Solar Thermophilic Anaerobic Reactor (STAR) for Renewable Energy Production

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To my parents, Fayz,
Malaka and Mohamed

ABSTRACT

El-Mashad, H.M. (2003). Solar thermophilic anaerobic reactor (STAR) for renewable energy production. Ph.D. Thesis, Wageningen University, Wageningen, The Netherlands.

Liquid and solid cattle manures are major waste streams in Egypt. The main objective of this research was maximising the net energy production from these wastes by using a solar energy heating system. High concentration of ammonia can strongly affect the gross methane production via inhibition of methanogenesis and reduced hydrolysis. The latter is only limited addressed so far in literature and therefore taken as a second objective of this study.

To be able to design a solar thermophilic anaerobic reactor (STAR) and its pumping system, the effect of temperature on the rheological properties of liquid cattle manure was measured experimentally. The effect of temperature and temperature fluctuations on the performance of completely stirred tank reactor (CSTR) systems operated at 50^{o}C and 60^{o}C treating liquid cattle manure was studied also experimentally. The temperature fluctuations of the reactor content in a STAR system, designed without extra equipment for heating during the night, shown to be in a range, which will not significantly affect the biological activity in the reactor.

Simulations were carried out to study the effect of the interaction between different reactor volumes and different insulation materials on the net thermal energy production from the STAR system at Egyptian climatic conditions. Using a flat plate solar collector, with areas equal to the reactor's cross section area, improves the efficiency for large reactors only slightly, while for small reactors a large improvement is achieved.

The feasibility of a non-mixed accumulation system (AC) for treatment of solid manure was studied experimentally at 40 and 50^{o}C and filling time of 60 days using a 10% (V/V) inoculum placed on the reactor bottom. The results showed a distinct stratification of intermediates along the reactor height. Leachate recirculation and distribution of the inoculum with the feed could improve the system performance: higher methane production with less stratification extent. The results of a mechanistic model, describing the biological process in AC system including the dispersion of intermediates and bacteria species between the system layers showed a very well agreement with the experimental data of the methane production.

Finally, a design of a STAR for solid cattle wastes was studied in a model. The simulation results show that a minimum reactor temperature of 44.5 during summer and 47.6^{o}C during winter could be achieved for a well-insulated reactor with an aspect ratio of 0.6.

The effect of different ammonia concentrations on the hydrolysis constant (k_h) of liquid cattle manure was also studied experimentally at 50 and 60^{o}C. Negative linear relations between k_h and both total and free ammonia concentrations were found at each studied temperature.

From a literature review it becomes clear that next to animal manure rice straw is an important waste stream from the Egyptian agriculture. Combined composting of digested manure mixed with rice straw could produce an attractive organic fertiliser.

Based on emergy analysis of the system, the STAR concept can be recommended from the sustainability point of view.

Contents

CHAPTER 1: GENERAL INTRODUCTION

1. General Introduction

1.1. Problem statement and fields of interest

All over the world, the population increase coincides with the depletion of non-renewable energy sources. Although Egypt is an oil exporter, some projections foresee a start of oil import as early as 2005-2010. This is due to the high rate of growth in the demand for electricity (around 7-8% per year); the continuing expansion of industry and the declining production levels of the oil fields (IEA, 2000). The increase of population, on the other hand, increases also the need for improved food production (*i.e.* increased land fertility). This requires more organic fertilisers (*e.g.* agricultural wastes). About 60% of the Egyptian cattle wastes is used as fuel by direct burning in low efficiency burners (Hamdy, 1998). The remainder is used as fertiliser or lost during handling. This situation forces the search for clean and renewable energy sources together with the conservation of the organic fertilisers. Biomass technologies can deal with these objectives. However, biomass energy is still more costly than fossil energy. According to Chynoweth *et al.* (2001), trends to limit emissions of greenhouse gases and subsidies of biomass energy would make it cost competitive.

Conversion technologies for the production of energy from biomass can be classified as biological or thermal (Claassen *et al.*, 1999). The choice between such technologies depends strongly on the material properties together with the social and economic situation. Anaerobic digestion is one of the biological technologies to produce renewable and clean energy (*i.e.* biogas) from biomass. Besides, it conserves the fertiliser value presented originally in the waste (Van Velsen and Lettinga, 1980). From the end of the last century onwards, anaerobic digestion has been applied in man-made environments for both energy production and as a cost-effective method for stabilisation of wastes and wastewaters (Lettinga 1996). The methane produced can be used for water or space heating, electricity or steam production or for other thermal energy demands (Ghosh, 1986). It can also be used as engine fuel. According to Chynoweth *et al*. (2001), methane production from anaerobic digestion is competitive in efficiencies and costs as compared to other bioenergy forms (*e.g*. synthesis gases and ethanol).

The production of biogas from the biomethanation process depends strongly on temperature. Anaerobic digestion can be achieved under psychrophilic (< 25^oC), mesophilic ($25-40^oC$) or thermophilic (> 45^oC) conditions. Digestion under thermophilic conditions has many advantages such as higher metabolic rates and a more effective destruction of pathogens and weed seeds (Van Lier, 1995). The latter advantage is extremely important for cattle wastes, as the effluent can be used as organic fertiliser free from pathogen and weed seeds. A big disadvantage is that under thermophilic conditions more energy is consumed for heating the reactor compared to mesophilic conditions, which may lead to sever overall reduction of the net energy production. This disadvantage could be overcome if other renewable sources such as solar energy can be used as a heat source. This will save fossil fuel or biogas consumed during the biomethanation process. This combination represents a kind of solar energy storage in the form of biogas. Moreover, this utilisation will reduce the environmental impact from using conventional energy resources. However, the system could be more costly compared to a conventional heating system. A few papers have been published about the incorporation of a solar heating system in the anaerobic digestion process. Axaopoulos *et al.* (2001) presented a mathematical model and experimental study on a solar-heated anaerobic digester treating swine manure at 35°C. Alkhamis *et al.* (2000) investigated experimentally the utilisation of solar energy for heating a bioreactor at mesophilic conditions. The main problem is that in applying solar energy for the energy supply of the reactor introduces effects of seasonal and daily fluctuations in the temperature level of the reactor. The impact in microbiological processes involved in the digestion is not known. Therefore in this thesis the feasibility of a Solar Thermophilic Anaerobic Reactor (STAR) is studied for treating liquid and solid manure under semi -arid regions (e.g. Egypt).

1.2. The objectives

The general objective of this research is to improve the efficiency of the conversion of agricultural wastes into useful energy and organic fertiliser. Form this general objective the more specific objective follows to study the application of a solar energy heating system in thermophilic anaerobic digestion of agricultural wastes, maximising the net energy production with production of a hygienic organic fertiliser. Related to this objective, the research also concerns the effect of high ammonia concentrations on the process stability under thermophilic conditions.

1.3. Overview this dissertation

To achieve the goal, desk studies are combined with both experiments and modelling studies.

This dissertation contains five *chapters* besides the introduction. *Chapter* 2 is a desk study concerning an overview of Egyptian agricultural wastes as potential renewable sources of energy and organic fertiliser. From *chapter* 2, we will conclude that anaerobic digestion gives the major contribution to achieve the goals. So the next *chapters* focus on the anaerobic digestion and incorporation of solar energy in this process. *Chapter* 3 is a literature review on aspects relevant to the focus of the thesis. This chapter starts with a general background of the anaerobic digestion process and the effect of ammonia on it. A review of implementation of solar energy in the anaerobic digestion process is also presented in this *chapter*.

Chapter 4 describes experimental results concerning the effect of temperature and temperature fluctuations on the performance of thermophilic (50-60°C) digestion of liquid cattle manure in a Completely Stirred Tank Reactor (CSTR) system. Additionally the rheological properties of dairy cattle manure under different temperatures have been measured. These experimental data have been used for a simulation model for determination of the net energy production from conventional heated CSTR and STAR systems with volumes and different insulation materials. In another simulation model, the experimental data were also used to design a STAR system suitable for small animal farms in Egypt. In the latter simulation model, the temperature dynamics and the evaluation of STAR are presented. Moreover, in *chapter* 4, the effect of high ammonia concentrations on the anaerobic hydrolysis of liquid dairy cattle manure under thermophilic conditions is experimentally investigated and presented.

The results in *chapter* 5 deal with the feasibility of the anaerobic digestion of solid cattle wastes in an accumulation (fed batch) system under high temperature conditions (40-50^{o}C). The effects of temperature, leachate recirculation and different inoculum addition modes on the system performance were experimentally studied. Moreover, a model for biochemical processes involved in a stratified accumulation system has been developed and validated with the experimental data. Finally, in this *chapter* a STAR system was modelled for a stratified accumulation system treating solid cattle manure.

Finally, the general discussion and conclusions of the results obtained in this thesis together with the system evaluation are presented in *chapter* 6.

CHAPTER 2: REUSE POTENTIAL OF AGRICULTURAL WASTES IN SEMI-ARID REGIONS: EGYPT AS A CASE STUDY

A modified version of this *chapter* was written as an article:

El-Mashad, H.M.; Loon, W.K.P. van; Zeeman, G.; Bot, G.P.A. and Lettinga, G. Reuse potential of agricultural wastes in semi-arid regions: Egypt as a case study. Submitted to Reviews in Environmental Science and Biotechnology

2. Reuse Potential of Agricultural Wastes in Semi-arid Regions: Egypt as a Case Study

Abstract

Agricultural wastes represent an important source of bio-energy and valuable products. In Egypt, 18% of the agricultural wastes is used directly as fertiliser. Another 30% is used as animal food. The remainder is burnt directly on the fields or is used for heating in the small villages, using low efficiency burners. These wastes can be used more efficiently as a source of energy and as organic fertiliser. The anaerobic bioconversion of these materials will result in a net energy production. The utilisation of agricultural wastes for the production of energy and compost, combined with using solar energy will save fossil fuel, improve health conditions and the general life quality in the villages.

2.1. Introduction

The fast population growth and the depletion of traditional energy sources triggered many countries to search for new and renewable energy sources. Egypt can be considered as a representative country in semi-arid regions. It is an agricultural country: agriculture provides about 37% of the total employment. Although yields for many agricultural crops in Egypt are among the highest in the world, the total arable land area is only 3.3 million-hectare. The yearly population growth, of about 2.7%, increases the demand for food and energy. This results in the application of intensive crop rotation, leading to an increased need for (chemical) fertilisers. The sandy soils that are usually found in land reclamation projects require fertilisers. Agricultural wastes can be used as a source of organic fertiliser. The application of these organic fertilisers will reduce the cost of chemical fertilisers as well as the energy consumption during their production. Furthermore, the controlled treatment of agricultural wastes represents a kind of human and animal health concern. This in fact is the "sustainability" concept, which stands for the idea that the present and coming generations should preserve resources, energy and a balanced healthy life environment for the future generations (Lettinga, 2001). According to Lettinga (2001) the relevant long-term sustainability commandments to be met for environmental technologies are:

1- Use of little if any mineral resources and energy,

2- Enabling production of resources/energy from wastes,

3- Pairing high efficiency with long term of life,

4- Applicable at any place and at any scale,

5- Plain in construction, operation and maintenance.

The International Energy Agency (IEA, 2000) mentioned that, although Egypt at the moment is an oil exporter, as early as 2005-2010 it will start to import oil. This is caused by an annual increase of electricity demand of around 7-8%. The Egyptian energy consumption has nearly tripled over the past two decades, from 17.6 in 1980 to 50.9 Mtoe (million tonnes oil equivalent) in 1999. Industrial demands tapped more than half (53.6%) of the nation's energy in 1997, while one quarter went to transportation (24.7%) and the remainder (22.1%) to residential use. At the same time, the carbon emission in Egypt increased from 11.7 million metric tons in 1980 to 31.6 milion tons in 1998. Egypt has signed the Koyoto Protocol for climate change, demanding stabilisation and curtailing emission of CO_2, methane and other greenhouse gases. For the time being Egypt is not bound to this obligation but for the future it will be subjected to fulfil the Koyoto Protocol. Figure 2.1 shows the energy production, consumption and CO_2 emission from fossil fuel in Egypt in the period 1990-1999 (IEA). The situation in Egypt is more or less representative for other semi-arid regions.

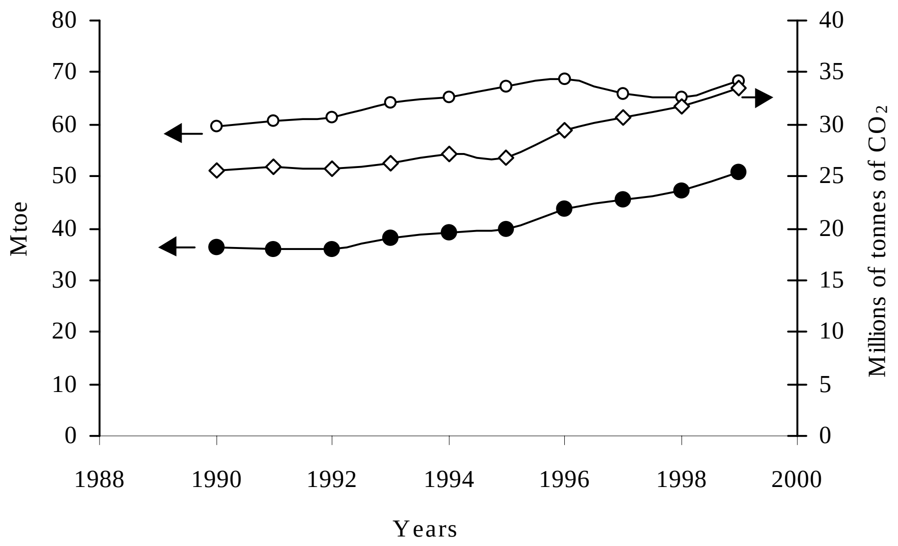


Fig. 2.1. Total energy production, consumption and total CO_2 from fossil fuels in Egypt (1990-1999):○, total primary energy production; ◊, total CO_2 from fossil fuels; ●, total primary energy consumption

Utilisation of biomass (*i.e.* agriculture crop residues) and animal wastes as a source of energy is important from an energetic as well as environmental viewpoint. Furthermore the incorporation of other renewable energy like solar energy in the treatment of agricultural wastes will increase the impact of such resources in solving energy and environmental problems. So far the reuse potential of agricultural waste in Egypt is not investigated. This paper deals with the inventory in three steps:

1- Identify the most important flows of waste, which are not reused.

2- Identify reuse techniques.

3- Combine it to the most promising reuse possibilities in Egypt as an example for semi-arid regions.

2. 2. Agricultural wastes in Egypt

2.2.1. Crop residues

Major crops in Egypt include wheat, maize, rice, cotton, clover, sugar cane, beans, and soybeans. Moreover, Egypt produces some vegetables and fruits. According to the Egyptian New and Renewable Energy Authority (2000), the potential of crop residues in Egypt contributes to about 50% of the total biomass potential. Hamdy (1998) mentioned that about 52% of the agricultural residues are burnt directly on the fields or in inefficient burners (less than 10% efficiency) in small villages. Both methods result in loss of energy as well as negative impact on the environment. Moreover, the traditional storage in the farms and on roofs gives a large chance for insects and other disease carriers to grow and re-attack human, animals or new crops. Hamdy (1998) revealed that about 30% of the agricultural residues is used for animal feeding and the rest (18%) is used as fertiliser. The updated Egyptian renewable energy strategy targets to supply 3% of the electricity generation by the year 2010 from solar and wind with additional contributions from biomass applications (Egyptian New and Renewable Energy Authority, 2000)

Table 2.1 shows the annual areas for crop production, and total wastes production for the most important crops in Egypt.

As shown in Table 2.1, the largest crop residues are wheat, maize, sugar cane and rice straw. Wheat and maize residues are almost totally used as animal feed. Sugar cane residues are burnt in sugar factories. However, rice straw is mostly burnt on the fields.

Table 2.1. The areas and total annual waste production for major Egyptian crops

	*Area (1000HA)**	*Total Wastes (1000 Ton)***
Wheat	984	5998
Maize	843	3814
Sugar Cane	134	3634
Rice, Paddy	650	2724
Tomatoes	189	1441
Seed Cotton	218	835
Broad Beans, Dry	140	467
Sugar Beets	61	440
Potatoes	76	380

*FAO (2001); ** Hamdy (1998)

2.2.2. Animal manure production

Egypt produces a huge amount of animal wastes. Table 2.2 shows the annual animal waste production. From Table 2.2 it can be read that the total amount of buffalo and cow manure is about 10 million-ton per year.

Table 2.2. The yearly wet manure production in Egypt

	Number *(1000 Head)**	*Total wet manure production* *(1000 Ton)***
Cattle	3635.6	5403
Buffaloes	3430.1	5097
Horses +Asses +Mules +Camels	3216.9	2348
Sheep + Goats	3982	729
Chickens + Ducks + Turkeys	99.1	< 1

*FAO (2001); ** Hamdy (1998)

The uncontrolled handling and storage of manure causes loss of organic matter and also pollution problems. Hamdy (1998) mentioned that about 60% of the cattle wastes (buffalo and cows) is used as fuel by direct burning in low efficiency burners (less than 10%); another 20% of the animal wastes is used as organic fertiliser, and the rest is lost in handling.

From the overviews in Tables 2.1 and 2.2, it can be concluded that rice straw and animal manure have the greatest potential to be used as a source of clean energy and organic fertiliser. It can also be concluded that a sustainable treatment of such resources is of vital concern for Egypt. According to Tabana (2000) a mixed crop-livestock system is the most important cattle production system, representing over 70% of all cattle in 1997, together with large numbers of buffaloes and some sheep and goats. In general the mixed crop-livestock system has less than 4 hectares of crops and less than 15 adult animals.

It can be recommended that a treatment system should be decentralised and small scale to limit the transport costs. In the following sections possible treatment methods for both rice straw and cattle manure are reviewed and analysed.

2.3. General technologies for biomass conversion

Viesturs *et al.* (1995) mentioned possible technologies for biomass conversion with energy production, which are summarised in Fig. 2.2.

The choice of a certain technique depends on the composition of the material as well as the advantages and the drawbacks of such technique. In the present study enzymatic hydrolysis and chemical hydrolysis (as presented in Fig. 2.2) are not considered for the complexity, high cost and/or the high-tech of such technologies to be applied on farm scale. Some general information on combustion and gasification is presented before. These techniques can be approved for farm scale use.

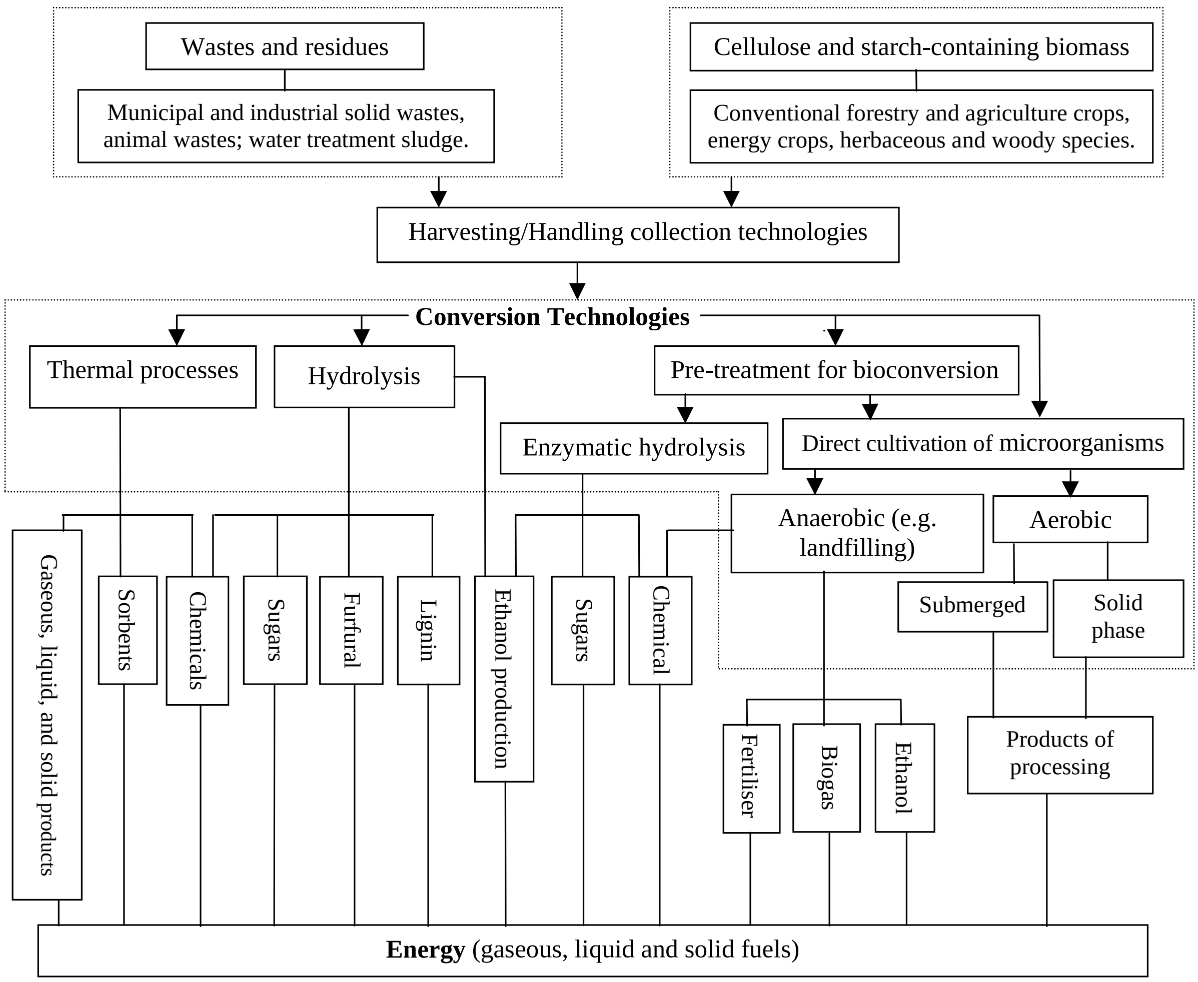


Fig.2.2. The general technologies of biomass conversion (adapted from Viesturs et al., 1995)

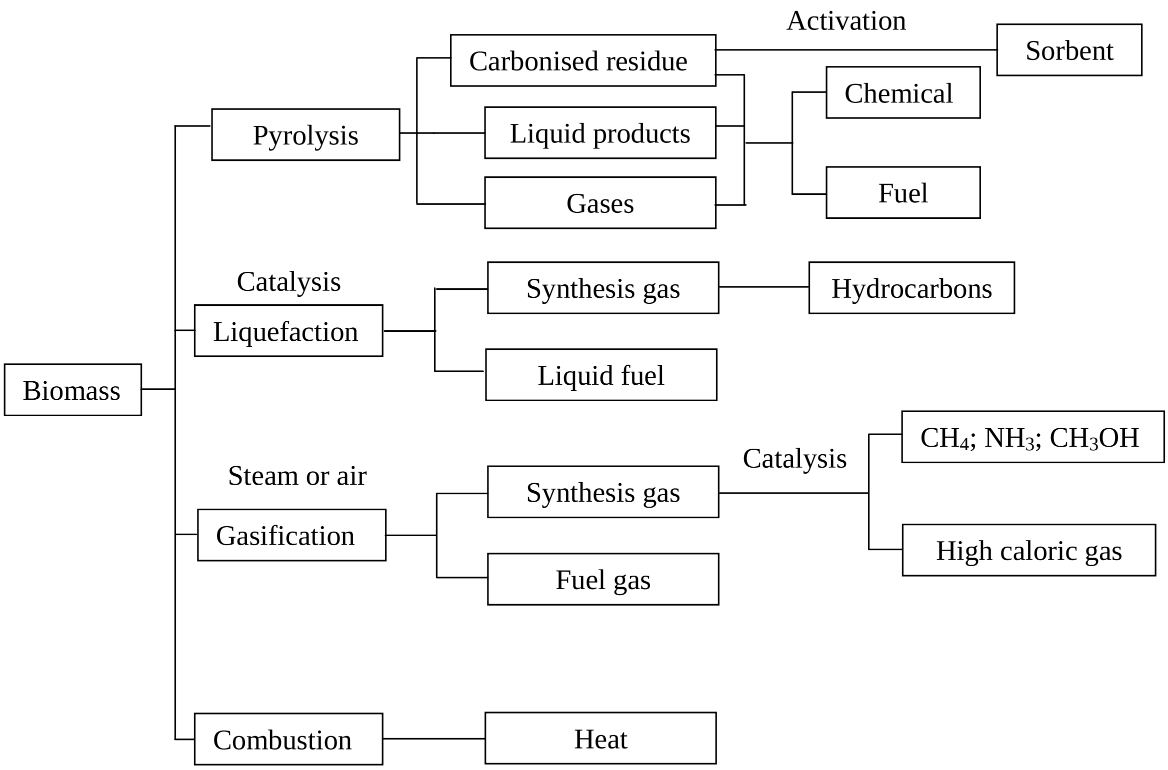


Fig.2.3. Thermal processes of biomass conversion (adapted from Viesturs et al., 1995)

2.3.1. Combustion

Combustion is one of the thermal processes used to release energy and valuable products from agricultural wastes. Figure 2.3 gives an overview of several thermal processes.

The combustion of solid phase wastes is largely a process of gasification followed by combustion of the gaseous products. Normal combustion is considered to take place in three steps namely, drying, gasification and combustion. However, there are no sharp limits between these stages. As can be seen from Fig 2.3 combustion unlike other processes can only release energy. Combustion has some advantages:

1- The volume of solid waste can be reduced up to 90 percent, with weight reduced up to about 60%.

2- The resulting ash could be used for building or road materials.

3- Modern plants convert waste to energy in the form of electricity, steam, or both, which provides some income to their operators.

The furnace efficiency depends on the gas temperature in the furnace, oxygen content and mixing of combustion air and temperature of the furnace walls. The efficiency of a furnace can be determined indirectly or directly. *Indirect efficiency* is determined by measuring or estimating various losses (*i.e.* radiation and convection; heat flue-gas losses, losses due to inflammable substances in the ashes). *The direct efficiency* is obtained by measuring the heat production estimated by measuring the water flow rate and the temperature differences between the outlet and the inlet of water in the furnace. The obtained value of heat production is divided by the effective calorific value of the fuel.

2.3.2. Gasification

Gasification is one of the thermo-chemical conversion processes, which uses heat to produce by bio-fuels chemical conversion. This process is limited to combustion and pyrolysis processes. Warnecke (2000) reviewed that, at temperatures higher than 400 K, the thermo-chemical processes are combustion, thermolysis and reactolysis. Gasification is an incomplete combustion of biomass, resulting in production of a synthetic gas, which is a mixture (called producer gas) of H_2, CO and traces of CH_4. One of the important features of gasification is that the reaction temperature can be kept as low as 600-650^oC, thereby preventing sintering and agglomeration of the ash inside the burning devices. Compared to combustion methods, the gases produced from gasification may be used as energetical or technological feedstock; while during combustion only the energetically use of heat from the raw material is possible (Viesturs *et al.,* 1995). Producer gas can be used in internal combustion engines, in direct heat applications and in methanol production, which is useful as fuel for heating as well as chemical feedstock for industries. Gasification offers a high potential as a small-scale method to convert biomass to a gaseous fuel which might be used in a number of farming operations, such as crop drying and fuelling engines on irrigation wells (Lepori *et al.,* 1980). Most preferred fuels for gasification have been charcoal and wood. However, biomass residues are the most appropriate fuels for on-farm systems. Gasification has been suggested as an alternative for combustion of low-density biomass materials and almost any carbonaceous fuel or biomass can be gasified under experimental or laboratory conditions (Rajvanshi, 1986; Kaupp, 1982;Wilen and Rautalin, 1995).

There are three types of gasifiers: updraft, downdraft and cross-draft (Rajvanshi, 1986). The choice of the gasifier type is dictated by the fuel, bulk density, size, moisture content, and ash content. Goss and Jain (2000) revealed that for rice husk down draft gasifiers with throat are known to generate best quality producer gas, having minimum tar for engines. Due to the high ash content of rice straw the fluidised bed gasifier systems are the most appropriate. Wilen and Rautalin (1995) revealed that the major advantage of a fluidised bed gasifier over downdraft is its flexibility with regard to feed rate and composition. Fluidised bed systems can also have a high volumetric capacity and the temperature can be easily controlled (Rajvanshi, 1986) However, these advantages are offset by the complexity of the system with large blowers for blowing air and augers for biomass feeding. Besides, fluidised bed systems produce more dust and tar as compared to downdraft gasifiers. Lepori *et al.* (1980); Natarajan *et al.* (1998); Rajvanshi (1986) revealed that fluidised bed technology seems to be suitable for converting a wide range of agricultural residues into energy, due to its inherent advantages of fuel flexibility, low operating temperature and isothermal operating condition. It has the advantage of being small in size, requiring relatively low capital investment, and it can be easily automated to minimise the use of full time operating labour. Warnecke (2000) revealed that fluidised beds have good heat and material transfer between the gas and solid phases with the best distribution, high specific capacity and fast heat up. These systems can be used for wide variations of fuel quality and a broad particle size distribution. Disadvantages of these systems are the high dust content in the gas phase and the conflict between high reaction temperatures with good conversion efficiency and low melting points of ash components.

2.4. Reuse of rice straw

2.4.1. Rice straw composition

Rice straw has three main components: organic matter, water, and ash. Rice straw has a high ash content compared to other grass species. Table 2.3 shows the elemental composition of rice straw (Zhang and Zhang, 1999).

The moisture content has a great effect on the calorific value. The higher the moisture content, the lower the dry matter content and the more energy is required for drying. This means that a lower calorific value will be obtained at controlled burning (Nilsson, 1981).

Table 2.3. The elemental composition of rice straw (moisture content 7.9%) relative to total solids (TS). STD is standard deviation

Components	*C*	*N*	*P*	*K*	*H*	*S*	*Ash*	*Volatile solids*
(%TS)	34.8	0.46	0.09	1.58	4.61	0.14	20.5	79.5
STD	± 0.4	± 0.02	± 0.01	± 0.02	± 0.05	± 0.01	± 0.2	± 0.45

Also for preventing degradation during long time storage and proper combustion of straw, the moisture content should be less than 18% (w.b.). Jenkins and Rumsey (1985) revealed that the moisture content of biomass used for energy systems has a large influence on the operating characteristics and economic success of these systems. Proper drying conditions must be supplied to reduce the high moisture content of the fuel prior to combustion. Otherwise, the combustion temperature will be lowered, causing incomplete combustion with high emissions of particles, carbon monoxide, and hydrocarbons. Korenaga *et al.* (2001) mentioned that low moisture content reduces the emissions of Polycyclic Aromatic Hydrocarbons (PAHs) during rice straw burning. The lowest emission of total particulate PAHs was obtained at 15% moisture content. So, a high moisture content in big bales may cause handling and emission problems.

The potential environmental benefits of diverting rice straw from open-field burning to controlled disposal will significantly reduce air pollution and the related health hazards (Kadam *et al.* 2000). As an alternative to combustion, rice straw can be used as an energy source via gasification and anaerobic digestion. The residue can be used as a soil amendment. Aerobic composting is not resulting in the production of gas, but in the production of heat, which results in evaporation of water and therefore the production of a dry, hygienic compost.

2.4.2. Rice straw combustion

The burning of rice straw can cause environmental pollution. Air emission from combustion can include particulate matter, carbon monoxide, nitrous oxides, acid gases, dioxins, and other hazardous organics and heavy metals. The temperature of the smoke is a critical factor in controlling emissions. Dioxins outside of the stack can occur if the smoke is not cooled. The removal of pollutants from the combustion gases can be achieved with a proper operation of the unit at constant burning temperature and the use of scrubbers followed by a fabric filter or an electrostatic precipitator. Rice straw is an economically interesting bio-fuel source but it causes severe slagging, fouling, and corrosion (Jenkins *et al.,* 1997).

The following characteristics of rice straw make it a difficult fuel to power plants or home heating (Forrest *et al.,* 1997):

1- The alkalinity (particularly the potassium and chlorides) of rice straw creates serious and costly slagging problems in the biomass power boiler. Large accumulation occurs on the boiler walls, creating unscheduled downtime for removing the slagging.

2- The high silica content of rice straw (averaging 15 -19%) results in a high ash content. This ash reduces the energy efficiency of the biomass boilers and should be disposed.

2.4.3. Combustion systems and their efficiencies

Many combustion systems with varying sizes and applications are used for solid fuel combustion. Nilsson (1981) described the straw furnaces commonly used in Sweden. Table

2.4 shows the types of these furnaces and their efficiencies. In general, the highest values have been obtained for the small-bale furnaces.

Table 2.4. Straw furnaces, and their efficiency (Nilsson, 1981)

Furnace type	*Efficiency (%)*
Over-burning magazine furnace	35-40
Under-burning furnace	55-65
Furnace equipped with feeding devices	60-75

Kofoed Nielsen *et al.* (1982) and Kofoed Nielsen and Nielsen (1983) studied the efficiency improvement of straw furnaces by cooling down the flue gas below dew point. The heat exchanger used has a gas scrubber. The results showed that the efficiency was increased from 70% to 90% of the effective calorific value of straw. The flow gas temperature was decreased from 300^{o}C to 45-50^{o}C after using the heat exchanger. The emission was reduced in the range of 15% to 70% of the original value without using the gas scrubber. Orth *et al.* (1983) revealed that various burning systems for agricultural wastes still have problems with burning straw with high efficiency and low emissions. The results showed that efficiencies of 50 to 70% can be reached. Streher (1980) applied some modifications for the through-burning boilers in order to achieve greater efficiency and less emission. These modifications were building a second cylinder to allow operation at higher temperatures; also a secondary combustion chamber leads to lower emission. Briquetting is believed to improve the efficiency of biomass utilisation (Tripathi *et al.,* 1998), however rice straw would probably require pre-treatment to enhance binding of its molecules (Forrest *et al.,* 1995).

In large-scale combustion systems such as electricity plants, the co-combustion of biomass fuel with coal may enhance the combustion process and mitigate the environmental impact of coal burning. Jenkins and Bhatnagar (1991) revealed that the use of paddy straw for power generation is a concept for at least a portion of the fuel. Van Doorn *et al.* (1995) revealed that, in a fluidised bed installation, lower combustion temperatures might prevent agglomeration. Compared with coal-firing the concentration of chlorine in the flue gas increased when increasing the amount of straw or sewage sludge. Co-combustion of straw has a beneficial effect on the SO_2 and NO_x emissions, although the effect on the SO_2 content is less pronounced compared with co-firing wood. Hartmann and Kaltschmitt (1999) concluded that if straw or residual wood is used in co-combustion with 10% coal, the environmental impact is much lower. Wood shows the lowest environmental impact compared to straw. CO_2 emissions released during the burning of biomass do not contribute to the anthropogenic greenhouse effect because the amount of CO_2 emitted into the atmosphere equals that removed during the plant growth.

The collection and handling of rice straw require fossil fuel for equipment operation. The amount of energy, which can be obtained from the rice straw combustion, must be higher than the energy consumption in the collecting and handling process of rice straw. Studies showed a positive net energy from biomass utilisation. Jenkins and Knutson (1984) studied the fossil fuel energy input for collection and processing of one ton of rice straw. The results showed that a total of 1325 MJ of fossil energy were required to collect, process and deliver 1 ton of straw (16000MJ) to a 25 MW power plant. The energy intensity of the straw when delivered to the plant was 1.083. Energy intensity is defined as the ratio of the embodied energy of fuel (heating value and fossil energy input) to the fuel heating value. On the other hand, Jenkins and Sumner (1986) mentioned that the energy yield ratio (energy output in fossil fuel equivalents divided by the fossil fuel input) for straw converted to electricity, including the fossil energy inputs to the power plant, was 4.2 for a power plant thermal efficiency of 25%. Smaller scale conversion of rice straw for use in on-farm drying was estimated to have an energy yield ratio of 9.6. Returning of ash from the power plant to the field to reduce the fertilisers requirements would decrease fossil fuel input to fertilisers only by about half, because fossil fuel energy would be expended in transporting the ash and spreading it on the field. Kadam *et al.* (2000) mentioned that transportation of loose straw is expensive, and densification of the straw is most probably necessary. Cubing of rice straw facilitates the transportation. Cubing was estimated to add another 620 $MJton^{-1}$ of fossil fuel input and would be justified energetically only when straw required transportation beyond 125 km (Jenkins and Sumner, 1986). From the results of Jenkins and Knutson (1984), it can be concluded that combustion of rice straw should take place decentralised in small-scale units.

2.4.4. Problems with rice straw combustion and gasification

Beside the problems of emissions, there are some other technical problems involved in the combustion and gasification of straw. The high concentration of alkali, sulphur, chlorine and silica in rice straw causes some problems for the devices (gasifiers, furnaces, and boilers). Vijil *et al.* (1984) and Liliedah *et al.* (1999) mentioned that a major potential problem encountered in fluidised beds, is bed sintering or agglomeration, which, in the worst case may result in total de-fluidisation and to unscheduled downtime. The word sintering in general implies a chemical process in which a porous substance becomes more solid by heating. Agglomeration also implies an increase in particle size but it is more a physical than a chemical process. The problems and the solutions of straw combustion and gasification can be summarised in Table 2.5.

To use combustion and gasification under farm conditions, it can be recommended to utilise leaching or blinding of straw with wood fuel as simple methods to reduce the high ash contents problems. Alternatively to direct burning and gasification, rice straw can be used as feedstock for anaerobic digestion.

Table 2.5. Problems of gasification and combustion and their solutions

Problem	*Solutions*
Agglomeration and sintering	1- Use of catalysts can promote the formation of combustible gases at relatively low temperatures (Viesturs *et al.,* 1995). 2- Co-combustion of rice straw with coal (Vijil *et al.,* 1984) and the blending of rice straw with wood fuel (Jenkins, 1991). 3- Limestone was the principal additive used in test boilers to maintain bed fluidisation (Thomas *et al.,* 1995). 4- High alumina sand reduced agglomeration in a circulating fluidised bed (CFB) but it did not change the composition of deposits on the super-heater tubes (Thomas *et al.,* 1995). 5- Use of a two-stage process, in two different reactors, including pyrolysis and char gasification (Hauserman, 1995). 6- By leaching with water, most of the potassium and chlorine are extracted from fuel. The extraction of both alkali metals and chlorine, along with some other elements, particularly sulphur and phosphor, are beneficial in terms of improving the fuel value of biomass materials, not only from the fouling standpoint but from those of corrosion and emission formation as well (Jenkins *et al.,* 1997). Leaching also facilitates the ignition and burning processes of rice straw (Di-Blasi *et al.,* 1999).
Problem due to the low softening and melting points of the ash	1- In laboratory tests, Steenari and Lindqvist (1998) found that kaolin was the most effective additive to enhance the melting point compared with dolomite.
Deposit of alkali compounds on heat exchanger surfaces which lead to a reduced effectiveness of the heat transfer	1- Special boiler designs with low furnace exit gas temperatures (815^{o}C), for burning crops residues, including grasses and straws (Thomas *et al.,* 1995). The design should include: adequate water-wall surface area or parallel heat exchange surfaces, and combustion air control to control gas temperatures, possibilities for removing large quantities of ash, and to clean tenacious deposits. 2- Leaching reduced the ash content by about 50 wt.% and caused some swelling thus enhancing gas/solid heat transfer (Di-Blasi *et al.,* 1999 and Dayton *et al.,* 1999). 3- Preliminarily combustion tests showed that the anaerobically digested rice straw residue combusted successfully without causing fouling problems even when the combustion temperature reached 1600^{o}C. In contrast, raw rice straw usually starts to cause fouling problems at around 1400^{o}C (Zhang and Zhang, 1999).

2.4.5. Biomethanation of rice straw

The anaerobic digestion process is one of the technologies commonly used for waste treatment. Beside the biogas produced from the anaerobic digestion, it is beneficial to use the digested residues as soil amendments as the availability of nitrogen and phosphorus increases. The high carbon content, high solid content and the low nitrogen content of rice straw requires the use of other sources of nitrogen and water. Nitrogen can be added in inorganic form (ammonia) or in organic form (urea, animal manure or food wastes). Hills and Roberts (1981) showed that adding either chopped rice or wheat straw to dairy manure enhanced the anaerobic digestion process and increased the methane production rate. Furthermore adding chopped rice straw to cattle dung enhanced the organic matter degradation to a high extent (35- 51%) compared with 27% in cattle dung alone (Somayaji and Khanna, 1994). The authors argued this enhancement to the increased availability of carbon for methane formation. Rice straw needs some pre-treatment to enhance its degradation. The effects of different pre-treatment methods, physical (mechanical), thermal (pressure cooker for 2 h at 60, 90 and 110^{o}C) and chemical (ammonia) treatment, on the digestion of rice straw were investigated at a temperature of 35^{o}C (Zhang and Zhang, 1999). The pre-treatment temperature (60^{o}C to 90^{o}C) has a significant effect on the digestibility of straw. With or without thermal pre-treatment, grinding resulted in a significant improvement in terms of solid reduction and biogas yield as compared with chopping or no-size reduction. Fungal pre-treatment of straw can make it a better substrate for methanogenesis (Mehta *et al.,* 1990). Biogas and methane production were increased by treating rice straw with white rot fungus *Phanerochaete Chrysosporium* (Ghosh and Bhattacharyya, 1999).

At mixed farms, where both animal manure and rice straw are available, co-digestion can be recommended as an option for the treatment of these two sources.

2.4.6. Composting of rice straw

Composting is a process in which the organic material is converted into organic fertilisers by means of biological activity under controlled conditions. The objectives of composting are to stabilise the organic matter; to reduce the malodour, to destruct the weed seeds and pathogens, and to produce a uniform organic fertiliser suitable for land application (Haga, 1990). Hamelers (2001) mentioned that the primary objective of a compost plant is to produce compost conforming to specific product standards with minimal emissions to the environment.

Micro-organisms including bacteria, fungi, and actinomycetes decompose rice straw. Aeration, temperature, nutrients, and moisture are factors that affect the rate and degree of rice straw decomposition. Aerobic decomposition may be quite rapid at the optimal nutrient, temperature and moisture levels. Cuevas (1993) mentioned the benefits of rice straw composting: income gains resulting from a healthy crop; improved soil texture, better aeration and water-holding capacity, increased fertility and less acidity. Compost reduces the need for chemical fertilisers, which contaminate surrounding waters and encourage algae blooms. Additionally, farmers become less dependent on off-farm inputs. Forrest *et al.* (1995) revealed that the high C/N ratios of rice straw make it a less desirable constituent in composting than other agricultural wastes. However, addition of rice straw to the composting material has a number of advantages: it adds texture to the material; it prevents a pile from getting too hot; and it is an ideal ingredient when it has been premixed with livestock manure.

Cuevas (1993) revealed that extensive composting, which requires three months for complete decomposition, is too slow for farmers who plant two or three rice crops a year. Rapid composting requires a mix of carbon-rich materials such as rice straw and nitrogen-rich materials like animal manure. The drawback of rapid composting is the extra work for the farmer. In addition to that drawback, it should be mentioned that the application of such activator could be hardly applied under small farms conditions. Kakezawa *et al.* (1992) studied the composting process of rice straw in a two-step composting process to produce compost with a high Cation Exchange Capacity (CEC) and humic acid content. The CEC and humic acid content of the compost produced from the fermented rice straw were higher than the unfermented one. Although compost has many advantages, farmers do not have incentives to apply it mainly due to the lack of knowledge.

2.4.7. Rice straw incorporation in soils

Rice straw can be used as soil amendment. Rice fields are commonly fertilised with organic matter, mainly rice straw, which is ploughed under after rice harvest (Weber *et al.,* 2001). Rice straw is resistant to decay and can interfere with succeeding years' operations if not plowed under to greater depths than standard operations call for (Kadam *et al.,* 2000). The direct incorporation of rice straw in the soil may have a bad effect on the next crop and also may cause increasing CH_4 emissions from the fields (Weber *et al.,* 2001). Anaerobic decomposition of rice straw results in an increase of toxic products, which can damage the crop. These products include volatile fatty acids, hydrogen sulphide and methane (Watanabe, 1984). To mitigate CH_4 from rice fields, non-stabilised organic amendments (*e.g.* animal manure, rice straw or green manure) should be minimised. It was found that compost had only a slightly stimulating effect on CH_4 emissions, especially in the common application range of 3-15 tons.ha^{-1} (Skea, 1995). Methane emission form rice straw incorporation depends strongly on the soil conditions (*e.g.* temperature and moisture content). Devêvre and Horwáth (2000) studied the effect of temperature (5, 15 and 25^{o}C) on the decomposition of rice straw in a rice paddy soil under aerobic and anaerobic (flooded) conditions. The results showed that flooding had a tendency to enhance methane emission however with decreasing temperatures CH_4 production became negligible.

2.5. Reuse of manure

Animal wastes are used as a source of energy and as organic fertilisers. The traditional handling and storage methods of animal wastes cause pollution problems and loss of organic matter. Due to the high moisture content of the manure, the application for direct combustion or gasification is not possible. However, the Egyptian farmers usually store the manure in big piles to dry. Pollution problems come from both the direct combustion and from the storage of these wastes (El-Hadidi, 1998):

1- Malodours and air pollution form gaseous emissions.

2- Diseases caused by attracted insects.

3- Water pollution due to leaching of liquids during rain.

4- Increased fire risk during dry period.

Only a few publications are available for cattle manure combustion and gasification. Dagnall *et al.* (2000) mentioned that anaerobic digestion and combustion are used to produce energy from farm livestock manure. They mentioned that the primary combustible feedstock is poultry litter with a moisture content of 20-50%. According to Dagnall *et al.* (2000), overall power generation efficiency could be as high as 27%. Gasification technologies can theoretically yield conversion efficiencies up to 35% but these are not yet proven for this feedstock. As mentioned above, the composition of the waste controls vastly the proper treatment method.

2.5.1. Manure composition

The composition of animal manure depends on the type of animal, the feeding strategy, the animal housing and the slurry collection and storage system (Zeeman, 1991). The composition of Egyptian cattle manure (Abd Elaty, 1985) is compared with both the Dutch liquid (Zeeman, 1991) and solid cattle manure (*chapter* 5.1) is shown in Table 2.6.

The results in the table show that Egyptian solid cow manure has almost the same total solids and volatile solids content, but liquid manure (*i.e.* low TS) has a low nitrogen content as compared to the Dutch one. The conservation of manure is an important issue for Egyptian agricultural sector as it is a good source of organic fertiliser. This stimulates the use of environmental friendly and healthy disposal methods such as composting and anaerobic digestion.

Table 2.6. The composition cow manure

Parameters	*Units*	*Dutch*		*Egyptian*
		Liquid manure	*Solid manure*	
Total Solid (TS)	(g kg^{-1})	85.4 - 95	250	109-272
Volatile Solid (VS)	(g kg^{-1})	71.2-80.8	189	75.3-222.2
Ammonia (NH_4^+N)	(g kg^{-1})	2.2-3.5	1.82	----
Dissolved COD (COD_{dis})	(g kg^{-1})	27.6-34.1	41.7	----
Volatile Fatty acids (VFA)	(g [COD]kg^{-1})	9.9-13.7	14.98	----
Kjeldahl nitrogen (Nkj)	(g kg^{-1})	4.2*	6.67	1.37- 6.83
Total COD	(g kg^{-1})	96.6-131	314.9	----

* Calculated based on the data of El-Mashad *et al.* (2001)

2.5.2. Biomethanation of manure

Anaerobic digestion is one of the technologies used to produce energy as well as to stabilise the waste. Energy production has remained an important factor, even at dropping energy prices. The atmospheric greenhouse effect, sustainable development and the ozone layer depletion have all contributed to the value of anaerobic digestion as a renewable energy source (De Baere, 2000).

The utilisation of animal manure as a feedstock for biogas production will save plant nutrients and improve health conditions and quality of life in the villages (El-shimi and Arafa, 1998). Biogas is a CO_2 neutral fuel and the increase of biogas utilisation will achieve CO_2 and methane emission decrease. However this reduction will depend on a careful handling of fresh and digested manure to avoid significant methane losses to the atmosphere.

Many researchers have studied the biomethanation of cow manure in detail. Many studied the mesophilic and psychrophilic digestion (*e.g.* Zeeman, 1991). Others studied thermophilic digestion (Varel *et al.,* 1977; Wiegant and Zeeman, 1986; Angelidaki and Ahring, 1993; Angelidaki and Ahring, 1994). Thermophilic digestion has many advantages over the mesophilic (Van Lier, 1995), such as higher metabolic rates, pathogen removal and improved physical-chemical properties. It is recommended to study the thermophilic digestion of liquid cow manure in CSTR systems and solid manure in accumulation systems (*chapters* 4.2; 4.3; 5.1; 5.2).

2.5.3. Manure composting

As mentioned before, about 20% of the Egyptian manure is used as soil fertiliser. The organic matter content in Egyptian soils is very poor (2%) and needs annual addition (El-shimi and Ararfa, 1998). However, heavy applications of raw animal wastes may damage crop plants as a result of excess ammonium and the presence of phytotoxic substances (*e.g.* phenolic acids and volatile fatty acids). Composting reduces these problems (Harada, 1990). The response of the crops varies with the different composted animal manure and the rate of application. Composts increase water-holding capacity, aggregation, soil structure, aeration and tilth together with higher concentration of plant nutrients (Maynard, 1991). All these factors result in higher crop yields.

Controlled conditions are important for composting. During composting, micro-organisms require water; carbon (energy source) and nitrogen (to maintain and build cells). The proper moisture content is around 60% and the suitable C/N ratio for composting is between 20 and 30. As composting proceeds, the C/N ratio decreases gradually to around 15 (Haga, 1990). Hamelers (2001) mentioned that a C/N value of 25 is considered sufficient. If the C/N ratio is too low, excess nitrogen lead to volatilisation of ammonia. On the other hand, a moisture content of 40-60% is generally considered optimal for the composting process (Hamelers, 2001). The high moisture content of manure (75-90%) causes disturbances of oxygen supply to the compost material by destroying its porous structure. Taiganides (1977) mentioned that it is difficult to achieve thermophilic composting of high–moisture cattle faeces without proper pre-treatment such as mixing with a bulking agent. Chang *et al.* (1980) used the formula of Rodale (1971) to calculate the carbon percentage depended on the ash content of the material.

From this formula, the C/N ratio of manure can be calculated to be 15.8 and 22.1 for Dutch and Egyptian cow manure respectively. This low ratio results in nitrogen loss as ammonia volatises. The high moisture content of manure and low C/N ratio both promote mixing with dry carbon-rich materials such as straw (Haga, 1990).

2.6. A proposed framework of the combination of biomethanation and composting for rice straw and manure

In general, it can be expected that application of biomass technology for semi-arid countries like Egypt can contribute to the fulfilment of future commitments under the climate convention (Egyptian New and Renewable Energy Authority, 2000).

The two most important unused agricultural waste flows in Egypt are rice straw and cow manure. To choose the suitable technique for disposal of these materials, the following objectives can be formulated:

1- Preserving nutrients by production of an organic fertiliser and/or compost.

2- Production of clean energy.

To choose the best technique or combination of techniques, which comply with these objectives, two important points should be considered:

1- The composition of the material.

2- The advantages and the drawbacks of the treatment methods especially with respect to environmental emissions.

Based on the data presented in previous sections, the potential techniques for different substrates can be summarised (Table 2.7).

Table 2.7. Possible techniques for treatment of cattle manure and rice straw

Technique	*Material*			
	Rice straw	*Solid manure*	*Liquid manure*	*Mixture manure/rice straw*
Thermal processes	+/-	+/-	-	-
Anaerobic digestion	+/-	+	+	+
Aerobic composting	+/-	+/-	-	+

Table 2.7 shows that rice straw can be used as a fuel for thermal processes but the sintering and agglomeration problems encountered in such systems should be considered. For the Egyptian situation, at using efficient furnaces (60%), a 0.7 Million Ton Oil Equivalent (1 MTOE = 41.9 GJ) could be recovered from rice straw combustion. For aerobic and anaerobic processes, rice straw needs some pre-treatment and/or blinding with other materials

like cattle manure. On the other hand, solid manure can be used as a substrate for thermal processes, provided that it has low moisture content. Moreover, it can be used as a substrate for aerobic composting provided that it has the proper moisture content and the C/N ratio. Furthermore it can perfectly be used in anaerobic processes. Based on our results (*chapter* 5.1), a methane yield of 18.3 *l* [CH_4] kg^{-1} [solid manure] could be recovered from an accumulation system at 60 days filling time and 50^{o}C. For liquid manure, the only option is to use it in the anaerobic digestion process. Based on the results of Zeeman (1991) for liquid cattle manure at mesophilic conditions (30^{o}C) a methane yield of about 13 *l* [CH_4] l^{-1} [liquid manure] could be recovered from batch systems operated at a digestion time of 125 days and 9.5 *l* [CH_4] l^{-1} [liquid manure] from CSTR systems operated at 10 days HRT. On the other hand, a methane yield of 16 *l* [CH_4] l^{-1} [liquid manure] could be recovered from thermophilic digestion at about 10% TS from a CSTR system operated at 20 days HRT and a temperature of 50^{o}C (El-Mashad *et al.,* 2001).

Taking these criteria a framework for disposal of both rice straw and cow manure is proposed in Fig. 2.4. As can be seen the cow manure (liquid or solid) can be anaerobically digested to produce biogas (*i.e.* methane). With or without addition of rice straw, anaerobic digestion of solid wastes has been applied up to TS concentration of ca 40% (Ten Brummeler, 1993). The anaerobic effluent can be post-treated possibly together with fresh rice straw addition via the composting process. Rice straw size reduction could precede the composting process. Based on the results of Zhang and Zhang (1999), about 30% of the effective calorific value of rice straw can be recovered in the form of methane.

The objective of the post-composting is increasing the solid concentration via evaporation of water and reduction of pathogens and weed seeds by the increased temperature (Hamelers, 2001). In order to achieve these objectives enough biodegradable carbon should be left after anaerobic digestion. The latter can be done by controlling the anaerobic process or by addition of fresh rice straw to the effluent. Modelling could show the most effective process.

Blending of rice straw with anaerobic effluent increases nitrogen content of rice straw. Additional benefit is the increased total solid, which enhances the porous structure. Bhumibhamon *et al.* (1988) developed this process leading to good composting of rice straw and cattle manure. Haga (1990) showed the good characteristics of compost produced from rice straw and manure mixture (Table 2.8).

From previous sections, it can be said that rice straw and cattle manure available at small farms can be well disposed if both streams are combined.

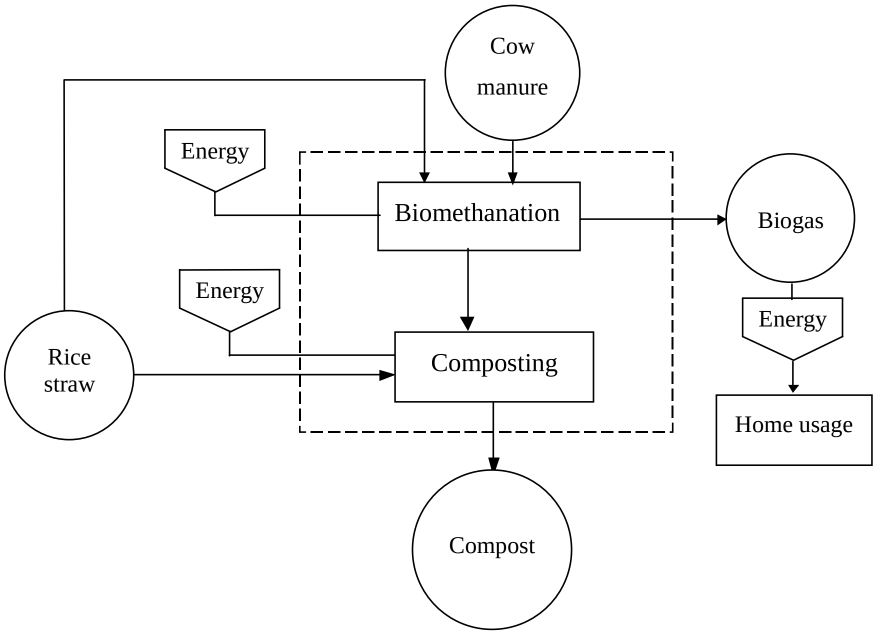


Figure 2.4. Flowchart of reuse of cow manure and rice straw.

Table 2.8. The characteristics of composted rice straw/manure mixture (Haga, 1990)

Moisture (%)	Total N (%*)	P_2O_5 (%*)	K_2O (%*)	CaO (%*)	MgO (%*)	Total C (%*)	C/N
77.6	2.16	2.15	2.31	2.31	0.96	36	16.7

* % of dry matter.

2.7. Conclusion and future perspective

It can be concluded that, the two major flows of unused agricultural wastes are rice straw and cattle and buffaloes manure. The combustion and gasification processes of rice straw have low efficiencies and have harmful effects on the environment as well as on burners and gasifiers. There are some techniques, which can be used to increase the efficiencies and to mitigate the environmental and operational problems of this process. However, a better option is to treat rice straw after blending with manure via biological conversion technologies. The most environmental friendly disposal of these two wastes is a two step process: firstly the anaerobic digestion of cow manure and rice straw; secondly composting the effluent of the anaerobic digestion together with the rice straw. To enhance the anaerobic digestion efficiency (*i.e.* net energy), solar energy can be used as a heating source for the biomethanation process. Utilisation of such renewable resources will lead to the saving of fossil fuel used for heating of substrates during the biomethanation process. The utilisation of such resources will also lead to reduce the environmental impact from using conventional energy resources. Based on these conclusions experimental and model research is developed. In this research thermophilic digestion of cow manure has to be investigated in more detail in connection to the consequences of the fluctuating energy supply from solar collectors.

CHAPTER 3: LITERATURE REVIEW

3.0. Introduction to the Chapter

In *chapter* 2, the thermophilic anaerobic digestion was considered as a core process for this dissertation. To increase the net energy production from thermophilic digestion, solar heating system was proposed. This *chapter* starts (in section 3.1) with a general background about the essence and the importance of the anaerobic digestion process. Moreover, the factors affecting the process and the most applied systems for animal manure digestion are also reviewed. Section 3.1 finishes with a mini review of the previous investigations on incorporation of solar energy in the anaerobic digestion process.

As high ammonia concentration is a key parameter affecting the process performance especially under thermophilic conditions, section 3.2 is dedicated to study the positive and the negative effects of the presence of ammonia on the digestion process. In this section, the mechanisms of the negative effect of ammonia on methanogenesis are also discussed together with the involvement of ammonia in the anaerobic digestion models. Finally, this section provides some practical procedures to alleviate the negative effects of high ammonia concentrations on the digestion process.

3.1. Anaerobic Digestion Process: A General Overview

This *chapter* concerns some general information on anaerobic digestion and the systems, which are commonly used for animal waste treatment. The essence and kinetics of the digestion process together with the most important factors affecting the process performance are reviewed. In addition, some ideas on the handling and utilisation of the produced biogas and the effluent (as fertilisers) are presented. Finally, implementation of solar energy in anaerobic digestion process is also reviewed.

3.1.1. Background

Anaerobic digestion (AD) is the process of biological degradation of organic matter, in the absence of oxygen, producing biogas, a mixture of methane, carbon dioxide and traces of other gases. AD is extensively applied for treatment of wastewater and agricultural wastes with 'relatively' high moisture content. As reviewed by Zeeman (1991), the digestion of agricultural residues was applied shortly after the Second World War during the period of energy shortage. Then the interest of the process application declined as a result of the reduction of the prices of conventional energy sources. After the energy crises in 1973, the interest of AD has been increased again. Many researches were carried out on the AD of animal wastes during the last four decades (*e.g.* Varel *et al.,* 1977; Van Velsen, 1981; Zeeman, 1991; Angelidaki and Ahring, 1994; Hansen *et al.,* 1998; Hill and Bolte, 2000).

The main objectives of digestion of animal slurry can be summarised as follow (Zeeman, 1991; Tafdrup, 1995; Lettinga, 2001):

1- Energy production and reduction of CO_2 emission by replacing fossil energy. Anaerobic digesters are attractive as sustainable energy conversion systems. This in fact is the mean aim for applying AD of animal slurries on farm (Zeeman, 1991). The net energy produced from the AD process depends on many factors, which are summarised in Table 3.1.1.

2- Reduction of the formation of malodorous compounds (Van Velsen, 1981).

3- Reduction of emission of greenhouse gases by reduction of CH_4 production and emission during manure storage.

4- Improvement of the fertilising value of farm manures (*e.g.* converting a large portion of organic nitrogen to ammonia), thus reducing consumption of the chemical fertilisers.

5- Reduction of pathogens and weed seeds of the effluent. The extent of removal of the pathogens depends on the digestion temperature.

6- Reduction of NH_3 emission in the case of using a combined digestion and storage system (*i.e.* accumulation system).

7- Enhancement of further processing of the animal slurry. For example, the dewaterability of the digested slurry is easier than that of undigested slurry.

Table 3.1.1. Parameters affecting the net energy production (*e.g.* Hawkes, 1980; Fischer *et al.,* 1986; Zeeman, 1991)

Parameters	*Items involved*
1-Feed stock characteristics	1- Type of animal from which the manure is collected. 2- The addition of bedding material with the manure. 3- Animal ration feeding. 4- Total solids content. 5- Volatile solids content. 6- Biodegradability of the substrate. 7- First order hydrolysis constant. 8- Ammonia concentration. 9- Viscosity and specific heat. 10- Influent temperature.
2- Reactor design	1- Reactor volume. 2- Reactor type (batch; accumulation; CSTR etc.,). 3- The reactor shape. 4- Type and thickness of the insulation. 5- Heating system and its efficiency. 6- Handling system of the manure (*e.g.* solid separation before digestion).
3- Operation conditions	1- Digestion or filling time in the case of batch or accumulation system, respectively. 2- Operation temperature (psychrophilic; mesophilic or thermophilic) 3- Loading rate (at a fixed substrate concentration) in the case of a CSTR. 4- Ambient temperature.

3.1.2. Chemical; physical and thermal properties of cattle manure

3.1.2.1. Chemical composition

As stated before, the chemical composition of the substrate is an important factor affecting the net energy production. Many factors affect the composition of cattle waste such as animal feeding; breeding system (*e.g.* using a bedding material or not); animal age and storage conditions (Zeeman, 1991). Cattle waste is a complex waste. It mainly consists of carbohydrate (cellulose and hemicellulose) next to fats and proteins. For example, cattle manure contains about 35% cellulose and hemicellulose and 8% lignin of TS (Wellinger, 1984). According to Zeeman (1991), cellulose and hemicellulose are anaerobically digestible while lignin is generally recognised as anaerobically inert. Chandler *et al.* (1980) found a reverse linear relation between the degradation of TS and lignin content.

3.1.2.2. Physical and thermal properties

The knowledge of physical and thermal properties of a material is important in designing efficient systems for handling and treatment of such material. As mentioned above, physical and thermal properties of the manure (*e.g.* viscosity and specific heat) affect the net energy production. For instance, higher viscosity of the material means high energy requirement to provide sufficient mixing for a digestion system (*e.g.* CSTR). Chen (1986) studied the rheological properties of sieved-beef cattle manure slurries at different total solid (TS) concentrations ranging from 2.6% to 19.3% and different temperatures (14 - 64^{o}C) and shear rates, ranging from 1 to 200 s^{-1}. To our knowledge, only a few reports about the rheological properties of dairy cattle manure are available (see *chapter* 4.1 of this thesis).

Achkari-Begdouri and Goodrich (1992) found an increase of the manure density of dairy cattle manure with an increase of its solids content in the range of about 2.5% to 14.2% TS. They also found a decreased linear relation between the increase of the total solids and both specific heat (at TS concentration $\leq$ 10% TS) and thermal conductivity (at TS concentration $\leq$ 8% TS). For beef cattle manure, Chen (1983) found a decrease of the specific heat with the increase of total solids in the range of 0.94 to 99.4% TS. Moreover he found also a decrease of both thermal conductivity and bulk density with increasing the TS concentration in the range of 2.8 to 95% TS.

3.1.3. The digestion process

The anaerobic digestion of complex organic wastes is a multistep process of series and parallel reactions (Pavlostathis and Giraldo-Gomez, 1991; Elmitwalli, 2000; Sanders, 2001). It consists of four major stages (see Fig. 3.1.1):

1- **Hydrolysis** in which particulate organic mater is converted by extracellular enzymes to monomer or dimeric components, such as amino acids, single sugars and Long Chain Fatty Acids (LCFA). Such compounds can pass the cell membrane.

2- **Acidogenesis** in which the hydrolysis products are fermented or anaerobically oxidised to Short Chain Fatty Acids (SCFA), alcohol and ammonia.

3- **Acetogenesis** in which alcohol and SCFA (other than acetate) are converted to acetic acid or hydrogen and carbon dioxide.

4- **Methanogenesis** in which acetic acid and CO_2 plus H_2 are converted to methane and carbon dioxide.

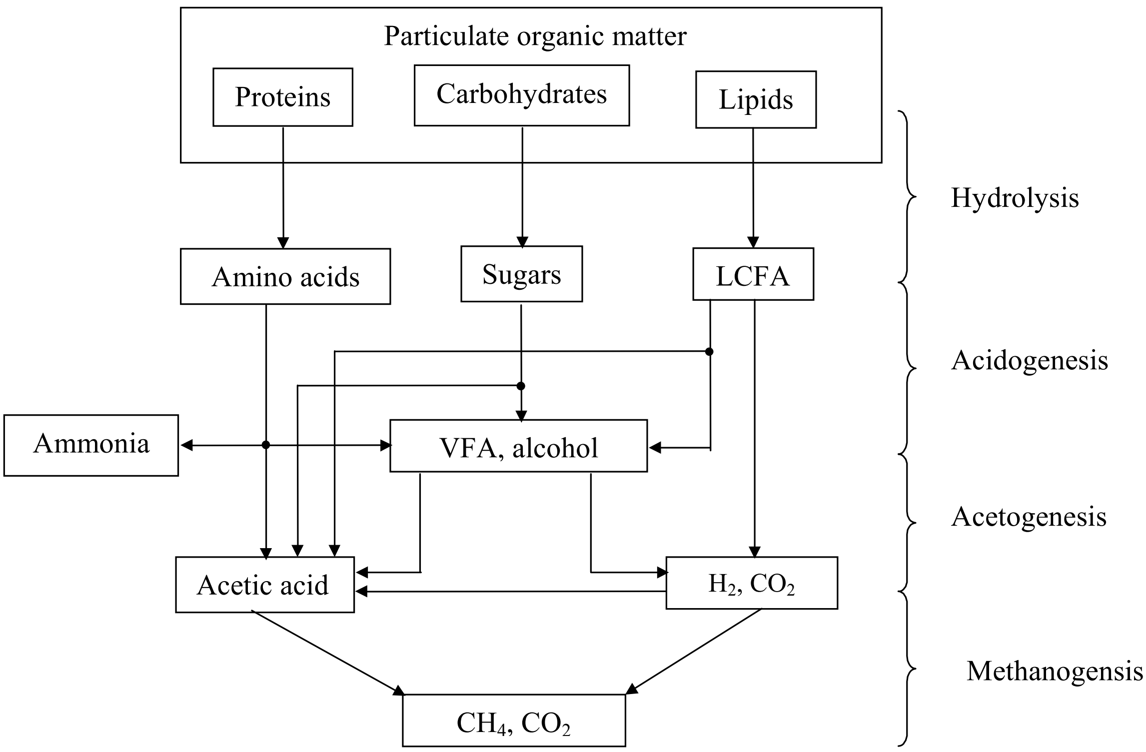


Fig.3.1.1. A simplified scheme for the anaerobic digestion of complex waste (adapted from Pavlostathis and Giraldo-Gomez, 1991; Elmitwalli, 2000; Sanders, 2001)

Generally, hydrolysis is the rate limiting step during the digestion of complex wastewaters and wastes like animal manures (*e.g.* Van Velsen, 1981; Zeeman, 1991).

3.1.4. Kinetics and modelling of the anaerobic digestion process

Many models have been developed and applied for different kinds of animal wastes. Hill (1983) mentioned that existing models fall into two categories:

1- Models that are highly accurate but need a lot of input parameters.

2- Simplified models, which are highly limited in their predictive ability.

For modelling of hydrolysis, first order kinetics are usually applied (*e.g.* Pavlostathis and Giraldo-Gomez, 1991; Sanders, 2001). This empirical approach is more useful for practice than the application of a mechanistic surface related model as developed by Sanders (2001). Latter model assumes that the hydrolysis rate depends on the surface available for enzymes. The available surface can not easily be measured for non-homogenous substrates like manure.

For modelling of methanogenesis, Monod -based kinetics are usually used. Hill (1983) presented a dynamic model to simulate non-steady as well as steady state digestion of animal wastes. He mentioned that any model that is derived for steady state conditions can not predict process failure under dynamic conditions. Hill (1982) reported a dynamic computer model that predicts digestor-operating conditions for the four major animal types (*i.e.* dairy, beef, poultry and swine). He validates the model at 35 and 60^{o}C using steady state data of pilot and full-scale methane fermentation plants. Hill and Bolte (1987) modelled the relationships between the VFA constituents in animal waste digesters based on experimental data of Hill *et al.* (1987) and literature data. The model predicts the VFA concentrations in successful and failing digesters. The failure of the digestor was predicted based on the ratio between propionate and acetate (P/A). For successful digestion, acetate concentration remains below 800 mg l^{-1}. A P/A ratio of approximately 1.4 is an indicator of digestor failure. Angelidaki *et al.* (1999) presented a comprehensive dynamic model of the process including the hydrolytic and fermentation process of 19 different chemical compounds. Hill *et al.* (2001) simulated the anaerobic digestion of dairy cattle and swine manure at low temperatures (10-20^{o}C). Batstone *et al.* (2002) presented a dynamic model (AD model No.1) for complex waste and wastewater. This model is a comprehensive model including all steps involved in the conversion of each constituent of a waste. More recently, Keshtkar *et al.* (2003) presented a mathematical model for non-ideal mixing continuos flow reactors for anaerobic digestion of cattle manure. In that model all steps of the digestion process were included.

Concluding, most of the above mentioned models were applied for either batch or completely stirred tank reactor (CSTR) systems. The dynamic model, including the hydrolysis, acidogenesis and methanogenesis, is preferred. Only a few references could be found on the modelling of an accumulation (AC) system but all on liquid slurries. Zeeman *et al.* (2000) modelled a well-mixed AC system treating sewage and swill. So, in *chapter* 5.3 of this thesis, a dynamic model for the process performance of a stratified AC system treating solid cattle manure is presented.

3.1.5. Anaerobic digestion systems for animal wastes

Many systems are applied for animal wastes (Zeeman, 1991). These systems can be classified as:

1- Batch reactors.

2- Continuous systems such as Completely Stirred Tank Reactor (CSTR) and plug flow reactors.

3- Accumulation systems (AC).

4- High rate systems like Upflow Anaerobic Sludge Blanket (UASB) reactors. This kind is usually used for the liquid fraction of the slurry.

The choice of any of the above systems depends on many factors such as:

1- The characteristics of the slurry (*e.g.* moisture content).

2- Technical and financial issues.

According to Lettinga (2001), batch, continuos solid state digesters and accumulation systems are relatively low in investment, operational and maintenance cost. The applied systems in the present study (*i.e.* batch, CSTR and AC) are described in detail.

3.1.5.1. Batch reactors

The system starts up with a certain amount of inoculum and is filled with fresh substrate. Such systems are used for solid state digestion "BIOCEL" (Ten Brummeler, 1993). This systems are simple in design and in operation and therefore potentially very attractive (Lettinga, 2001). Although the system is simple, it has two distinct phenomena: the accumulation of the intermediates in the first period (Veeken and Hammelers, 1999) and great differences in the gas production rate over the digestion time (Zeeman, 1991). To overcome the latter phenomenon, Zeeman (1991) proposed operating two different batch reactors out of phase. In practice for the digestion of biowastes 'BIOCEL', 14 digesters are consecutively used to give a continuously biogas production to be used in heat/power generation (Ten Brummeler, 1999).

3.1.5.2. Completely stirred tank reactor (CSTR)

This system is characterised by continuous and constant rates of both feeding and discharging. This assures a constant working volume. The system has a complete mixing of both substrate and bacteria. The Hydraulic Retention Time (HRT) is equal to the Solid Retention Time (SRT). At constant temperature and loading rate, a constant biogas production rate will be obtained. This system was applied by many authors (Van Velsen, 1981; Zeeman, 1991; Angelidaki and Ahring, 1994 and Hansen *et al.,* 1998) and applied most frequently in practice for sludge and slurry digestion. Fischer *et al.* (1986) mentioned on one hand the advantages of CSTR systems: (1) it can be used for manure with high-suspended solids concentrations; (2) it provides good contact between substrate and micro-organisms; (3) it provides a homogenous temperature throughout the tank; (4) it prevents scum layer formation. On the other hand, Fischer *et al.* (1986) mentioned the disadvantages of the CSTR systems: (1) the required energy for mixing; (2) the possibility of undigested sludge substrate leaving the digester.

3.1.5.3. Accumulation system (AC)

In the operation of an AC system a fraction of the reactor volume is always filled with inoculum, to provide enough methanogenic activity. AC and continuous stirred tank reactor (CSTR) systems are both continuously fed systems, but while the effluent from a CSTR is continuously removed, the effluent in an accumulation system is removed only once, at the end of the filling period. The CSTR has a constant digestion volume, while that of the AC-system is increasing in time. Wellinger and Kaufmann (1982) showed for the first time, the operation of an accumulation system (AC) for the digestion of liquid animal manure in practice. According to Zeeman (1991), the AC system is the simplest system for on farm practice as it combines storage and digestion. As manure cannot be used as a fertiliser during the winter period storage of some months is always necessary in medium and low temperature climates.

3.1.6. Factors affecting the process performance/stability

3.1.6.1. Interaction between operation conditions and feed composition (e.g. inhibition)

According to Van Velsen and Lettinga (1980) the major part of the environmental factors that affect the digestion performance concerns the composition of the feed (*e.g.* the presence of the inhibitory or toxic compounds like ammonia). Hawkes (1980) revealed that each species of the microbial population involved in the digestion process requires both carbon and nitrogen. If there is too little nitrogen present the bacteria will be unable to produce enzymes. On the other hand, high concentrations of nitrogen especially in the form of ammonia may cause inhibition of bacterial growth. The role of ammonia during anaerobic digestion will be discussed in detail (see *chapter* 3.2 of this thesis).

The digester's pH is affected by the interaction between the composition of the substrate (*e.g.* VFA and ammonia concentrations) and the operation conditions. The pH value may affect all process steps. For hydrolysis, Sanders (2001) mentioned that the simplest relationship between pH and enzyme activity is the 'bell shaped' curve with maximum enzyme activity at pH between about 6 and 8. She mentioned also that the net effect of pH on the hydrolysis rate is specified by the optimum pH of different enzymes present in the digester and the effect of pH on the substrate solubility. Koster (1989) mentioned that if the rate of methanogenesis is lower than acidogenesis, the pH might reach values below 6, which is fatal for methanogenic bacteria. An optimum pH near neutrality (*ca* 6.3-7.8) should be maintained in the anaerobic reactor (Grady and Lim, 1980; Van Haandel and Lettinga, 1994). As will be stated in *chapter* 3.2, the pH is an important parameter affecting the inhibition/toxicity of the system. Little inhibition by volatile acids will occur at neutral pH (Grady and Lim, 1980). Contrary to free ammonia concentration which is increased with pH, the un-ionised molecules of VFA (UVFA) is reduced with pH increase (Koster, 1989). In the digestion of cattle waste, high pH is frequently found even at lower HRT. During the digestion of cattle waste at thermophilic conditions (55-60^{o}C), Varel *et al.* (1977) revealed that the decrease of the process efficiency at the highest applied loading rates might be due to inhibition caused by high concentrations of ammonia rather than high concentrations of VFA. This is because high pH usually was remained, which reduces the UVFA.

3.1.6.2. Temperature

Temperature is an important factor affecting the performance of anaerobic digestion. Like many biological process, the digestion rate increases with increasing temperature up to an optimum (Hawkes, 1980). According to Grady and Lim (1980), the exact effect of temperature on a system performance depends on the characteristics of the waste and can only be determined experimentally. Temperature affects all process steps: it affects hydrolysis and bacterial growth (Sanders, 2001). Results of Veeken and Hamelers (1999) on digestion of 6 different biowastes showed that the Arrhenius equation perfectly describes (R^2 = 0.984-0.999) the relation between the first order hydrolysis constant (k_h) and the temperature (20-40^{o}C). Hashimoto *et al.* (1981b) studied the effect of temperature (30–60^{o}C) on the ultimate methane yield from beef cattle manure in batch fermentors. The results showed that temperature affects the production rate of CH_4 but does not increase the amount of CH_4 that can be produced from a unit mass of substrate.

Anaerobic digestion can be achieved under psychrophilic (< 25^{o}C), mesophilic (25-40^{o}C) and thermophilic (>45^{o}C) conditions (Van Lier, 1995). The digestion under mesophilic and psychrophilic conditions has been studied and reviewed in detail by Zeeman (1991).

Digestion under thermophilic conditions has many advantages and disadvantages as reviewed by many authors (*e.g.* Buhr and Andrews, 1977; Van Lier, 1995; Duran and Speece, 1997).

The advantages include:

1- Increased reaction rates as a result of the higher growth rates of thermophilic micro-organisms. But these micro-organisms have lower growth yields. The applicable residence time may approach one third of those under mesophilic conditions (Ahring *et al.,* 1995).

2- Improved solids-liquid separation. Mechanical de-watering of thermophilically digested sewage sludge is better than that of mesophilically digested sludge (*e.g.* Hobson *et al.,* 1981; Van Velsen and Lettinga, 1980). The opposite however is also reported. Maibaum and Kuehn (1999) mentioned that the dewaterability of effluent from thermophilic digestion (55^{o}C) of a mixture of chicken slurry and the organic fraction of municipal solid wastes was significantly worse than that from mesophilic digestion (35^{o}C).

3- Increased destruction of pathogenic organisms. According to Bendixen (1994) many pathogens in manure and slurry may survive for longer periods under mesophilic conditions. At thermophilic conditions (*i.e.* 50-55^{o}C) many pathogens are eliminated within some hours.

Possible disadvantages of the thermophilic process:

1- Higher energy requirement for system operation than at mesophilic conditions.

2- Poor effluent quality. Effluent has high concentrations of dissolved material (Buhr and Andrews, 1977). However, Ahring (1994) mentioned that no difference could be found in the effluent VFA of mesophilic and thermophilic digesters.

3- The lower growth yields of thermophilic micro-organisms result in longer start-up times and may make the process more susceptible to toxicity and to changes of temperature or other environmental conditions.

4- Poor process stability especially in the presence of high ammonia concentration (see *chapter* 3.2 of this thesis).

3.1.6.3. Detention time

The detention is one of the most important design parameters, which determines the economics of the digesters. Generally, while the methane production rate (l [CH_4] l^{-1} [reactor] day^{-1}) from the same substrate decreases with HRT the methane yield [l [CH_4] l^{-1} [substrate]) increases (*e.g.* Varel *et al.,* 1980; Zeeman, 1991). During mesophilic digestion of liquid piggery manure, at detention times exceeding 15 days there was only a slight increase in methane yield while a sharp decrease was noticed at detention times below 15 days (Van Velsen and Lettinga, 1980). According to Van Velsen and Lettinga (1980), the critical detention time depends on the chemical and physical characteristics of the waste. The results of Zeeman (1991), on the digestion of dairy cattle manure, showed that at higher detention time a considerable part of the gas originates from the suspended organic material. Various approaches have been proposed to reduce the HRT, such as increasing digester temperature and retaining biomass solids in the reactor to have longer SRT than HRT (Dugba and Zhang, 1999).

3.1.6.4. Mixing

Mixing is one of the parameters affecting the process performance. Grady and Lim (1980) mentioned that an adequate mixing prevents the development of unfavourable environments to methanogenic population (*e.g.* regions of low pH). Mixing also maintains a uniform temperature in the reactor and can help in exposing larger surface area of the substrate to biological attack as a result of breaking of the substrate particles. Moreover, mixing prevents the formation of the scum layer. Hobson *et al.* (1981) mentioned that if the digester is not properly mixed, layering occurs. Under such conditions there could be a series of cultures growing under different conditions at different reactor heights. Proper mixing of a digester depends strongly on the reactor shape (Metcalf and Eddy, 2003). For example, the rectangular tanks possess difficulties in mixing compared to cylindrical and egg-shaped reactors.

According to Verhoff *et al.* (1974) and Hobson *et al.* (1981), the most common applied systems for mixing the content of the digesters are (1) gas mixing, (2) mechanical stirring, and (3) mechanical mixing by means of sludge recirculation. The selection of the mixing system is affected by the density of substrate (*i.e.* solid concentration). According to Metcalf and Eddy (2003), the power input, which is affected by the applied mixing system, per unite volume of liquid can be used as a rough measure of mixing effectiveness.

The effect of mixing on the digestion process is rather contradictory (Stroot *et al.,* 2001). The results of Stroot *et al.* (2001) on the codigestion of municipal solid waste and biosolids (*e.g.* primary sludge) at 35°C, showed that by reducing the extent of mixing better performance was achieved. The manually shaking for 2 minutes daily achieved a better performance of the system. The results of Zeeman (1991), on AC system treating cow manure at 15°C and 100 day filling time using 15% inoculum, showed a negative effect of mixing on the breakdown of VFA especially propionic acid. She mentioned that the most likely explanation for that is the destruction of the adjacent structure between the H_2 consuming and propionic acid oxidising bacteria, which results in an increase of the H_2 concentration in the immediate vicinity of the latter bacteria. Consequently, retardation of propionic acid degradation occurs. In the digestion of olive mill wastewater in batch digestion at 35°C, Hamdi (1991) found that methane production decreases with increasing agitation rate. Lee *et al.* (1995) studied the effect of mechanical agitation (at 30 rpm for 10 minutes every 3 and 6 hours intervals) and gas recirculation (at 24 *l* of the gas for 10 minutes every 3 and 6 hours intervals) on the performance of a CSTR treating swine slurry at 38°C. The results showed that the highest methane production rate was achieved with gas recirculation at 6 hours intervals.

3.1.7. Gas handling and utilisation

According to Dohne (1980) the properties of biogas are similar to those of natural gas and it may be used in stead of natural gas. Most equipment used for natural gas can be operated with biogas after suitable modification. Methane produced by AD can be used to produce electricity for on farm use or sale to electricity companies. In this case, combined heat and power (CHP) generation could be applied. This implies that a part of the heat produced during electricity generation could be recovered for heating up the reactor. Consequently, little if any of energy could be added to the digester via other sources (*e.g.* direct biogas combustion or solar heating systems). The biogas needs to be scrubbed to remove impurities and may then be compressed and sold to fuel companies (Kelleher *et al.,* 2002). The upgrading of biogas depends on the application. According to IEA Bioenergy (2001), unlike using biogas in boilers, the application of biogas in vehicles engines requires a high upgrading of its quality (*i.e.* at least 95% methane). Bartlett *et al.* (1980) mentioned that for economical usage of biogas, the energy produced must be utilised on site. This is due to the excessive cost of storing. They revealed also that gas storing for seasonal use (*e.g.* drying) is not feasible. Hobson *et al.* (1981) mentioned that biogas may be used in a boiler to provide hot-water for some processes on farms or for digester heating. It can also be used to generate electricity or for powering machines. For large scale, they proposed that the gas can be purified and the methane fed into natural-gas distribution.

In many villages in rural areas, biogas could directly be used on-site for example for cooking, replacing the environmentally unfriendly burning of biomass or the use of non-renewable energy source. To optimise the net biogas yield, solar energy can be used for the energy requirements of the anaerobic digestion process. In this thesis the utilisation of solar energy as a heating source is a main aim of the investigations.

3.1.8. Effluent utilisation as fertilisers

As stated above the effluent from a digestion system (*i.e.* digestate) can be used as a hygienic organic fertiliser. According to Al Seadi (2001), the utilisation of the digestate as a fertiliser is the only sustainable application of it. Such application requires a high quality digestate to assure a save application for human and environment. According to Wellinger (1984), the anaerobic digestion of cattle manure efficiently reduces the number of pathogens bacteria and viruses. Moreover it improves the distribution of the fertiliser in the field as it reduces the viscosity. The reports about the effect of anaerobic digestion on fertiliser's value are rather conflicting. Allan (2003) concluded that there is no effect of the AD process on crop yield compared to raw manure at similar nitrogen rates. Moreover, there was no significant effect of AD on and viability of weed seeds compared to the raw manure. Based on experimental results obtained on tomato (Jothi *et al.,* 2003), a remarkable reduction in the nematode population was achieved with an increase in plant growth and yield after application of digested cow dung at 40 days detention time. On the other hand, the digestion process increases the ammonia concentration in the effluent, which may increase ammonia volatilisation. Many means can be applied to reduce this volatilisation. Yang *et al.* (2003) mentioned that ammonia volatilisation from application of cattle slurry can be reduced by injection of slurry into soils rather than application on surface.

3.1.9. Application of solar energy for heating biogas units

A few reports were found concerning the application of solar heating system in the anaerobic digestion of animal wastes. Hills and Stephens (1980) investigated the feasibility of using solar energy for batch heating of the influent for a mesophilic (35± 1^{o}C) 110 liter CSTR. In their study, breadbox and solar pond solar collectors were tested. The results showed that the breadbox collector was more efficient than the solar-pond collector. However, the solar bond was recommended for on farm application because the simplicity and the accuracy of the scaled up application of this collector. Alkhamis *et al.* (2000) designed and operated a lab scale digester (53 *l*) operated with a flat plate solar collector. A PID (proportional-integral and differential) controller was designed and installed to maintain a constant temperature of 40^{o}C in a water jacket around the digester. The results showed that using the PID controller, a prompt response could be obtained for a temperature change of less than 1 K. Moreover, an economic analysis of the incorporation of solar heating system was also carried out. This analysis showed an economic feasibility of the system under Jordan situation. Axaopoulos *et al.* (2001) developed a mathematical model for simulation of reactor treating swine manure heated with solar energy. The model was calibrated with experimental data from a 45 m^3 operated at 6 days HRT at an aimed temperature of 35^{o}C. The solar heating system consists of four flat plate solar collector of 8 m^2 each mounted on the reactor roof at a tilt angle of 22^{o}. The model results showed a well agreement with the measured values of the reactor temperature. A reactor temperature in the range of 32.4-34.2^{o}C could be achieved under Naxos Island (ϕ=37^{o} 06') in Greece.

3.2. Ammonia and Anaerobic Digestion Process: A Review

Abstract

Ammonia plays a key role in the performance and stability of anaerobic reactors operated on feedstocks with high content of protein and non-protein nitrogenous compounds. Many researchers studied the effect of ammonia on the performance of digesters treating agricultural as well as industrial wastes. The mechanism of the ammonia inhibition and the inhibition thresholds has also been studied. Many methods have been proposed to perform a successful digestion at high ammonia concentrations. This article reviews the published researches of the last four decades, which concern ammonia issues in the anaerobic digestion process, focused.

3.2.1. Introduction

Anaerobic digestion (AD) is a microbial degradation process of organic matter in the absence of oxygen. Such processes occur naturally in soils and in the digestive tract of ruminant animals. AD has been applied for many decades as a key method for stabilising wastes like sewage; industrial and agricultural wastes. Many factors affect the AD process performance and its stability, among them the feed composition and more especially the ammonia concentration. A high ammonia concentration not only adversely affects the anaerobic microflora (Van Velsen and Lettinga, 1980) but also affects the growth of mammalian cells (McQueen and Bailey, 1991). Ammonia frequently is considered as the primary cause of digester failure because of its direct inhibition of microbial activity. Rick *et al.* (1997) revealed that ammonia, present in poultry litter, may be an important inhibitory component that helps in breaking the cycle of *Salmonellae* transmission from litter to the birds. The initial inhibition of salmonella growth by ammonium depends on the extracellular pH and type of anion forming the ammonium salt.

A high concentration of ammonia can cause inhibition and also total cessation of the microbial conversion process (*i.e.* toxicity) depending on many factors such as the applied ammonia concentration; operation conditions (*e.g.* SRT, temperature etc.,) and most important, the extent of adaptation of the micro-flora to the applied ammonia concentration. According to Yang and Speece (1985) it is important to assess for a given toxic substance at a specific concentration range its reversible or irreversible toxicity characteristics. In case the toxicity is irreversible, the adverse operational consequences would be relatively serious for a microbial process with low cell synthesis characteristic like methanogenesis. For aerobic micro-organisms with comparatively high cell synthesis characteristics, the effect will be less dramatic. Biomass re-growth would be prohibitively long with a low cell synthesis microbial process. However, if the toxicity is reversible, re-growth would not be a major factor. The presence of a high concentration of a toxic compound obviously will cause causes a decrease in the rate of methane production (Benjamin *et al.,* 1984). If the compound is extremely toxic, it may lead to kill of all the organisms for at least one step in the metabolic sequence. In this case, methanogenesis can not resume. Unless the toxic compound is removed or detoxified from the wastewater, *e.g.* by dilution or by reactions, which lower its activity in the aqueous phase, such as sorption at the digestion process can not be attained. If the compound does not completely inhibit the metabolism, some bacterial activity will remain depending on the SRT. The culture even may eventually acclimate to the compound leading to a similar specific metabolic rate as in the absence of the toxicant. Alternatively, methanogenesis may proceed at a lower specific rate than in the absence of toxicant.

The main aim of this article is to review the most important aspects of the role of ammonia in anaerobic digestion processes:

1- The need of presence of ammonia for metabolism of organisms.

2- The mechanisms of its inhibition, which is very important to get a good process performance and high stability and possibilities to model the ammonia effect on the anaerobic digestion process.

3- Relation between operational conditions and ammonia concentration.

4- Adaptation of the micro-flora to high ammonia concentrations.

5- Methods, which can be applied to alleviate ammonia inhibition.

6- Furthermore, it is aimed to find out the research gaps in the issues concerning the ammonia and anaerobic digestion process.

3.2.2. Positive effect of ammonia presence

3.2.2.1. Importance of ammonia for metabolism of organisms

The nitrogen needed for their growth, the bacteria obtain directly from NH^+_4-N or by the activity of proteolytic and deaminative bacteria in the digester system and the presence of proteins and non-protein nitrogenous compounds in the feedstock. These compounds are first degraded to amino acids, then are deaminated to ammonia or when urea is produced, as metabolic end product, ammonia will result from the direct conversion of this compound. All bacterial steps require ammonia-N as nitrogen source for cell mass synthesis. Fermentative bacteria can usually utilise both amino acids and ammonia but methanogenic bacteria merely use ammonia for the synthesis of bacteria cells (Hobson and Shaw, 1971; Hobson and Richardson, 1983). Total ammonia nitrogen (TAN) concentrations of approximately 200 mg l^{-1} are believed to be beneficial to the anaerobic process (Sung and Liu, 2001). This depends on the substrate concentration and the yield. For the effluent from the anaerobic digestion of swine manure, ammonia accounts for more than 70 percent of the nitrogen in the digester effluent and only 43 percent in the influent (Fischer *et al.,* 1979). These amounts of ammonia in fact depend on the substrate. Most of the original influent organic nitrogen will be converted to NH^+_4-N and a small percentage (6.5 %) will be used in cell production (HulshoffPol, 2000). A bacterial nitrogen content is calculated to be 0.124-g [N] g^{-1} [bacteria] according to the empirical formula ($C_5H_7NO_2$) as established by Loehr (1977) and used by Hill and Cobb (1996). Based on the stoichiometry presented by Hill (1982) and Husain (1998), the amount of bacteria per mole for different types of substrate is shown in Table 3.2.1.

Table 3.2.1. The amount of different bacteria species produced from different substrates

Numbers of moles Substrate (s)	*Bacteria type*	*Mole of bacteria*
1 mole of glucose	Acedogenesis	0.1115
1 mole of propionate	Hydrogenogenesis	0.0458
1 mole of butyrate	Hydrogenogenesis	0.0545
2.073 mole of hydrogen + 1 mole of carbon dioxide	Homoacetogenesis	0.0487
3.813 mole of hydrogen + 1 mole of carbon dioxide	Hydrogen methanogenesis	0.022
1 mole of acetate	Acetogenesis	0.022

Exceptionally high ammonia-nitrogen concentrations (exceeding 3000 mg l^{-1}) generally occur in liquid animal manure. These wastes usually contain nitrogen in the form like urea; proteins and amino acids. The organic nitrogen compounds are degraded during digestion (mineralization) and released the nitrogen in the inorganic ($NH^{+}{}_{4}N$) form (Velsen and Lettinga, 1980). Table 3.2.2 summarises the typical nitrogen and ammonia contents for various types of animal wastes.

Table 3.2.2. Typical nitrogen and ammonia content for various animal wastes (Hill and Cobb, 1996)

Waste type	*g [TKN] g^{-1} [TS]*	*g [$NH^{+}{}_{4}$-N]g^{-1} [TS]*
Swine	0.0600	0.0308
Beef feedlot (confinement)	0.0262	0.0154
Dairy	0.0214	0.0115
Poultry (broiler)	0.0500	0.0308
Poultry (caged layer)	0.0800	0.0308

Contrary to Hill and Cobb (1996) who mentioned that there exists a typical characteristics composition of manure, Zeeman (1991) reported that the composition of animal manure depends on the type of animal, the feeding strategy applied, the animal housing and the slurry collection and storage system. She reported literature data for the nitrogen and ammonia content of cow slurry found in various countries (Table 3.2.3).

Table 3.2.3. The composition of cow slurry in different countries (Zeeman, 1991)

Country	*g [TKN]g^{-1} [TS]*	*g [$NH^{+}{}_{4}$-N]g^{-1} [TS]*
The Netherlands	0.04632	0.03097 -0.0316
Great Britain	0.05159	0.02513
USA	0.03288	0.006803
India	0.014101	n.d
Switzerland	0.04334 - 0.04349*	0.02013- 0.02288 *
Germany	0.03294-0.051829	0.00706-0.02769

n.d not determined
* g g^{-1} [VS].

Based on the substrate composition of the biodegradable fraction, the theoretical amount of ammonia produced under anaerobic conditions can be calculated. Assuming a complete conversion (100% biodegradability), the amount of CH_4; CO_2 and ammonia (NH_3) produced can be calculated according to Cobb and Hill (1990a):

$$C_aH_bO_dNz+[b-4(a-\frac{d}{2})-3z]\,H^+ \rightarrow (a-\frac{d}{2})CH_4+(\frac{d}{2})\,CO_2+(z)\,NH_3.$$

The reaction shows that z moles of NH_3 are produced per each mole of the organic substrate. Sobotka *et al.* (1983) determined the molecular formulas of the organic matter fraction (VS) for a number of wastes and Cobb and Hill (1990a) used these formulas for calculating the theoretical methane production. Similarly we calculated the theoretical NH_3 production. Molecular formulas of wastes according to Sobotka *et al.* (1983) and calculated amounts of CH_4; CO_2 and NH_3 according to Cobb and Hill (1990a) are presented in Table 3.2.4.

Table 3.2.4. The estimated waste composition formulas and calculated CH_4 and NH^+_4-N production during anaerobic digestion of different wastes

Waste type	*Molecular formula / 1 C (According to Sobotka et al., 1983)*	*Theoretical CH_4 produced ($l\ g^{-1}$ [VS] destroyed)*	*Theoretical CO_2 produced ($l\ g^{-1}$ [VS] Destroyed)*	*CH_4 (%)*	*Theoretical NH_3 produced (mg g^{-1}[VS] destroyed)*
Dairy	$CH_{1.773}O_{0.83}N_{0.056}$	0.471	0.334	58.5	34.23
Beef	$CH_{1.82}O_{0.88}N_{0.042}$	0.44	0.346	56.0	25.09
Swine	$CH_{1.655}O_{0.767}N_{0.0634}$	0.515	0.320	61.7	40.23
Poultry	$CH_{1.864}O_{0.909}N_{0.113}$	0.407	0.339	54.6	64.11
Municipal solid waste	$CH_{1.59}O_{0.567}N_{0.024}$	0.698	0.276	71.7	17.76

It can be seen from Table 3.2.4 that the digestion of poultry wastes gives the highest ammonia content and municipal solid waste gives the lowest. From the data in Tables (3.2.2, 3.2.3 and 3.2.4), it can be concluded that despite the mentioned variations in the composition of animal manure from country to another, knowledge of the composition gives the potential capability for calculating the expected amount of ammonia produced in the anaerobic digestion of that particular waste (assuming 100% biodegradability).

3.2.2.2. Ammonia and the buffer capacity of a system

One of the most important parameters affecting digester stability concerns the system buffer capacity. The bicarbonate-ammonia buffer is the primary parameter controlling the pH and process stability (Georgacakis *et al.* 1982). The buffer capacity of a solution is determined from the concentrations of each buffer present, their pK values and the pH of the solution (Butler, 1964). As a result of the extremely high concentrations of ammonia-nitrogen prevailing in the mixed liquid on manure digester, the system has a high buffer capacity and consequently a dramatic pH-fall below a certain critical value for instance about 6 can hardly occur (Van Velsen and Lettinga, 1980). Obviously (*e.g.* Georgacakis, 1982) the formation of VFAs may decrease the buffering capacity of the system according to Equation 3.2.1 but the formation of NH_3 which produced at the same time will increase the bicarbonate concentration according to Equation 3.2.2:

$$HAc + NH_4HCO_3 \rightarrow NH_4Ac + H_2CO_3 \qquad (3.2.1)$$

$$\begin{array}{llllll} NH_4^+ & + OH^- & + H^+ & + HCO^-{}_3 & \Leftrightarrow NH^+{}_4 + HCO^-{}_3 + H_2O & \\ \downarrow & \uparrow & \uparrow & \downarrow & & (3.2.2) \\ (NH_3 + H_2O) & (CO_2 + H_2O) & & (salt) & & \end{array}$$

However, in case the $NH^+{}_4$-N would raise to much high values (*e.g.* Albertson, 1961*)* that a significant rise in pH would occur, *i.e.* beyond the normal optimum range for methane bacteria, the bacterial activity will decline which then results in an accumulation of VFAs. These accumulating VFA tend to reduce the pH allowing the bacteria time to recover and to establish a new stability at a lower gas production level. For wastes with a low nitrogen content, the original bicarbonate alkalinity of the waste is the chief source of process stability, *i.e.* to prevent pH drop due to an accumulation of VFAs. The concentration of the ammonium ion and of free ammonia are interrelated via the digester mixed-liquor pH according to the following equation (Kroeker *et al.,* 1979):

$$NH_3 \leftrightarrow NH_4^+ + OH^- \qquad (3.2.3)$$

When the pH decreases the equilibrium will shift to the right. Since solubility of gases compounds like H_2S; H_2; CH_4 and CO_2 decreases with increasing temperature, gases will be easily stripped from the solution and consequently their concentrations in the effluent of the thermophilic reactors are lower than in the effluent of mesophilic digester. The decreased solubility of CO_2 implies a comparable higher reactor pH under thermophilic conditions (Van Lier, 1995). However a substantial stripping of NH_3 can only be achieved at significantly higher pH values (Liao *et al.,* 1995).

3.2.3. Negative effects of ammonia (*i.e.* inhibition/toxicity)

Unlike the importance of the presence of ammonia for bacterial growth, high concentrations of ammonia may cause a serious disturbance in the process performance *i.e.* cause a distinct decrease of the microbial activities (Sung and Liu, 2001), just like higher concentrations of alkaline earth-metal salts, heavy metals and sulfides it may lead to toxicity or inhibition problems (Kroeker, 1979). Inhibition is usually indicated by a decrease in the steady state methane gas production rate and increasing VFA concentrations, while toxicity is manifests a total cessation of the methanogenic activity (*e.g.* Kroeker, 1979). An anaerobic digestor is rather well comparable with a rumen system. In the ruminant stomach absorption of ammonia through the rumen wall seems to prevent the occurrence of inhibitory concentrations (Zeeman, 1991).

The process stability in an anaerobic digestor depends upon maintenance of a delicate biochemical balance between the acidogenic and methanogenic organisms. Process instability manifests usually by a rapid increase in the concentration of volatile acids with a concurrent decrease in methane gas production. Such an unstable situation may happen as a result of ammonia levels up to 3200 mg l^{-1} at even these methane still can be produced (Robertson *et al.,* 1975). The strong inhibitory effect of $NH^+{}_4N$ clearly was demonstrated by the studies of Koster (1989) in batch VFA-Fed experiments at various ammonia concentrations (0.68-2.601

g l^{-1}) and conducted with granular sludge originated from an industrial UASB reactor treating wastewater from beet-sugar factory. Figure 3.2.1 shows the assessed negative correlation between the activity (assuming the activity at 680 mg l^{-1} is 100%) and total ammonia concentration.

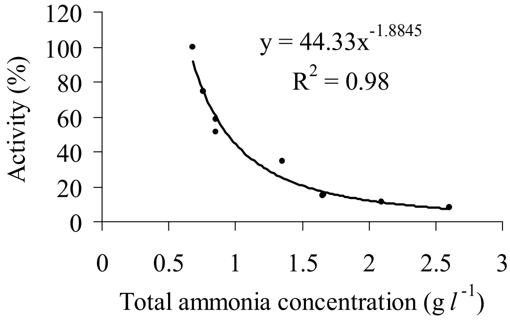


Fig.3.2.1. Relation between the activity and total ammonia concentrations (Koster, 1989)

Krylova *et al.* (1997) observed a significant decrease in the number of proteolytic and methanogenic bacteria when $NH^{+}_{4}N$ concentrations exceeding 7800 mg l^{-1} were presented in a digestor treating poultry manure. Chamy *et al.* (1998) demonstrated that the high protein content of wastewater from the salmon industry leads to distinct limitations of the anaerobic digestion of this wastewater at 37°C, mainly due to the accumulation of ammonia in the media. They found a negative correlation between the biodegradability and total solid content. At concentrations exceeding 3500 mg l^{-1}, it was not possible to increase the total solids to obtain the same biodegradation as at lower ammonia concentrations.

3.2.3.1. Factors affecting ammonia inhibition/toxicity

Temperature is one of the factors affecting the threshold of ammonia inhibition/toxicity. The pH also plays a significant role in the inhibitory/toxic threshold. There is an incessant relation between increase of the free ammonia concentration and both temperature and pH. According to Mc Carty and McKinney (1961) and McCarty (1964) ammonia nitrogen concentrations in the range 200-1500 mg l^{-1} have no clear adverse effect on methanogenesis, while concentrations in the range of 1500-3000 mg l^{-1} are inhibitory at pH exceeding 7.4. Ammonia concentrations exceeding of 3000 mg l^{-1} are supposed to be toxic regardless of the pH and free ammonia concentrations exceeding 150 mg l^{-1} are severely toxic. In spite of the high alkalinity, the final pH depends the operating conditions, being lower as the HRT was decreased due to the lower ammonia concentrations (Guerrero *et al.,* 1999). However the effect of HRT can not be separated from the temperature effect. In the next sections, the relation between ammonia and both mesophilic and thermophilic conditions is elucidated.

Mesophilic condition

Different inhibition thresholds of total ammonia or free ammonia have been reported in literatures for different operation conditions. Under mesophilic condition, inhibitory NH_3 concentration of 80-150 mg [N] l^{-1} at a pH of 7.5 have been reported (Koster and Lettinga, 1984; Braun *et al.,* 1981). At 30-35°C, De Baere *et al.* (1984) mentioned that the free ammonia-N should be kept below concentration of 80-100 mg l^{-1} for optimal system performance. Free ammonia concentrations higher than 200 mg [N] l^{-1} were shown to be inhibitory for the digestion of wastewaters from the sea food processing industry at 37°C (Omil *et al.,* 1995).

As mentioned above, high ammonia concentrations are found naturally in animal wastes. However, many researches were carried out by adjusting ammonia concentration. Sievers and Brune (1978) studied the effect of different C/N ratio in the anaerobic digestion of swine waste at $35^oC\pm1$ and at 15 days retention time. The C/N ratio was adjusted by the addition of urea or glucose. The results showed that at C/N ratio of 1.7, methane production fell to zero and the free ammonia level rose to over 500 mg l^{-1}. The addition of urea to mesophilic digestion (35^oC) of cattle manure (Sterling *et al.,* 2001) resulted in a decrease of total biogas production rate by a proximately 30% after addition of 1500 mg l^{-1} and 50% after addition of 3000 mg l^{-1} compared with the rate at control digesters.

The total ammonia concentrations at which process failure occurs in the mesophilic temperature range are much higher for the digestion of pig manure than for cow manure (Zeeman *et al.,* 1983; Zeeman *et al.,* 1985a). According to the authors cow manure apparently contains compounds having an additional effect on the inhibition by ammonia. Possibly, compounds formed during the acidification step exert an inhibition action on methanogenesis. They did not define such compounds. For swine manure digestion, at 35^oC and 15 days HRT, Fischer *et al.* (1979) and Fischer *et al.* (1984) found that a stable process could be achieved even at NH_4^+-N and pH increased up to 4.24 g l^{-1} and 7.9 respectively. While at NH_4^+-N concentration of 6083 mg l^{-1} the digester was unstable.

At 36^oC, Vidal *et al.* (2000) mentioned the ammonia production has two antagonistic effects: free ammonia causes a partial inhibition of the process but it also controls the pH and therefore inhibition by accumulation of VFA is avoided and the overall process improved. In their experiments on acetic acid solution at 35 ^oC, Kroeker *et al.* (1979) revealed that methane production rate was decreased to about one third of its value by increasing the ammonia concentration from 2070 to 5020 mg l^{-1}. However at ammonia concentration 5020 mg l^{-1}, the free ammonia concentration was 257 mg l^{-1} the toxicity or total cessation of bacterial activity was not evidenced.

The addition modes of ammonia and operation conditions affect the process performance. Bhattacharya and Parkin (1989) studied the effect of slug and continuous additions of ammonia on anaerobic acetate and propionate utilisation at 40; 25 and 15 days SRT. Massive slug doses of ammonia immediately stop bacterial activity. Smaller slug doses give lower-SRT systems a better chance to recover. At 15 days SRT, slug addition of 8000 mg [ammonia] l^{-1} was tolerated. This may be explained by the higher dilution rates, at the shorter SRT, accelerate recovery from toxic slugs. With continuous addition of ammonia, high-SRT systems can tolerate higher concentrations than low-SRT systems. For the treatment of fishmeal processing wastewaters, Guerrero *et al.* (1997) used a Upflow Anaerobic Filter (UAF) operated at 37 ^oC. The change of recycling ratio (F/R) from 1:10 to 1:5 after 215 days from the start up caused the appearance of high concentrations of VFA (especially butyrate and valerate), ammonia (up to 6.5 g [N-TA] l^{-1} and 1.3 g [N-FA] l^{-1}).

Thermophilic compared to mesophilic condition

Like mesophilic conditions, many researches were done to study the effect of high ammonia concentrations on the performance of thermophilic anaerobic digestion of different substrates.

In thermophilic (60^oC) anaerobic digestion of cattle waste, Varel, *et al.* (1977) found that at the high loading rates (3 days SRT) the system efficiency decreased. They attributed this to the inhibition caused by a general overabundance of solutes such as ammonia, and fatty acids. Swine manure fermentation at 55°C (Van Velsen, 1979a) and 40°C (Stevens and Schulte, 1979) resulted in lower gas production than fermentation at 35°C. The lower gas production was attributed to free-ammonia inhibition. Sánchez *et al.* (2000) observed a decrease of methane production when the temperature was increased from 35°C to 60°C during batch digestion of cattle manure at digestion time of 33 days. This behaviour is due to the higher degradation rate of organic nitrogen to ammonia nitrogen observed at 60°C. Angelidaki and Ahring (1994) studied the effect of temperature in the range 40-64°C on the anaerobic digestion of cattle manure at two ammonia concentrations (2500 and 6000 mg [N] l^{-1}) in continuously fed lab scale reactors at 15 days HRT. The results demonstrated a higher sensitivity to increased temperatures at higher ammonia loads. Poor performance (rapid increase of VFA concentrations) was observed at free ammonia concentrations exceeding approx. 700 mg [N] l^{-1}.

In the digestion of source separated biowaste at 37°C and 55°C**,** Gallert and Winter (1997) stated that the effluent from the thermophilic reactor has a high ammonia concentration compared to the mesophilic one, this may be presumably from protein degradation. In the mesophilic and thermophilic reactors, the calculated free ammonia concentrations were 30 and 126 mg l^{-1} respectively; these free ammonia concentrations are too low to influence methanogenesis significantly. On the other hand, Kayhanian (1994) studied the operational and inhibitory limits of ammonia concentration in high-solids anaerobic digestion of the biodegradable organic fraction of MSW at 54-60°C. He observed that total ammonia concentrations of 1000 mg l^{-1} (calculated free ammonia 60 mg l^{-1}) or higher adversely affect the performance of the high-solids anaerobic digestion process. Wile the optimum total ammonia concentration 600-800 mg l^{-1} (calculated free ammonia 22-24 mg l^{-1}), process failure occurred at 2500 mg l^{-1}.

Figure 3.2.2a shows the relation between effluent VFA and total ammonia concentrations for different substrates under different experimental conditions. Although there is a clear trend between both parameters for every individual study, the effects of both temperature and pH under every experiment conditions have not to be overlooked. So, the VFA concentrations were plotted (Fig.3.2.2b) against the calculated free ammonia concentrations for the same experimental conditions shown in Fig. 3.2.2a. As can be seen from Fig. 3.2.2b that there is a high correlation (r = 0.74) between both parameters.

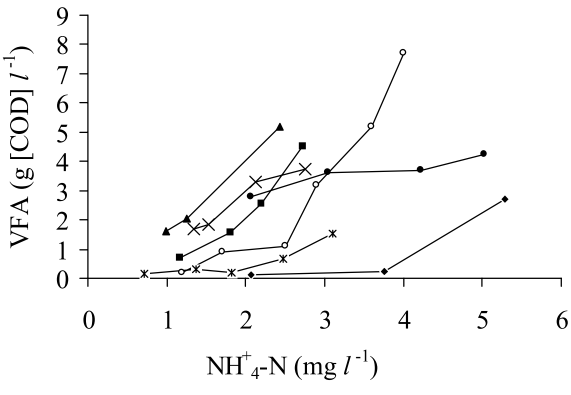


Fig.3.2.2a. Relation between VFA concentrations and total ammonia concentrations: ▲, data of Varel (1977) at 3 days HRT and 60°C; ×, data of Varel (1977) at 6 days HRT and 60°C; ■, data of Varel (1977) at 9 days HRT and 60°C; ○, data of Zeeman (1991) at 10 days HRT and 30°C; ●, data of Kroeker (1979) at 15 days HRT and 35°C; жс, data of Fujishima et al (2000) at 15 days HRT and 35°C; ♦, data of Van Velsen (1981) at 15 days HRT and 30°C

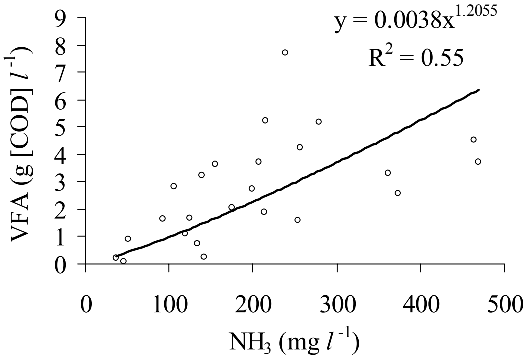


Fig.3.2.2b. Relation between VFA concentrations and free ammonia concentrations

It can be concluded that the published results are rather conflicting regarding to total ammonia inhibition. However, it should be mentioned that free ammonia is the main inhibitory component for methanogenesis instead of total ammonia. This is due to the fact that the bacterial cell wall is far more permeable for un-dissociated molecules than for ions (Van Velsen and Lettinga, 1980).

From the results above it is clear that unlike the importance of the presence of ammonia for a successful performance of anaerobic digestion, the presence of high concentrations of ammonia / free ammonia concentrations will adversely affect the process performance. But the extent of the detrimental effect depends highly on factors like the adaptation of microflora.

3.2.4. Adaptation of microflora

3.2.4.1. Importance of adaptation

Although many reports show the importance of bacterial acclimation, most of these reports do not show whether the adaptation is the result of a metabolic change of the already present microflora or from growth of new culture adapted to a different ammonia concentration. The results of Zeeman *et al.* (1985b) obtained during the digestion of cow manure clearly show that adaptation to high ammonia of 3000 mg [NH^+_4-N] l^{-1} at 50°C can indeed take place. Whether the adaptation is the result of internal changes in the predominant species of methanogenic bacteria, or of a shift in the methanogenic population, was not clear. According to Koster (1986) the adaptation of the methanogenic population to high ammonia concentrations can not be attributed to growth of a new type of bacteria, but to slow adaptation of the original population during the period of stagnation of the methane production which lasted approximately 6 months in his experiments.

Ammonia nitrogen becomes toxic or inhibitory in a digester above a threshold limit of 1700 to 1800 mg l^{-1} only when the rate of its formation exceeds the rate of the acclimation of methane forming organisms (Van Velsen, 1981). According to Melbinger and Donnellon (1971) an ammonia concentration of 2700 mg l^{-1} does not affect the gas production in acclimated high-rate digesters. The feasibility of methane fermentation for treating a waste depends largely on the ability of methanogenic bacteria to acclimate to adverse environmental factors. Van Velsen 1981; Van Velsen and Lettinga (1980) found clear evidence for this in daily fed experiments with digested sewage sludge conducted at an ammonia nitrogen concentration exceeding 1700 mg l^{-1}. Inhibition manifested but this inhibition only is temporary provided sufficient time is taken to allow the bacteria to acclimate. This acclimation explains the successful digestion found at ammonia concentrations exceeding 1500 mg l^{-1} at 30°C at pH levels exceeding 7.5 (Van Velsen, 1979a and b) and even at ammonia concentrations of 1900-2000 mg l^{-1} as found by Koster (1986). Van Velsen (1981) also studied the influence of ammonia nitrogen concentrations in the range 2070-5290 mg l^{-1} in a continuous digestion experiments with piggery waste at 30°C. The digester population already was adapted to 1900 mg [ammonia nitrogen] l^{-1}. The results obtained show that the gas production found at 2070 mg [ammonia nitrogen] l^{-1} is 33 % higher than that at 5290 mg [ammonia nitrogen] l^{-1}. Koster and Lettinga (1988) studied the effect of extreme ammonia concentrations in the batch digestion of potato juice at 30°C. They found that methanogenesis still occurred even at 11.8 g [ammonia-N] l^{-1}, but at 16 g [ammonia-N] l^{-1} little if any methanogenic activity was left. In their experiments the adaptation potential of the granular sludge used in that study was 6.2. They observed that after an adaptation process for a period of about117 days during which the sludge was enabled to adapt to various ammonia concentrations exceeding the initial toxicity threshold level of 1.9 g l^{-1} a 6.2 times higher NH^{+}_{4}-N concentrations than the initial toxicity threshold level could be accepted. Even at extremely high ammonia concentrations toxicity is reversible to a great extent. On the other hand the results of Koster and Lettinga (1988) also show that the maximum specific methanogenic activity (SMA_{max}) of adapted granular sludge (2.315 g l^{-1}) on potato juice as feed decreases as the increasing of total ammonia concentration (Fig. 3.2.3). In Fig. 3.2.3 also the data of Van Velsen (1981) found during the batch of piggery waste with sludge adapted to 2.42 g l^{-1}.

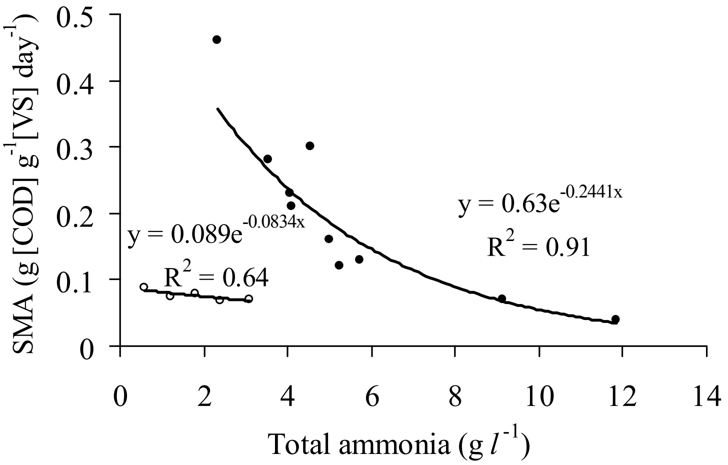


Fig.3.2.3. Relation between MSA and total ammonia concentration: ●, granular sludge adapted to 2.315 g l^{-1} (Koster and Lettinga, 1988); ○, digested piggery waste adapted to 2.42 gl^{-1} (Van Velsen, 1981)

The results of Hashimoto (1986) obtained in continuously fed digesters and conducted with cattle waste, show that ammonia inhibition begin at about 2500 mg l^{-1} with sludges not previously acclimated to high ammonia concentrations under thermophilic (55°C) and mesophilic (35-37°C) conditions as well. The inhibition begins at about 4000 mg l^{-1} for thermophilic fermentors using sludge previously acclimated to ammonia concentrations between 1400 and 3300 mg l^{-1}. Webb and Hawkes (1985) studied the variation of methane yield during the digestion of poultry manure at different influent concentration and ammonia nitrogen levels at 35°C. Addition of extra NH_4Cl to raise the ammonia concentration to 3744 mg l^{-1} gave 81 % inhibition in the gas production with using a seed adapted to approximately 960 mg [NH_4^{+}-N] l^{-1}, whereas no inhibition manifested with using a seed adapted to approximately 3390 mg [NH_4^+-N] l^{-1}. In the digestion of swine manure at 35°C and 20 days detention time, a stable operation was achieved at a free ammonia concentration of 663 mg l^{-1} (Georgacakis *et al.,* 1982). The stability at such high free ammonia levels was attributed to the acclimation of the bacteria to high nitrogen levels and the high bicarbonate alkalinity. They considered the system in steady state condition when the biogas production, pH and ammonia remained unchanged for at least 35 days during an acclimation period of 70 days. Lay *et al.* (1997) studied the effect of ammonia in the range 1670-6600 mg l^{-1} on methane production from a high-solids (4-10% TS) organic waste at 37°C at 20 days HRT. Rather than free ammonia concentrations, high ammonium concentrations were found the more significant factor in affecting the methanogenic activity of a well-acclimatised bacterial system. Free ammonia was the most affecting component when using a non-acclimated bacterial culture. Sung and Liu (2001) studied the effect of the total ammonia nitrogen on acetoclastic methanogenic activity, in the digestion of soluble non-fat dry milk, at 55°C and HRT of 7 days. The total ammonia (TAN) background concentrations in the reactors were 400,1200 and 3050 mg l^{-1}. The results showed that biomass acclimated to higher TAN could alleviate the inhibition effect of high ammonia concentration. The lethal TAN concentrations were around 10,000 mg l^{-1} regardless of acclimation concentrations. For effluents from fish meal plant, which contain ammonia concentration up to 4 g l^{-1}, Soto *et al.* (1991) considered anaerobic digestion only feasible after an adaptation period.

3.2.4.2. Required period for adaptation

The time required for complete acclimation increases with the ammonia concentrations (Robbins *et al.,* 1989). Adequate acclimation may take about 2 months or even longer. Once adapted to an ammonia-nitrogen concentration of 1700 mg l^{-1} the methanogenic sludge also seems to be acclimated to significantly higher concentration, *viz.* of 2750 mg l^{-1} at the minimum (Van Velsen and Lettinga, 1980). Adaptation of bacteria to increasing ammonia levels depends largely on the rate of ammonia formation, which on its turn is determined by the loading rate and the hydraulic retention time. In un-adapted cultures, free ammonia levels of about 150 mg l^{-1} cause growth inhibition, but much higher concentrations can be accommodated by methanogenic cultures which have undergone a period of gradual adaptation. The stable operation of mesophilic anaerobic fermentation at ammonia concentrations exceeding 2000 mg l^{-1} can be attributed to the acclimation of methanogens to high ammonia concentrations (*e.g.* Braun *et al.,* 1981). According to Van Velsen (1981) a digester, seeded with sewage sludge, treating liquid pig manure can be started up successfully at sludge loads up to 0.126 kg [COD] kg^{-1} [VS] day^{-1}. The digester should be fed at this loading rate for a period of 2.5 months in order to allow the sludge to adapt.

Van Velsen (1979,b) studied in batch experiments at 30°C ± 2 the effect of ammonia concentration up to 5000 mg l^{-1} on digested sewage sludge (acclimated to 815 mg[ammonia nitrogen] l^{-1}) and digested piggery waste (acclimated to 2420 mg [ammonia nitrogen] l^{-1}). The substrate consisted of a mixture of acetic, propionic and butyric acids. When using digested sewage sludge, methanogenesis still can take place at ammonia concentrations as high as 5000 mg l^{-1}, although the lag phase amounted to 50 days. Once the methane formation has begun, the VFA were eliminated simultaneously, except propionic acid. Propionic acid was not eliminated at all even after 90 days of incubation. With digested piggery manure, the methane production started immediately after incubation at ammonia nitrogen concentrations in the range 605-3075 mg l^{-1}. However, the maximum gas production rate was found to decrease slowly with increasing ammonia nitrogen, while a lag-phase manifests for the elimination of propionic acid. Acetic acid and butyric acid were eliminated simultaneously, whereas the elimination of propionic acid started only after 18 days of incubation. Due to the differences of the acclimation thresholds for each sludge type it is not possible to conclude whether the type of the sludge or the acclimation threshold is the reason for the aforementioned differences.

Figure 3.2.4a shows the duration of the lag phase period found in the experiments conducted by Van Velsen (1979,b), for digested sewage sludge adapted to ammonia concentration of 815 mg l^{-1}, and those of Rollon (1999), conducted with a sludge adapted to low ammonia concentration of 46 mg l^{-1}. A linearly relation between the length of lag phase and the total ammonia concentration was found by Van Velsen (1979,b), while Rollon (1999) found that the lag phase length did not vary significantly with ammonia concentrations < 1.5 g l^{-1}. The lag phase observed during the experiments carried out by Rollon was considerably longer as compared to those of Van Velsen. An increase of the lag phase with increasing free ammonia concentrations (Fig. 3.2.4b) was also observed by Poggi-varaldo, *et al.* (1991) in batch digestion of acetic acid. It was not clear why no increase in lag phase with increase of ammonia was observed by Rollon (1999) but was for an adapted sludge as observed by Van Velsen (1979,b).

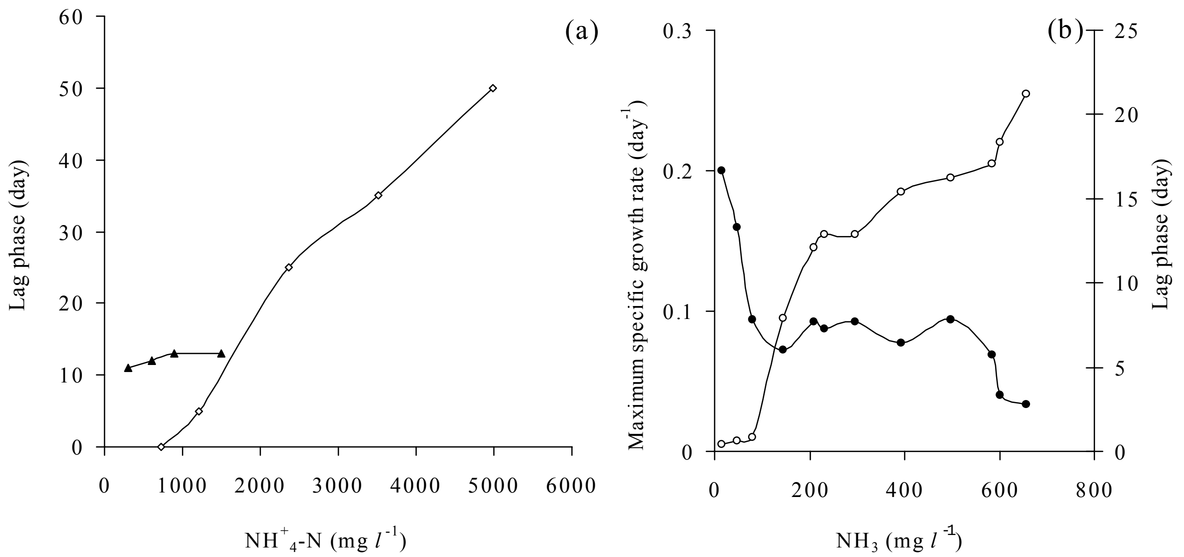


Fig.3.2.4a. Relation between lag phase and total ammonia concentration: ▲, data of Rollon (1999);◊, data of Van Velsen (1981). Fig.3.2.4b.Relation between free ammonia concentrations and duration of the lag phase and maximum specific growth rate (data of Poggi-varaldo et al., 1991): ○, lag phase; ●, maximum specific growth rate

Experiments under thermophilic conditions (55°C) with swine manure (62.5 g [VS] l^{-1} and at free-ammonia concentration of 410 mg l^{-1}) were conducted at 25 days HRT (Hashimoto, 1983). Stable conditions could only be achieved after an adaptation period of more than 170 days. Methanogenic activity is almost nil at a concentration of 6000 mg [NH_4^+-N] l^{-1}, recovery starting only after 38 days (Soto *et al.,* 1991). A stable methane production in the digestion of cattle manure at 15 days HRT and 55°C could be maintained at ammonia concentrations up to 6000 mg [N] l^{-1} after 6 months of operation (Angelidaki and Ahring, 1993a). In a UASB reactor treating cattle manure at 55°C, Borja *et al.* (1996) showed that ammonia concentrations of 5000 mg [N] l^{-1} can inhibit the process but a stable digestion could be maintained with ammonia concentrations up to 7000 mg [N] l^{-1} after 6 months of operation.

From the above, it is clear that adaptation is of big importance to obtain successful digestion at high ammonia concentrations of 1700 mg l^{-1} and higher. The adaptation period depends on the applied ammonia concentration and organic loading rate.

3.2.5. Mechanisms of ammonia inhibition

Various researchers speculated about the mechanism of the ammonia inhibition during the anaerobic digestion process. Evidence has been obtained that ammonia may inhibit all these sub-processes of the digestion process, *i.e.* hydrolysis, acidogenesis and methanogenesis.

3.2.5.1. Mechanisms on hydrolysis and acidogenesis

There are only few reports dealing with the effect of ammonia on the hydrolysis step. According to Zeeman (1991) not only methanogenesis but also hydrolysis is inhibited at high ammonia concentrations. She observed this in digestion experiments with cow manure in a CSTR at 30^{o}C. Also from the results of Van Velsen (1981) obtained in the digestion of liquid swine manure, a more or less linear drop in the hydrolysis was found in relation to both total and free ammonia concentration (see Table 3.2.5). Our recent results (*chapter* 4.3) in the batch digestion of dairy cattle manure at 20 days SRT showed a strong negative linear relation between the hydrolysis constant and both the total and the free ammonia concentrations (Table 3.2.5). The results also showed that acidogenesis apparently is the rate-limiting step at free ammonia concentrations ≤ 0.25 g l^{-1}. Although the results did not reveal the mechanism of the ammonia effect on hydrolysis, Zeeman (1991) explained the possible effects of ammonia on the hydrolysis as follows:

1- NH_4^+-N inhibition.

2- Inhibition due to accumulation of intermediates like VFAs and H_2.

3- The simultaneous presence of higher concentrations of NH_4^+-N and accumulated intermediates causes the inhibition of the hydrolysis.

4- Inhibition due to specific organic compounds present in urine instead of due to NH_4^+-N.

Table 3.2.5. Relations between both total hydrolysis (H_R, % of total COD added) and hydrolysis constant (K_h, day^{-1}) and total and free ammonia concentrations ($g\ l^{-1}$).

Relation	*Reactor*	*Digestion time / HRT (days)*	*Temperature (^oC)*	*Substrate*	*NH^+_4-N range ($g\ l^{-1}$)*	*NH_3 range ($g\ l^{-1}$)*	*Reference*
$H_R = -3.71[NH^+_4\text{-}N] + 77.1$; $R^2 = 0.99$ $H_R = -76.31[NH_3] + 73.2$; $R^2 = 0.97$	CSTR	10	30	Piggery waste	2.07- 5.29	0.047- 0.2	Van Velsen (1981)
$H_R = -4.16[NH^+_4\text{-}N] + 22.8$; $R^2 = 0.87$ $H_R = -57.3[NH_3] + 19.3$; $R^2 = 0.74$	CSTR	10	30	Cow manure	1.2- 4.9	0.04- 0.26	Zeeman (1991)
$K_h = -0.02\ [NH^+_4\text{-}N] +0.09$; $R^2 = 0.95$ $K_h = -0.24\ [NH_3] + 0.09$; $R^2 = 0.97$	Batch using adapted sludge to 1.1 g $[NH^+_4\text{-}N] l^{-1}$	20	50	Dairy cow manure	1.06-3.77	0.079- 0.235	*Chapter* 4.3
$K_h = -0.02\ [NH^+_4\text{-}N]+ 0.1$; $R^2 = 0.92$ $K_h = -0.23\ [NH_3] + 0.1$; $R^2 = 0.94$	Batch using adapted sludge to 1.1 g $[NH^+_4\text{-}N]\ l^{-1}$	20	60	Dairy cow manure	1.22-3.56	0.146- 0.359	*Chapter* 4.3

Based on a modelling study of Vavilin *et al.* (1996), a NH_3 concentration of 990.5 mg l^{-1} seems to be inhibitory for hydrolysis step of cattle manure. Inhibition of the enzyme activity and the reduction in the number of methanogenic bacteria (determined via the most probable number per cm^3) was observed by Krylova *et al.* (1997) during the digestion of poultry manure. The authors did not mention the types of enzymes, which were affected by high concentrations of ammonia. In our recent results (*chapter* 4.2), we concluded that not the enzyme activity but the enzyme production is affected by high NH_3 concentrations. However the mechanism of hydrolysis inhibition is not clear. The results of Rollon (1999) on the anaerobic degradation of fish processing wastes showed that increasing $NH^+{}_4N$ concentrations (600-1500 mg l^{-1}) resulted in a slow decrease of the methanogenesis rate. Protein hydrolysis becomes inhibited at a concentration of 600 mg l^{-1}. Fujishima *et al.* (2000) mentioned that increasing the concentration of ammonia nitrogen from 740 to 3500 mg [N] l^{-1}, in the digestion of sewage sludge using batch experiments at 35°C, resulted in significantly decrease of glucose degradation rate. They attributed this to an inhibitory effect on the glycolytic pathway via which glucose is acidified. The degradation of glucose is slightly more inhibited at 55 than at 37°C at an ammonia concentration of 3-3.7 g l^{-1} (Gallert and Winter, 1997). According to Koster and Lettinga (1988), based on batch tests at 30°C, contrary to methanogenesis, the acidogenic population in the granular sludge was hardly affected by high ammonia concentrations in the range 4051-5734 mg [N] l^{-1}, while the methanogenic population lost 56.5 % of its activity under these conditions. Guerrero *et al.* (1999) studied the anaerobic hydrolysis and acidogenesis of wastewaters from a fishmeal factory in a CSTR at 37°C and 55°C and at HRT ranging from 6 to 48 hr. The results showed that most of protein was converted into VFA and ammonia, even at the lowest HRT. Consequently, the content of total ammonia in these reactors reached extremely high values in both cases (15-17 g l^{-1}), which corresponds to free ammonia concentration up to 0.66 g l^{-1} at 37°C and 1.64 g l^{-1} at 55°C. Although a more efficient operation of both hydrolysis and acidogenesis was achieved at 55°C, they recommended mesophilic systems if a two-phase system was considered for the overall treatment of these effluent, since toxic effects from ammonia would impede a stable operation in the methanogenic reactor at thermophilic conditions.

3.2.5.2. Mechanisms on methanogenesis

Two mechanisms for the adverse effect of high ammonia concentrations on methanogenesis have been reported. A high concentration of ammonia can either affect acetate or hydrogen consuming bacteria. According to Zeeman (1991), the mechanism of $NH^+{}_4$-N inhibition is more complicated than the relation between residual VFA concentration and $NH^+{}_4$-N concentration. Wiegant and Zeeman (1986) proposed a scheme (see Fig.3.2.5) for the NH_4^+-N (100- 4500 mg l^{-1}) inhibition in the thermophilic digestion of cow manure. This scheme illustrates an inhibition of the hydrogen consuming methanogens by NH_4^+-N, while the acetate consuming bacteria are not directly inhibited by NH_4^+-N. The propionate accumulated via ammonia-promoted inhibition of the hydrogen-utilising bacteria may play an important role in the accumulation of acetate in stressed digesters. According to them, the energy of the propionic breakdown strongly depends on the hydrogen partial pressure. The accumulation of propionic acid inhibits the thermophilic acetate utilising methanogens. When both propionic acid and NH_4^+-N are present, the breakdown of acetic acid is even more inhibited. They attributed the resistance of acetate utilising bacteria to the adaptation of the inoculum to ammonia concentration of 3000 mg [N] l^{-1}. Figure 3.2.5 shows the proposed scheme by Wiegant and Zeeman (1986).

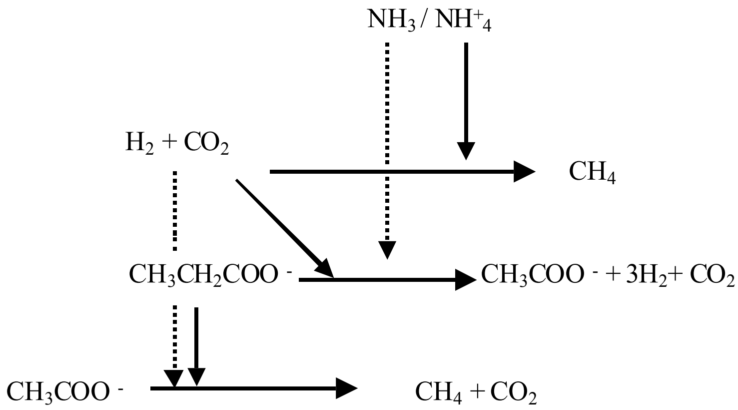


Fig.3.2.5. A proposed scheme for the inhibitory action of ammonia in thermophilic digestion of cow slurry. Horizontal arrows: inhibited reaction; vertical arrows: inhibiting action. Possible inhibiting actions are dotted (Wiegant and Zeeman, 1986).

Hobson and Shaw (1976) investigated the effect of NH_4Cl on pure cultures of *Methanobacterium Formicicum* at 38 ^oC, isolated from piggery wastes. The results show that at ammonia nitrogen concentration of 2471 mg l^{-1} partly inhibited growth of *M. Formicicum* and gas production at pH 7.1; while ammonia nitrogen concentrations of 3294 mg l^{-1} completely inhibit the bacterium. Hobson and Shaw did not attempt to distinguish between the ammonium ion and free ammonia concentration. According to Koster and Lettinga (1984), the acetate-consuming methanogenic bacteria are more strongly affected by ammonium-nitrogen than hydrogen-consuming methanogenic bacteria at 30^oC above the threshold level of about 1700 mg l^{-1}. They concluded this based on the observation that acetate accumulates during batch digestion of a mixture of acetic, propionic and butyric acids. The authors used granular sludge obtained from an industrial UASB reactor treating beet-sugar wastewater. Koster and Koomen (1988) mentioned that at a temperature, pH and ammonia concentration of 37 ^oC, 7.8 and 4.9 g l^{-1} respectively, washout of hydrogenotrophic methanogens from digesters treating slurries in CSTR system will not occur. The authors attributed this to the higher HRT of such systems (at 20-30 days) compared to the minimum required cell retention time (*i.e.* 30.1 h). Robbins *et al*. (1989) studied the effect of adding ammonia concentrations (*viz.* 0.8,1.6,2.4,3.2 and 4.8 g l^{-1}) on the performance of anaerobic digestion of dairy cattle manure at 37 ^oC and HRT 16 days. The results show clearly that the methanogenic activity of acetate utilisation was most affected by changes in the total ammonia. The results also showed that, after each change in the ammonia level in the digester, acetate utilisation was inhibited but after acclimation it returned to a normal value. The maximum growth rate of unacclimated mesophilic acetoclastic methanogens was reduced by free ammonia concentration in a three-stage pattern (Poggi-varaldo *et al.,* 1991). The authors calculated the maximum growth rate from the accumulative biogas production after a lag phase period. The length of such a period depends on the free ammonia concentration (see Fig.3.2.4b). Figure 3.2.4b shows these stages: rapid inhibition (0-113 mg l^{-1}), plateau (114-540 mg l^{-1}) and further rapid inhibition (541-700 mg l^{-1}). The stage pattern of inhibition suggested that more than one mechanism of free ammonia concentration is acting on the mixed culture. In the first stage, a cation exchange-distortion caused by ammonia can be considered as a probable cause for inhibition of methane producing bacteria. The inhibition in the third stage could be related to osmotic effects of the ammonium salt or to a mechanism of inhibition by ammonium ion at the level of the bacteria membrane site where methane synthesis occurs. According to the author the second interpretation would require further research. Hunik *et al.* (1990) measured the maximum growth rate of acetoclastic methanogens at extremely high NH^{+}_{4}-N concentrations in the range between 7700 and 10400 mg l^{-1} and at pH between 7.8 and 7.93. They used an inoculum from laboratory-scale poultry manure digester. The inoculum contained about 10000 mg l^{-1}. The results support the hypothesis of an ammonia-facilitated H^{+} toxicity (Sprott and Patel, 1986). They attributed the increase of the cell pH to the increase of ammonia concentration. According to Angelidaki and Ahring (1993,a), the SMA of acetate-utilising methanogens at 55°C, present in a lab scale CSTR treating cattle manure, decreased at ammonia concentration of 6 g [N] l^{-1} more than the hydrogenotrophic population. Hansen *et al.* (1998) found that at a free ammonia concentration of 1.1 g [N] l^{-1} or more, acetate constituted the main part of the VFA, during the digestion of swine manure in CSTR at different temperatures (37,45,55 and 60°C). This indicates that acetate utilising methanogenic bacteria are primarily inhibited. The H_2 -utilising methanogens had a much higher apparent specific growth rate than acetate utilising methanogens. The apparent specific growth rate was calculated from methane production rate (MPR) assuming MPR is proportional to the growth of methanogenic bacteria. The results show that the acetate-utilising methanogens can be regarded as rate limiting during anaerobic digestion of swine manure with a high content of ammonia. Ammonia toxicity tests on the acetate-and hydrogen-utilising populations were performed by Borja *et al.* (1996) using digested cattle manure at 55°C. The results show a higher sensitivity of aceticlastic methanogens compared to the hydrogenotrophilic methanogens. The specific growth rate for aceticlastic methanogens was halved at ammonia concentrations of 4000 mg [N] l^{-1} (*i.e.* NH_3 of 280 mg l^{-1}), compared to 7500 mg [N] l^{-1} (*i.e.* NH_3 of 520 mg l^{-1}) for the hydrogenotrophic methanogens. It should be mentioned that the main differences between the experiments of Borja *et al.* (1996) and those of Wiegant and Zeeman (1986) are the amount and the type of inoculum used and the background concentrations of ammonia in the inoculum.

From the aforementioned mechanisms on the various process steps, one can conclude that acetoclastic methanogens can be negatively affected by high ammonia concentrations either directly or indirectly (*i.e.* via accumulation of propionic acid). Moreover, although ammonia adversely affects the hydrolysis, the mechanism of such effect is still not completely clear.

3.2.6. Kinetics and modelling

Ammonia is believed to affect the kinetic parameters of the anaerobic digestion process. Hobson (1983*)* concluded that inhibition appears to start at ammonia concentration about 1800 mg l^{-1}. He said that the inhibition is so far confined to the methanogenic bacteria. He proposed an equation, which applies to acetate or hydrogen utilisation as fellow:

$$\mu^{*}{}_{m} = \mu_{m} - \mu_{m}\frac{([NH_4^{+} - N] - 1800)}{1700} \qquad (3.2.4)$$

u^*_m is the actual um of the bacteria at an ammonia concentration between 1800 and 3500 mg l^{-1}.

Below or above these concentrations u^*_m is either u_m or zero. Hobson used experimental data obtained from anaerobic digestion of piggery waste at HRT of 16.3 days at

35 °C with ammonia concentration of 2155 mg l^{-1} to test this equation. The results showed that the residual acids averaged a concentration of 336 mg l^{-1} (as acetic acid) and the acids concentrations predicted by the model 230 mg l^{-1}. According to Hobson (1983) propionate will be almost absent in the uninhibited piggery waste digestions until near the washout retention time. Degradation of butyrate would be affected only at short retention time by ammonia inhibition. Hashimoto (1982) used Contois kinetics, which uses a kinetic parameter K, to predict the gas production from cattle manure. This kinetic parameter is reported to increase with the increase of the influent VS. According to Zeeman (1991) in case the NH_4^+-N concentration and VS concentration are correlated, K could be correlated with the NH_4^+-N. The results of Zeeman (1991) in cattle manure digestion up to 7% VS indicated that not the VS concentration but the NH_4^+-N concentration of the manure is affecting the process performance. Hill (1985) mentioned that the use of the equation of Andrews (1968) could be extended to any type of substrate. For animal waste digestion, VFA and ammonia are the two inhibitors. Hill and Barth (1977) modified this equation by incorporating the inhibition of unionised ammonia and VFA in the growth kinetics of the methane formers as fellows:

$$\mu = \frac{\mu_m}{1 + \frac{K_s}{VA} + \frac{VA}{K_{ia}} + \frac{NH_3}{K_{i2}}} \qquad (3.2.5)$$

Hill and Cobb (1996) proposed a simplified model for nitrogen relationships within anaerobic fermenters. In this model they assumed hat more than 99% of ammonia nitrogen in the fermenter is in the ionic form (NH_4^+-N) and less than 1 % in the NH_3-N form. This was assumed from the fact that normally the pH of operating fermenters in the range 6-7.5, far below the pK_a of ammonia (*i.e.*, pK_a = 9.24). With this simplification, the mathematical representation of the nitrogen accounts only for the influent nitrogen concentration; effluent nitrogen concentration, HRT; biological conversion of ON-N to NH_4^+-N and bacterial synthesis of NH_4^+-N to ON-N. Angelidaki *et al.* (1999) developed a comprehensive model describing the bioconversion of complex substrate to biogas. The free ammonia concentration, pH and temperature are included in the model as modulating factors. The model shows that there exists a clear correlation between the level of inhibition and the free ammonia concentration. As long as the free ammonia concentration is kept below 800 mg l^{-1} the process is running relatively undisturbed. However, when free ammonia concentration increases over 800 mg l^{-1} the process is inhibited. These results are accordance with their previous results (Angelidaki and Ahring, 1993,a and 1994). Siegrist and Batstone (2001) modelled the inhibition of ammonia with a non competitive inhibition term ($K_{I,NH3}$). The results of the model show that, at steady state, for a mesophilic sewage sludge reactor operated at 20 days HRT acetic acid starts to accumulate if free ammonia exceeds 35 mg l^{-1} (NH_4^+-N of 1700 mg l^{-1} and pH 7.3). For thermophilic sewage sludge reactor operated at 6 days HRT acetic and propionic acid starts to accumulate if free ammonia exceeds 140 mg l^{-1} (NH_4^+-N of 1500 mg l^{-1} and pH 7.4). $K_{I,NH3}$ values were 6 and 36 mg l^{-1} for mesophilic and thermophilic condition respectively.

It can be concluded that some of the available models are empirical and that none of them do consider the state of the sludge, whether it is adapted sludge or not. As we did not evaluate the available models, we can not recommend any of them. A more detailed study is needed to evaluate them for the digestion of different substrates. We are the opinion that the sludge adaptation-state should be considered.

3.2.7. Ammonia mitigation

Although high ammonia concentrations are considered as inhibitory or even toxic for the anaerobic digestion microflora, many researches have been dedicated to find means to improve the performance of the digesters treating wastes exposed to high ammonia concentrations. These means can be consisted of either adjustment of the influent composition or of the operation condition and/or by using some additives (*e.g.* chemicals).

3.2.7.1. Control of operation conditions

The problems associated with ammonia inhibition in a high-solids anaerobic digestion process, can be reduced by one or more of the following methods (Kayhanian, 1994):

1- Dilution of the digester content in order to lower the ammonia concentration in the liquid phase.

2- Adjusting the C/N ratio of the feedstock.

3- Using some kind of external ammonia absorption process.

The rate of ammonia formation of the inhibition threshold possibly can be controlled by applying a proper feeding regime to the digester *e.g.* using the (volatile acid / alkalinity) ratio as a key parameter (Melbinger and Donnellon, 1971). In batch and in continuos experiments with piggery manure conducted at 37 ^{o}C, Braun *et al.* (1981) showed that by means of pH –controlled operation and a suitable choice of temperature, inhibition of NH_4^+-N could be prevented. Consequently, in this way the need to dilute the substrate with high ammonia contents could be prevented. For digestion of swine manure with low solid concentration at 35 ^{o}C, Hill and Bolte (2000) found that NH_4^+N never exceeds 700 mg l^{-1} *i.e.* a concentration that does not cause any inhibition effect to the process. Although they could provide the biological and technical criteria of using dilute waste, they did not give the economic feasibility of the system. Since the addition of diluting water may improve the gas yield but also increases the required size of the digester to treat a fixed amount of waste, and the amount of energy required to heat that amount of waste to operational temperature. To overcome these dilution problems, an increase of the HRT can be considered instead. To optimise digester operation it is important to be able to estimate how the extent the gas yield may be depressed at a given NH_4^+N concentration (Webb and Hawkes, 1985). Chamy *et al.* (1998) mentioned alternative solutions to resolve the ammonia inhibition problem, viz. the pH control of the media so as to diminish the effect of free ammonia; implement a nitrification-denitrification process or to strip out the ammonia. Angelidaki and Ahring (1994) mentioned that decreasing the process temperature could be a good option for overcoming ammonia inhibition.

In lab-scale experiments, Cintoli *et al.* (1995) studied the ion exchange pre-treatment of pre-screened piggery wastewater followed by anaerobic treatment in UASB and UASB-AF reactors. Granular sludge, with three months acclimation period, was used for starting up UASB and UASB-AF reactors. They concluded that the combination of ion exchange by zeolite and anaerobic digestion in a UASB or UASB-AF reactor represents a solution to achieve a substantial reduction of the pollution of piggery wastewaters. This combination can achieve a reduction of the ammonium concentration from 1500 mg l^{-1} to 400-500 mg l^{-1} and organic removal up to 80 % at a 2 days HRT.

The possibility of protecting methanogenic bacteria from the inhibitory action of organic matters (*e.g.* phenol, long chain fatty acids) and inorganic compounds (*e.g.* heavy metals, sulfide and ammonia) has been studied (Hanaki *et al.,* 1994) by cell immobilisation using polyvinyl alcohol (PVA) beads. The results obtained show that, while inhibitory effect of some compounds can be reduced by immobilising the bacteria, the inhibition action by ammonia could not be reduced because a high pH within the bead can not relieve the inhibitory effect caused by free ammonia. Hansen *et al.* (1999) found that the addition of granules from a thermophilic UASB treating VFA, or increasing HRT from 15 days to 30 days, positively affects the methane yield from swine manure at 55 ^{o}C. The latter may be attributed to the increased SRT. So it can be concluded that increasing the SRT represents an option to mitigate the negative effect of high ammonia concentrations

Another approach is the co-digestion concept. In batch studies on the co-digestion of cattle slurry with poultry manure, Callaghan *et al.* (1999) found that the co-digestion of cattle slurry with poultry manure (7.5 and 15 % TS) gives higher cumulative methane production while the system with the lower concentration of poultry manure gives higher specific methane yield comparing with cattle slurry alone. This was thought to be due to high concentration of free ammonia concentration. The precise concentration of unionised ammonia at which inhibition occurs is open to debate. With 7.5 %TS chicken manure and cattle slurry mixture, the NH_4^+-N concentration was 3250 mg l^{-1} and NH_3 concentration 263.5 mg l^{-1}, whereas with 15 % TS chicken manure and cattle manure mixture these values were 8800 and 1087 mg l^{-1} respectively.

3.2.7.2. Utilisation of additives

Different additives have been proposed as helpful means to mitigate the inhibition/toxic effects of ammonia. Angelidaki and Ahring (1993b*)* studied the effect of the addition of the clay mineral bentonite and bentonite-bound oil (BBO) on thermophilic anaerobic digestion (55^{o}C) of cattle manure at different ammonia concentrations (2500 to 5000 mg l^{-1}). They observed a positive effect of bentonite and BBO addition; *i.e.* addition of these components resulted in more rapid recovery of the process. When ammonia was increased directly from 2500 to 6000 mg l^{-1} neither bentonite nor BBO had a positive effect on the alleviation of ammonia inhibition. However, they did not come up with an explanation of the effect of bentonite on ammonia inhibition. They attributed the effect of bentonite to the presence of cations such as Ca^{2+} and Na^{+} since these ions seem to counteract the inhibitory effect of ammonia (MCarty and McKinney, 1961;Sprott and Patel, 1986). In the anaerobic digestion of poultry manure, Krylova *et al.* (1997) found that the addition of 10 %(w/v) of powdered phosphorite (a rock with a high concentration of phosphates) enhanced the production of biogas and methane at 7 .8 g l^{-1}. Hansen *et al.* (1999) studied several methods to improve the methane yield from swine manure at 55 ^{o}C at high ammonia concentrations (6000 mg [N] l^{-1}). Firstly, addition of 1.5 % (w/w) activated carbon, secondly, addition of 10 % (w/w) glauconite (greenish ferric-iron silicate mineral) and finally, addition of 1.5 % (w/w) activated carbon and 10 % (w/w) glauconite. The results show an increase of methane yield to about 1.88,1.34,2.91 times the value without any additions respectively.

3.2.8. Post treatment

There are many methods to reduce effluent ammonia concentrations. Many researchers have studied this issue in detail. It would be too long to mention even a part of the results published under this topic. But Siegrist (1996) mentioned the feasible chemical and biological processes to recycle or eliminate ammonium from digester supernatant:

- Precipitation of ammonium as $MgNH_4PO_4$ by addition of phosphoric and magnesium oxide. This method is feasible but most expensive due to required chemicals as well as drying of the precipitate but the precipitate (struvite) is a useful product.

- A partial removal of ammonia could be achieved by ammonia stripping followed by a biological polishing process.

- Nitrification of ammonium in the biological step of the treatment plant and denitrification of nitrate in tertiary filtration by addition of readily degradable compound. Denitrification with methanol will be the cheapest solution with today's methanol price.

- Separate intermittent nitrification / denitrification of the digester supernatant. This method is used if digester supernatant inhibits nitrification substantially or if the anoxic zone is too small for organic carbon addition.

- A combination of nitrification and an another process called ANAMMOX (anaerobic ammonium oxidation) is used for removal of ammonium from wastewaters having high ammonia concentrations (Jetten *et al.,* 1999).

3.2.9. Conclusions and future perspectives

From the end of the last century onwards; anaerobic digestion has been applied in man-made environments for both energy production and as a cost -effective method for waste stabilisation and wastewater treatment (Lettinga, 1996). The anaerobic process is relatively easily disturbed and methanogenic bacteria are fairly susceptible to toxic or inhibiting compounds like ammonia. Many researchers have comprehensively studied the role of ammonia; the inhibition mechanisms and the effect of ammonia on the process kinetics. Most of these researchers focused on the methanogenic step. Research has been directed to the development of methods to alleviate the inhibition or toxic effect of high ammonia concentrations aiming to obtain better performance and stability of the process. It is also believed that hydrolysis is the rate limiting step in the anaerobic digestion of complex wastes and wastewaters (Zeeman and Sanders, 2001), but so far few reports have been published concerning the effect of ammonia on the hydrolysis step. Further research is required to get more insight about the effect of ammonia on the different kind of enzymes involved in the hydrolysis step for different wastes.

Nomenclature

CSTR	Continuous stirred tank reactor.
FA	Free ammonia concentration.
F/R	Recycling ration (feeding/ recycling flow rate)
HRT	Hydraulic retention time.
K_{i2}	Inhibition coefficient of ammonia
K_{ia}	Inhibition coefficient of acids
K_s	Saturation constant
MC	Moisture content.
MPB	Methane producing bacteria.
MSW	Municipal solid waste.
NH_3	Concentration of unionised ammonia
OLR	Organic loading rate
ON-N	Organic nitrogen.
SMA	Maximum specific methanogenic activity.
TA	Total ammonia concentration
TKN-N	Total Kjeldahl Nitrogen
TS	Total Solids.
u*m	The actual μ_m.
u_m	The maximum uninhibited growth rate
VA	Concentration of unionised acids
VFA	Volatile fatty acids.
VS	Volatile solids.
VSS	Volatile suspended solids
UASB	Up flow anaerobic sludge blanket reactor
μ	Specific growth rate
μ_m	Maximum specific growth rate

CHAPTER 4: DIGESTION OF LIQUID COW MANURE

4.0. Introduction to the Chapter

This *chapter* concerns experimental and modelling results obtained on liquid cattle manure. Firstly, the effect of temperature on the rheological properties of liquid cattle manure was measured. Secondly, the effect of temperature and temperature fluctuation (downward and upward) on the performance of thermophilic CSTR systems treating cattle slurry was assessed experimentally. Thirdly, the effect of high ammonia concentrations on thermophilic anaerobic hydrolysis of cattle slurry was also investigated experimentally.

The experimental data from CSTR systems were used as a base for model investigations for calculating the thermal efficiency of STAR. The *chapter* finishes with a design of STAR system for liquid manure treatment in small animal farms in the Egyptian situation. The results presented in this *chapter* were written in five separate papers:

4.1. El-Mashad, H.M.; Loon, W.K.P. van; Zeeman, G. and Bot, G.P.A. Rheological properties of cattle manure. Submitted to Bioresource Technology.

4.2. El-Mashad, H.M.; Zeeman, G.; Loon, W. K.P. van; Bot, G.P.A. and Lettinga, G. Effect of temperature and temperature fluctuation on thermophilic anaerobic digestion of cattle manure. Submitted to Bioresource Technology.

4.3. El-Mashad, H.M.; Zeeman, G.; Loon, W.K.P. van; Bot, G. P.A. and Lettinga, G. Effect of ammonia on thermophilic anaerobic hydrolysis of dairy cattle manure. Submitted to Bioresource Technology.

4.4. El-Mashad, H.M.; Loon, W.K.P. van and Zeeman, G (2003). A model of solar energy utilisation in the anaerobic digestion of cattle manure. Biosystems Engineering 84 (2): 231-238.

4.5. El-Mashad, H.M.; Loon, W.K.P. van; Zeeman, G.; Bot, G.P.A. and Lettinga, G. Design of a solar thermophilic anaerobic reactor (STAR) for small animal farms. Condensed version is submitted in part to Biosystems Engineering.

4.1. Rheological Properties of Dairy Cattle Manure

Abstract

Rheological properties are important for the design and modelling of handling and treatment of fluids. In the present study, the viscosity of liquid manure (about 10 % Total Solids) has been measured at different shear rates (2.38-238 s^{-1}). The effect of temperature on the viscosity at different shear rates was studied as well. The results showed that manure has non-Newtonian flow properties, because the viscosity strongly depends on the applied shear rate. The results showed also that manure behaves like real plastic materials. The power-law model of the shear stress and the rate of shear showed that the magnitude of the consistency coefficient decreases for increasing the temperature with high values of the determination coefficient. Moreover, the results showed that the Arrhenius-type model fits very well the temperature effect on manure viscosity (R^2 at least 0.95) with calculated activation energy of 17.0 ± 0.3 kJ mol^{-1}.

4.1.1. Introduction

Nowadays animal farms need to function efficiently both in the economical and ecological fields. The disposal of dairy farm manure is important both from hygienically and sustainable viewpoints. In the design of manure handling and treatment systems, thermal and rheological properties are important.

Viscosity is the physical property, which influences the flow regime and the pressure drop for a flowing fluid. It is, for instance, an important parameter for the design of heat exchangers to heat up manure during its conditioning and treatment, for instance, during anaerobic digestion (*chapter* 4.5). The rheological properties also determine size, type and power of the pump. Beside this, apparent viscosity can be employed as a process control parameter (Moeller and Torres, 1997). Knowledge of the flow behaviour is needed for calculating energy demand, process control and selection of the proper equipment (Kaya and Belibağli, 2002). Moeller and Torres (1997) showed that wastewater sludge is neither Newtonian nor plastic but behaves like a pseudo plastic fluid. Slurries are generally non-Newtonian fluids (Chen, 1986). So in this research the apparent viscosity has to be considered.

Anaerobic digestion is a widely used technology for disposal of manure. It is applied under different temperature ranges: psychrophilic (< 25°C), mesophilic (25-40°C) and thermophilic (>45°C) conditions (Van Lier, 1995). In arid and semi-arid regions, the mesophilic and thermophilic digestion are applied.

It is very well known that temperature generally affects the viscosity of materials. The effect of temperature on the apparent viscosity at a specific shear rate is generally expressed by an Arrhenius-type model (Bhandari, 1999 and Marcotte *et al.,* 2001). Literature shows some studies on thermal properties and bulk density of beef and dairy cattle manure (*e.g.* Chen, 1983 and Achkari-Begdouri and Goodrich, 1992). The data reported on the rheological properties of manure and the temperature effect on its viscosity are limited: Chen and Hashimoto (1976), Hashimoto and Chen (1976) studied the rheological properties of fresh and aerated livestock waste slurries. Chen (1986) studied the effect of temperature and solids concentrations on rheological properties of sieved beef-cattle manure. In the present study, viscous behaviour of non-sieved dairy cattle manure with different total solid concentration and different composition is studied.

The objectives of this study are:

1- To determine the viscous behaviour of the non-sieved dairy cattle manure.

2- To study the effect of temperature and composition on the apparent viscosity of manure at different rates of shear.

4.1.2. Materials and methods

4.1.2.1. Cattle manure

The manure used in this study was produced from dairy cows (Frisian Holstein) weighing about 650 kg. The diet is free of any antibiotic addition. There were some variations in the manure composition, as all experiments were not performed from the same batch of manure (see Table 4.1.1). The manure was refrigerated (4^oC) until used.

4.1.2.2. Manure analysis

The manure used in the present study has been analysed following APHA (1992) for Total Solids (TS), Volatile Solids (VS), Kjeldahl-nitrogen (Nkj). Total ammonium (NH_4^+-N) was determined by the steam distillation method (APHA, 1992). Total COD (CODt) was measured as described by Zeeman (1991). The dissolved COD (COD_{dis}) and Volatile Fatty Acids (VFA) concentrations were measured for diluted (about 20 times) and homogenised samples. The homogenised samples were centrifuged at 3500 rpm for 10 minutes. The measurements were completed as described by Zeeman (1991) and Van Lier (1995). All analyses were performed in duplicate. Manure density was calculated based on water fractions (Achkari-Begdouri and Goodrich, 1992).

4.1.2.3. Manure viscosity measurement

Manure apparent viscosity was measured by using a Haake model rotoviscometer. The detailed description of this rotoviscometer is presented by Den Ouden (1995). The geometries used were a serrated cup and bob with an air gap at the bottom. The deformation applied was shear in the narrow slit by rotating the bob (Fig. 4.1.1). Before starting measurements, the manure was heated up using hot water recirculation around the sample. At the desired temperature, the apparatus was started to get the required rate of shear.

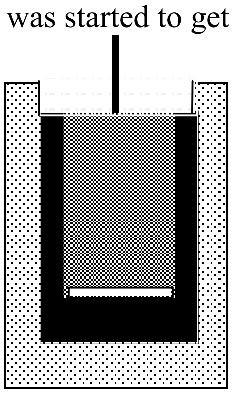


Fig.4.1.1. The rotoviscometer: with ▓, the bob; █ , the sample; and ░ , water jacket

4.1.3. Results and discussion

4.1.3.1. Relation between shear stress and rate of shear

Table 4.1.1 shows the composition and some physical properties as measured for the two manures used in the viscosity measurements.

Table 4.1.1. Thermal and physical characteristics of manure

	Unit	*Manure1*	*Manure2*
Total Solids	(g l^{-1})	91	107
Volatile Solids	(g l^{-1})	73	86
CODt	(g l^{-1})	111	124
COD_{dis}	(g l^{-1})	17.3	19.9
Total FVAs	(g [COD] l^{-1})	5.4	7.1
N-Kj	(g l^{-1})	3.9	4.2
NH_4^+-N	(g l^{-1})	1.7	1.8
Density	(kg m^{-3})	1037	1044

Figure 4.1.2 shows the plot of shearing stress against rate of shear for the manure1 (Table 4.1.1). This relation could not be presented for the manure2 (Table 4.1.1) while not enough manure was available. However, it could be used to measure other properties. As can be seen, manure is a non-Newtonian fluid as the ratio of shear stress to rate of shear is not constant but it depends on the rate of shear. This ratio is called apparent viscosity (Coulson and Richardson, 1964). The exhibition of this non-Newtonian behaviour may be due to the existence of large molecules like the cellulosic materials, which have not been biodegraded in the animal digestion system. It can also be seen that shear stress is higher at the lower temperatures for the same rate of shear. Moreover it can be seen that the relation between shear stress and rate of shear becomes linear only at higher rates of shear (> 50 s^{-1}). This kind of material is called 'real plastic', which is intermediate in behaviour between Bingham plastic and pseudo plastic (Coulson and Richardson, 1964). Kumar (1972) mentioned that when the slurry was below 5% total solids content, it showed Newtonian flow properties, and above 6% it showed non-Newtonian (pseudo plastic) flow properties. Hashimoto and Chen (1976) mentioned that livestock waste slurries are pseudo plastic materials.

It should be mentioned that, compared with similar studies, in the present study the dilution of the raw samples was not applied for two reasons:

1- In practice, the handling and most treatment processes are applied without dilution.

2- Addition of water affects the ratio between different components of the manure, which affects the magnitude of viscosity.

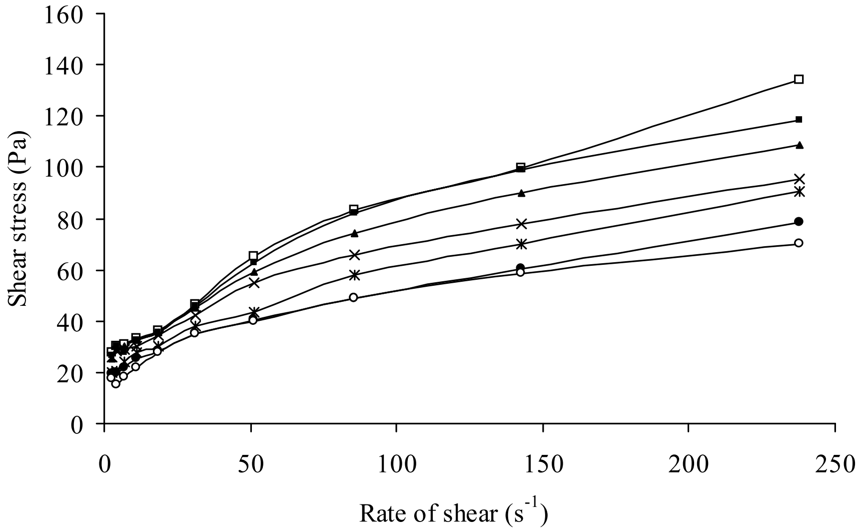


Fig.4.1.2. Relation between shear stress and rate of shear at different temperatures:
□, *30°C;* ■, *35°C;* ▲, *40°C; x, 45°C;* ⁎, *50°C;* ●, *55°C;* ○, *60°C*

The experimental data were fitted to the power law model. Chen and Hashimoto (1976) and Hashimoto and Chen (1976) used the power law to describe the relation between shear stress and the rate of shear of fresh and aerated livestock waste slurries. This law was also successfully used by Kaya and Belibağli (2002) to describe the rheological behaviour of pekmez (a common grape product in Turkey) and by Moeller and Torres (1997) for anaerobically digested sludge. The power law can be written as follows:

$$\tau = k\gamma^{n} \qquad (4.1.1)$$

τ	Shear stress	Pa
γ	Rate of shear	s^{-1}
k	consistency coefficient	$Pa.s^{n}$
n	flow behaviour index	---

The value of *n* indicates the sensitivity of viscosity for rate of shear. The lower the value of *n* the more sensitive is viscosity for rate of shear (Agote *et al.,* 2001). The calculated values are shown in Table 4.1.2.

Table 4.1. 2. Calculated parameters of the Power-law model for shear stress with temperature (T), flow behaviour index n and consistency coefficient k.

T (°C)	*n*	*k(Pa.s^n)*	*R^{2*}*
30	0.211	21.3	0.85
35	0.348	16.1	0.93
40	0.325	16.7	0.96
45	0.295	17.2	0.94
50	0.332	13.0	0.97
55	0.309	12.7	0.97
60	0.342	10.5	0.97

* No of observations =10.

From this table it can be observed that the magnitude of the consistency coefficient (k) decreases if temperature (T in ^oC) increases ($k = -0.3\ T + 29$; $R^2 = 0.85$). This result is in agreement with Kaya and Belibagli (2002), who used a comparable biological material: organic solid in water, high viscous, non-Newtonian fluid. The power-model describes the flow behaviour of manure adequately, as the R^2 values are a least 0.85. It is significant that the values of $n \neq 1$, confirming the non-Newtonian behaviour of manure. The power law is applied also for both pseudo plastics and dilatant materials (Coulson and Richardson, 1964). Similar results were also obtained by Moeller and Torres (1997) for anaerobically digested sludge.

4.1.3.2. Effect of temperature on apparent viscosity

Since turbulent flow regime resembles the situation in practice during anaerobic digestion (*e.g.* CSTR systems) and internal fracture during the viscosity measurement is avoided, rates of shear of 85.7; 142.8 and 238 s^{-1} were used for determining the relation between apparent viscosity and temperature. This is the (more or less) linear part of the curves shown in Fig. 4.1.2.

Table 4.1.3 shows the apparent viscosity of the two manures at different temperatures and different rates of shear. As can be seen apparent viscosity decreases with the increase of rate of shear and of temperature. The effect of temperature (T, in ^oC) can be described by a linear relation ($\mu = AT + B$). The parameters (A and B) are mentioned together with R^2 values (Table 4.1.3).

Table 4.1. 3 .The apparent viscosity of the tested manure at different temperatures

Temperature (^oC)	*Apparent viscosity (Pa.s)*			
	Manure1 (91 g [TS] l^{-1})			*Manure2 (107 g [TS] l^{-1})*
	Rate of shear			*Rate of shear*
	85.7 s^{-1}	*142.8 s^{-1}*	*238 s^{-1}*	*238 s^{-1}*
30	0.97	0.70	0.56	0.72
35	0.96	0.70	0.50	0.64
40	0.87	0.63	0.46	-----
45	0.77	0.55	0.40	0.58
50	0.68	0.49	0.38	0.52
55	0.57	0.42	0.33	0.43
60	0.57	0.41	0.30	0.37
A	-0.016	-0.011	-0.009	-0.011
B	1.47	1.05	0.81	1.05
R^2	0.966	0.969	0.987	0.978

It can also be seen that total solid concentration is an important parameter too: the higher the TS content the higher is the apparent viscosity. This is in agreement with the results of Chen (1986) obtained for the viscosity of sieved beef- cattle manure. The results are also in agreement with the results of Jelinek (1977), who stated that there is a direct proportional correlation between total solids and both density and viscosity of swine manure.

The effect of temperature on the apparent viscosity at these specified shear rates was further evaluated using the Arrhenius model (Marcotte *et al.,* 2001):

$$\mu = A \exp\left(E_a / RT_{abs}\right) \tag{4.1.2}$$

Where:

μ	Apparent viscosity	Pa.s
A	Frequency factor	Pa.s
E_a	Activation energy	J mol^{-1}
R	Universal gas constant	J $mol^{-1}.K^{-1}$
T_{abs}	Absolute temperature	K

The linear plots of the Arrhenius model for the two kinds of manure are shown in Figs 4.1.3a and 4.1.3b. The calculated frequency factor and the calculated activation energy are shown in Table 4.1.4. The activation energy has a constant high value of 17.0 ± 0.3 kJ mol^{-1} for all experiments. This high value indicates the sensitivity of the viscosity to the temperature change (Bhandari *et al.,* 1999).

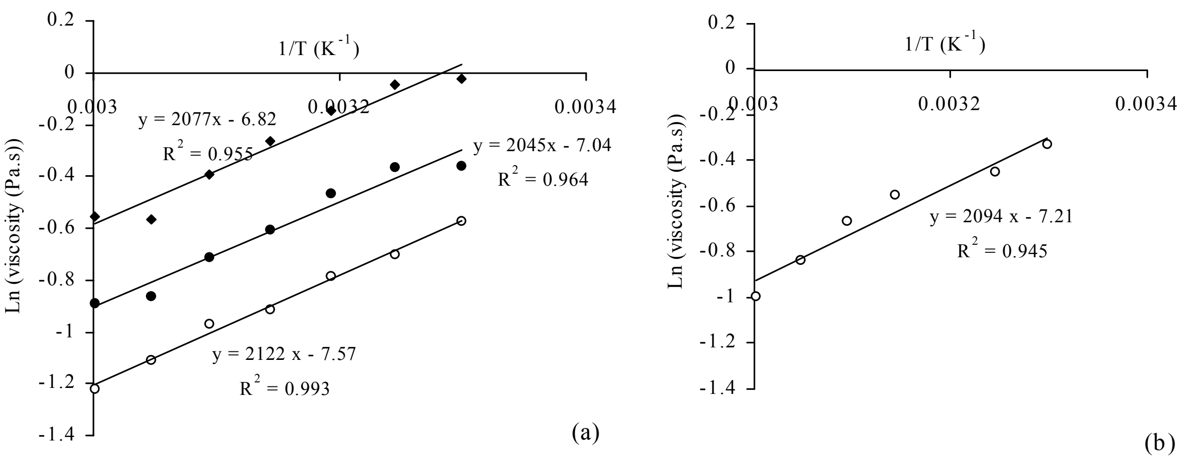


Fig.4.1.3. Arrhenius plots for natural logarithm of apparent viscosity of the manure as a function of inverse absolute temperature at different rates of shear: ♦, 85.7 s^{-1}; ●, 142.8 s^{-1}; ○, 238 s^{-1}. (a) manure of 91 g [TS] l^{-1} and (b) manure of 107 g [TS] l^{-1}

Table 4.1.4. The calculated frequency factor (A) and activation energy (Ea)

Rate of shear (s^{-1})	*Manure1 (91 g [TS]l^{-1})*		*Manure2 (107 g [TS]l^{-1})*	
	A (Pa.s)	*Ea (kJ mol^{-1})*	*A(Pa.s)*	*Ea (kJ mol^{-1})*
85.7	0.0011	16.9	---	---
142.8	0.0009	16.7	--	--
238	0.00052	17.3	0.00074	17.00

Chen (1986) obtained a comparable value (18 ± 5 kJ mol^{-1}) of activation energy for sieved beef cattle manure. This value was obtained from the Arrhenius plot: the logarithm of limiting viscosity against the reciprocal of absolute temperature. According to Chen (1986) the limiting viscosity is defined as the viscosity approached at very high shear rates. This limiting viscosity should never be less than the sum of the viscosity of the solution and the viscosity due to the concentration of the particles (Einstein viscosity). It must be stressed that different definitions are used for the activation energy depending on application of the Arrhenius equation. Gaskell (1992) explained the physical meaning of this activation energy. The activation energy is the energy barrier that a flow unit must overcome to squeeze successfully between its neighbours.

4.1.4. Conclusions

The rheological behaviour of liquid cattle manure has been studied. The effect of both total solids and temperature on the apparent viscosity has also been included. The results show that manure is a non-Newtonian material and it behaves like a real plastic material. The relation between shear stress and rate of shear is only linear at higher rates of shear for all temperatures studied (30-60^oC). The higher the solid content the higher is the apparent viscosity. The results also show that the temperature effect on the apparent viscosity of manure can be described very well by an Arrhenius-type model with R^2 values of at least 0.95. A value of 17.0 ± 0.3 kJ mol^{-1} for activation energy is obtained, which is comparable to that of sieved beef-cattle manure (Chen, 1986).

4.2. Effect of Temperature and Temperature Fluctuation on Thermophilic Anaerobic Digestion of Cattle Manure

Abstract

The influence of temperature, 50 and 60°C, at Hydraulic Retention Times (HRT's) of 20 and 10 days, on the performance of anaerobic digestion of cow manure has been investigated in completely stirred tank reactors (CSTR's). Furthermore, the effect of both daily downward and daily upward temperature fluctuations has been studied. In the daily downward temperature fluctuation regime the temperatures of each reactor was reduced by 10°C for 10 hours while in the daily upward fluctuation regime the temperature of each reactor was increased 10°C for 5 hours. The results show that the methane production rate at 60°C is lower than that at 50°C at all experimental conditions of imposed HRT except when downward temperature fluctuations were applied at an HRT of 10 days. It also was found that the free ammonia concentration not only affects the acetate-utilising bacteria but also the hydrolysis and acidification process. The upward temperature fluctuation affects the maximum specific methanogenesis activity more severely as compared to imposed downward temperature fluctuations. The results clearly reveal the possibility of using available solar energy at daytime to heat up the reactor (s) without the need of heat storage during nights, especially at an operational temperature of 50°C and at a 20 days HRT, and without the jeopardising of the overheating.

4.2.1. Introduction

The depletion of non-renewable energy sources leads to the need to search for other - renewable – resources available at local conditions. There exist many renewable sources, such as sunlight, wind and biomass, while agricultural wastes represent an important source of bio-energy. The anaerobic digestion process is one of the technologies used to produce energy as well as to reduce the organic content of waste. Energy production remains an important process, even at moderate energy prices in non-oil-producing countries. The climate problems due to the greenhouse effect, the recognised need for sustainable development and problems due to the ozone layer depletion have all contributed to the recognition of the value of anaerobic digestion as a technique to produce renewable energy (De Baere, 2000).

Among the many factors affecting the anaerobic digestion process, temperature is an important one. Anaerobic digestion can proceed under psychrophilic (< 25°C), mesophilic (25-40°C) and thermophilic (>45°C) conditions. The digestion under thermophilic conditions offers many advantages such as higher metabolic rates, consequently higher specific growth rates but frequently also higher death rates as compared to mesophilic bacteria (Van Lier, 1995; Duran and Speece, 1997). Chen *et al.* (1980) revealed that there is a kinetic advantage in fermentation of livestock manure at thermophilic over mesophilic temperature. However, the kinetic advantages in conducting the digestion process at 60°C rather than at 50°C are insignificant. An important advantage of the thermophilic process undoubtedly is that it provides a high destruction of pathogens and weed seeds. Larsen *et al.* (1994) concluded that thermophilic as well as mesophilic digestion with thermophilic pre-treatment will result in sufficient reduction of vegetative pathogenic bacteria (both *E. coli* and *Enterococci*) and intestinal parasites usually found in animal wastes. This cannot be said for mesophilic digestion when used alone. *Salmonella* and *Mycobacterium paratuberculosis* are inactivated within 24 h at thermophilic conditions while it needs weeks or even months at mesophilic temperatures (Sahlström, 2003). This in fact is an important criterion for the animal waste treatment since the effluent can be used as a soil conditioner. Some researchers, like Mackie and Bryant (1995) mentioned that thermophilic (60^{o}C) anaerobic digestion of cattle waste is more stable than mesophilic (40^{o}C) at different HRT's (*viz.*10, 15, and 20 days).

On the other hand, thermophilic treatment suffers from some drawbacks such as lower stability compared to mesophilic treatment (Buhr and Andrewa, 1977; Wiegant, 1986; Van Lier, 1995). According to Duran and Speece (1997), thermophilic systems produce somewhat poorer effluent quality. Moreover, the lower growth yield combined with their high growth rates of thermophilic organisms leads to longer start-up times, while it also renders these processes more susceptible to toxicity and changes in operational and environmental conditions. According to insights of Angelidaki and Ahring (1994) the optimum temperature for digestion of substrates with high ammonia loads differs from the optimum temperature at low ammonia loads. Due to the temperature/ammonia interactionship the effect of temperature cannot be examined independently when the ammonia concentration is in the inhibitory range. According to results of Ahring *et al.* (2001), increasing the operational temperature from 55^{o}C to 65^{o}C results in an immediate unbalance between the fermenting, acids-producing micro-organisms and acids-consuming micro-organisms. Another drawback of thermophilic operation comprises its energy requirements and this may reduce the net energy production from thermophilic compared to mesophilic digestion.

To maximise the net energy production from anaerobic digestion we need to consider the steps involved in the digestion process (*e.g.* the hydrolysis step) and the factors affecting these steps (*e.g.* temperature). Particularly the complementary use of other available renewable energy resources such as sunlight should be considered. Utilisation of solar energy as a source for reactor heating will save fossil fuel or biogas used for heating and represents in this way a kind of solar energy storage in the form of biogas. However, the incorporation of such a renewable energy source obviously is accompanied with further investments. In order to keep the (total) system as simple as possible, a system design could be considered where the reactor is heated up during period of sunshine without heat storage to maintain the desired temperature during night-time. Such a mode of operation might negatively affect the process stability, as the reactor will be subjected to temperature fluctuations between day and night. This effect will be more pronounced for small reactor volumes. Moreover, this mode of operation might lead to overheating in case the control system is not working properly or when there is an excess of solar energy. Speece (1983) is one of the many researchers postulating that anaerobic digestion is sensitive to sudden change of environmental conditions. According to Van Lier (1995) the effect of temperature shocks depends strongly on the imposed temperature change, the duration of the shock and also on the bacterial composition of sludge. As already mentioned by Van Lier *et al.* (1996) for large-scale thermophilic anaerobic installations, such as UASB reactors, it is of utmost importance that the treatment system can tolerate moderate temperature fluctuations. According to Kroeker *et al.* (1979) temporary diurnal temperature fluctuations as high as 8^{o}C in the anaerobic digestion of swine manure did not significantly affect the process stability at a process temperature of 35^{o}C at retention times of both 30 and 6 days. Evidently a serious lack of information exists on the temperature fluctuation effect on the performance of thermophilic anaerobic digestion of farm wastes (*i.e.* cow manure), and consequently, this effect deserves to be investigated in more detail.

Objective

The objective of the present study is to investigate the influence of temperature and temperature fluctuation on thermophilic anaerobic digestion of cow manure using a CSTR system. Therefore the following effects were investigated experimentally:

1- Assess the differences of the digestion process of cow manure using a CSTR system at two temperatures (50 and 60^{o}C) and at two different HRT's (20 and 10 days).

2- Assess the effect of temperature fluctuations on the performance of the process:

a- An imposed daily downward temperature fluctuation of 10^{o}C for a period of 10 hours.
b- An imposed daily upward temperature fluctuation of 10^{o}C for a period of 5 hours.

4.2.2. Materials and methods

4.2.2.1. Experimental set up

Twelve experiments in six experimental runs have been carried out. After 'steady state' has established, at least three sets of analysis were conducted, in duplicate, and then the next run was started. 'Steady state' was defined as the situation where a stable methane production coincides with stable effluent volatile fatty acids concentrations. Table 4.2.1 presents the experimental set up.

4.2.2.2. Experimental reactors and inoculum

Two CSTR reactors with a working volume of 8 l each were used in this study. The reactors were operated in a daily draw-fill mode. The imposed operation temperatures are shown in Table 4.2.1. The reactors were heated using hot water recirculation through a water jacket surrounding the reactors. In the first run, the reactors were seeded with 8 *l* thermophilic sludge obtained from a 2700 m^3 reactor from VAGRON (Groningen, The Netherlands), a system treating municipal waste at a temperature of 52-57^{o}C at a retention time of 18 days. One week after inoculation, feeding was started. For each of the next experimental runs the inoculum was taken from the previous run except for the fifth run. After finishing the fourth run, the reactors were operated batch wise for about 2 months at constant temperatures of 50 and 60^{o}C. Some characteristics of the inoculum used in the fifth run are shown in Table 4.2.2.

Table 4.2.1. The experimental set up

	First run	*Second run*	*Third run*	*Fourth run*	*Fifth run*	*Sixth run*
The aim is studying the effect of :	Constant temperature	Downward temperature fluctuations	Constant temperature	Downward temperature fluctuations	Upward temperature fluctuations	Upward temperature fluctuations
HRT (days)	20	20	10	10	10	20
Temperature (^oC)	50 ^oC (R^{20}_{50})	50^oC for 14 hours and 40^oC for 10 hours (R^{20}_{50d}).	50^oC (R^{10}_{50})	50^oC for 14 hours and 40^oC for 10 hours (R^{10}_{50d}).	50^oC for 19 hours and 60^oC for 5 hours (R^{10}_{50u}).	50^oC for 19 hours and 60^oC for 5 hours (R^{20}_{50u}).
	60 ^oC (R^{20}_{60})	60 ^oC for 14 hours and 50 ^oC for 10 hours (R^{20}_{60d}).	60^oC (R^{10}_{60})	60^oC for 14 hours and 50^oC for 10 hours (R^{10}_{60d}).	60^oC for 19 hours and 70^oC for 5 hours (R^{10}_{60u}).	60^oC for 19 hours and 70^oC for 5 hours (R^{20}_{60u}).
Mixing	Continuously at 6 rpm	Continuously at 6 rpm	Intermittent *at 50 rpm for 1 minute every 10 minutes	Intermittent* at 50 rpm for 1 minute every 10 minutes	Intermittent* at 50 rpm for 1 minute every 10 minutes	Intermittent* at 50 rpm for 1 minute every 10 minutes
Organic loading rate (g [COD]l^{-1} day^{-1})	2.9	2.9	5.25	5.25	6.1	3.05
Elapsed time before 'steady state' (days)	49	49	35	42	31	62

*With continuos mixing at 50 rpm for 10 minutes before feeding the reactors

Table 4.2.2. Characteristics of the inoculum used in the fifth run with standard deviations between brackets

Parameter	*Inoculum for R^{10}_{50u}*	*Inoculum for R^{10}_{60u}*
Total solids (g l^{-1})	42.3 (0.4)	47.3 (0.2)
Volatile solids (g l^{-1})	31.5 (0.4)	36.9 (0.2)
VFA (mg [COD] l^{-1})	22.1 (2.8)	92.4 (1.3)
Ammonia (mg l^{-1})	1215.8 (25.6)	1223.2 (8.7)
SMA (g[COD]g^{-1}[VS]day^{-1})	0.1(0.003)*	0.12 (0.002)**

* At 50°C; ** at 60°C

4.2.2.3. Feedstock

The reactors were fed with diluted cow manure originating from dairy cows weighing about 650 kg. The diet of the cows was free of any antibiotic addition. There were some variations in the manure composition as it was not possible to obtain enough manure at one time to carry out all the experiments. The manure was stored in a refrigerator (4°C) until used. Before feeding, the manure was diluted with tap water to give a 5 % TS feedstock. The dilution used in these experiments was to mitigate the high ammonia concentration effect. In many countries less protein rich feed is used, resulting in a lower NH_4^+-N content of the manure. Important characteristics of the manure used are given in Table 4.2.3.

Table 4.2.3. The composition of the influent with standard deviation between brackets

Parameter	*Unit*	*First and second Experiments*	*Third and Fourth Experiments*	*Fifth and Sixth Experiments*
Total Solids	g l^{-1}	50 (1.3)	50 (0.3)	50(0.6)
Volatile Solids	g l^{-1}	40.1 (0.5)	41.6 (0.01)	40.3(0.03)
Total COD	g l^{-1}	57.9 (4.8)	52.5 (2.0)	60.9 (3.8)
Dissolved COD	g l^{-1}	9278.2 (662.7)	6619.4 (113.1)	9482 (225.7)
Total VFA's	mg [COD] l^{-1}	3299.3 (280.9)	1983 (37.5)	2985.9 (148)
Acetate (C2)	mg [COD] l^{-1}	2014.2 (31.5)	1361 (28.9)	1952.5 (68.9)
Propionate (C3)	mg [COD] l^{-1}	488.5 (8.6)	383.5 (6.7)	606.1(19.3)
Iso-butyrate (i-C4)	mg [COD] l^{-1}	143.9 (6.7)	50.1 (1)	66.5 (1.2)
Butyrate (n-C4)	mg [COD] l^{-1}	128.1 (2.4)	155.8 (0)	187.7 (23.6)
Iso-valerate (i-C5)	mg [COD] l^{-1}	524.7 (330)	0.0 (0)	129.4 (33.6)
Valerate (n-C5)	mg [COD] l^{-1}	0.0 (0)	32.4 (1)	43.7(1.4)
N-Kj	mg l^{-1}	1978.6 (26.7)	1861.3 (62.5)	2116.6 (108.2)
NH_4^+-N	mg l^{-1}	854.4 (15.2)	949.8 (47.9)	947.9 (13.9)

4.2.2.4. Analysis

The total COD (COD_t) was analysed as described by Zeeman (1991). The dissolved COD (COD_{dis}) and the VFA concentrations were measured in a 20 times diluted samples after they were centrifuged for 10 minutes at 3500 rpm followed by membrane filtration (0.45 µm, Schleicher and Schuell ME 25, Germany) and diluted with formic acid. COD_{dis} was measured using the micro method (Jirka and Carter, 1975). The VFA's were determined by gas chromatography using a Hewlett Packard 5890 equipped with a 2 m × 4 mm glass column, packed with Supelcoport (100-200 mesh) coated with 10 % Fluorad FC 431. The temperatures of the column, injection port and flame ionisation detector were 130, 220, 240°C, respectively. The carrier gas was nitrogen saturated with formic acid (40 ml per min). TS, VS, Kjeldahl-nitrogen (Nkj) were analysed as described by APHA (1992). The total ammonium concentration (NH_4^+-N) was determined by steam distillation (APHA, 1992). Methane produced was collected in gasbags after the CO_2 had been removed by passing the biogas through a 3-6 % NaOH solution. The daily methane production was measured by using a wet gas meter. The methane production was recalculated for Standard Temperature and Pressure (STP). The pH was measured daily, whereas VFA was measured once weekly for 20 days HRT and twice a week for 10 days HRT till 'steady state'. Once 'steady state' was reached, all effluent analyses were carried out immediately, thereby preventing the need to store samples. The maximum specific methanogenic activity test (SMA) has carried out in duplicate, by VFA (acetate) depletion for two feeds as described by Van Lier (1995). The initial sludge concentration was 3 g [VS] l^{-1} and acetate concentration in both feeds was about 1.5 g [COD] l^{-1}. The results of the second feed were used for the SMA calculations. The average results of all analysis and standard deviations of each analysis set are presented.

4.2.3. Data processing

4.2.3.1. Calculations

The dissociation constant of aqueous ammonia (pKa) decreases with an increase of the absolute temperature T (K) in the range of 273-373 K. Free ammonia concentration can be calculated from the following formula (Perry and Chilton, 1973; Poggi-Varaldo *et al.,* 1997):

$$NH_3 - N = \left(NH_4^+ - N\right) \times \left[1 + \frac{10^{-pH}}{10^{-\left(0.1075 + \frac{2725}{T}\right)}}\right]^{-1} \qquad (4.2.1)$$

Percentages of total hydrolysis (H); acidogenesis (A); and methanogenesis (M) were calculated according to the following equations, respectively:

$$H\,(\%) = \left(\frac{CH_4\ as\ COD + Effluent\ COD_{dis}}{Influent\ COD_t}\right) \times 100. \qquad (4.2.2)$$

$$A\,(\%) = \left(\frac{CH_4\ as\ COD + Effluent\ VFA\ as\ COD}{Influent\ COD_t}\right) \times 100. \qquad (4.2.3)$$

$$M\,(\%) = \left(\frac{CH_4\ as\ COD}{Influent\ COD_t}\right) \times 100. \qquad (4.2.4)$$

4.2.3.2. Statistical analysis

Data were analysed by using the data analysis toolbox in EXCEL software. The applied statistical analysis was ANOVA single factor with replications. To compare the mean values, the values of the Fisher's least significant difference (Fisher's LSD) at t = 0.05 was calculated for each studied HRT. As the type of manure used in upward temperature fluctuation reactors is different and the bacteria involved in the upward temperature fluctuation reactors probably differ from all other reactors, the data of these reactors were analysed separately.

4.2.4. Results and discussion

4.2.4.1. Methane yield at steady state operation

The appearance of 'Steady state' conditions in the operation of the various experimental runs was confirmed by calculating the Nitrogen Ratio (NR), defined as the ratio between total Kjeldahl nitrogen (Nkj) entering an anaerobic reactor and the Nkj leaving the reactor. We found (see Fig. 4.2.1 a and b) that NR equals to almost unity. According to Cobb and Hill (1990b) this parameter is a reliable indicator of the fermentor 'steady state'. Based on experimental data, they concluded that the system is operating under 'steady state' if the NR = 1.00 ± 0.05.

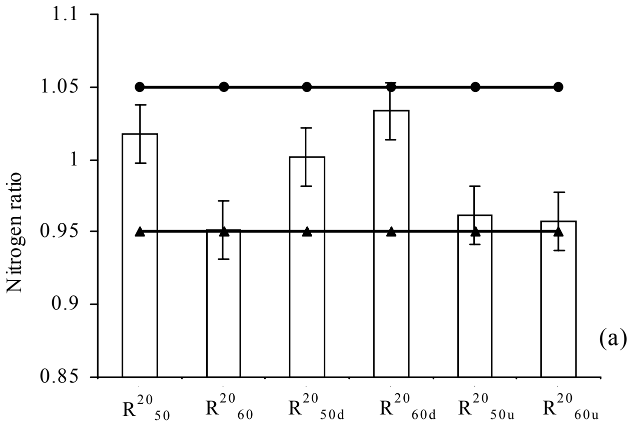


Fig. 4.2.1,a. Nitrogen ratio at 20 days HRT: ▲, lower limit; ●, upper limit

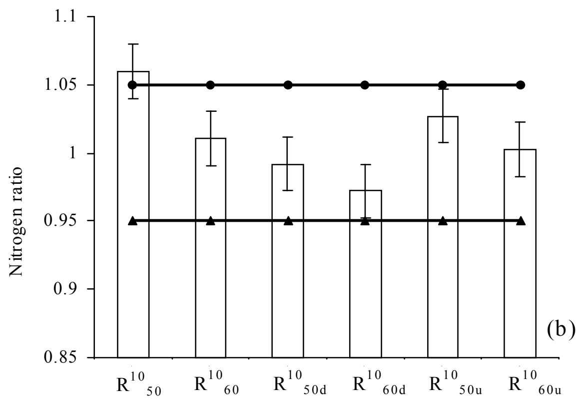


Fig. 4.2.1,b. Nitrogen ratio at 10 days HRT: ▲, lower limit; ●, upper limit

It can be seen from Fig. 4.2.1,a and b that for all reactors the NR is in the range specified by Cobb and Hill, except for one small surplus of 1.06 at R^{10}_{50}, but considering the measuring accuracy, it is still in the range. Our results are also in accordance with results found by Varel *et al.* (1977) in the thermophilic digestion of cattle waste. They found that little if any nitrogen is lost from the system and most of it is present in the effluent as ammonia or microbial cells.

4.2.4.2. Ammonia and pH

The measured pH-values and assessed values for the total and free ammonia (NH_3) concentrations are summarised in Tables 4.2.4 and 4.2.5. From these data it can be observed the pH values and free ammonia concentrations in the reactors operated at higher temperatures are higher compared to those operated at lower temperature. One exception exists: in case of R^{10}_{60u} the accumulation of VFA causes a drop of the pH. The statistical analysis (Table 4.2.6) showed a significant effect of temperature/temperature fluctuations on the pH and the free ammonia concentration at both studied HRT's. The NH_3 concentration is affected by the temperature and pH (Equation 4.2.1). The lower pH value in R^{10}_{60u} caused a lower NH_3 concentration.

The pH of the digester liquid and its stability as well comprises an extremely important parameter, since methanogenesis only proceeds at high rate when the pH is maintained in the neutral range. Most methanogenic bacteria function optimally at pH 7-7.2, and the rate of methane production declines at pH-values below 6.3 or exceeding 7.8 (Bitton, 1994; Van Haadel and Lettinga, 1994). The pH is known to influence enzymatic activity, because each enzyme has a maximum activity within a specific and a narrow pH range.

As the free ammonia concentration depends on the pH value, we need to consider the relevant prevailing chemical equilibria in the reactors. According to a review made by Georgacakis *et al.* (1982), the process stability largely depends on the chemical equilibria established between the three primary buffers-agents, *i.e.* VFA, bicarbonate and ammonia. A plot of the pH values against the values of the ratio of NH^+_4-N/VFA as measured in this study and those measured in a previous study of Zeeman (1991) dealing with mesophilic anaerobic digestion of cow manure shows a strong negative correlation (Fig. 4.2.2). It should be mentioned that the data of the reactors operated at upward temperature fluctuation regime are not included in this regression. The trend of the data of the present study (Fig. 4.2.2) is confirmed by the data of Zeeman (1991). The differences observed between both studies arise, likely, from the variations in the manure composition. According to Georgacakis *et al.* (1982) the NH_3/VFA ratio can be used as an operational parameter reflecting the digester stability for high nitrogen wastes.

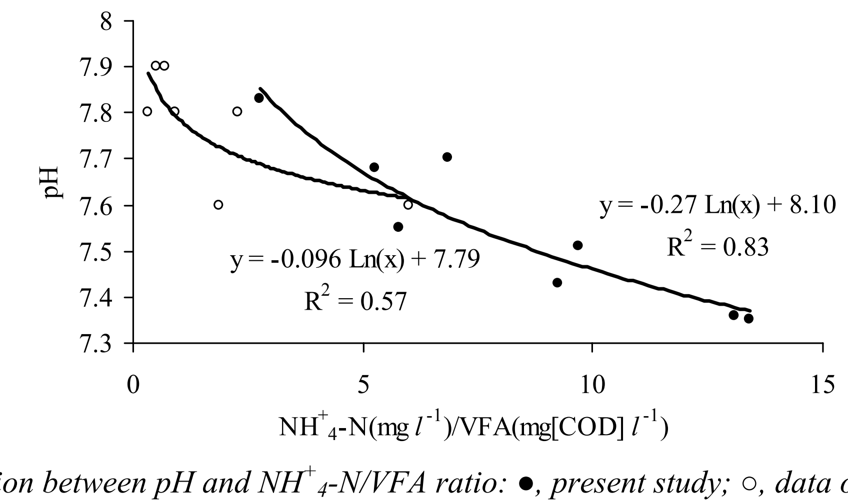


Fig. 4.2.2. Relation between pH and NH^+_4-N/VFA ratio: ●, present study; ○, data of Zeeman (1991)

Table 4.2.4. Average values and 'standard deviations' (values between brackets) of the studied parameters during steady state of the experiments conducted at 20 days HRT

Parameters	R^{20}_{50}	R^{20}_{60}	R^{20}_{50d}	R^{20}_{60d}	R^{20}_{50u}	R^{20}_{60u}
Hydrolysis (%)	49.1 (1.7)	47.0 (0.8)	43.4 (1.7)	38.4 (1.3)	42.0 (1.5)	37.7 (0.7)
Acidogenesis (%)	39.1 (1.7)	34.8 (0.8)	34.4 (1.7)	27.73 (1.3)	33.04 (1.5)	23.2 (0.7)
Methanogenesis (%)	38.8 (1.7)	34.2 (0.8)	34.2 (1.7)	27.48 (1.3)	32.94 (1.5)	21.3 (0.7)
COD_{dis} (mg l^{-1})	5949.8 (303.1)	7456.5 (279)	5310.5 (305.1)	6288.9 (255.9)	5547.8 (124.5)	10018.1 (167.6)
VFA (mg [COD] l^{-1})	201.1 (44.8)	388.6 (65.5)	99.8 (39.5)	142.6 (10.6)	63.2 (14.7)	1198.2 (34.3)
Non acidified COD_{dis} (mg l^{-1})	5748.7 (338.3)	7067.9 (332.7)	5210.7 (269.4)	6146.3 (251.8)	5484.6 (120.9)	8819.9 (140)
pH	7.68 (0.05)	7.83 (0.0)	7.51 (0.04)	7.7 (0.04)	7.43 (0.03)	7.62 (0.02)
Nkj (mg l^{-1})	1944.5 (134.1)	2079.8 (103.7)	1976.3 (47.6)	1914.9 (112.5)	2193.4 (30)	2209.8 (60.7)
NH^{+}_{4}-N (mg l^{-1})	1056.9 (40.9)	1075.3 (29.7)	967.8 (47.5)	979.9 (26.5)	1042.1 (32.9)	1107 (10.5)
NH_3 (mg l^{-1})	131.5 (4.6)	281.8 (21.9)	70.4 (12.1)	188.1 (43.3)	81.1 (1.2)	210.3 (3.1)

Table 4.2. 5. Average values and 'standard deviations' (values between brackets) of the studied parameters during steady state of the experiments conducted at 10 days HRT

Parameters	R^{10}_{50}	R^{10}_{60}	R^{10}_{50d}	R^{10}_{60d}	R^{10}_{50u}	R^{10}_{60u}
Hydrolysis (%)	33.4 (1.4)	32.4 (1.5)	27.9 (1.4)	32.1 (1.5)	35.0 (0.7)	31.3 (2.4)
Acidogenesis (%)	28.2 (1.4)	24.1 (1.5)	21.6 (1.4)	23.6 (1.5)	24.9 (0.7)	15.0 (2.4)
Methanogenesis (%)	28.0 (1.4)	23.7 (1.5)	21.5 (1.4)	23.6 (1.5)	24.7 (0.7)	8.9 (2.4)
COD_{dis} (mg l^{-1})	2810.2 (202.8)	4569.8 (181.0)	3359.5 (131.4)	4610.0 (106.4)	6288.6 (397)	13685.9 (682.0)
VFA (mg [COD] l^{-1})	75.4 (6.0)	173.6 (32.8)	80.2 (12.2)	122.9 (22.7)	101.4 (21.7)	3740.4 (1279)
Non acidified COD_{dis} (mg l^{-1})	2734.8 (182)	4396.2 (193.0)	3279.3 (138.1)	4487.1 (100.2)	6187.2 (410.5)	9945.5 (655.0)
pH	7.36 (0.03)	7.55 (0.04)	7.35 (0.03)	7.43 (0.02)	7.48 (0.04)	7.26 (0.13)
Nkj (mg l^{-1})	1741.5 (61.4)	1735.6 (10.7)	1755.2 (114.6)	1785.3 (33.9)	2063.5 (74.8)	2109.4 (24.0)
NH^{+}_{4}-N (mg l^{-1})	985.2 (27.1)	1004.5 (47.3)	1075.5 (40.1)	1138.9 (61.7)	1041.9 (18.1)	1113.3 (51.9)
NH_3 (mg l^{-1})	57.5 (1.2)	151.5 (8.9)	51.7 (3.5)	108.0 (9.4)	97.7 (8.3)	94.9 (17.0)

4.2.4.3. Hydrolysis, acidification and methanogenesis

The assessed values (in percentages) of hydrolysis, acidogenesis and methanogenesis of the total COD at 'steady state' are summarised in Tables 4.2.4 and 4.2.5. As expected, at long HRT (Table 4.2.4) the higher values are found compared to those found at short HRT (Table 4.2.5), unlike the differences in the manure composition. These findings are in agreement with the results of Zeeman (1991) on the anaerobic digestion of cow manure under mesophilic conditions.

Hydrolysis

The statistical analysis of the data found for the percentage hydrolysis show significant differences between most of the reactors (Table 4.2.6).
At HRT of 20 days and at constant temperature, the percentage hydrolysis found for the reactor operated at 50°C ($R^{20}{}_{50}$) is significantly higher than for the reactor operated at 60°C ($R^{20}{}_{60}$). From the data in Table 4.2.6 it can be seen that the total ammonia concentrations in these two reactors are rather similar (no significant differences) but the free ammonia concentrations are quite different (significant differences), *i.e.* it is substantially higher in the reactor operated at 60°C. This may the main reason for the lower hydrolysis. Zeeman (1991) found in the digestion of cattle manure under mesophilic conditions that the extent of hydrolysis is inversely proportional to the free ammonia concentration. However, the underlying reason of this effect is still unknown.

At HRT of 10 days no significant difference in the extent of hydrolysis is found between both temperatures ($R^{10}{}_{50}$ and $R^{10}{}_{60}$), although also here the free ammonia concentration between both reactors is significant. This might indicate that the negative effect of high free ammonia concentration is compensated by the positive effect of higher temperature on hydrolysis (Veeken and Hammelers, 1999; Sanders, 2001).

Tables 4.2.4 and 4.2.5 also show the results found for the percentage hydrolysis at imposed changes in temperatures. The temporary drop in temperature at both HRT's negatively affects the amount of hydrolysis except for $R^{10}{}_{60d}$. The reason for the deviating behaviour at $R^{10}{}_{60d}$ is not clear. Comparing the results of $R^{20}{}_{50d}$ and $R^{20}{}_{60d}$ confirms the negative effect of free ammonia concentration on hydrolysis as found for $R^{20}{}_{50}$ and $R^{20}{}_{60}$.

An upward change in temperature results in a significant higher hydrolysis at $R^{20}{}_{50u}$ than at $R^{20}{}_{60u}$. A significant higher hydrolysis is also obtained at $R^{10}{}_{50u}$ compared to $R^{10}{}_{60u}$. The reduced hydrolysis, found in the reactors exposed to downward change in temperature as compared to the values found for reactors operated at a constant temperature (Table 4.2.7) indicates that the process of hydrolysis is affected by downward temperature rather than the acidogenesis and methanogenesis.

Table 4.2.6. Statistical analysis results at downward and upward temperature fluctuation

Parameters	*Compared reactors couples (the two reactors shown in the same column)*									
	Temperature effect						*Downward fluctuation effect*			
	R^{20}_{50}	R^{20}_{50d}	R^{20}_{50u}	R^{10}_{50}	R^{10}_{50d}	R^{10}_{50u}	R^{20}_{50}	R^{20}_{60}	R^{10}_{50}	R^{10}_{60}
	R^{20}_{60}	R^{20}_{60d}	R^{20}_{60u}	R^{10}_{60}	R^{10}_{60d}	R^{10}_{60u}	R^{20}_{50d}	R^{20}_{60d}	R^{10}_{50d}	R^{10}_{60d}
Hydrolysis	S	S	S	NS	S	S	S	S	S	NS
Acedogenesis	S	S	S	S	S	S	S	S	S	NS
Methanogenesis	S	S	S	S	S	S	S	S	S	NS
VFA	S	NS	S	S	S	S	S	S	NS	S
COD_{dis}	S	S	S	S	S	S	S	S	S	NS
pH	S	S	S	S	S	S	S	S	NS	S
NH^{+}_{4}-N	NS	NS	S	NS	S	S	S	S	S	S
NH_3	S	S	S	S	S	NS	S	S	NS	S

S, significant differences; NS, non significant differences

Table 4.2.7. The reduction in H, A and M at downward temperature fluctuation relative to the values at constant temperature

	Compared reactors couples (the two reactors shown in the same column)			
	R^{20}_{50}	R^{20}_{60}	R^{10}_{50}	R^{10}_{60}
Parameters	R^{20}_{50d}	R^{20}_{60d}	R^{10}_{50d}	R^{10}_{60d}
Hydrolysis	11.5	18.5	16.5	0.9
Acedogenesis	12.1	20.4	23.3	1.9
Methanogenesis	11.8	19.5	23.4	1.6

Acidogenesis

The results in Tables 4.2.4 and 4.2.5 show that the higher the temperature the higher the COD_{dis} in the effluent. They also show that more than 94 % of COD_{dis} consists of non-acidified matter for all studied reactors, except for R^{20}_{60u} and R^{10}_{60u}. Figure 4.2.3 shows the relation between non-acidified COD_{dis} and both the free and total ammonia concentrations, although without the data of the reactors operated at upward temperature fluctuation regime. Figure 4.2.3 indicates on one hand the existence of a clear correlation (R^2 = 0.71) between non-acidified COD_{dis} and free ammonia concentration, but on the other hand such a correlation does not exist between non-acidified COD_{dis} and total ammonia concentration. These results indicate that the high free ammonia concentration also affects the acidogenic bacteria. Results of Hansen *et al.* (1998) in the digestion of swine manure digestion at 15-day HRT and at a high concentration of free ammonia (0.75-2.6 g l^{-1}) demonstrate some inhibition of hydrolysis and acidification. The results of Rollon (1999) obtained in the anaerobic treatment of fish wastewater revealed a slight but distinct inhibition of acidogenesis at increasing the NH^+_4N concentrations from 0-1.5 g l^{-1}.

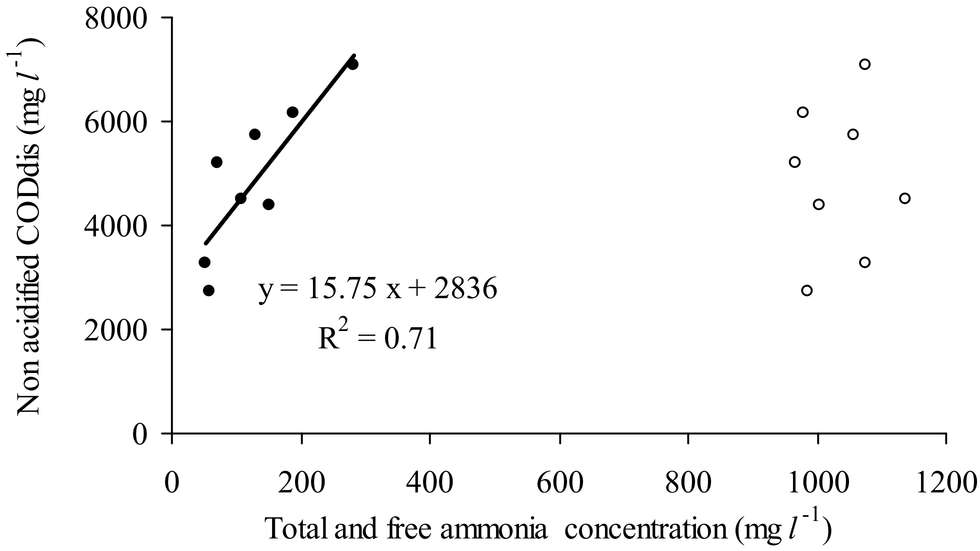


Fig.4.2.3. Relation between non-acidified COD_{dis} and both free and total ammonia concentrations: ○, for total ammonia; ●, for free ammonia

Methanogenesis

Tables 4.2.4 and 4.2.5 show the results of measurements of the effluent VFA concentration. A higher effluent VFA's is found at both studied HRT at higher imposed operational temperatures. With respect to the effect of HRT the results are opposite to theory, viz. an increasing VFA concentration with higher loading rate, except for $R^{20}{}_{60u}$ and $R^{10}{}_{60u}$ where we found the highest VFA concentration. The latter may be attributed to the difference in the manure used at both HRT. A statistical analysis of the data shows a significant effect of both temperature/temperature fluctuations on the VFA concentration at both studied HRT (Table 4.2.6).

The temporary temperature drop reduces significantly the effluent VFA for each reactor compared to systems operated at constant temperature, except for $R^{10}{}_{50d}$. This lower VFA-concentration might be explained by the positive effect of decreased temperature on the free ammonia concentration, because this will become lower. On the other hand, a lower temperature also will result in decrease of the maximum growth rate of the bacteria involved. The observed positive effect of the imposed temporary temperature drop on effluent VFA concentration is in accordance with the result of Angelidaki and Ahring (1994) who found that a temperature reduction from 55 to 40°C resulted in a decrease of the effluent VFA concentration. The data obtained in the temporary temperature raise show that the VFA content of the effluent of both $R^{20}{}_{50u}$ and $R^{10}{}_{50u}$ is lower compared to $R^{20}{}_{60u}$ and $R^{10}{}_{60u}$.

The data of VFA concentrations for all studied reactors, except those of the reactors operated at upward temperature fluctuation regime, have been plotted against the total and free ammonia concentrations. Although there is some scattering, the results reveal a high correlation coefficient (R^2 = 0.84) between effluent VFA's and NH_3 concentration (Fig. 4.2.4). Although the free ammonia concentration range in this study is different from that of Angelidaki and Ahring (1994), their results also give a strong relation between these two parameters. It can also be seen from this figure that the correlation between total ammonia concentration and VFA is very poor. The strong accumulation of VFA in $R^{20}{}_{60u}$ and $R^{10}{}_{60u}$ may be attributed to the effect of the extreme temperature and not to free ammonia concentrations.

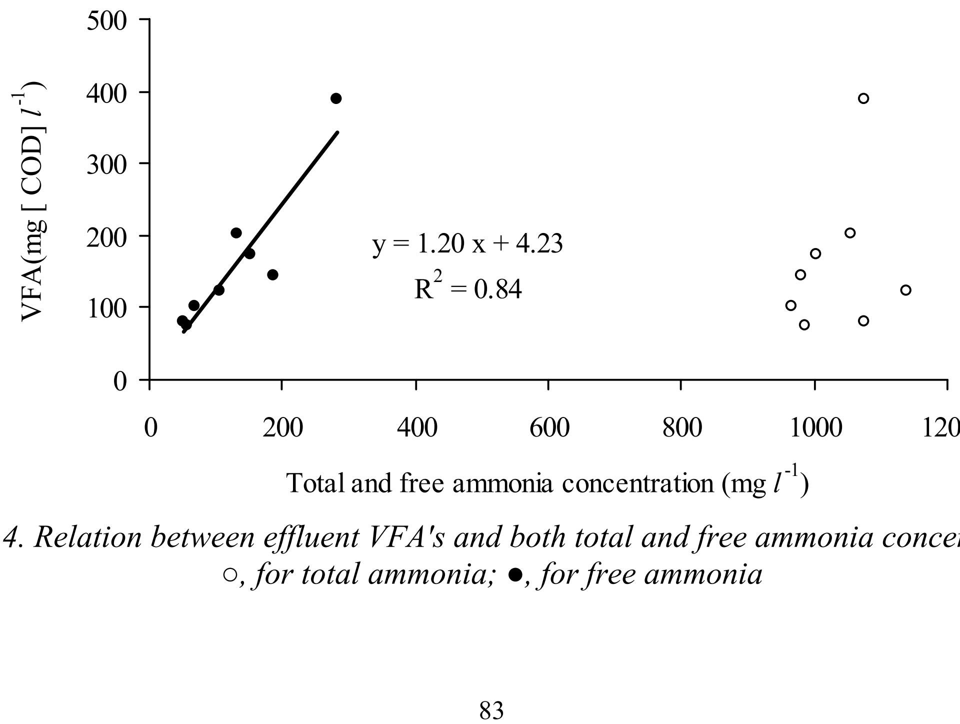


Fig.4.2.4. Relation between effluent VFA's and both total and free ammonia concentrations: ○, for total ammonia; ●, for free ammonia

The results in Table 4.2.8 show the individual fraction of VFA of the total VFA concentrations in the various reactors. It can be seen that at HRT = 20 days acetate constitutes more than 80% of the total VFA, except for R^{20}_{60u}. On the other hand, at HRT = 10 days the higher VFA's (>C_2) become more predominant. About 60 % of the total VFA at 60°C and about 37 % at 50°C and at 60°C particularly propionate is dominant (about 30 %) while at 50°C it is only present in small quantities (0.5%).

Acetate represents more than 80% of the total VFA for R^{20}_{50u} and R^{10}_{50u}. For R^{20}_{60u} and R^{10}_{60u}, both propionate and acetate are present at higher concentrations in the effluent while the higher VFA's (> C_3) are only present in minor amounts. The results of Varel *et al.* (1980) obtained in the thermophilic digestion of cattle waste at 65°C also demonstrated that acetate and other VFA are presented at higher concentrations in thermophilic systems compared to systems operated at lower temperatures. In experiments with a UASB reactor treating synthetic wastewater at mesophilic conditions (30°C), Visser *et al.* (1993) found that a short term, *i.e.* during a period of 8-9 h, exposure of the reactor to a temperature shock of 55°C and 65°C, the propionate and butyrate degradation recovered rapidly whereas that of acetate proceeded slowly. According to Van Lier (1995) the optimum temperature for propionate degradation is 55/60°C, and consequently it looks reasonable to attribute the observed inhibition of propionate and acetate degradation in both R^{20}_{60u} and R^{10}_{60u} to the exposure of the higher temperature.

Methanogenic activity

To quantify the effect of temperature and temperature fluctuation on the activity of methanogenic bacteria, maximum specific methanogenic activity (SMA) was performed on acetate as a sole substrate. Table 4.2.9 summarises the values assessed of SMA for the sludges in the various experimental runs.

From these data it can be seen that the maximum specific methanogenic activity (SMA) of the effluent from the reactor operated at 50°C or from the reactor originally operated at 50°C, exceeds that from the reactors operated at 60°C or which originally were operated at 60°C. These results are in agreement with the methane production rates found in all studied reactors, except R^{10}_{60d}. The SMA becomes lower in reactors operated at the shorter HRT, which can be attributed to the faster volume turnover, because it leads to a reduction of the ratio active cells/VS. For the imposed downward and upward temperature changes both results show that the SMA is higher at 50°C compared to any of the other temperatures studied. Apparently the microflora present in the reactors is mainly thermophilic of nature with an optimum temperature around 50°C. The imposed temporary upward temperature change more severely affects the SMA as compared to the imposed downward temperature change. This is quite similar to observations made by Lau and Fang (1997) in a study dealing with the effect of temperature shocks on the activity of bio-granules in a UASB operated at 55°C. They found a distinctly more severe effect on the SMA with a 10°C temperature increase (for 8 days) than a shock of 18°C temperature decrease (for 16 days). Furthermore, they found that a temperature shock had a less adverse effect on the acetotrophic methanogens than on the other methanogens. The SMA activity test at 30°C has been performed on sludge from all reactors operated under temperature fluctuation regimes. The assessed SMA at 30°C clearly is very low and for all effluents, but particularly for the effluent from the reactor originally operated at 60°C.

Table 4.2.8.Average measured VFA fractions during 'steady state'. The numbers between brackets are the percentages from the total VFA

Reactor	*VFA fractions (mg [COD] l^{-1})*						
	C_2	C_3	*i*-C_4	*n*-C_4	*i*-C_5	*n*-C_5	*Total*
R^{20}_{60u}	378.8 (31.6)	620.5 (51.8)	14.6 (1.2)	18.1 (1.5)	144.8 (12.1)	21.4 (1.8)	1198.2
R^{10}_{60u}	2508.8 (67.1)	733.3 (19.6)	110.6 (3.0)	133.7 (3.6)	217.7 (5.8)	36.2 (1.0)	3740.4
R^{20}_{60}	311.0 (80)	28.6 (7.4)	0.0 (0.0)	49 (12.6)	0.0 (0.0)	0.0 (0.0)	388.6
R^{10}_{60}	71.0 (40.9)	52.0 (30)	0.0 (0.0)	28.9 (16.6)	0.0 (0.0)	21.7 (12.5)	173.6
R^{20}_{60d}	141.2 (99.1)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.90 (0.6)	0.6 (0.3)	142.6
R^{10}_{60d}	108.7 (88.4)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	14.3 (11.6)	122.9
R^{20}_{50u}	52.0 (82.4)	0.0 (0.0)	0.0 (0.0)	10.3 (16.2)	0.9 (1.4)	0.0 (0.0)	63.2
R^{10}_{50u}	89.7 (88.4)	2.7 (2.7)	7.5 (7.4)	1.5 (1.5)	0.0 (0.0)	0.0 (0.0)	101.4
R^{20}_{50}	178.7 (88.9)	0.0 (0.0)	0.0 (0.0)	22.4 (11.1)	0.0 (0.0)	0.0 (0.0)	201.1
R^{10}_{50}	47.7 (63.2)	0.4 (0.6)	0.0 (0.0)	27.1 (35.9)	0.3 (0.4)	0.0 (0.0)	75.5
R^{20}_{50d}	99.8 (100)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	99.8
R^{10}_{50d}	77.4 (96.5)	2.8 (3.5)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	80.2

Table 4.2.9. Maximum specific methanogenic activity with standard deviation between brackets

Reactor	*Test temperature*	*SMA (g [COD] g^{-1} [VS] day^{-1})*
R^{20}_{50}	50°C	0.24 (0.007)
R^{20}_{60}	60°C	0.21 (0.003)
R^{20}_{50d}	30°C	0.05 (0.001)
	40°C	0.11 (0.005)
	50°C	0.21 (0.006)
R^{20}_{60d}	30°C	0.01 (0.004)
	50°C	0.23 (0.013)
	60°C	0.21 (0.018)
R^{10}_{50}	50°C	0.15 (0.002)
R^{10}_{60}	60°C	0.1 (0.006)
R^{10}_{50d}	30°C	0.06 (0.004)
	40°C	0.15 (0.036)
	50°C	0.15 (0.003)
R^{10}_{60d}	30°C	0.04 (0.0004)
	50°C	0.17 (0.007)
	60°C	0.15 (0.016)
R^{20}_{50u}	30°C	0.02 (0.006)
	50°C	0.11 (0.007)
	60°C	0.08 (0.014)
R^{20}_{60u}	30°C	---
	60°C	0.09 (0.01)
	70°C	0.07 (0.02)
R^{10}_{50u}	30°C	0.02 (0.001)
	50°C	0.09 (0.006)
	60°C	0.07 (0.001)
R^{10}_{60u}	30°C	0.03 (0.01)
	60°C	0.07 (0.02)
	70°C	0.04 (0.006)

4.2.5. General discussion

The results of the present study clearly demonstrate that a stable digester operation at thermophilic conditions (50 and 60°C) is well possible on cattle manure, as manifested in a constant methane production accompanied with constant low VFA concentration in the effluent. Moreover, the results demonstrate that such a stable operation also can be achieved after imposing short-term (10 hours) downward temperature changes to the system. This also is possible when imposing daily short term (5 hours) upward temperature drops of 10°C for reactors originally operated at 50°C, but not in the case for reactors originally were operated at 60°C.

The results clearly show that the use of solar energy for heating the reactor contents without heat storage or auxiliary heater during nights will not affect the reactor stability. The heat losses from the reactor during night-time never will reduce the reactor(s) temperature to the same extent as we studied here. The magnitude of temperature decrease or increase depends on many factors such as reactor size; thickness and type of insulation; ambient temperature; available solar collection area and the control system configuration. According to our results (*chapter* 4.5) the daily temperature fluctuation in a well insulated 10 m^3 CSTR will be in the order of magnitude of ± 1°C.

According to Visser *et al.* (1993) imposed temperature fluctuations may affect the bacteria type involved in the process, at temperatures exceeding the maximum value for growth, anyhow decay may exceed the growth rate of bacteria, and this irrevocably then will result in a decrease in the reactor removal capacity. Zinder *et al.* (1984) mentioned that the thermophilic *Methanothrix* enrichment is capable to grow at temperatures up to 70°C while *Methanosarcina* sp. grows faster at 55°C than a *Methanothrix* culture, while at 60°C, the doubling time of the two cultures are quite similar (*ca.*30h). They also mentioned that *Methanosarcina* sp., a predominant aceticlastic thermophilic methanogens, is sensitive to temperature elevations above 60°C. They postulated that the digester might withstand minor temperature fluctuations when operated closer to the optimum temperature of *Methanosarcina* sp., (55 to 58°C).

As far as the effect of the free ammonia concentration concerned there apparently exists an incessant relation with both temperature and pH, which likely may be attributed to the fact that the bacterial cell wall is far more permeable for un-dissociated molecules than for ions (Van Velsen and Lettinga, 1980). Many researchers have postulated that the high NH_3 concentration can inhibit thermophilic digestion more seriously compared to mesophilic digestion (Zeeman *et al.,* 1985; Wiegant and Zeeman, 1986; Angelidaki and Ahring, 1993,a). According to early findings of McCarty and McKinney (1961) free ammonia concentration exceeding 150 mg l^{-1} will be inhibitory. But according to Koster and Lettinga (1988); Braun *et al.* (1981); Kroeker *et al.* (1979), NH_3 concentration under mesophilic conditions already is inhibitory in the range 80-150 mg [N] l^{-1} at a pH of 7.5. The observed process inhibition by ammonia appeared to be a result of too high concentrations of free ammonia rather than to the high concentration of the ammonium ion. However, they also revealed that even at free ammonia concentration as high as 257 mg l^{-1}, toxicity or total cessation of bacterial activity was not evidenced but inhibition occurred. Dealing with the anaerobic digestion of cow manure at much higher concentrations compared to those used in this study, Zeeman *et al.* (1985) demonstrated that the high concentration of free ammonia is the main factor responsible for the poor performance of thermophilic digestion of cow manure. The hypothesis that the temperature will enhance ammonia inhibition of methanogenesis due to the increase of the fraction of unionised ammonia, already was used by Van Velsen (1981) previously to explain the poor results obtained in the thermophilic digestion of piggery wastes as compared to mesophilic digestion. From the results of the present study, it is reasonable to conclude that the free ammonia concentration particularly affects the acetate-utilising bacteria. As far as reversibility of the ammonia toxicity, the results of Angelidaki and Ahring (1994) revealed that an imposed temperature drop from 55 to 40°C in a digester operated at 15 days HRT resulted in relief from the inhibition caused by high concentration of free ammonia.

Our results clearly show that hydrolysis is the most seriously affected process step in the anaerobic digestion of animal manure in the temperature range of 50-60ºC. Whereas the rate of the hydrolysis step is negatively affected by lower temperatures as appeared from the results of a CSTR operated under steady state conditions at 50 and 60ºC, a short term temperature decrease from 60 towards 50ºC also negatively affects hydrolysis. The latter indicates that not the enzyme activity but the enzyme production is affected by high NH_3 concentrations.

4.2.6. Conclusions

The effect of two different temperatures (50 and 60°C) and of short-term temperature fluctuation on the anaerobic digestion of cow manure were investigated in CSTR's at two different HRT's (10 and 20 days). Stable operation at both constant and fluctuated temperatures was realised. Beside the effect of temperature/temperature fluctuation on the process performance some others conclusions can be drawn:

- Hydrolysis is negatively effected by temperature in the temperature range of 50 to 60ºC as appeared from the results of CSTR's operated with animal manure under 'steady state' conditions.
  - The negative effect of the temperature on hydrolysis is possibly caused by increased NH_3 concentrations, which prevail at higher temperature.
  - The inhibition of the hydrolysis at increased temperature is not reversible, as was clearly demonstrated by the results found in experiments dealing with short-term temperature drops.
- Acidogenesis is negatively effected by increased NH_3 concentrations, which prevail when the operational temperature is increased.
- Methanogenesis is likewise negatively affected by increased NH_3 concentrations.

4.3. Effect of Ammonia on Thermophilic Anaerobic Hydrolysis of Dairy Cattle Manure

Abstract

The first order hydrolysis constant (k_h) of dairy cattle manure has been determined in batch anaerobic reactors at temperatures of 50 and 60°C to study the effect of varying reactor temperatures. In addition also the effect of high ammonia concentrations (1-3.7 g l^{-1}) on the k_h values was studied under the same experimental conditions. The results obtained in the investigations show that at each studied temperature, the k_h value linearly decreases with both the increase of total and the free ammonia concentrations. However, the mechanism underlying the observed effect is still unknown. The results also show that at most of the studied conditions, the temperature increase did not positively affect k_h values. This likely can be explained by a possible positive effect of the temperature on the k_h value is compensated by the negative effect of high ammonia concentrations on the k_h. Acidogenesis looks the rate-limiting step at free ammonia concentrations of $\leq$ 0.250 g l^{-1} while at free ammonia concentration >0.25 g l^{-1}, methanogenesis is the rate-limiting step.

4.3.1. Introduction

Anaerobic digestion already is universally used for many years for the treatment of agricultural wastes and wastewaters. To optimise the process performance, the behaviour of each individual step involved in the digestion process (*i.e.* hydrolysis, acidogenesis and methanogenesis) should be investigated on its either the stimulatory or inhibitory/toxic components. Depending on the characteristics of the waste, any of these steps may be affected by toxicity (Bhattacharya and Parkin, 1989).

Ammonia comprises one of the inhibitory components, and since exceptionally high ammonia-nitrogen concentrations (exceeding 3 g l^{-1}) frequently occur in animal manure (Van Velsen and Lettinga, 1980), it is a very reliant compound to be investigated on its effect on digestion processes. High concentrations of ammonia cause inhibition or even total cessation of the process, at least temporary. The threshold concentration causing inhibition or toxicity depends on the applied ammonia concentration, on the prevailing process temperature and the extent of adaptation of the microflora present in the reactor (Van Velsen, 1981; Koster, 1989). Webb and Hawkes (1985) mentioned that the inhibitory effects of intentionally raised NH^+_4N levels are lower than those resulting from naturally produced NH^+_4N. In the digestion of piggery wastes at 37°C, Braun *et al.* (1981) found that addition of NH_4Cl up to total ammonia concentration of 2.96 - 4.85 g [NH^+_4-N] l^{-1} even had a stimulatory effect on the amount of methane ultimately produced (higher accumulated methane) and also on the rate compared to supplied ammonia concentrations up to 2.18-3.39 g [NH^+_4-N] l^{-1}. However these researchers did not explain that phenomenon.

Many studies have been carried out to assess the effect of ammonia on the digestion of animal manure both at mesophilic and thermophilic conditions. Most of the research conducted so far focused on the methanogenic step (Zeeman *et al.,* 1985; Angelidaki and Ahring, 1993a; Hansen *et al.,* 1998). Moreover many researchers explored the mechanisms of the ammonia effect on specific methanogenic bacteria. Some proof was gathered for the hypothesis that acetate-consuming methanogenic bacteria are more strongly affected by ammonium-nitrogen than hydrogen-consuming methanogenic bacteria (Koster and Lettinga, 1984; Koster, 1989; Angelidaki and Ahring, 1993a). Contrary to the previous mentioned mechanism, Wiegant and Zeeman (1986) proposed a mechanism for NH_4^+-N (0.1- 4.5 g l^{-1}) inhibition in the thermophilic digestion of cow manure. This mechanism illustrates an inhibition of the hydrogen consuming methanogens by NH_4^+-N, while the acetate-consuming bacteria are not directly inhibited by NH_4^+-N.

Only few researchers so far studied the effect of ammonia on hydrolysis. Under mesophilic conditions, according to Zeeman (1991) there exists an inverse relation between hydrolysis of dairy cattle manure and both the total and the free ammonia concentrations. An increase of ammonia (2.07-5.3 g l^{-1}) by addition of urea to a system digesting piggery waste resulted in clear drop of the metabolic rate of hydrolytic bacteria (Van Velsen, 1981). However it was not clear whether the increase of the pH or the increase of ammonia or a combination of both was the reason for the decline in the rate. In a kinetic study conducted by Vavilin *et al.* (1996), the methane production rate was found to decrease substantially, which could be due to inhibition of the hydrolysis step by the prevailing high NH_3 concentration of 0.991 g l^{-1}.

So far, to our knowledge, no studies have been dedicated to the effect of ammonia on the hydrolysis constant under thermophilic conditions, and therefore the objectives of the present study were:

1- To determine the first order hydrolysis constant (k_h) of dairy cattle manure at two different temperatures (50 and 60°C) using batch reactors.

2- To assess the effect of addition of high ammonia concentrations (in the form of NH_4Cl) on the process performance and on the k_h value at the same experimental conditions.

4.3.2. Materials and methods

4.3.2.1. Experimental set up

The multiple flask reactor set-up (Sanders, 2001) was used in the present study. This system consists of a set of eight identical 300-ml serum flasks, which represent one large reactor. At the start of the experiment, all serum flasks have the same contents (Table 4.3.1); the manner the process of hydrolysis proceeds is assumed to be similar in all sepate flasks (Sanders, 2001). Each flask contained an amount of manure to give the initial composition shown as in Table 4.3.1. Additionally, an amount of inoculum (digested cow manure) and NH_4Cl stock solution (in the experiments with adding NH_4Cl) were added to a total ammonia concentration in the range of 1-3.7 g l^{-1}. Then the flasks were filled with distilled water to a working volume of 100 ml (200 ml as headspace). For every experimental flask, an accompanying flask was used as a control for correction of CH_4 and for assessment of the COD_{dis} and VFA produced from inoculum. No nutrients were applied in any of the assays and pH control was also not applied in order to avoid possible inhibition due to a high salt concentration (Koster and Lettinga, 1988). The manure was collected and stored as described in *chapter* 4.2.

Table 4.3.1. Substrate composition in the experimental reactors

Parameter	*Total COD*	*COD_{dis}*	*Total VFA*	*N-Kj*	*NH^+_4-N*
Unit	g l^{-1}	g l^{-1}	g [COD] l^{-1}	g l^{-1}	g l^{-1}
Value	57.88	9.29	3.31	1.96	0.85

After filling, the contents of the serum flasks were mixed manually and next the flasks were flushed with N_2 for three minutes and sealed with rubber stoppers and aluminium caps. The bottles were incubated statically at the desired temperatures (50^{o}C and 60^{o}C). After the content of the bottles reached the incubation temperature (*i.e.* after about 1 h) the gas at headspace of each bottle was released to reach the atmospheric pressure equilibrium.

At different time intervals (see Figs. 4.3.1- 4.3.3) after the start of the experiments, one of the serum flasks and one control flask were selected randomly to analyse their contents. For these two serum flasks gas pressure and composition were measured through the rubber septum. The gas pressure was measured using a portable membrane pressure unit, Wal 0 - 4 bar absolute (Wal Mess- und Regelsysteme, Oldenburg, Germany). The gas composition was measured in duplicate. Then the contents of the selected flask-containing sample were analysed, in duplicate, for VFA, dissolved COD and ammonia. While for the control, the contents were analysed for VFA and COD_{diss} also in duplicate.

The biodegradability assay was carried out in duplicate at 50^{o}C using the same serum flasks, containing the manure of same composition as used for hydrolysis constant calculations. The amount of methane produced was monitored, for 83 days. Control bottles were also used. At the termination of the experiment the contents of the bottles were analysed for VFA and COD_{dis}.

4.3.2.2. Inoculum

The reactors were inoculated with adapted (*ca* 1.1 g [NH^+_4-N] l^{-1}) digested cow manure originating from a 'steady state' thermophilic laboratory scale Completely Stirred Tank Reactor (CSTR) operated at HRT of 20 day and temperatures of 50 and 60^{o}C. The amount of inoculum was calculated to give the same activity potential (g [COD removed] l^{-1}day^{-1}) at both temperatures. The added amount of inoculum was calculated to be enough to prevent VFA accumulation at a 20 days Solid Retention Time (SRT), with addition of 25% extra of inoculum. This was done assuming a hydrolysis constant of 0.07 day^{-1} (Zeeman, 1994). The methanogenic activity of the inoculum used was measured by VFA depletion (Van Lier, 1995). The characteristics of the inoculum used are presented in Table 4.3.2.

Table 4.3.2. Characteristics and amount of inoculum

Parameter at T =	*50°C*	*60°C*
Specific methanogenic activity (g [COD]g^{-1} [VS] day^{-1})	0.24	0.21
COD_{dis} (g l^{-1})	5.95	7.46
VFA (g[COD] l^{-1})	0.20	0.39
Total ammonia (g l^{-1})	1.06	1.08
pH	7.68	7.83
Free ammonia (g l^{-1})	0.131	0.282
VS (g l^{-1})	21.6	33.5
Inoculum amount (g[VS]g^{-1} [COD added])	0.086	0.098

4.3.2.3. Analysis

The samples for VFA and COD_{dis} measurements were diluted (20 times). These samples were centrifuged at 3500 rpm for 10 minutes. The samples were membrane-filtered using 0.45µm (Schleicher & Schuell ME, Germany). COD_{dis} was measured using the micro method (Jirka and Carter, 1975). The VFAs were determined by gas chromatography, for the membrane-filtered samples, using a Hewlett Packard 5890 equipped with a 2 m × 2mm glass column, packed with Supelcoport (100-120 mesh) and coated with 10 % Fluorad FC 431. The temperatures of the column, injection port and flame ionisation detector were 130, 220 and 240°C, respectively. The carrier gas was nitrogen saturated with formic acid (40 ml per min). Total COD was measured as described by Zeeman (1991). Ammonia nitrogen was measured by distillation method (APHA, 1992). Total solids (TS) and volatile solids (VS) were measured as described by APHA (1992). All measurements were performed in duplicate.

The biogas composition (CH_4; CO_2; N_2; O_2) was determined in duplicate in a 100 µl sample using Fisons instrument gas chromatography model GC 8000 Interscience. The GC was equipped with columns connected in parallel (split 1:1): (1.5m × 2mm) Teflon, packed with chromosorb 108, (60-80mesh), and (1.2mx2mm) stainless steel, packed with molecular sieve 5A, (60-80 mesh). Helium was used as a carrier gas (45 ml/min). The oven, detector and injection temperatures were 40, 100 and 110°C respectively. A mixture of 2.94% O_2; 20% N_2; 24.8%CO_2, and 51.76% CH_4 was used as a standard.

4.3.3. Data processing

4.3.3.1. Methane production

The total methane production (for sample and inoculum flasks) was calculated from the accumulated methane in the headspace and the dissolved methane. The later was calculated according to Henry's law. The amount of methane in the headspace can be calculated as follows:

$$M_{CH_4} = \frac{CP_h V_h p_r}{RTV_L} \qquad (4.3.1)$$

M_{CH_4} = amount of methane production (g [COD] l^{-1})
C = conversion factor, theoretically, 64 g [COD] mol^{-1} [CH_4 at standard temperature of 0^oC and standard pressure of 1 atm.].
P_h = the pressure in the headspace, (Pa).
V_h = the headspace volume, (m^3)
p_r = percentage of the methane in the headspace (%).
R = universal gas constant (8.31 $Jmol^{-1}$ K^{-1})
T = temperature (K).
V_L = the liquid volume (*l*).

4.3.3.2. Biodegradability calculation

Biodegradability was calculated according to:

$$\text{Biodegradability} = \frac{(accumulated\, CH_4\, as\, COD)100}{Total\, COD\, added} \qquad (4.3.2)$$

4.3.3.3. Hydrolysis constant calculation

The first order hydrolysis constant was calculated using the equation derived by Sanders (2001) on the basis of the equation of Eastman and Ferguson (1981):

$$\ln\left(\frac{X_{SS,Eff} - X_{SS,Inf}(1 - f_h)}{X_{SS,Inf}\, f_h}\right) = -k_h t \qquad (4.3.3)$$

Where: $X_{SS,Eff}$ = concentration of total particulate in the effluent (biodegradable + non biodegradable part) ,(g l^{-1})
$X_{SS,Inf}$ = concentration of total particulate in the influent, (g l^{-1}).
f_h = biodegradable fraction of particulate part, $\in [0,1]$.
k_h = first order hydrolysis constant, (day^{-1}).
t = the digestion time , (day).

4.3.3.4. Some other calculations

Calculations of free ammonia concentrations and the percentages of the hydrolysis, acidogenesis and methanogenesis have been calculated as described in *chapter* 4.2.

4.3.4. Results and discussion

4.3.4.1. Biodegradability

The calculated biodegradability of the total COD after a 83 days digestion period amounted to 39.53%. A comparable value (0.36-0.4 (g [VS destroyed] g^{-1} [VS added])) for dairy cattle manure has been reported by Hill (1982) and Zeeman (1991). It should be mentioned here that we assessed the biodegradability merely at 50°C since from literature it is known that the temperature does not affect the biodegradability. So Hashimoto *et al.* (1981b); Veeken and Hamelers (1999) and Mahmoud (2002) found a very similar biodegradability for cattle manure in the temperature range 30-60°C as well as for 6 different types of solid biowaste in the temperature range 20-40°C and for primary sludge between 15-35°C. The COD_{diss} and VFA concentrations at the end of the biodegradability assay amounted to 1.1 g l^{-1} and 0.062 g [COD] l^{-1} respectively. From these data the amount of removed dissolved COD was calculated at about 88%. The biodegradability of the particulate COD was calculated to be 30.2%, which is used for the hydrolysis constant calculations. At mesophilic conditions a removal efficiency of about 69% could be calculated from the data published by Zeeman (1991). The assessed higher removal efficiency for COD_{diss} in the present study can be attributed either to the better accessibility of the refractory particles for biodegradation after the imposed long term exposured to the high temperature (50°C) or to the attachment of the small particles to the large particles. According to Elmitwalli (2000) in the batch digestion of membrane filtered (0.45 μm) sewage, the particle size of finely dispersed matter increases.

4.3.4.2. Hydrolysis

Table 4.3.3 summarises the average pH values and both the total and the free ammonia concentrations measured in all reactors over the experimental course, together with the calculated k_h values and determination coefficient (R^2) for k_h calculations. It should be mentioned that in the first reactors (R_{1-50} and R_{1-60}), the calculated k_h values apply for condition where no additional NH_4Cl has been supplied. From the data in Table 4.3.3 reveal that at R_{1-50} and R_{1-60}, the calculated k_h are very similar at both studied temperatures, although the ammonia concentrations in the R_{1-60} reactor were substantially higher. Figure 4.3.1 shows the course of the ammonia concentration over the whole experimental period for both studied temperature conditions (R_{1-50} and R_{1-60}). A quite evident increase of total ammonia manifests at both temperature conditions, but at 60°C the amount of ammonia produced is clearly higher. This may be attributed to the higher hydrolysis rate of protein under the higher temperature (Sanchez *et al.,* 2000).

Table 4.3.3. Measured average and standard deviation (±) of pH and concentrations of both total and free ammonia concentrations as well as k_h and R^2 values which are calculated from equation (4.3.3) with $f_h = 0.302$

Parameters	*Reactors*							
	$R_{1\text{-}50}$	$R_{1\text{-}60}$	$R_{2\text{-}50}$	$R_{2\text{-}60}$	$R_{3\text{-}50}$	$R_{3\text{-}60}$	$R_{4\text{-}50}$	$R_{4\text{-}60}$
Total ammonia (g l^{-1})	1.06	1.22	2.20	2.06	3.20	2.31	3.77	3.56
	±0.04	±0.07	± 0.07	±0.05	± 0.12	± 0.18	±0.14	±0.18
Free ammonia (g l^{-1})	0.079	0.146	0.137	0.250	0.215	0.301	0.235	0.359
	±0.03	±0.04	±0.06	±0.08	±0.11	±0.09	±0.15	±0.16
pH	7.43	7.40	7.33	7.44	7.36	7.45	7.30	7.30
	±0.13	±0.14	±0.17	±0.20	±0.22	±0.13	±0.28	±0.20
k_h (day^{-1})	0.075	0.072	0.056	0.06	0.037	0.04	0.038	0.023
R^2	0.91	0.96	0.97	0.81	0.96	0.89	0.93	0.70

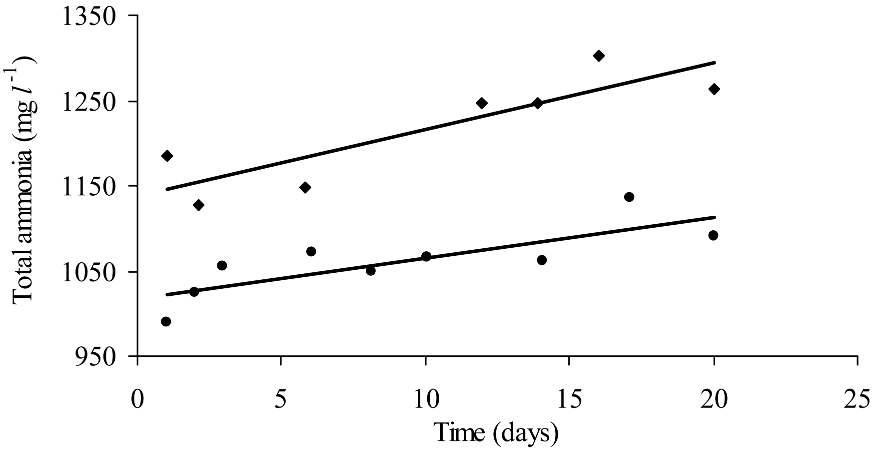


Fig.4.3.1. Total ammonia concentration over the whole experiment time: ■, 60°C; ●, 50°C

In the second and the third experiment we increased the ammonia concentrations by supplying NH_4Cl (reactors $R_{2\text{-}50}$, $R_{3\text{-}50}$, $R_{4\text{-}50}$ and $R_{2\text{-}60}$, $R_{3\text{-}60}$, $R_{4\text{-}60}$). From the data in Table 4.3.3 it is clear that the average pH did not differ significantly among the reactors as a result of NH_4Cl addition. The same observations were made also by Rollon (1999) in digestion experiments with fish processing wastewater where NH_4Cl was supplied. Moreover we found that the addition of NH_4Cl did not raise the pH to the same values obtained in CSTR operated at the same temperatures (see *chapter* 4.2). The latter may be attributed to the slightly acidic NH_4Cl added (Angelidaki and Ahring, 1994) and to the higher VFA concentrations prevailing in the system especially during the first period of the experiments (Fig. 4.3.3 a and b).

From the results presented in Table 4.3.3 it can be concluded that the hydrolysis of cow manure can be described 'perfectly' by first order kinetics (values of R^2 are at least 0.7), which according to Veeken and Hamelers (1999) would demonstrate that hydrolytic enzymes have occupied all available degradable adsorption sites of the manure. Such a complete occupation may either be the results of the presence of a sufficient amount of hydrolytic enzymes on the surface of the manure in the first phase of the process or the result of a fast growth of the hydrolysing bacteria (Hobson, 1985; Pavlostathis and Giraldo-Gomez, 1991; Veeken and Hamelers, 1999).

The results in Table 4.3.3 reveal that at each of the studied temperatures the calculated k_h decreases with both an increase of the total ammonia and the free ammonia concentration as well, and apparently more or less linearly according to a relation $k_h = A X + B$, where X represents either total or free ammonia concentration (g l^{-1}). The constants (A and B) are mentioned together with R^2 values (Table 4.3.4).

Table 4.3.4. Regression parameters (A, B and R^2) for fitting of hydrolysis constant as a function of total and free ammonia concentrations ($k_h = AX + B$)

Parameter	*Effect of total ammonia*		*Effect of free ammonia*	
	Temperature		*Temperature*	
	50°C	*60°C*	*50°C*	*60°C*
A (l g^{-1}day^{-1})	-0.015	-0.021	-0.242	-0.231
B (day^{-1})	0.089	0.098	0.092	0.11
R^{2*}	0.95	0.92	0.97	0.94

*n = 4

The results in Table 4.3.4 show a very strong negative correlation between the k_h values and both total and free ammonia concentrations. Similar results have been published by Zeeman (1994) for the digestion of cattle manure at mesophilic conditions. It should be mentioned that the k_h value increases with the imposed temperature (Veeken and Hammelers, 1999; Sanders, 2001 and Mahmoud, 2002). In all the reactors except $R_{3\text{-}60}$ and $R_{4\text{-}60}$, the assessed k_h values are more or less the same at both studied temperatures. This might explain that the positive effect of higher temperature on k_h is compensated by the negative effect of ammonia. At $R_{3\text{-}60}$ and $R_{4\text{-}60}$, the negative effect of high ammonia is prevailing.

4.3.4.3. Acedogenesis

As can be seen from the data in Tables 4.3.5 and 4.3.6 the calculated acidogenesis percentages after 20 days are almost constant at 50°C at all applied ammonia concentrations. This means that the high total ammonia and free ammonia concentrations do not affect the acidogenic bacteria. It can also be seen that the percentages of acidogenesis are almost the same as the assessed percentages of methanogenesis. However, from the data presented in Tables 4.3.3, 4.3.5 and 4.3.6 it can be concluded that at 60°C and at high concentrations of total ammonia ($\geq$ 2.06 g l^{-1})/free ammonia ($\geq$ 0.25 g l^{-1}) the process of acidogenesis is clearly affected. According to Koster and Lettinga (1988) acidogenic populations in the granular sludge are hardly affected by ammonia in the concentration range 4.1-5.7 g l^{-1} at 30°C. On the other hand results of Rollon (1999) obtained in the anaerobic degradation of fish processing wastes showed that a clear inhibition occurs of the protein acidogenesis already at ammonia concentrations as high as 1.5 g l^{-1}. Our results (see Tables 4.3.5 and 4.3.6) reveal an accumulation of COD_{dis} but no accumulation of VFA at temperatures of 50 and 60°C and at lower ammonia concentrations. These results lead to the conclusion that the acidogenesis step is rate limiting at free ammonia concentration of ≤ 0.250 g l^{-1}.

4.3.4.4. Methanogenesis

The assessed percentages methanogenesis of the total added COD at 50°C and at 60°C with and without NH_4Cl addition are summarised in Tables 4.3.5 and 4.3.6 and depicted in Fig. 4.3.2, a and b. The ammonia concentrations shown in these Figures are the average over 20 days (Table 4.3.3). As can be seen that the addition of NH_4Cl increases the lag phase from about 2 days to about 5 days. Similar results were obtained by Van Velsen (1981) who studied the digestion of piggery waste at 30°C in batch digestion using sewage sludge adapted to 0.815 g l^{-1}. The results clearly show that methanogenesis still occurs at high ammonia concentrations (1.21-4.99 g l^{-1}), although the lag phase increases with increasing ammonia concentrations, even reaching 50 days at ammonia concentration of 4.99 g l^{-1}. It can also be seen (Fig. 4.3.2, a and b) that at both temperatures studied, the adverse effect of ammonia is more pronounced in the first period (*ca* first 13-14 days) of the experiments. To quantify this effect on methanogenesis, we plotted the values of accumulated methane production versus the time during the period (excluding the lag phase) where VFA are available (Fig. 4.3.3 a and b). The slopes of these plots give the maximum methane production rates (g [COD] l^{-1} day^{-1}). In these plots, conform theory, the Y intercepts were set to zero. The methane production rates assessed from these plots are summarised in Table 4.3.7 and from these data it can be seen that the maximum methane production rate declines with increasing ammonia concentration. Similar results were also obtained by Koster and Lettinga (1984). Apparently the differences between that rates at different ammonia concentrations are more pronounced at 60°C compared to that at 50°C.

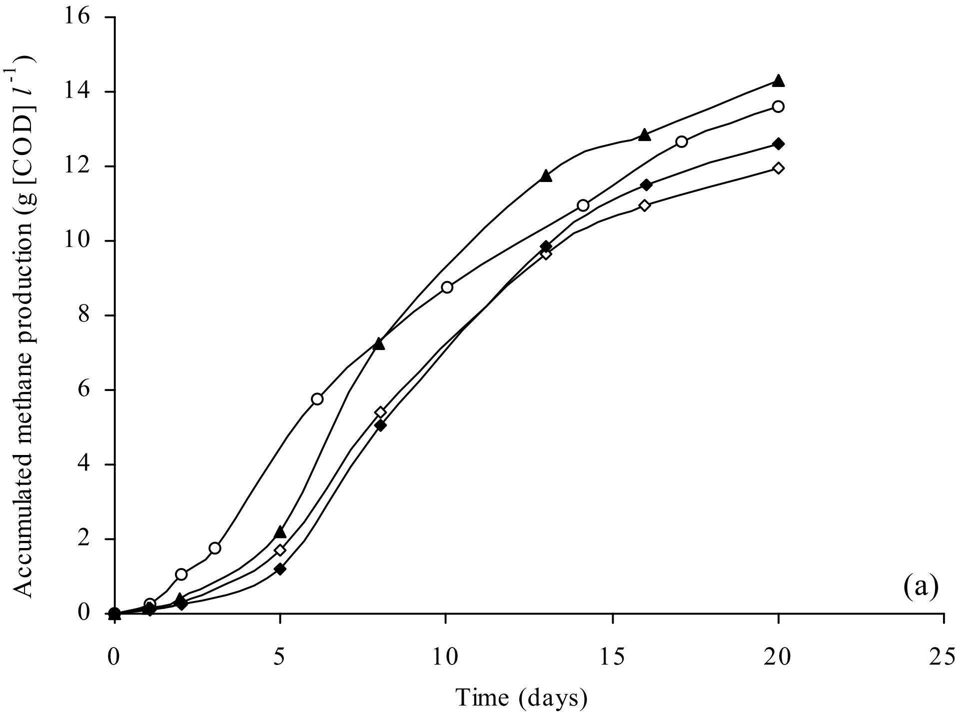


Fig.4.3.2, a. Accumulated CH_4 at 50°C at different ammonia concentrations: ○, 1.06 g l^{-1}; ▲, 2.2 g l^{-1}; ◊, 3.2 g l^{-1}; ♦, 3.77 g l^{-1}

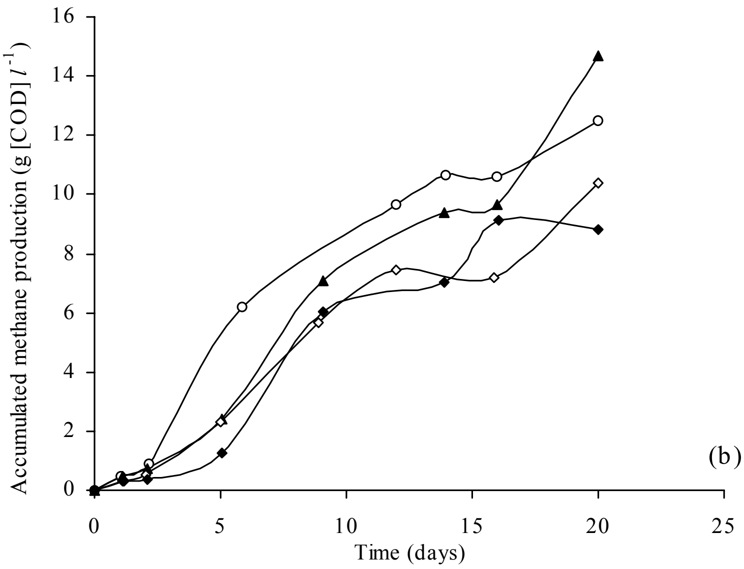


Fig.4.3.2,b. Accumulated CH_4 at 60°C at different ammonia concentrations: ○, 1.22 g l^{-1}; ▲, 2.06 g l^{-1}; ◊, 2.3 g l^{-1}; ♦, 3.6 g l^{-1}

Moreover, apparently at 50°C the differences on the accumulated methane at the end of experiments between all studied ammonia concentrations are insignificant. On the other hand, at 60°C the accumulated CH_4 in $R_{3\text{-}60}$ and $R_{4\text{-}60}$ is lower than that at other reactors. The data in Table 4.3.3 show that the total ammonia concentrations at both temperatures are comparable, but the calculated maximum free ammonia concentration at 50°C 0.235 g l^{-1} is significantly lower than the values of 0.301 and 0.358 g l^{-1} found at 60°C. This may be the reason for the observed low accumulated amount of CH_4 at $R_{3\text{-}60}$ and $R_{4\text{-}60}$. Various inhibitory thresholds values of the free ammonia concentrations for methanogenic bacteria have been reported in literature. According to results of Webb and Hawkes (1985) obtained at 35°C and with adapted seed sludge ammonia concentration of 3.39 g l^{-1}, corresponding to free NH_3 concentrations of 0.33-0.37 g l^{-1} can be handled with little inhibitory effect.

Table 4.3.5. Measured parameters at all reactors operated at 50°C after 20 days

Parameter	*Reactors*			
	$R_{1\text{-}50}$	$R_{2\text{-}50}$	$R_{3\text{-}50}$	$R_{4\text{-}50}$
Accumulated CH_4 (g[COD] l^{-1})	13.62	14.29	11.96	12.6
COD_{dis} (g l^{-1})	7.82	5.23	5.23	4.85
VFA (g [COD]l^{-1})	0.117	0.097	0.114	0.313
Acetate (g [COD] l^{-1})	0.069	0.084	0.079	0.115
Propionate (g [COD] l^{-1})	0.00	0.013	0.035	0.032
Ammonia (g l^{-1})	1.091	2.217	3.267	3.907
pH	7.48	7.6	7.71	7.72
Hydrolysis* (%)	37.0	33.7	29.7	30.2
Acidogenesis* (%)	23.7	24.9	20.9	22.3
Methanogenesis* (%)	23.5	24.7	20.7	21.8

* Calculated as a percentage of the total COD added.

Table 4.3.6. Measured parameters at all reactors operated at 60^oC after 20 days

Parameter	*Reactors*			
	$R_{1\text{-}60}$	$R_{2\text{-}60}$	$R_{3\text{-}60}$	$R_{4\text{-}60}$
Accumulated CH_4 (g [COD] l^{-1})	12.51	14.7	10.4	8.83
COD_{dis} (g l^{-1})	7.86	6.53	7.91	4.88
VFA (g [COD] l^{-1})	0.216	0.541	1.556	1.446
Acetate (g [COD] l^{-1})	0.165	0.344	0.20	0.349
Propionate (g [COD] l^{-1})	0.051	0.158	1.095	0.822
Ammonia (g l^{-1})	1.263	2.048	2.343	3.73
pH	7.51	7.44	7.44	7.4
Hydrolysis* (%)	35.2	36.7	31.6	23.7
Acidogenesis* (%)	22.0	26.3	20.7	17.8
Methanogenesis* (%)	21.6	25.4	18.0	15.3

* Calculated as a percentage of the total COD added.

Table 4.3.7. Maximum methane production rate (MMPR) driven from the maximum slopes of Fig. 4.3.2, a and b during the period from day 5 to day 14

Parameters	*Reactors*							
	$R_{1\text{-}50}$	$R_{1\text{-}60}$	$R_{2\text{-}50}$	$R_{2\text{-}60}$	$R_{3\text{-}50}$	$R_{3\text{-}60}$	$R_{4\text{-}50}$	$R_{4\text{-}60}$
MMPR (g [COD] l^{-1} day^{-1})	0.871	0.803	0.86	0.688	0.688	0.611	0.675	0.527
R^2	0.96	0.95	0.89	0.92	0.89	0.95	0.84	0.81

Figure 4.3.3 a and b show the course of total VFA concentration in relation to the imposed SRT. Apparently for both studied temperatures VFA accumulated in the first period (*i.e.* during the lag phase), after *ca* 5 days the VFA concentration decreased. The rapid accumulation of VFA indicates that the processes of hydrolysis and acidification almost start immediately, at least at substantially higher rate than methanogenesis (Zeeman, 1991; Ten Brummeler, 1993; Veeken and Hamelers, 1999). At the termination of the experiments conducted at 50^oC, the VFA concentrations drop to values as low as 0.313 g [COD] l^{-1} at $R_{4\text{-}50}$ (Table 4.3.4). It also is clear that in the reactors operated at 60^oC after 20 days a distinctly higher VFA concentration is found than in the systems operated at 50^oC. It also can be seen (Fig. 4.3.3a and 4.3.3b; Tables 4.3.5, 4.3.6) that at both temperatures the higher VFA-concentration is found at the higher ammonia concentration, results which are very similar to those of Zeeman *et al.*, (1985) and Zeeman (1991), who found an exponential increase of VFA with NH_4^+-N increase (1.2-4.9 g l^{-1}) at both mesophilic and thermophilic conditions.

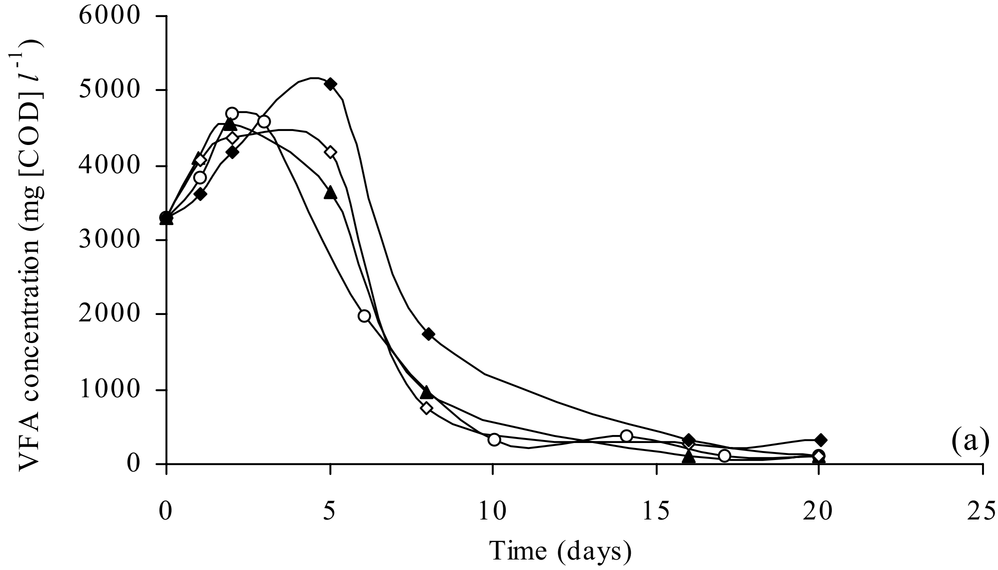


Fig.4.3.3,a. VFA concentrations at 50°C at different ammonia concentrations : ○, 1.06 g l^{-1}; ▲, 2.2 g l^{-1}; ◊, 3.2 g l^{-1}; ♦, 3.77 g l^{-1}

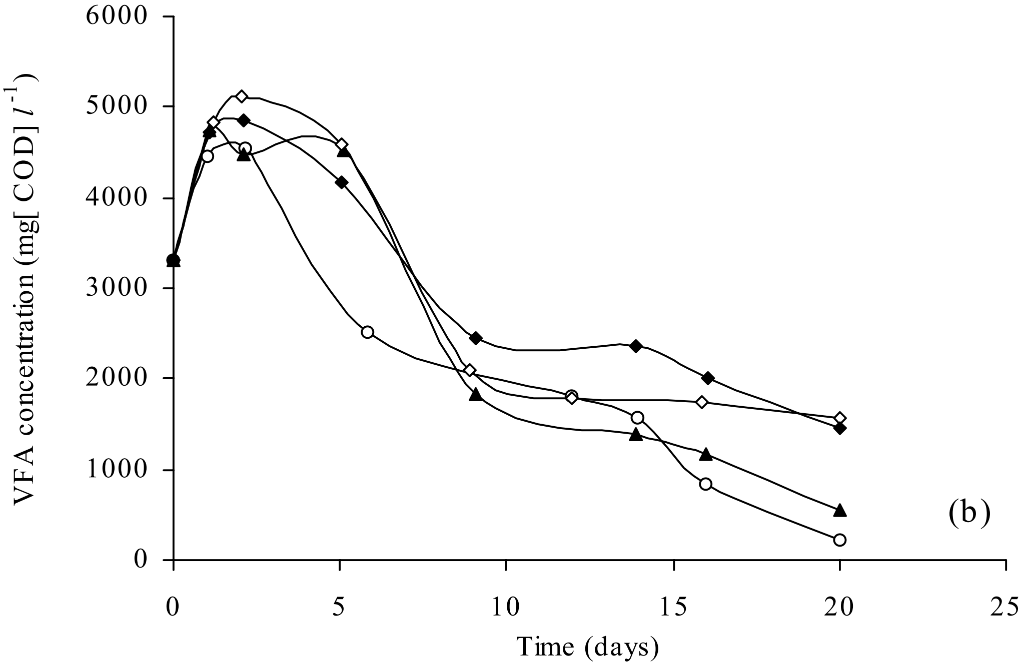


Fig.4.3.3,b. VFA concentrations at 60°C at different ammonia concentrations: ○, 1.22 g l^{-1}; ▲, 2.06 g l^{-1}; ◊, 2.3 g l^{-1}; ♦, 3.6 g l^{-1}

Tables 4.3.5 and 4.3.6 present the values of the various assessed parameters at the end of the experiments (*i.e.* after 20 days). They show that at 50°C acetate represents the major constituent of VFA. This is also the case for 60°C in the reactors operated at average ammonia concentrations of 1.2 and 2.06 g l^{-1}, but at average ammonia concentrations of 2.3 and 3.5 g l^{-1} propionate represents the major VFA-constituent at 60°C. Apparently under these conditions of high ammonia concentrations the accumulation of propionate can be attributed to an indirectly effect of the high $NH^{+}{}_{4}N$ concentration, *i.e.* an inhibition of hydrogen utilising bacteria (Wiegant and Zeeman, 1986).

4.3.5. Final discussion and conclusions

The results of our present study demonstrate that in the anaerobic (batch) digestion at a temperature of 50°C, a total ammonia in the range of 1-3 g l^{-1}, *i.e.* a free ammonia concentration of 0.079-0.235 g l^{-1} does not have a severe detrimental effect on methanogenesis at a SRT of 20 days, at least when using an inoculum adapted to total and free ammonia concentrations of 1.1 g l^{-1} and 0.13 g l^{-1} respectively. This also applies for the process of acidogenesis. However, when conducting the digestion at 60°C using an adapted inoculum to total ammonia and to free ammonia concentrations of 1.1 g l^{-1} and 0.282 g l^{-1} respectively, both acidogenesis and methanogenesis clearly are adversely affected at total ammonia and free ammonia concentrations of respectively of 2.3 g l^{-1} and 0.3 g l^{-1} or more. Our results clearly reveal that at both studied temperatures the hydrolysis is adversely affected by high ammonia concentrations: there exists a negative correlation between the first order hydrolysis constant and both total and free ammonia concentrations.

Our study also reveals that the rate-limiting step is seriously affected by the imposed digestion temperature and ammonia concentration as well. These findings are in accordance with those of Speece (1983) and Pavlostathis and Giraldo-Gomez (1991), who came to the conclusion that the rate-limiting step in the anaerobic digestion is related to the nature of the feedstock, the operational temperature and the imposed loading rate. Acidogenesis apparently is the rate-limiting step at free ammonia concentrations $\leq$ 0.25 g l^{-1}, while it is methanogenesis at free ammonia concentration >0.25 g l^{-1}. However, according to Van Velsen and Lettinga (1980) and Zeeman and Sanders (2001) the hydrolysis step is generally considered as the rate-limiting step in anaerobic digestion systems of complex wastes and wastewater.

Though the negative effect of ammonia on hydrolysis is clear, the mechanism of that effect is not clear sufficiently yet, because according to Zeeman (1991) possible explanations of ammonia effect on the hydrolysis can be the following:

1- NH_4^+-N inhibition.

2- Inhibition due to accumulation of intermediates like VFA's and H_2.

3- Inhibition due to the simultaneous presence of higher concentrations of NH_4^+-N and accumulated intermediates.

4- Inhibition due to specific organic compounds present in urine instead of due to $NH4^+$-N.

Further research is required to elucidate the reason(s), by conducting experiments using sludge adapted to different ammonia thresholds on the hydrolysis.

4.4. A Model of Solar Energy Utilisation in the Anaerobic Digestion of Cattle Manure

Abstract

The anaerobic digestion of cow manure has a higher destruction of pathogens and weed seeds under thermophilic conditions compared to mesophilic conditions. To maintain such conditions, solar energy can be used. In this research, the consequences of the use of solar energy under Egyptian conditions are evaluated. In this study, experiments are combined with modelling. In the experimental part, anaerobic digestion on laboratory scale is studied in two continuously stirred tank reactors at 50 and 60^{o}C. Daily temperature fluctuations in the tank caused a decrease in methane production rate of only 12 and 20% at 50 and 60^{o}C respectively. The results are used in a model for the thermal energy demand. In the model the net thermal energy production as a function of reactor volumes, thermal insulation and additional preheating of the influent is evaluated. The model results show that for continuously stirred tank reactors, additional preheater is not advised since it decreases the efficiency. The results also show that a maximum overall heat transfer coefficient of 1 $Wm^{-2}K^{-1}$ is needed for reaching at least 50% of energy efficiency. Furthermore, adding a solar energy system improves the efficiency for large reactors only slightly, while for small reactors a large improvement is achieved. An energy efficiency of 90% can be reached.

4.4.1. Introduction

As the cost of fuel rises, the use of renewable and sustainable energy systems becomes more viable. Agricultural residues represent an important source of bio-energy and valuable products. Technologies for energy production from such resources can be classified as biological (fermentation) or thermal (gasification, pyrolysis, burning). Anaerobic digestion is a biological process by which complex organic materials can be transformed, in the absence of oxygen, into biogas (a mixture of methane; carbon dioxide and traces of other gases). The main objectives of anaerobic digestion are waste stabilisation and energy recovery. Ghosh (1986) mentioned that farm digesters produce a high methane-content gas which, without cleanup, can be used for water or space heating, electricity or steam production to meet other thermal energy demands. It is also technically feasible to utilise methane gas as engine fuel. An important additional benefit is the conservation of the fertiliser value, originally present in the waste (Van Velsen and Lettinga, 1980). The anaerobic digestion process has a key role in environmental pollution control: methane is an important greenhouse gas, but if captured for use, it acts instead as a good renewable energy source (McCarty, 2001). Anaerobic digestion can be achieved under psychrophilic (< 25^{o}C), mesophilic (25-40^{o}C) or thermophilic (>45^{o}C) conditions. Digestion under thermophilic conditions has many advantages such as higher metabolic rates (Van Lier, 1995) and a higher destruction of pathogens and weed seeds (Bendixen, 1994; Lund *et al.,* 1995). The latter is very important since the effluent can be used as a soil conditioner. The major drawbacks of thermophilic compared with mesophilic treatment are less stability and higher energy requirements (Buhr and Andrewa, 1977; Wiegant, 1986; Van Lier, 1995).

The completely stirred tank reactor (CSTR) is the most generally applied system for slurry digestion. To keep the reactor temperature constant, external source of heating is used.

This source may be fossil fuel or produced biogas, but this lowers the energy efficiency. If another renewable energy resource such as thermal solar energy could be integrated in the process then a high gas production can be achieved with high energy efficiency. Egypt has a high solar intensity, the annual global radiation is between 7-9 GJm^{-2}. Utilisation of solar energy in the anaerobic digestion process will lead to the saving of fossil fuel or biogas. Hamdy (1998) mentioned that, in Egypt, about 60% of the cattle wastes are used as fuel by direct burning in low efficiencies burners (less than 10%); another 20 % of the animal wastes are used as organic fertiliser, and the remainder is lost in handling. Therefore, in Egyptian rural areas, the produced gas has to be used as a direct fuel source. So using it for cogeneration of heat and power (CHP) is not a good option here; even not when the waste heat was used to maintain the thermophilic conditions in the reactor.

The combination of solar energy and biogas production represents a kind of solar energy storage in the gas. The incorporation of solar energy in the anaerobic digestion process may affect the process stability, which is resulting from the daily fluctuations of the available solar energy. So far this effect is not known and has to be investigated.

Objectives

The objectives of the present study are:

(1) experimental determination of the effect of both temperature and temperature fluctuation on methane production from thermophilic anaerobic digestion of cow manure;

(2) determining in a model the effect of reactor size, outside insulation and separate preheating on net energy production; and

(3) study the possibility of solar energy utilisation in this process.

4.4.2. Materials and methods of the experimental work

Two experimental runs of anaerobic digestion have been carried out. In the first run, two reactors were kept at a constant temperature: one at 50°C and one at 60°C, respectively. After about 50 days "steady state" was reached characterised by constant methane production rate together with constant volatile fatty acid concentration (El-Mashad *el al.,* 2001). To test the reproducability of the result, this "steady state" maintained during 9 days. Then a second run was performed, in which the reactor temperatures were reduced 10°C for 10 hours daily for both reactors. The magnitude of temperature reduction was chosen based on simple model calculations of temperature reduction of a 2 m^3 reactor operated at 50°C, with overall heat transfer coefficient of 5 $Wm^{-2}K^{-1}$, in worst case scenario by applying first order cooling model. The worst case conditions were considered as a constant ambient temperature of 15°C and the longest sunset hours under Egyptian situation of 16 hours and there is no auxiliary heating during sunset hours. The results of these calculations showed that the reactor temperature dropped to about 40°C. From these calculations, a temperature reduction of 10°C was chosen.

4.4.2.1. Experimental reactors

Two CSTR reactors (cylindrical vertically oriented), each with a working volume of 8 liters, were used in this study at a hydraulic retention time (HRT) of 20 days. The diameter of the reactor is 0.18 m and its height is 0.45 m. The reactors were continuously mixed at 6 rpm using a gate type mixer (diameter 0.12 m). The reactors were heated by hot water recirculation through a water jacket surrounding the reactors. The reactors were seeded with 8 liters of thermophilic sludge obtained from a 2700 m^3 reactor from the VAGRON, (Groningen, NL) treating municipal waste at a temperature of 52-57^oC and a retention time of 18 days. One week after inoculation, the feeding was started. The system feeding was performed once a day. Because the feeding process requires only 10 minutes, no heat recovery from the effluent is possible here. In the second run, the feeding regime was started at about 8 o'clock in the morning, then the temperature of the water in the jacket was reduced for both reactors. The reactors reached the reduced temperature after about 20 minutes. Around 6 o'clock in the evening the temperature returned back to 50^oC and 60^oC, respectively.

4.4.2.2. Feedstock

The feeding consisted of diluted cow manure. The manure used in this study was produced from dairy cows weighing about 650 kg. The cows were fed on a ration consisting of 70% grass and 30% maize as well as about 5 kg of concentrated feed per day. The diet contained also 0.1 kg of minerals and vitamins without any antibiotic addition. The manure was stored in a refrigerator at 4^oC until used. Before feeding, the manure was diluted with tap water to yield a 5% total solid (TS) feedstock. In Table 4.4.1, the influent composition is given. The influent composition has been measured as described in *chapter* 4.2.

Table 4.4.1. The influent composition

Parameter	*Value*	*Unit*
Total solid (TS)	5	%
Volatile solid (VS)	80	% of TS
NH_4^+N	0.85	g l^{-1}
Dissolved chemical oxygen demand	9.3	g l^{-1}
Volatile fatty acids (VFA)	3.3	g [COD] l^{-1}
Total nitrogen	2	g l^{-1}
Total chemical oxygen demand (Total COD)	57.9	g l^{-1}

4.4.2.3. Methane measurement

Produced methane was collected in gas bags after removing CO_2 by passing the biogas through a glass column containing 150ml of 3% NaOH solution. The solution was changed twice a day. The amount of NaOH required was calculated as follows (Anaerobic Lab Work, 1992):

$$V_{NaOH} = \frac{2V_{CH_4}}{0.7C_{NaOH}} \qquad (4.4.1)$$

where: V_{NaOH} is the tolerated volume of NaOH in *l*; V_{CH4} is the volume of methane, when it is time to replace the NaOH solution, in *l*; and C_{NaOH} the concentration of NaOH in g l^{-1}.

The daily methane production was measured using a wet gas meter. The methane production has been recalculated for standard temperature and pressure.

4.4.3. Modelling

For calculating the energy consumption for heating the substrate and maintaining the desired reactor temperature, a model has been made. To achieve this, two systems have been modelled: a CSTR without pre-heater and one preceeded by a pre-heater as schematically shown in Fig. 4.4.1. This system has been proposed for the sake of using the available solar energy to heat the feedstock during daylight. The heat required for the preheating process and the constant temperature of the reactors can also be achieved by using a conventional heater. Since the experimental results showed that the reactor operated at 50°C has higher methane production compared with the reactor operated at 60°C, all calculations have been performed at a digestion temperature of 50°C.

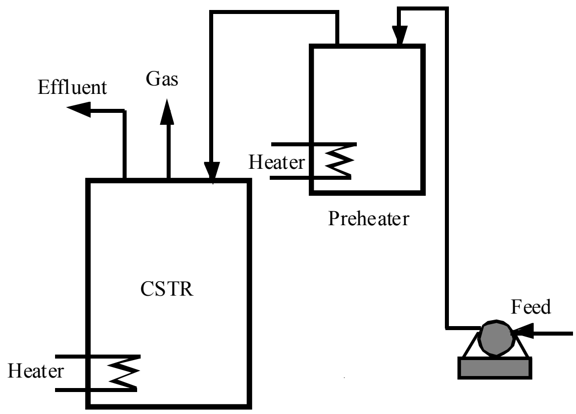


Fig.4.4.1. Continuous stirred tank reactor (CSTR) with pre-heater

4.4.3.1. Pre-heater heat model

The pre-heater is assumed to be a batch process. In the preheating process, the influent temperature is increased from ambient temperature, to the digestion temperature (50°C). The assumption that manure increased from ambient temperature was based on the fact that the system of animal breeding varies from roofed stable to open roof stables, which consequently affects the manure temperature. It is assumed that the preheating is accomplished within ten hours. The pre-heater temperature is represented by the following equation:

$$\rho V_{pre} C_p \frac{\mathrm{d}T_{pre}}{\mathrm{d}t} = E_{pre} - U_{pre} A_{pre} (T_{pre} - T_a) \qquad (4.4.2)$$

where: T_{pre} is the preheater temperature in K; V_{pre} is the preheater volume in m^3; ρ is the manure density in $kg\ m^{-3}$; C_p is the specific heat of manure in $J\ kg^{-1}\ K^{-1}$; t is the time in s; E_{pre} is the power needed for preheater in W; U_{pre} is the overall heat transfer coefficient of the preheater in $Wm^{-2}K^{-1}$; A_{pre} is the preheater surface area in m^2; T_a is the ambient temperature in K.

It should be mentioned that Equation (4.4.2) does not include the heat capacity of the pre-heater material since this is negligible compared to the heat capacity of the loaded manure. Density and specific heat of the manure are calculated from its solid content (Achkari-Begdouri and Goodrich, 1992).

For calculating the product $U_{pre}A_{pre}$, it is assumed that the pre-heater has a cylindrical shape, its height equals 60% of its diameter (*i.e.* aspect ratio is 0.6). The overall heat transfer coefficient *U* has been calculated for different insulation types and different thickness, assuming the heat transfer coefficient to the ambient air (h_o) equals 10 $Wm^{-2}K^{-1}$ (Beek and Muttzall, 1975).

$$\frac{1}{U_{pre}} = \frac{1}{h_o} + \sum_{i=1}^{n} \frac{d_i}{k_i} \qquad (4.4.3)$$

where: d_i is the thickness of material i in m; k_i is the thermal conductivity of material i in $Wm^{-1}K^{-1}$.

The calculated values for different types of insulation are shown in Table 4.4.2 and will be used in further calculations. These calculations will be also used for the reactor.

Table 4.4.2. The calculated overall heat transfer coefficient for different insulation materials thickness with thermal conductivity of 0.04; 0.3 and 0.8 $Wm^{-1}K^{-1}$ for rock wool; straw loam and bricks, respectively (Gaskell, 1992)

Material and thickness	*Calculated U, $Wm^{-2}K^{-1}$*
10 cm bricks + 11 cm rock wool	0.33
40 cm straw loam	0.67
30 cm straw loam	1
40 cm bricks or concrete	1.7
9 cm straw loam	2.5
8 cm bricks or concrete	5

4.4.3.2. Continuous stirred tank reactor heat model

The CSTR operation mode is characterised by constant flow rates of both the influent and the effluent, leading to a constant reactor volume in time. The reactor temperature can be described by the following equation:

$$\rho V C_p \frac{\mathrm{d}T_R}{\mathrm{d}t} = \phi_V \rho C_p (T_{in} - T_R) + E_r - UA_r (T_R - T_a) \qquad (4.4.4)$$

where: V is the reactor volume in m^3; T_{in} is the influent temperature in ^oC; T_R is the reactor temperature in ^oC; ϕ_V is the flow rate m^3s^{-1}; U is the overall heat transfer coefficient of the reactor in $Wm^{-2}K^{-1}$; Ar is the reactor surface area in m^2; E_r is the heater power in the reactor in W.

Because convective heat losses by gas are small compared to that of the manure, it is assumed that only the flow rate and heat capacity of the manure has to be considered in the convective term ($\phi_V \rho C_p (T_{in} - T_R)$). Equation (4.4.4) does not contain the direct solar gain due to absorption through the reactor walls, because the absorption part depends significantly on many factors like the location of the reactor installation (indoor or outdoor), shading conditions and colour. So, the model presented here is the most simple case. It should also be mentioned that the reactor has a cylindrical shape with an aspect ratio of 0.6. The aspect ration was chosen based on the calculations of Beuger (2002).

The product of the overall heat transfer coefficient and surface area of the reactor can be calculated also from the data given in Table 4.4.2.

4.4.3.3. Ambient air temperature

Minimum, maximum and average daily air temperatures for some days every month were available at 10 days interval for Egyptian conditions. The measured data was obtained from Wunderground weather report during years 1999 and 2000 (Wunderground, 2000). To obtain typical data for the daily minimum, maximum and average temperatures over the whole year, the available data were interpolated. Figure 4.4.2 shows the daily minimum (T_{min}), average (T_{av}) and maximum (T_{max}) air temperatures. As can be seen from this figure, the temperature starts to increase by the beginning of March (day 60) and starts decreasing by mid August (day 250).

The characteristic time $(V\rho C_p / UA)$ for the reactor is in the order of days, but hourly data are needed in this model because: (1) every day fresh manure needs to be heated from ambient temperature to reactor temperature; and (2) available solar energy highly fluctuates during the day.

The hourly ambient temperature has been obtained by approximation of the available daily temperatures (minimum, maximum and average) by a sine function. For this function the minimum temperature was assumed to be at three o'clock in the morning, and the maximum temperature at three o'clock in the afternoon.

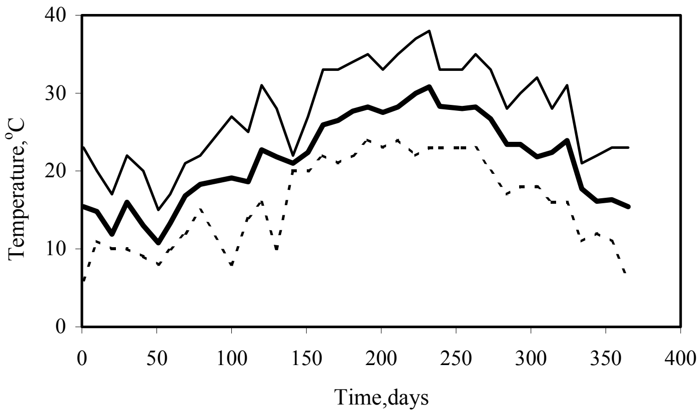


Fig.4.4. 2. Ambient air temperature over a whole year under Egyptian conditions:
-------, T_{min}; ━━━━━, T_{av} ; ————— , T_{max}

4.4.4. Results and discussion

4.4.4.1. Methane production

Firstly, the effect of temperature level is investigated. Table 4.4.3 shows the average methane production rate (MPR), expressed as *l* [CH4] m^{-3} [reactor] day^{-1}, during steady state conditions together with the standard deviations between the observations. For the first run, "steady state" conditions were reached after 50 days and maintained during another 9 days to obtain some replications of the measurements. From Table 4.4.3 it can be seen that methane production rate at a reactor temperature of 50^{o}C, denoted by R_{50}, is higher than that at a reactor temperature of 60^{o}C, denoted by R_{60}. This may be attributed to the effect of free ammonia concentration under the higher temperature (see *chapter* 3.2). It should be mentioned that the magnitude of free ammonia concentration (NH_3-N) depends on many factors like, ammonium nitrogen (NH^+_4-N) concentration; pH and temperature (Angelidaki and Ahring, 1993a).

Table 4.4.3. Mean methane production rate (MPR) during constant and fluctuating (FL) temperatures and its standard deviation (SD) during 'steady state'

Reactor	*Temperature, ^{o}C*	*Mean MPR, $l[CH_4]m^{-3}[reactor]\ day^{-1}$*	*SD of MPR, $l[CH_4]m^{-3}[reactor]\ day^{-1}$*	*Number of observations*
R_{50}	50	394	20	9
R_{60}	60	347	8	9
R_{50FL}	50+40	348	17	15
R_{60FL}	60+50	279	14	15

Secondly, the effect of fluctuating temperatures is investigated. The daily temperature fluctuation, due to adding once per day fresh manure at ambient temperature, is small. The hydraulic retention time of 20 days results in a fresh manure supply of 5% of the reactor volume per day. The accompanying temperature drop is always less than 2^{o}C. If solar energy is used as a heating source, without auxiliary heating or heat storage, temperature drops during the night. Here, an extreme daily temperature drop of 10°C during 10 hours is considered (see section 2). The temperature regime of 14 hours at 50°C and 10 hours at 40°C denoted as R_{50FL}; and the regime of 14 hours at 60°C and 10 hours at 50°C denoted by R_{60FL}. A small, but significant decrease of methane production rate can be observed at fluctuating temperature conditions. It can be seen from Table 4.4.3 that "steady state" conditions, for the second run, were reached after 55 days, from the end of the first run, and maintained during 15 days. Average values and standard deviations of methane production rate during "steady state" conditions are shown in Table 4.4.3.

From the influent composition (Table 4.4.1), it can be calculated that 2.9 kg [COD] per m^3 [reactor] is added daily. Now the methane yields during steady state are determined at about 136, 120, 120 and 96 *l* [CH_4] kg^{-1} [COD added] for R_{50}, R_{60}, R_{50FL} and R_{60FL}, respectively. It can be seen that temperature fluctuations have a minor effect: R_{50F} is 12% lower than R_{50} and R_{60FL} is 20% lower than R_{60}. In this case, the influence of temperature fluctuations on the methane production is higher at higher temperatures. From these results it can be concluded that it is possible to use the available solar energy to heat the reactor without severe effect on the methane production or process stability at 50°C because, in practice the reactor temperature is not reduced to the severe conditions studied here.

4.4.4.2. Model for net thermal energy production

There are many parameters, which affect the net energy produced from the anaerobic digestion process, such as the feed composition. Here, it should be mentioned that the undiluted fresh manure has 8.6% volatile solids (VS) and the dilution used in these experiments was to mitigate the high ammonia concentration effect. In many countries, less protein rich feed is used, resulting in a lower NH_4^+-N content of the manure. In the experiments, daily 5% of the reactor volume is replaced with diluted manure (4% VS). When operated with non-diluted manure, a reactor volume of 1 m^3 per cow is needed. Since the volatile solids concentrations do not affect the process stability (*i.e.* inhibition) while the ammonia concentrations do (Zeeman, 1991). Based on the experimental results, the methane yield per kg VS added was calculated to be 197 *l* [CH_4] kg^{-1} [VS added] at 50°C. By using manure with 8.6% VS, the loading rate (at 20 days HRT) would be 4.3 kg [VS] m^{-3} [reactor] day^{-1}. The multiplying 197 *l*[CH_4]kg^{-1} [VS added] by 4.3 kg [VS]m^{-3} [reactor]day^{-1} produces 845 *l*[CH_4]m^{-3}[reactor] day^{-1} . The daily net thermal energy production (NTEP) at 50°C, has been calculated using a methane calorific value of 37 MJm^{-3} (Hill and Bolte, 2000).

Specific net thermal energy production (SNTEP) is defined as net energy production per cubic metre of the reactor: it is the caloric value of the produced methane minus the energy needed for heating the feed, and the heat losses to the environment. Table 4.4.4 shows the calculated SNTEP of different reactor volumes preceeded by pre-heaters expressed as a percentage of the energy potential production. The larger the reactor volume, the higher is the SNTEP. This may be attributed to the fact that the surface area to the volume ratio decreases with increasing reactor volume. For insulation material with a heat transfer coefficient of 5 $Wm^{-2}K^{-1}$, it is not possible to obtain a system SNTEP of 50% even with a reactor size of 200 m^3. For large reactors (larger than 100 m^3, needed for 100 cows) it is possible to use 30 cm of straw loam as insulation (U = 1 $Wm^{-2}K^{-1}$) to obtain at least 70% of the energy potential. It should be mentioned that straw loam, commonly used as a building material, is a mixture of straw and loam (Mink, 2000).

Table 4.4.4. The annual specific net thermal energy production as a function of different reactor volumes and different insulation (details, see Table 4.4.2) expressed as a percentage of the energy potential of methane produced (11.4 GJm^{-3} [reactor] $year^{-1}$) including a pre-heater

Reactor volume, m^3	*Reactor diameter, m*	*Proportion of energy produced ,%*					
		Insulated bricks	*40 cm loam*	*30 cm loam*	*40 cm bricks*	*9 cm loam*	*8 cm bricks*
2.0	1.62	70.2	58.1	46.1	22.1	---	---
4.0	2.04	72.7	63.1	53.6	34.5	10.6	---
10	2.77	75.2	68.1	61.1	47.0	29.5	---
20	3.49	76.7	71.1	65.5	54.3	40.3	---
40	4.39	77.8	73.4	68.9	60.0	49.0	15.7
100	5.96	79.0	75.7	72.5	65.9	57.7	33.2
150	6.83	79.5	76.6	73.7	68.0	60.8	39.4
200	7.52	79.7	77.0	74.5	69.3	62.8	43.3

It can be concluded that, applying insulation materials with $U \leq 1$ Wm^{-2} K^{-1}, the reactor volume larger than 100 m^3 does not affect the SNTEP too much. From this table, it can also be concluded that for small farms (2 cows) it is possible to achieve 70% system SNTEP, but this requires at least 10 cm bricks together with 11 cm of rook wool (k = 0.04 $Wm^{-1}K^{-1}$) to insulate the system (U = 0.33 $Wm^{-2}K^{-1}$).

Table 4.4.5 shows the effect of insulation type on the annual SNTEP of different CSTRs without pre-heaters. Conclusions similar to those related to Table 4.4.4 can be drawn: SNTEP increases with increasing reactor volume, so smaller reactors need better thermal insulation to achieve equal SNTEP as large reactors. But comparing these data with the data presented in Table 4.4.4, it can be concluded that the external pre-heater reduces the net thermal energy production by roughly 3% compared with the system without pre-heater. On the other hand, adding the fresh manure will reduce the reactor temperature by about 2^{o}C, which may reduce the biogas production. Furthermore, the addition of the pre-heater will increase the cost and needs more space without adding any benefits to the system, it can be concluded that the adding of a pre-heater is not necessary. For the solar application, the time of adding the new manure to the system should be specified according to the interaction between the available solar energy and the system configurations.

Table 4.4.5. The annual specific net thermal energy production as a function of reactor volumes and different insulation (details, see Table 4.4.2) expressed as a percentage of the energy potential of methane produced (11.4 GJm^{-3}[reactor] $year^{-1}$) without a pre-heater

Reactor volume, m^3	*Reactor diameter, m*	*Proportion of energy produced ,%*					
		Insulated bricks	*40 cm loam*	*30 cm loam*	*40 cm bricks*	*9 cm loam*	*8 cm bricks*
2.0	1.62	73.8	61.9	50.2	26.6	---	---
4.0	2.04	76.2	66.8	57.5	38.7	15.3	---
10	2.77	78.6	71.7	64.8	51.0	33.8	---
20	3.49	80.0	74.6	69.1	58.2	44.5	3.4
40	4.39	81.2	76.9	72.5	63.8	52.9	20.4
100	5.96	82.4	79.1	75.9	69.5	61.5	37.5
150	6.83	82.8	78.0	77.2	71.6	64.6	43.6
200	7.52	83.0	80.5	77.9	72.8	66.5	47.4

4.4.4.3. Model for net thermal energy production including solar energy

To avoid combustion of the produced methane for maintaining the required temperature inside the CSTR, the required energy for heating can be produced by a thermal solar collector system. Table 4.4.6 shows the system SNTEP after incorporation of the input energy, which can be covered by a solar collector system, mounted on the reactor roof. This is performed for different reactor sizes and different insulation materials under Egyptian conditions. Beam and diffuse solar radiation are calculated based on the equations presented by Sukhatme (1997). The solar energy calculations were based on a flat plate solar collector with a tilt angle equal to the latitude of Cairo (30.1°) and overall heat loss coefficient from the collector of 5 $Wm^{-2}K^{-1}$.

To calculate the system SNTEP after applying the solar energy (E_T), the following equation can be used:

$$E_T = \frac{\sum_{i=1}^{365} E_i - (1-P_i)I_i}{\sum_{i=1}^{365} E_i} \qquad (4.4.5)$$

where : P_i is the percentage of daily heat requirements which can be covered by solar energy for day i; I_i is the daily heat requirements to heat the reactor at the desired reactor temperature level; and E_i is the potential energy production based on daily methane production in the CSTR .

Table 4.4.6. The annual specific net thermal energy production as a function of different reactor volumes, without pre-heater (s), and different insulation includes the solar system mounted on the reactor roof

Reactor volume, m^3	*Reactor diameter, m*	*Proportion of energy produced ,%*					
		Insulated bricks	*40 cm loam*	*30 cm loam*	*40 cm bricks*	*9 cm loam*	*8 cm bricks*
2.0	1.62	99.0	87.2	75.4	51.8	22.3	-
4.0	2.04	96.3	86.9	77.5	58.8	35.4	-
10	2.77	93.4	86.5	79.6	65.8	48.6	-
20	3.49	91.8	86.3	80.9	69.9	56.2	15.1
40	4.39	90.5	86.2	81.8	73.1	62.3	29.7
100	5.96	89.2	86.0	82.8	76.4	68.4	44.4
150	6.83	88.7	86.0	83.2	77.6	70.6	49.6
200	7.52	88.5	85.9	83.4	78.3	72.0	52.9

Comparing the data in Table 4.4.5 and Table 4.4.6, it can be seen that the solar energy incorporation has a pronounced effect on the SNTEP of the small reactors. The magnitude of the increase of SNTEP, when including solar input depends on the reactor volume. Furthermore, the higher U values of the reactor the lower is SNTEP. As can be seen it is possible to obtain a system SNTEP higher than 90% but this is relevant for the small reactors and low U value insulation. On the other hand, the incorporation of solar collectors mounted on the reactor roof increase the system SNTEP of about 6% with a reactor volume of 200 m^3.

Concluding, the available specific surface area of the reactor (m^2 [roof] m^{-3} [reactor]) decreases with the increase of the reactor height and hence with the reactor volume. Since land occupation is one of the drawbacks of using solar energy, mounting the solar system on the reactor roof is the best option. When extra land has to be used for solar energy installation, this will in turn increase the fixed cost of the system.

4.4. 5. Conclusions

The specific net thermal energy production (SNTEP) from the anaerobic digestion of cattle manure has been studied in a model. The model results are based on experimental determination of methane production rate from continuous stirred tank reactors. The model studied the effect of preheater addition; different insulation materials and solar energy heating system on the SNTEP from different reactors volumes without considering the heat recovery from the effluent. Based on the results obtained from this study the following conclusions can be drawn:

(1) The experiments showed that the methane production rate during anaerobic conditions of cow manure at 50^oC is higher than that at 60^oC. This may be due to the higher free ammonia concentration at 60^oC compared to that at 50^oC.

(2) A daily temperature fluctuation of 10^{o}C is decreasing the methane production with only 12% at digestion temperature of 50^{o}C.

(3) It is possible to use solar energy for applying thermophilic anaerobic digestion of cow manure at 50^{o}C under Egyptian conditions with a minor effect on gas production rate.

(4) The larger the reactor size, the larger is the net specific thermal energy production.

(5) From the energy efficiency viewpoint, it is not recommended to use a pre-heating step before the continuous stirred tank reactor since this leads to increase system costs without adding any benefits to the system.

(6) The smaller the reactor, the better insulation is required to obtain high specific net thermal energy production (SNTEP), therefore the investment costs for small reactors are relatively high.

(7) A thermal insulation value for the reactor of about 1 W $m^{-2}K^{-1}$ seems to be sufficient to provide a SNTEP of at least 50%. If the reactor volume is at least 10 m^3; the SNTEP increases to at least 65%.

(8) Incorporation of solar energy can increase the system SNTEP over 90%, but this is only possible for small, well-insulated systems.

(9) Using solar energy, the maximum SNTEP is found for small reactors with good thermal insulation ($U < 1$ $Wm^{-2}K^{-1}$), while for bad thermal insulation ($U > 1$ $Wm^{-2}K^{-1}$) the maximum SNTEP is found for large reactors.

(10) For large reactor volumes (100 m^3 or more), it is not recommended to use solar energy by roof solar collectors since the extra efficiency is low.

(11) With solar energy system mounted on the reactor roofs, it is possible to obtain at least 75% of the energy potential for moderate insulation ($U =1$ W $m^{-2}K^{-1}$).

4.5. Design of A Solar Thermophilic Anaerobic Reactor (STAR) for Small Animal Farms

Abstract

A 10 m^3 completely stirred tank reactor has been designed for anaerobic treatment of liquid cow manure under thermophilic conditions (50^{o}C) using a solar heating system mounted on the reactor roof. A simulation model of two systems, including a heat recovery unit to heat up the feeding, has been developed. The first system is a simple one and the second is an integrated system, including an extra chamber for the pumps and the heat recovery unit. The control system is based on simple on/off strategy. An auxiliary heater, operated with the produced biogas, can be used during cold months. The measured and calculated design parameters are presented. The simulation results showed that the temperature fluctuation of the reactor during nights is less than 1^{o}C. This demonstrates that the reactor could be operated without harm for the microbial activity. The results showed that an annual net thermal energy production and overall annual energy efficiency of 100% and 95% respectively could be obtained from the integrated system.

4.5.1. Introduction

Agricultural wastes can be one of the renewable sources. A possible technology to release energy from agricultural wastes is anaerobic digestion. This technology has a lot of advantages from environmental; agricultural and sustainability viewpoints (Van Velsen and Lettinga, 1980; De Baere, 2000).

The digestion under thermophilic conditions has many advantages. On the other hand, the thermophilic treatment requires higher energy consumption compared to mesophilic treatment. Electricity, oil or part of the produced biogas is used to keep the reactor at the desired temperature. The use of such kinds of fuel is uneconomical and not renewable (Axaopoulos *et al.,* 2001). Using solar energy or other renewable sources to heat up the reactor could be a good alternative. To keep the system as simple as possible, the system could be constructed without heat storage during nights. This leads the system subject to daily temperature fluctuation. Axaopoulos *et al.* (2001) presented a mathematical model and experimental study on a solar-heated anaerobic digester treating swine manure at 35^{o}C. Alkhamis *et al.* (2000) investigated experimentally the utilisation of solar energy for heating a bioreactor. They also designed, installed and tested PID (proportional, integral and differential) controller to maintain a constant temperature of 40^{o}C in the water-jacket around the bioreactor. Florides *et al.* (2002) mentioned that computer modelling of thermal systems has many advantages. The most important are the elimination of the expenses of building prototypes, the optimisation of the system components, estimation of the amount of energy delivered from the system, and prediction of temperature variations of the system.

In Egypt, about 70 % of the animal farms is small or medium size (< 15 adult cattle) (Tabana, 2000). While long distance transportation of manure is difficult, small or medium size reactors are preferable. The possibility of using solar energy to heat up an anaerobic digester treating cow manure was studied (see *chapter* 4.4). The expected increase of the system efficiency after applying solar energy heating system was modelled. The results showed that it is possible to increase the annual specific net thermal energy production by about 15 % by mounting a solar collector on the reactor roof. The case was worked out for a 10 m^3 continuous stirred tank reactor (CSTR), treating manure produced from 10 cows, insulated with 30 cm straw loam without heat recovery from the effluent. The dynamic behaviour of the system related to the environmental and the operation disturbances was not studied in *chapter* 4.4.

The problems in the design rules, the interaction with the available solar energy, the effect of fluctuating temperatures on the reactor performance and the energy output to satisfy the local energy demand. Therefore, in the present study, a dynamic modelling approach was chosen. Two different configurations of the Solar Thermophilic Anaerobic Reactor (STAR) are modelled. In both systems cattle manure is treated in a CSTR of 10 m^3 at thermophilic conditions (50°C). The dynamic behaviour of the system, interrelated to the activity of bacteria, is incorporated. The simulation is worked out for Egypt as an example for Mediterranean or subtropical conditions. The main objective is to design a thermophilic CSTR reactor with high-energy efficiency including a simple and reliable control strategy. In the optimisation, the following aspects are considered:

1- The effect of adding a heat recovery unit, to heat up the influent by extracting the heat from the effluent, on the system performance.

2- A simple control system using the biogas produced as an auxiliary heating source during cold months.

3- Integrated design includes an extra chamber for pumping system and heat recovery unit aiming at the reuse of heat produced from both pumping system and stirring motor.

4.5.2. Measurements

To perform the model study many parameters are needed. Most manure characteristics used in the simulation are measured. Total solids (TS); Volatile solids (VS); Kjeldahl-nitrogen (Nkj) were measured according to APHA (1992). Total COD (COD_t); the dissolved COD (COD_{dis}) and Volatile fatty acids (VFA) concentrations were analysed as described by (Zeeman, 1991 and Van Lier, 1995). Total ammonium (NH_4^+-N) was determined by steam distillation method (APHA, 1992). For Prandtl number calculations the manure viscosity is measured at different temperatures (*chapter* 4.1). Manure viscosity was measured with a rotoviscometer (Haake model). The density; thermal conductivity and specific heat of manure were calculated based on water and solid fractions (Achkari-Begdouri and Goodrich, 1992). Table 4.5.1 shows some physical and thermal properties of manure used for the simulation.

Table 4.5.1. Thermal and physical characteristics of manure

Parameter		*Unit*	*Value*
Total Solids		kg m^{-3}	107
Volatile Solids		kg m^{-3}	86
Total COD		kg m^{-3}	124
Dissolved COD		kg m^{-3}	19.9
Total VFA		kg [COD] m^{-3}	7.07
N-Kj		kg m^{-3}	4.24
NH_4^+-N		kg m^{-3}	1.83
Density		kg m^{-3}	1043
Specific heat		J kg^{-1} K^{-1}	3901
Thermal conductivity		$Wm^{-1}K^{-1}$	0.577
Viscosity	30^{o}C	Pa s	0.722
	50^{o}C		0.516

The available measured data for solar energy were the monthly average daily solar radiation on a horizontal surface, as well as the monthly average daily hours of bright sunshine (CLAC, 1997). The different radiation components were calculated according to the equations presented by Duffie and Beckman (1974); Duffie and Beckman (1991) and Sukhatme (1997). The calculations are based on assumptions that the collector is tilted at an angle equal to the latitude angle and is facing due south (*i.e.* azimuth angle =0).

Biogas production rate was estimated based on the results of earlier experiments (*chapter* 4.2) assuming the biogas contains 40% CO_2.

The hourly ambient temperature has been obtained by fitting the available (minimum, maximum and average) measured daily temperatures by a sine function (*chapter* 4.4).

4.5.3. Mathematical model of the studied systems

Schematic diagrams of the systems presented in this study are shown in Fig. 4.5.1. The simple system configuration (Fig.4.5.1a) consists of a CSTR system, a heat recovery unit, a pumping system and a flat plate solar collector. The raw manure is pumped through the heat recovery unit while it is preheated via extracting heat from the effluent. The reactor is kept at the desired temperature by using hot water from the solar collector. If the water temperature is lower than 50^{o}C the water flow to the system is stopped. The system is insulated by 10 cm bricks and 11 cm rock wool. The integrated system (Fig.4.5.1b) consists of the same components as the simple one. In this system, the solar collector is mounted on top of the reactor so it includes an extra gas volume. Moreover a chamber is added for pumps and heat recovery installation. The purpose of this chamber is to recover some of the heat produced during pump operation.

Figure 4.5.2 shows a diagram of the overall heat balance of the integrated system including the state variables. An analogous diagram for the simple system can be drawn after eliminating the gas volume and the pump chamber.

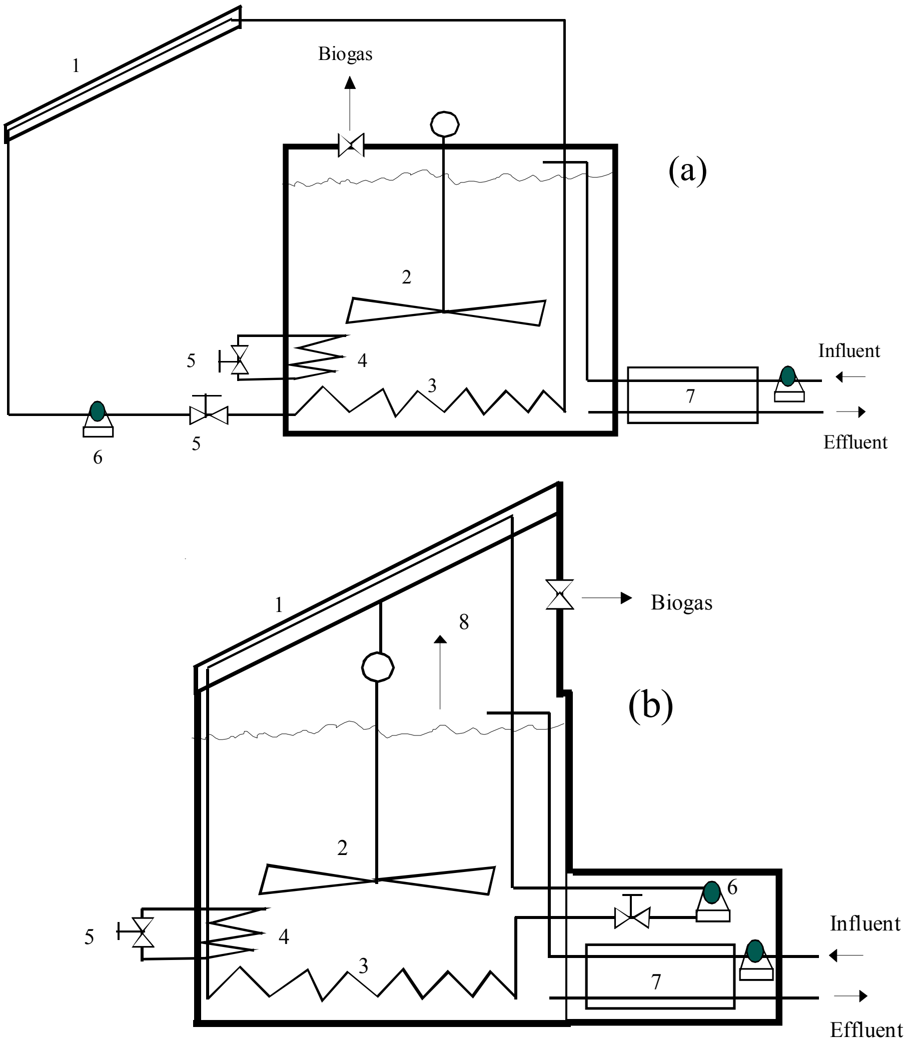


Fig.4.5.1. A schematic of the systems configuration; (a) is the simple system and (b) is the integrated one: 1, solar collector; 2, agitator; 3, heat exchanger; 4, auxiliary heater; 5, control; 6, pump; 7, heat recovery unit; 8, extra gas volume

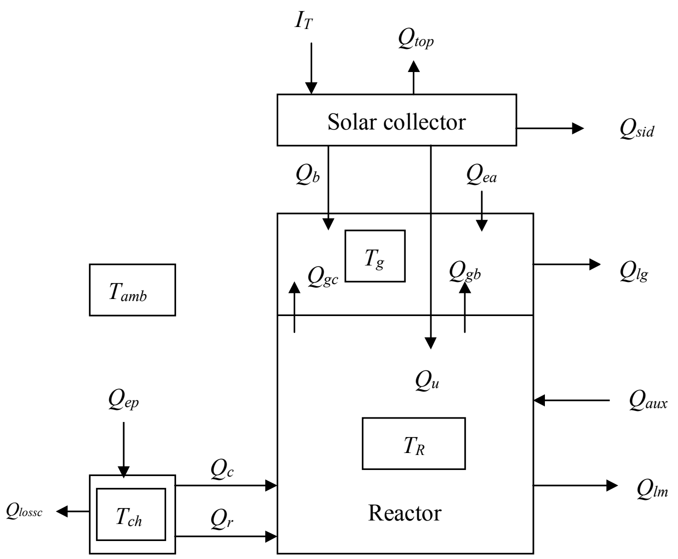


Fig.4.5.2. Overall heat balance diagram including all temperatures and heat flows, details see nomenclature list

4.5.3.1. Solar collector

As the time constant of the reactor is much larger compared to the solar collector, the solar collector is assumed to operate at steady state. The heat gain from the solar collector system can be calculated from Hottel-Whillier-Bliss equation (Duffie and Beckman, 1974; Sukhatme, 1997):

$$Q_u = F_R \; A_P \; (S - U_L \; (Tf_{in} - T_{amb})). \tag{4.5.1}$$

Where the value of the collector heat-removal factor (F_R) is given by

$$F_R = \frac{\dot{m} \; C_{pw}}{A_P \, U_L}\left[1 - \exp - \left(\frac{A_P \, U_L \, F^{\backslash}}{\dot{m} \, C_{pw}}\right)\right] \tag{4.5.2}$$

The overall heat losses coefficient (U_L) was calculated from the sum of the loss coefficients through the top, the sides and bottom. The top loss coefficient was calculated from the empirical equation of Klein (1975). It was calculated based on the hourly temperatures of the absorber plate in the monthly average day from a reasonable assumption of U_L (Sukhatme, 1997). Then the calculated absorber plate temperature was used to calculate the hourly values of U_L and a yearly average value of U_L was calculated as an average of these hourly values.

To calculate the outlet temperature (Tf_{out}) from the solar collector apart from incident solar flux (S) also the heat loss to the environment was considered:

$$Tf_{out} = \frac{F_R \; A_P \, (S - U_L \, (Tf_{in} - T_{amb}))}{\dot{m} \, Cp_w} + Tf_{in} \tag{4.5.3}$$

Since inlet and outlet temperatures of the solar collector (Tf_{in} and Tf_{out}) are dynamic and interrelated, the Simulink tool in Matlab program (version 5.3.1) was used to calculate both parameters by adding an extra energy balance around the reactor heat exchanger. From such energy balance equation the following solution can be derived:

$$Tf_{in} = Tf_{out} + (T_R - Tf_{out})(1 - e^{\left(\frac{-U\,A}{mCp_w}\right)}) \tag{4.5.4}$$

To obtain the maximum possible radiation on a tilted surface, the tilt angle of the collector should be chosen to maximise the sum of three components: direct; sky and ground diffuse radiation. Al-Ismaily and Probert (1995) used a simplified correlation to calculate the optimal tilt angle as follow (accurate within 2^o):

$$B_{opt} = \phi + \tan^{-1}\left(-1.319.\tan\delta\right). \tag{4.5.5}$$

The yearly-optimal tilt angle is obtained by averaging the monthly optimal tilt for the whole year. For Cairo, this angle is almost equal to the latitude (30.1^o).

The solar system array consists of a flat plate solar collector. Table 4.5.2 shows the parameters used in the simulation.

Table 4.5.2. System parameters used in the simulation for one solar collector

Parameter	*Unit*	*Value*
Latitude	^{o}	30.13
Length of the absorber plate	m	2
Width of the absorber plate	m	3 (3×1)
Thickness of the plate	m	0.002
Back insulation thickness	m	0.12
Side insulation thickness	m	0.05
Thermal conductivity of the insulation	W m^{-1} K^{-1}	0.05
Overall loss coefficient of the solar collector	W m^{-2} K^{-1}	4.66
Thermal conductivity of the plate material	W m^{-1} K^{-1}	200
Plate absorptivity	--	0.95
Glass covers number	--	2
Glass cover emissivity/absorptivity	--	0.88
Tube centre to centre distance	m	0.1
Outer diameter of the tube	m	0.011
Inner diameter of the tube	m	0.009
Heat transfer coefficient of the water to the tube	W m^{-2} K^{-1}	325
Water flow rate	l hr^{-1} m^{-2}	50

4.5.3.2. Heat exchangers

To calculate the required heat exchanger length (*i.e.* the heat exchanging surface area) inside the reactor, the overall heat transfer resistance per unit of length was calculated. This resistance was calculated based on the film resistance inside the heat exchanger; the conduction resistance of the heat exchanger walls and the resistance of heat convection inside the reactor. The convective heat transfer coefficients have been calculated based on the proper Nusselt number correlations.

The logarithmic mean temperature difference (LMTD) for the heat exchanger is calculated from the wrap-around heat exchanger equation (Dahl and Davidson, 1995), where the inlet temperature to the heat exchanger equals the outlet temperature from the solar collector and vice versa:

$$LMTD = \frac{(Tf_{out} - T_R) - (Tf_{in} - T_R)}{\ln\left[\frac{(Tf_{out} - T_R)}{(Tf_{in} - T_R)}\right]} \qquad (4.5.6)$$

To calculate LMTD the yearly average temperatures of the inlet and outlet flow of the solar collector were assumed to be constant at 60 and 70^{o}C respectively.

For the heat recovery from the out going manure, a coaxial heat exchanger is applied. The warm outgoing manure flows in the central tube, while the cold ingoing manure flows in the outer cylinder (Fig. 4.5.3).

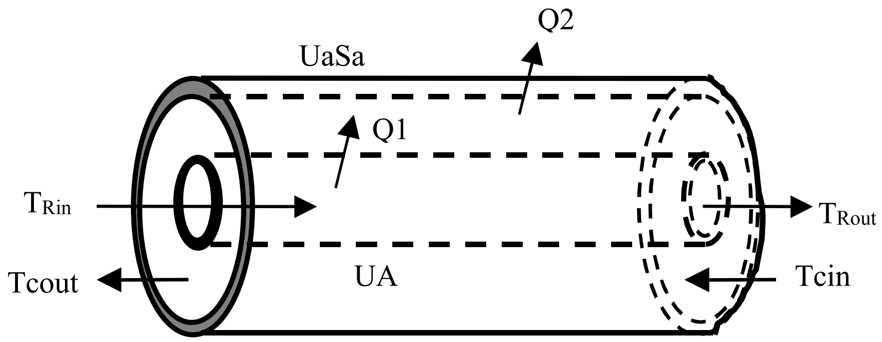


Fig.4.5.3. A section of the heat recovery unit

For the design of the heat recovery unit, some assumptions were formulated:

1- Counter flow, single-pass, single-wall heat exchanger.

2- Constant overall heat transfer coefficient.

3- Equal volume flow in both directions.

4- The heat losses to surroundings are included.

5- The cold manure enters the heat recovery unit at ambient temperature.

The same procedures used for the heat exchanger inside the reactor were used to estimate the required length of the heat recovery unit considering the appropriate correlations for heat transfer coefficient calculation. By using the assumptions above, a heat balance includes the heat losses along the heat recovery unit (Fig. 4.5.4).

The temperature gradient in the hot tube with out going flow is governed by the local temperature difference between cold and warm tube (Smith, 1997):

$$\frac{\mathrm{d}T_R}{\mathrm{d}x} = \frac{-U_{\mathrm{Re}} A_{\mathrm{Re}}}{L\,\rho\,\phi_v C\mathrm{p_m}} \left(T_R(x) - T_c(x)\right) \tag{4.5.7}$$

The temperature gradient in the cooler in going flow is also governed by the local temperature difference between cold tube and warm tube and between cold tube and ambient:

$$\frac{\mathrm{d}T_c}{\mathrm{d}x} = \left(\frac{-1}{L\,\rho\,\phi_v C\mathrm{p}_m}\right) \left[UaSa\left(T_c(x) - T_a\right) - U_{\mathrm{Re}} A_{\mathrm{Re}} \left(T_R(x) - T_c(x)\right)\right] \tag{4.5.8}$$

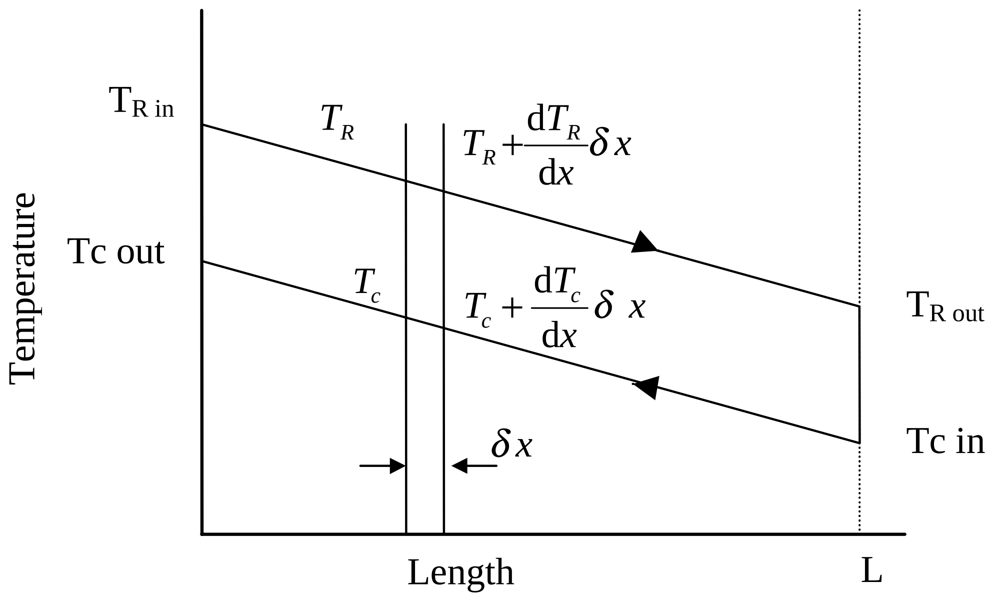


Fig.4.5.4. Heat balance over the length of the heat recovery unit

These two equations of the heat balance were solved numerically to calculate the temperature of the preheated manure ($T_{preh} = T_{cout}$) and the temperature of the discharge manure ($T_{R\ out}$). The mathematical solution is shown in Fig. 4.5.4. From these calculations, the effectiveness (*E*) of the heat exchanger was calculated as follow (Smith, 1997):

$$E = Max\left[\left(\frac{T_{R\ in} - T_{R\ out}}{T_{R\ in} - T_{c\ in}}\right), \left(\frac{T_{c\,out} - T_{c\ in}}{T_{R\ in} - T_{c\ in}}\right)\right] \tag{4.5.9}$$

To calculate the effectiveness, a yearly average of the inlet manure and both the ambient air temperature and the air temperature inside the pumps chamber were used. The calculated annual effectiveness was used to estimate the hourly temperature of the preheated manure as follows:

$$T_{preh} = E\,T_R + (1 - E)\,T_{amb} \tag{4.5.10}$$

Table 4.5.3 shows the parameters used in the simulations of the heat recovery unit.

Table 4.5.3. Parameters used in the simulation of heat recovery unit

Parameter	*Unit*	*Value*
Material thermal conductivity (steel)	W m^{-1} K^{-1}	50
The outer diameter of the internal pipe	m	0.073
The inner diameter of the internal pipe	m	0.066
The inner diameter of the outer pipe	m	0.107
Insulation thickness	m	0.1
Insulation thermal conductivity	W m^{-1} K^{-1}	0.04
Overall transfer coefficient tube	W m^{-2} K^{-1}	20.71
Pipe length	m	7.22
Effectiveness	%	60

4.5.3.3. The reactor

Although in the experimental installation the system is fed once daily. Varel *et al.* (1977) mentioned that greater efficiencies might be obtained with continuous feeding. The modelled system is a CSTR system, which means that the reactor is kept at a constant volume and at a uniform temperature. However, the temperature is time dependent.

For modelling of the integrated system, three heat balances were formulated: for the reactor effective volume, the extra gas volume, and the pump chamber. For the effective volume the following heat balance can be formulated:

$$\rho V C_{p_m} \frac{\mathrm{d}T_R}{\mathrm{d}t} = -Q_{man} + Q_u + Q_{aux} - Q_{lm} + Q_c - Q_{gb} - Q_{gc} \qquad (4.5.11)$$

In which, the accumulation of heat in the reactor is caused by energy needed to heat up the manure from the preheated temperature to the reactor temperature ($-Q_{man}$), heat gain from the solar collector (Q_u), the auxiliary heat (Q_{aux}) and the losses to the surroundings (Q_{lm}). In addition, the manure is in contact with the pump chamber (Qc) and gas volume (Q_{gb} & Q_{gc}).

It should be mentioned that the heat capacity of the reactor material is neglected compared to the heat capacity of the manure itself. Similar heat balance for the simple reactor system can be formulated after eliminating the terms concerning the extra gas volume and pump chamber.

The extra gas volume exchanges heat directly with the back of the solar collector (Q_b) and with surroundings (Q_{gl}). It gains energy from the agitation motor (Q_{ea}) and from the effective volume of the reactor (Q_{gb} and Q_{gc}):

$$\rho_g V_g C_{p_g} \frac{\mathrm{d}T_g}{\mathrm{d}t} = Q_b + Q_{gb} + Q_{ea} + Q_{gc} - Q_{gl} \qquad (4.5.12)$$

Hill (1983b) used the data of Chen and Hashimoto (1981) of 28.8 Wm^{-3} for the tank mixing and assumed transfer and electrical motor efficiencies of 60%. This amount of power was also used to calculate the energy consumption for mixing in the present study assuming the agitator is operated for 10% of the time.

The heat balance of the air inside the pump chamber includes the heat gain from the pumps motor (Q_{ep}), the heat exchange with environment (Q_{lossc}) and with the reactor (Q_c) as follows:

$$\rho_{air} V_{ch} C_{p\,air} \frac{\mathrm{d}T_{Ch}}{\mathrm{d}t} = Q_{ep} - Q_{lossc} - Q_c \qquad (4.5.13)$$

As the time constant of both the biogas volume and the air inside the pump chamber is very small compared to that of the reactor, it was assumed that they are at quasi steady state. The temperatures of both biogas and the air inside the pump chamber were obtained by solving their equations explicitly. It should be mentioned that the power of the manure pumps and the solar collector pumps were calculated based on the total heads required for the liquid flow and assuming the pumping efficiency of 50% (Hill, 1983b). Table 4.5.4 shows the parameters used in the simulations of the system.

Table 4.5.4. Design parameters of the system

Parameter	*Unit*	*Value*	
		Simple system	*Integrated system*
Volume	m^3	10	10
Aspect ratio (height/diameter)	---	0.6	0.6
Hydraulic retention time	days	20	20
Overall heat transfer from the reactor to ambient	$W\ m^{-2}\ K^{-1}$	0.33	0.33
Gas Volume	m^3	---	3.66
Area of heat losses from the gas volume	m^2	----	6.23
Area covered by solar collector	m^2	----	4.88
Pumps power	W	19.4	19.4
Agitator power	W	480	480
Volume of the pumps chamber	m^3	---	1
Heat loss area of the pumps chamber	m^2	---	4.87
Chamber surface attached to the reactor	m^2	----	1.09
Heat exchanger parameter			
Material thermal conductivity (steel)	$W\ m^{-1}\ K^{-1}$	50	50
Overall heat transfer coefficient	$W\ m^{-2} K^{-1}$	247	247
The outer diameter of the pipe	m	0.0579	0.058
The inner diameter of the pipe	m	0.0508	0.051
Length of the heat exchanger	m	2.35	2.35

4.5.3.4. The control system

Temperature has to be controlled because it affects the performance of the biomethanation process. An on/off differential controller is proposed to control the system. Van Straten and Van Boxtel (1996) mentioned that on/off control is widely used. The main reasons are the low costs, the simple controller rules, which are easy to implement in hardware logic and the intuitive appeal and easy understanding. In the present study, the control system can be divided into three subsystems as follows:

Control of the solar collector

The solar collector pump starts operating when the hourly heat gain is positive.

Control of the reactor

The flow gauge of hot water into the reactor begins to open when the outlet temperature of the solar collector (Tf_{out}) is equal or higher than 50^{o}C. The flow stops when Tf_{out} is less than 50^{o}C or the reactor temperature exceeds 50^{o}C.

Control of the auxiliary heater

If the reactor temperature is below 45^{o}C (set point), the auxiliary heater starts to operate. The power of the auxiliary heater is high enough to keep a constant temperature of 45^{o}C, which is the lower limit for these conditions (Van Lier, 1995).

4.5.4. Results and discussion

The model structure was worked out in Matlab + Simulink software for numerical solution. Buzàs *et al.* (1998) mentioned that for solar thermal systems, block-oriented solution seems to be appropriate as it provides a high flexibility in the case of changing the system layout.

4.5.4.1. The solar heating system

Figure 4.5.5 shows the calculated monthly average daily-absorbed energy under Egyptian situation. This amount of energy is the total amount absorbed on the monthly average day. The latter is the day in each month, which has the extraterrestrial radiation nearly equals to the mean value of that month (Sukhatme, 1997). As can be seen June and December have the largest and lowest energy respectively. It can also be seen that the months from July to September have almost the same absorbed energy. In March smaller irradiation with respect to September can be observed, however at the same position of the sun. This is probably due to the presence of clouds (measured data not shown).

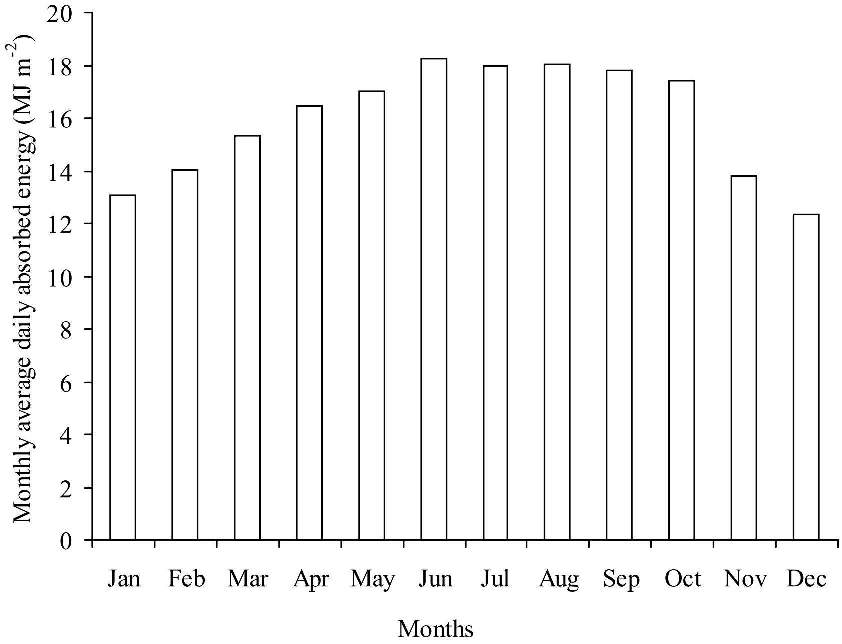


Fig.4.5.5. Monthly average daily absorbed energy

As mentioned before, The solar system array mounted on a tilt angle of 30.1^{o} and faces south. Figure 4.5.6 shows the hourly absorbed energy of the monthly average day of March; June; September and December (*i.e.* day number 75; 162; 258 and 344). As can be seen the longest and the shortest days are in June and December respectively. As it is well known, the energy absorbed increases during the day to reach the maximum around noon, then decline. On the other hand, although the maximum value is found in September around noon, the total energy absorbed (*i.e.* $\int(S\mathrm{d}t)$) in June is higher than that for September. This may be attributed to the fact that the solar incident angle at the collector at noon is smaller at larger tilt angle in winter and vice versa in summer (Fig. 4.5.7). The chosen tilt angle in fact does not adversely affect the system efficiency. It will be chosen to maximise the flux absorbed during winter when most energy is needed.

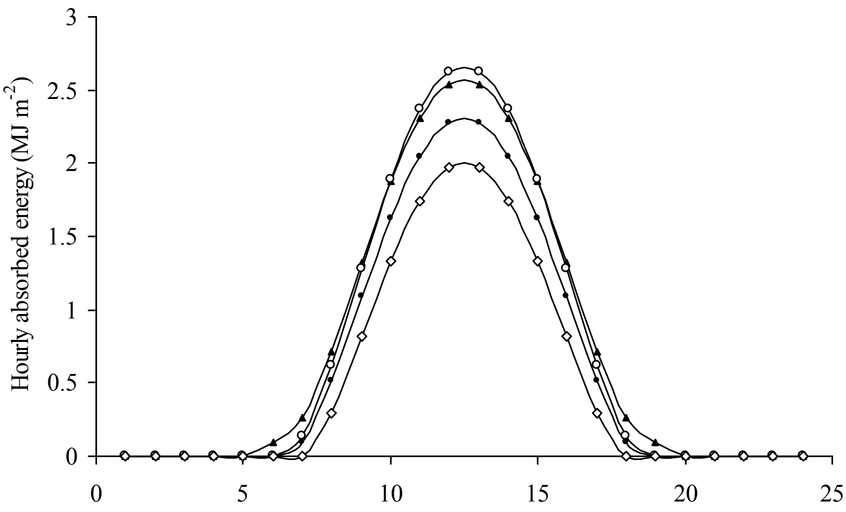


Fig.4.5.6. The daily variation of absorbed energy under Egyptian situation: ●, March; ▲, Jun; ○, Sep; ◊, Dec

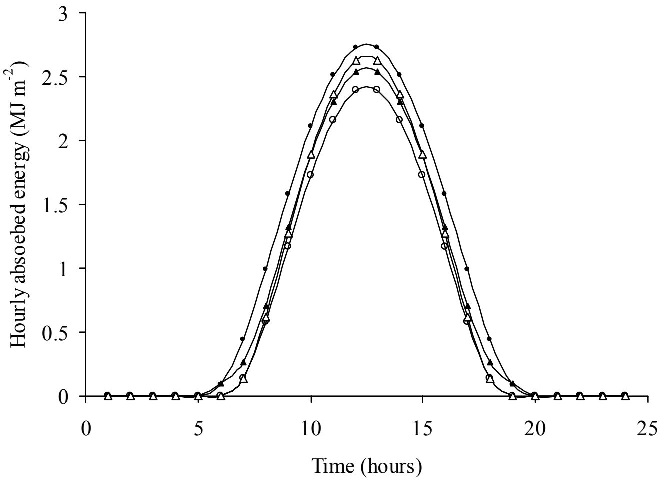
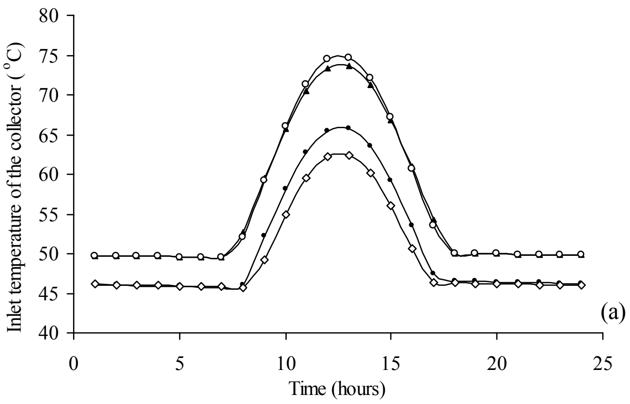


Fig.4.5.7. Effect of tilt angle on daily variation of hourly average absorbed energy under Egyptian situation during summer and winter: ●, Jun tilt angle 1.9^o; ▲, Jun tilt angle 31.1^o; ○, Sep tilt angle 1.9^o; ◊, Sep tilt angle 31.1^o

Figures (4.5.8, a and b and 4.5.9, a and b) show the temperature of the inlet and the outlet temperatures of the solar collector for the simple and the integrated system respectively. As can be seen from these figures inlet and outlet temperature changes are in accordance with the differences in both monthly and hourly absorbed fluxes and ambient temperature (Fig.4.5.11). Moreover, the integrated system has higher values of inlet and outlet temperatures, which may be attributed to the higher temperature of the reactor in this system.



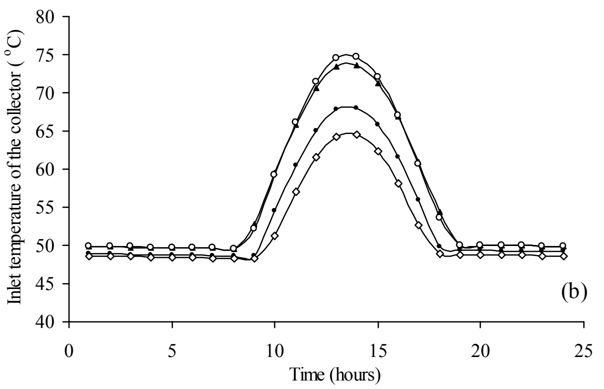


Fig.4.5.8. Daily inlet temperature of the collector, (a) and (b) for simple and integrated system respectively: ●, March; ▲, Jun; ○, Sep; ◊, Dec

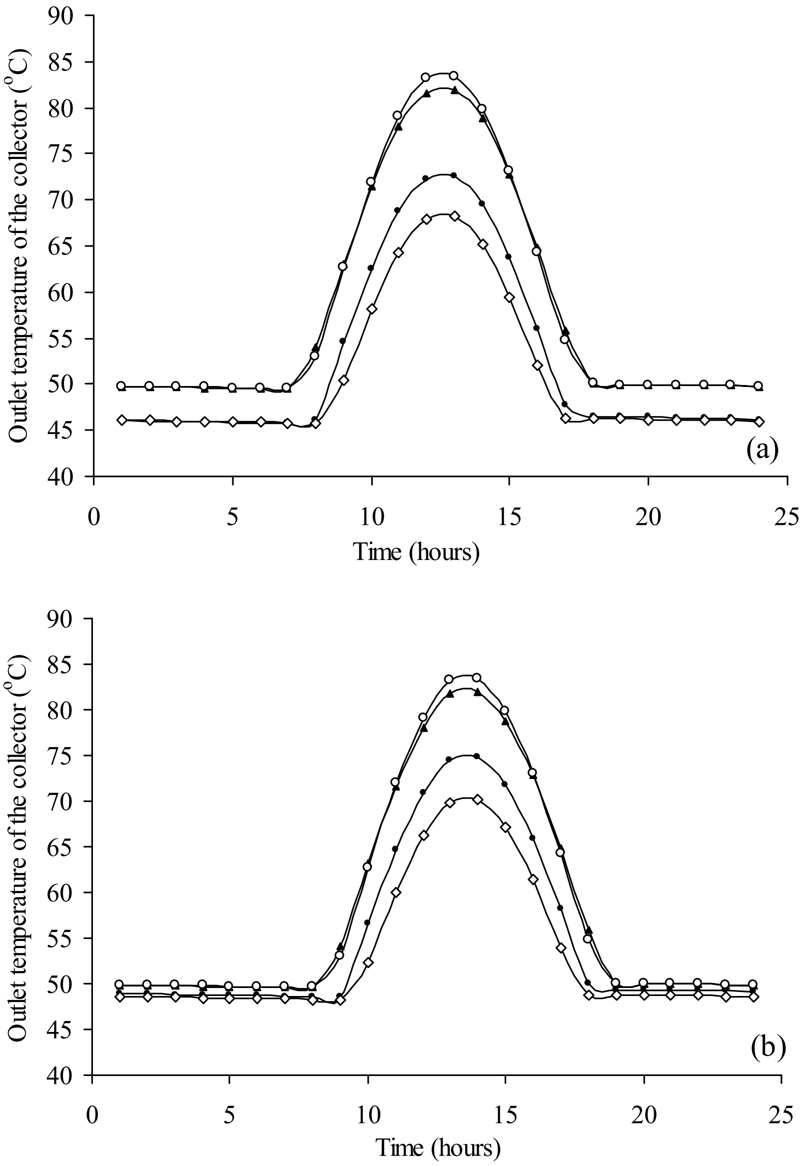
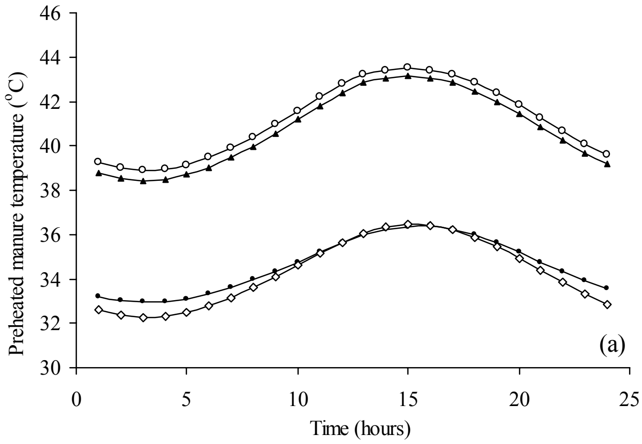


Fig.4.5.9. Daily outlet temperature of the collector, (a) and (b) for simple and integrated system respectively: ●, March; ▲, Jun; ○, Sep; ◊, Dec

4.5.4.2. The heat recovery unit

Figure 4.5.10 shows the preheated manure temperature after passing the heat recovery unit. As can be seen, by using the heat recovery unit, the feed temperature can be increased by about 10-20^{o}C, depending on raw manure temperature and/or ambient temperature (Fig.4.5.11). The smallest increase of the raw manure temperature coincides with the higher ambient temperature, because the driving force of heat transfer in this case is small. Furthermore, it can also be seen from Fig. 4.5.10 that the highest preheated manure temperatures can be obtained during the months, which have high ambient temperature (Fig. 4.5.11). This may be due to smaller environmental heat losses and higher raw manure temperatures. The necessity of the heat recovery will be discussed in the system evaluation section.



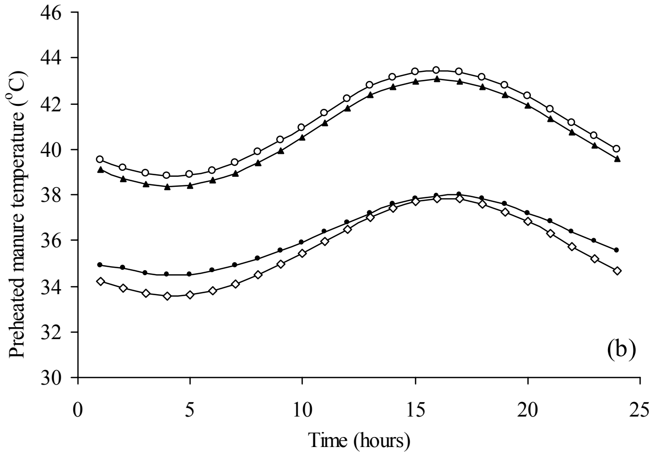


Fig.4.5.10. Temperature of preheated manure, (a) and (b) for simple and integrated system respectively: ●, March; ▲, Jun; ○, Sep; ◊, Dec

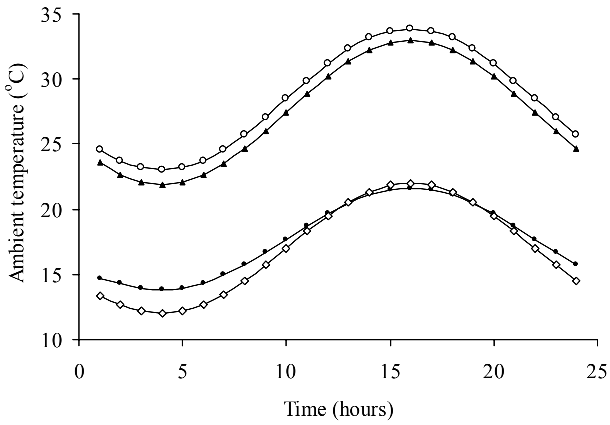


Fig.4.5.11. Ambient air temperature: ●, March; ▲, Jun; ○, Sep; ◊, Dec

4.5.4.3. The reactor

Figure 4.5.12 shows the hourly reactor temperature profile during the same four days for both studied systems. As can be seen the reactor temperature follows the seasonal and daily changes in solar flux. It can also be seen that the reactor temperature profiles are almost the same in June and September for both studied systems. This may be attributed to the differences in solar flux incident as well as the difference in the ambient temperature. The ambient temperature affects the reactor temperature because it influences the levels of preheated temperature and heat losses. It can also be seen that the daily temperature fluctuation is less than 1°C and the seasonal variation is less than 5°C. The results in *chapter* 4.3 showed that the effect of a daily temperature fluctuation of 10°C for 10 hours (*i.e.* the reactor operating at 40°C for 10 hours) has a minor effect on the methane production rate from CSTR operated at 50°C. It can be concluded that the systems could be operated successfully without extra heat storage during nights as well as without harming the activity of bacteria. Moreover, the simulation showed that on/off control strategy could be applied with great reliability in such slow reacting multi-component system.

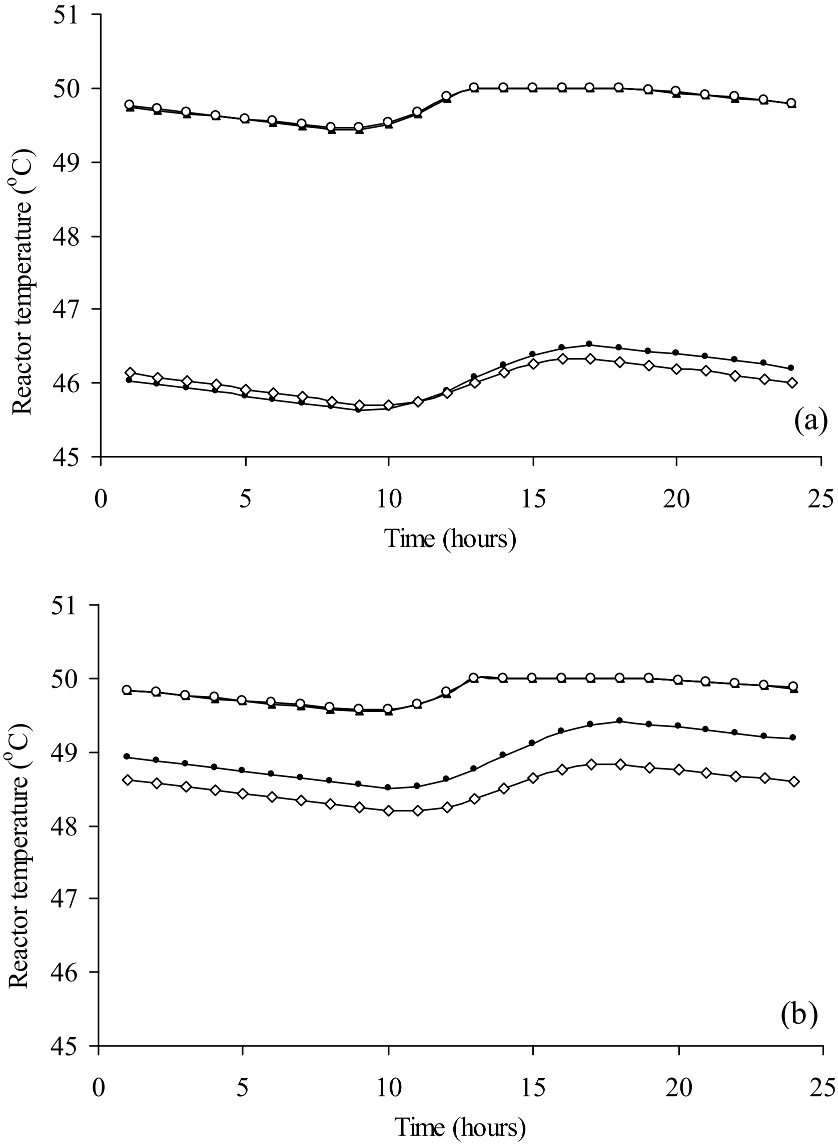


Fig.4.5.12. Daily profile of the reactor temperature, (a) and (b) for simple and integrated system respectively: ●, March; ▲, Jun; ○, Sep; ◊, Dec; note that simulations for June and September are almost on top of each other.

Figure 4.5.13 shows the temperature of the biogas in the integrated system. The temperature of the biogas reaches maximum of about 53°C and minimum of about 50°C. The maximum temperature occurs around noon in September for the same previous reasons.

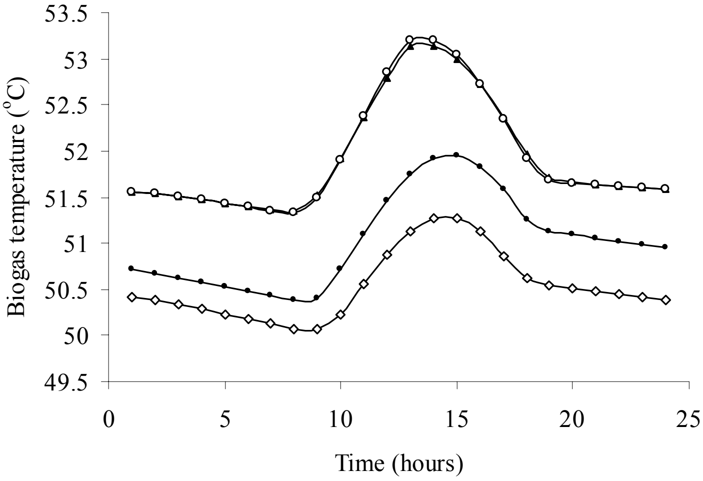


Fig.4.5.13. Biogas temperature: ●, March; ▲, Jun; ○, Sep; ◊, Dec

Figure 4.5.14 shows the temperature of the air inside the pump chamber in the integrated system. The temperature of the air reaches a maximum of about 46°C and a minimum of about 18°C. The maximum temperature occurs around noon in September. The increase of the air temperature, inside the chamber coincides with the start of the solar collector pump operation.

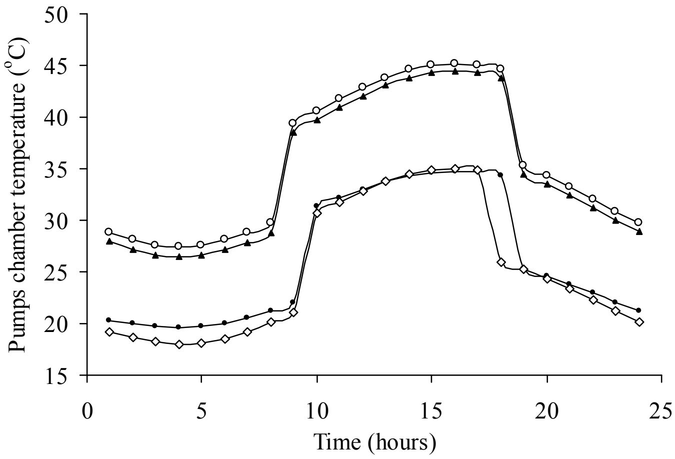


Fig.4.5.14. Pumps chamber temperature: ●, March; ▲, Jun; ○, Sep; ◊, Dec

4.5.4.4. System evaluation

Based on the presented model, the system with and without heat recovery was evaluated. The evaluation is based on annual energy input from different sources together with the temperature variations. Table 4.5.5 shows the amount of energy from each source for both systems as well as the effect on the system performance of adding the heat recovery unit. The model results show that with heat recovery, no auxiliary heat is required for the integrated system. This means that the specific net thermal energy production (SNTEP, *chapter* 4.4) is 100%. It should be mentioned that the electrical energy consumption was translated into thermal energy assuming a conversion factor for fossil-fuel equivalence of electricity of 11.08 kJ/Wh (Singh, 1978). The results in *chapter* 4.4 showed that SNTEP of about 93% could be obtained from a 10 m^3 CSTR (without either heat recovery; pump chamber and the control system) insulated with 10 cm bricks together with 11 cm of rock wool ($U_r = 0.33$ $Wm^{-2}K^{-1}$).

Table 4.5.5. The annual systems evaluation

Parameter	*Simple system*		*Integrated system*	
	With Heat recovery	*Without heat recovery*	*With Heat recovery*	*Without heat recovery*
Solar Energy (GJ)	20.19	21.16	20.01	20.81
Heat recovery unit (GJ)	11.73	------	11.96	------
Pumps and agitator (GJ, electrical)	1.76	1.76	1.76	1.76
Pumps and agitator (GJ, Thermal equivalent)	5.43	5.43	5.43	5.43
Auxiliary heater (GJ)	0.91	5.42	00	4.33
Total Energy input (GJ, Thermal equivalent)	38.26	32.01	37.4	30.57
Annual average temperature of the reactor (^oC)	48 ±2*	45 ± 4.4	49±1.3	46± 3.5
Minimum reactor temperature (^oC)	44.8	36.5	45.7	39.4
Annual average temperature of the biogas (^oC)	------	------	51±1.4	48 ±3.6
Annual average temperature of pumps chamber air (^oC)	------	------	30± 9	29±9

*± Standard deviation

For the system without heat recovery, it can be seen that lower reactor temperatures have been obtained. This in turn increases the driving force for heat gain from the solar collector. It can also be seen that the heat recovery unit affects the average and minimum hourly temperatures of the reactor considerably.

From the technological point of view the integrated system can be recommended. However the integrated system will be more expensive due to higher construction cost for inclusion of biogas volume and pumps chamber. Because the temperature in the biogas volume will be moderate no explosion danger is to be expected.

4.5.5. Conclusions

Two CSTR systems treating cattle manure were modelled and the results of their performance are presented. The first system is a simple system and the second is an integrated one, which includes extra volume of biogas in the top of the reactor and an extra chamber for the pumps and the heat recovery unit. Based on the results obtained from the simulations, the following conclusions can be formulated:

1- A maximum daily temperature fluctuation of less than 1K can be realised in both systems. A maximum annual temperature variation of about 5K can be realised in both systems, depending on the seasonal variations of both ambient temperature and solar flux.

2- The solar energy heating system can be used for the thermophilic anaerobic reactor while the occurring temperature variation does not decrease the activity of micro-organisms. So from the sustainability point of view, the incorporation of solar energy in biogas production unit increases the beneficial potential of anaerobic digestion in environmental pollution and resource conservation.

3- The annual electrical energy consumption is 48.8 kWh m^{-3}. Using the integrated system, an overall energy efficiency of 95% can be achieved by using the solar heating system and a heat recovery unit.

4- The on/off control can be applied effectively in such multi-component system.

5- The integrated system can be recommended from the technological and energetical point of view. Moreover operation and maintenance of the integrated system will not be more complicated compared to the simple one.

Nomenclature

A	Surface area of the reactor heat exchanger	m^2
A_{che}	Area of heat losses to environment	m^2
A_{chr}	Area of heat transfer from the pumps chamber to the reactor	m^2
A_{cross}	Cross section area of the reactor	m^2
Ag	Surface area of the gas volume	m^2
A_p	Absorber plate area	m^2
Ap	Area of the absorber plate	m^2
A_r	Surface area of the reactor	m^2
A_{Re}	Area of heat transfer of the heat recovery unit	m^2
B_{opt}	Optimum tilt angle	^{o}
Cp_{air}	Specific heat of air	$J\ kg^{-1}\ K^{-1}$
Cp_g	Specific heat of the biogas	$J\ kg^{-1}\ K^{-1}$
Cp_m	Specific heat of manure	$J\ kg^{-1}\ K^{-1}$
C_{Pw}	Specific heat of water	$J\ kg^{-1}\ K^{-1}$
F'	Collector efficiency factor	%
F_R	The collector heat-removal factor	%
I_T	Solar flux on a tilted surface	W
L	Length of heat recovery unit	m
m	Flow rate of water inside the solar collector	$kg\ s^{-1}$
Q_1	Heat gain (loss) from the manure inside the heat recovery unit	W
Q_2	Heat losses from the heat recovery unit to surroundings	W
Q_{aux}	Auxiliary heat add to the reactor	W
Q_b	Bottom heat loss from the solar collector	W
Q_c	Heat losses the pump chamber to the reactor	W
Q_{ea}	Electrical energy consumption in agitation	W
Q_{ep}	Rate of heat gain from the pump	W
Q_{gb}	Heat losses by from the liquid via biogas bubbles	W
Q_{gc}	Heat losses by convection from the liquid to biogas	W
Q_{gl}	Heat losses from the gas volume to ambient	W
Q_{lm}	Heat losses from the effective volume of the reactor	W
Q_{lossc}	Heat losses from the pump chamber to environment	W
Q_{man}	Heat required to heat up the preheated manure to the reactor temperature	W
Q_r	Heat recovered from the effluent	W
Q_{sid}	Sides losses from the solar collector	W
Q_{top}	Top losses from the solar collector	W
Q_u	Useful heat gain rate from the collector	W
S	Hourly incident solar flux absorbed in the absorber plate	$W\ m^{-2}$
S_a	Outer surface area of the heat recovery unit	m^2
t	Time	s
Tch	Temperature of the air in the pump chamber	^oC
T_{amb}	Ambient temperature	^oC
T_c	Local temperature manure	^oC
T_{cin}	Temperature of cold manure	^oC
T_{cout}	Temperature of preheated manure $= T_{preh}$	^oC
Tf_{in}	Water inlet temperature to the solar collector; assumed to be equal water outlet temperature from the reactor	^oC

Tf_{out}	Water outlet temperature from the solar collector; assumed to be equal water inlet temperature to the reactor	^{o}C
T_g	Biogas temperature	^{o}C
T_p	Temperature of the absorber plate	^{o}C
T_{preh}	Temperature of preheated manure	^{o}C
T_R	Operation temperature of the reactor	^{o}C
U	Overall heat transfer coefficient of the reactor heat exchanger	$W\ m^{-2}\ K^{-1}$
U_a	Overall heat loss coefficient from the recovery unit to environment	$W\ m^{-2}\ K^{-1}$
U_{Bttom}	Bottom loss coefficient	$W\ m^{-2}\ K^{-1}$
U_{che}	Heat losses coefficient to environment from the pump chamber	$W\ m^{-2}\ K^{-1}$
U_{chr}	Heat transfer coefficient from the pump chamber to the reactor	$W\ m^{-2}\ K^{-1}$
Ug	Heat loss coefficient from the gas volume	$W\ m^{-2}\ K^{-1}$
U_{gas}	Overall transfer coefficient of biogas	$W\ m^{-2}\ K^{-1}$
U_L	Overall losses coefficient from the collector	$W\ m^{-2}\ K^{-1}$
U_r	Overall heat loss coefficient from the reactor	$W\ m^{-2}\ K^{-1}$
U_{Re}	Overall heat transfer coefficient of the heat recovery unit	$W\ m^{-2}\ K^{-1}$
V	Reactor volume	m^3
V_{ch}	Volume of the pump chamber	m^3
V_g	Biogas volume	m^3
ϕ	Latitude	^{o}
δ	Declination angle	^{o}
ρ	Manure density	$kg\ m^{-3}$
ϕ_v	Volumetric loading rate	$m^3\ s^{-1}$
ϕ_{Vg}	Biogas production rate	$m^3\ s^{-1}$
ρ_g	Biogas density	$kg\ m^{-3}$
ρ_{air}	Density of air	$kg\ m^{-3}$

CHAPTER 5: DIGESTION OF SOLID COW MANURE

5. 0. Introduction to the Chapter

The results presented in this *chapter* concern the experimental and modelling results of the treatment of solid animal wastes in an accumulation system (AC). In the experimental part, the feasibility of using an AC system for treatment of solid animal wastes was studied at mesophilic and thermophilic conditions. Furthermore, the effect of leachate recirculation and the effect of different modes of inoculum addition were investigated as means for improvement of the system performance. In addition, results from two different models were presented. The first model concerns the biological process involved in the digestion of solid manure in an AC system. The model was validated with the experimental results. The second model concerns the design of a STAR system for treating solid animal wastes. The results presented in this *chapter* were written in four separate papers:

5.1. El-Mashad, H.M.; Zeeman, G.; Loon, W.K.P. van; Bot, G.P.A. and Lettinga, G (2003). Anaerobic digestion of solid animal waste in an accumulation system at mesophilic and thermophilic conditions, start up. General set up of this *chapter* is published in Water Science and Technology 48 (4): 217-220.

5.2. El-Mashad, H.M.; Zeeman, G.; Loon, W.K.P. van; Bot, G. P.A. and Lettinga, G. Effect of inoculum addition modes and leachate recirculation on anaerobic digestion of solid cattle manure in an accumulation system. To be submitted

5.3. El-Mashad, H.M.; Loon, W.K.P. van; Zeeman, G.; Bot, G.P.A. and Lettinga, G. A model for anaerobic digestion of solid cattle wastes in a stratified accumulation system. To be submitted

5.4. El- Mashad, H.M.; Loon, W. K.P. van; Beuger, A.L.; Boxtel, A.J.B. van; Zeeman, G. and Bot, G.P.A. Design of a layered accumulation system for thermophilic anaerobic digestion of solid manure heated with solar energy. To be submitted

5.1. Anaerobic Digestion of Solid Animal Waste in An Accumulation System at Mesophilic and Thermophilic Conditions, Start Up

Abstract

The anaerobic digestion of solid animal wastes has been studied in an accumulation system (AC) at a filling time of 60 days at 40 and 50°C. Poor mixing conditions during the digestion process of solid wastes promote stratification of substrate and of intermediate products along the reactor height. The effect of stratification has been followed in the AC system. The effect of two different moisture contents on the process performance and on the components stratification has also been elucidated. The results obtained show a pronounced stratification of both COD_{dis} and VFA concentrations along the AC system height. Using adapted sludge, a short or no lag phase was noticed. The results also showed that methanogenesis was the rate limiting step in the AC system, especially for the top layers. Moreover, the higher the moisture content of the manure, the better the observed process performance and the lower the stratification profiles can be observed.

5.1.1. Introduction

On farm anaerobic digestion of animal manure is an attractive technique for the production of both energy and stabilised organic fertiliser. Literature on manure digestion deals mainly with liquid manure (*i.e.* TS < 100g l^{-1}) digestion (*e.g.* Velsen, 1981; Zeeman, 1991 and Hill and Bolte, 2000), although many smaller farms, in various countries all over the world, still produce mainly solid manure, depending on the rations and the breeding system (*e.g.* the bedding material).

According to Pathak *et al.* (1985) and Ghosh and Lall (1988) slurry fermentation of low solid feeds suffer from a number of factors, which adversely affect the economic feasibility of the digestion process. It requires (1) the supply and handling of large volumes of external water and leads to substrate dilution, (2) the installation of relatively large digesters to accommodate the voluminous feed (slurry), (3) the handling and dewatering of large volume of digester effluents at considerable capital and operating costs, and 4) the expenditure of large amounts of energy for digester heating, feed slurry pumping, and effluent dewatering and disposal. On the other hand dry fermentation may suffer from problems related to its low moisture content, *i.e.* mass transport limitation and poor diffusion, and distribution of microorganisms throughout the substrate mass. Callaghan *et al.* (1999) mentioned that total solid contents of 27 % make chicken manure unsuitable for digestion, as it is difficult to mix systems with solids levels of above 10 % adequately by conventional mixing methods. Pathak *et al.* (1985) showed that the anaerobic digestion of high-solid cattle dung and cattle dung and rice straw mixtures remains unaffected at total solids concentrations up to about 15 %. At total solids concentrations in the range of 7.7%-15% no clear differences were observed in the amount of gas produced. Hill (1980) studied the anaerobic digestion of dairy manure (average TS of 20 %) in fed batch reactors, which were manually mixed once daily. Approximately 25 % of the volatile solids were destroyed after a period of 13 weeks. According to Makaly Biey *et al.* (2000), anaerobic solid state fermentation produces both energy in the form of biogas and a humus-like end-product called humotex and according to De Baere *et al.* (1985) solid wastes (30-35% TS) digested at thermophilic (50-

55^{o}C) conditions can be qualified as highly stabilised and as a hygienically acceptable compost.

For on farm application the anaerobic digestion system should be as simple as possible to operate and in agreement with the on farm practice. Wellinger and Kaufmann (1982) demonstrated for the first time the practical feasibility of an accumulation system (AC) for the digestion of liquid animal manure in practice. According to Zeeman (1991), the AC system is the simplest system for on farm practice as it combines storage and digestion. Since manure cannot be used as a fertiliser during the winter period it needs to be stored always for a period of some months in regions with a medium and low temperature climate. AC and continuous stirred tank reactor (CSTR) systems both comprise a continuously fed system, but while the effluent from a CSTR is continuously removed, the effluent in an accumulation system is removed only once, *i.e.* at the end of the filling period. The CSTR has a constant effective digestion volume, while that of the AC-system is increasing in time. In operating the accumulation system a fraction of the reactor volume is always needed for seed sludge, in order to provide sufficient methanogenic activity. The reactor is filled within the filling period and emptied once. The filling period is determined by the needed storage capacity and by the time needed to provide enough stabilisation (Zeeman *et al.,* 2000).

Previous studies dealing with AC systems focused on mesophilic and psychrophilic conditions for liquid manure. So far the anaerobic digestion of solid animal wastes, to our knowledge, has not been studied in an AC system. In the present investigation we therefore focused our research on the feasibility of solid manure digestion on the basis of the knowledge gained previously in the laboratory on liquid manure digestion (*e.g.* Zeeman, 1991) and on the solid state digestion of house hold waste (*e.g.* Ten Brummeler, 1993).

The objectives

The objectives of the research were:

1- To optimise the performance of an accumulation system for the anaerobic treatment/storage of solid manure at mesophilic and thermophilic conditions.

2- To assess the effect of the moisture content on the process performance as well as on the stratification of different components along the reactor height.

3- To assess the effect of layer stratification on the process performance.

4- To improve the insight in the hydrolysis step under such conditions.

5.1.2. Materials and methods

5.1.2.1 Experimental set up

Accumulation system

Two experimental runs have been carried out. In the first run the seed sludge consisted of 10% (V/V) thermophilic (50^{o}C) batch-wise digested horse dung. The maximum specific methanogenic activity (SMA) of the seed sludge, assessed by the VFA depletion method described by Lier (1995), amounted to 0.10 and 0.11 g[COD]g^{-1} [VS]day^{-1} at 40°C and 50°C respectively. After inoculation of the reactors, the feed for the first four days was supplied to the system and next the reactors were flushed with N_2 for 15 minutes and incubated at the desired temperatures. Feeding was made once a week. After 60 days, the reactors were opened and sampled as described below and then the reactors were re-flushed with nitrogen for 15 minutes and operated in batch-mode for about 50 days. Finally, an analysis sequence has been done for both batch reactors.

In the second run, 10% (V/V) digested manure from the first run was used as seed material. The feeding procedures were the same as during the first experiment, but after a filling time of 60 days, the reactors were continued batch wise for another 20 days. After 80 days the reactors were opened and sampled as described below.

Batch systems (stabilisation experiments)

To elucidate the development of methanogenesis over the reactor height, an additional stabilisation experiment was conducted. Samples of 100 g were taken, from different reactor heights at the end of the second run and put in 300 ml serum bottles. Two samples were taken from each reactor height and at each operational temperature. The bottles were closed and flushed with N_2 for 3 minutes and incubated statically at the analogous temperature for 104 days. The methane produced from the bottles was measured periodically by using a Marriotte flask containing a 5 % NaOH solution. The methane produced was recalculated for standard temperature and pressure (STP).

5.1.2.2. Substrates used

The cow manure used in the experiments originated from fattening animals. It consisted of feces, urine, and bedding material. The animals are fed concentrated, antibiotic free diets. The manure was stored in a refrigerator (4°C) until used. No pre-treatment was applied for the manure. The chemical characteristics of the substrate are mentioned in Table 5.1.1.

Table 5.1.1. Substrate characteristics, standard deviations are between brackets.

Parameters	*First run*	*Second run*
TS (g kg^{-1})	250.1 (2.4)	164.7 (5.8)
VS (g kg^{-1})	189.4 (1.4)	136.2 (4.2)
COD (g kg^{-1})	314.9 (4.9)	194.7 (3.8)
C_2 (g [COD]kg^{-1})	6.7 (0.1)	4.2 (1.6)
C_3 (g [COD]kg^{-1})	6.7 (0.1)	2.4 (1.0)
i-C_4 (g [COD]kg^{-1})	0.5 (0.0)	0.2 (0.1)
n-C_4 (g [COD]kg^{-1})	1.1 (0.0)	1.5 (0.6)
b-C_5 (g [COD]kg^{-1})	0.0 (0.0)	0.6 (0.2)
n-C_5 (g [COD]kg^{-1})	0.1 (0.0)	0.3 (0.1)
VFA (g [COD]kg^{-1})	15.0 (0.3)	9.11 (3.5)
COD_{dis} (g kg^{-1})	41.7 (2.4)	36.8 (9.5)
Nkj (g kg^{-1})	6.7 (0.1)	6.5 (0.1)
NH_4^+N (g kg^{-1})	1.8 (0.2)	2.1 (0.2)

5.1.2.3.Experimental reactors

Two cylindrical AC reactors, each with a working volume of 30 liters were used in this study. The aspect ratio of the reactor (reactor effective height/reactor diameter) is about 1.7. The filling time was chosen based on the period of the year when any crops don't grow due to low temperature conditions. For Mediterranean conditions this will be maximal 2 months. Figure 5.1.1 shows a simple scheme of the experimental reactor. It consisted of an AC reactor (1), fed manually through a funnel (2). After feeding the reactor was closed by a gas tight valve (3). The outlet biogas was passed through a 15% NaOH solution (4) to absorb CO_2, then the methane produced was measured by a wet gas meter (5). The gas volume was re-calculated for STP. The reactors were incubated at 40^oC and 50^oC for both experimental runs.

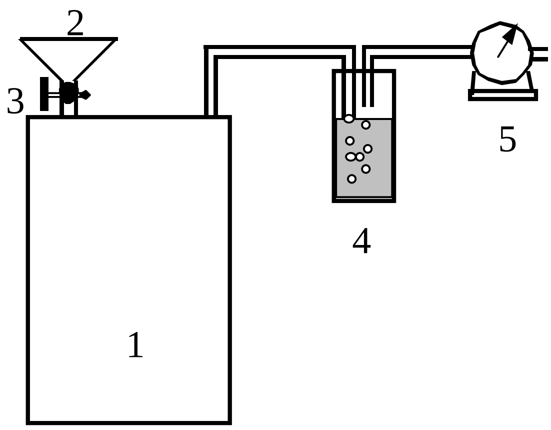


Fig.5.1.1. A schematic of the the experimental AC system with 1, AC reactor; 2, funnel; 3, gas tight valve; 4, sodium hydroxide solution; 5, gas meter

5.1.2.4. Sampling and analyses

At the end of both runs, samples were taken from different heights along the AC reactor (see Figures 5.1.5 and 5.1.6). For the batch-wise stage, in the first run, a composite sample was taken from each reactor. At the end of the stabilisation experiments, the bottles were analysed for COD_{dis} and VFA.

All analyses have been done in duplicate after dilution and mixing for 3 minutes using a food mixer. The total COD was measured for diluted samples according to Zeeman (1991). The mixed diluted samples for VFA and COD_{dis} measurements were centrifuged for 10 minutes at a 3500-rpm on samples prepared by membrane filtration (0.45 µm). COD_{dis} was measured using the micro method (Jirka and Carter, 1975). The VFA's were determined by gas chromatography using a Hewlett Packard 5890 equipped with a 2 m × 2mm glass column, packed with Supelcoport (100-120 mesh) and coated with 10 % Fluorad FC 431. The temperatures of the column, injection port and flame ionisation detector were 130, 220, 240^oC, respectively. The carrier gas was nitrogen saturated with formic acid (40 ml per min). Total ammonium (NH_4^+-N) was determined by the steam distillation method according to Standards Methods (APHA, 1992). Nkj was also measured according to Standards Methods (APHA, 1992).

5.1.2.5. Calculations

The percentages of hydrolysis (H), acidogenesis (A) and methanogenesis (M) have been calculated as described in *chapter* 4.2 of this thesis.

5.1.3. Results and discussion

5.1.3.1. Methane production

Methane production rate from the AC system

Figure 5.1.2 shows the course of the methane production rate (MPR) from both reactors during the first run. A lag phase of about one week at 50°C and about two weeks at 40°C prevailed, which likely is the result of adaptation of the microflora to the experimental conditions. Such 'long' lag phase did not manifest during the second run, *i.e.* lag phase were one week (Fig. 5.1.3), likely because of the use of an adapted seed material in that case (Ten Brummeler, 1993). As can be seen from Fig. 5.1.2, no noticeable difference between both reactors manifested. Figure 5.1.3 shows the methane production rate in the second run. The cessation of gas production at 50°C in the period from day 49 to day 62 is due to interruption in the heating system. From both Figures, it can be noticed that opposite to the CSTR system, inconstant MPR is obtained (Zeeman, 1991).

In the second run (Fig. 5.1.3), as expected the methane production rate at 50 °C exceeds that observed at 40°C. According to observations made by De Baere *et al.* (1985) thermophilic (50-55°C) solid state fermentation gives a markedly improved gas production compared to mesophilic conditions (30-40°C). However contrary to De Baere *et al.* (1985), Ten Brummeler (1993) observed an optimum temperature of 40°C for Municipal Solid Wastes (MSW) digestion. Ten Brummeler attributed the lower digestion rate at 55°C to the lower hydrolysis rate at 55°C compared to 40°C.

Comparing the results of the two runs, the methane production rate found at 50 °C during the second run is higher than that at the first run. One reason for this might be the higher moisture content in the influent in this run compared to that of the first run, which may lead to an improved mixing of the substrate with the seed sludge by the produced biogas. A second reason could be the lower viscosity at the higher temperature, which also results in better mixing between the seed material and the substrate. Ten Brummeler (1993) mentioned that the negative effect of high total solid concentrations on the overall decomposition (methane production rate) in dry anaerobic digestion can be attributed to factors such as: the lower water availability for the microorganisms involved; the high concentration of inhibiting compounds at higher total solids concentrations and substrate limitation due to insufficient mixing of substrate and bacteria at higher total solids concentrations. According to Ten Brummeler, a higher viscosity of the medium requires a longer period of mixing for a proper mixing up of the substrate and inoculum.

Opposite results were obtained at 40°C, which may be attributed to the loss of methanogenic activity at 40°C after the long batch incubation period in the first run combined with the lower μ_{max} at 40°C compared to that at 50°C. In order to enable a comparison between both situations, the accumulated amount of methane during the filling time was calculated based on the total COD added to the system. The calculated amounts during the first run amounted to 51.6 and 58 *l* kg^{-1} [COD added] at 40 and 50^{o}C, while they were 52.9 and 125.9 *l* kg^{-1} [COD added] during the second run at 40^{o}C and 50^{o}C respectively. There is no significant difference between both runs at 40^{o}C, contrary to 50 ^{o}C.

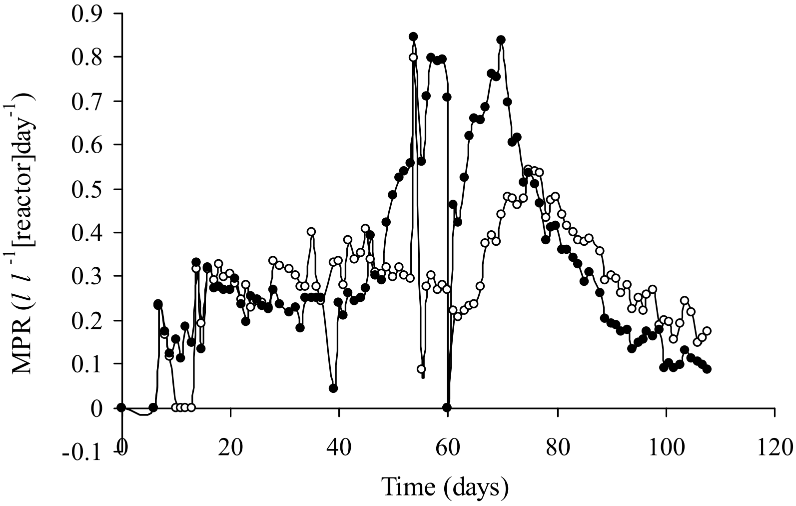


Fig.5.1.2. Methane production rate at the first run: ○, MPR at 40^{o}C; ●, MPR at 50^{o}C. At day 60 reactors were opened for sampling then operated batchwise

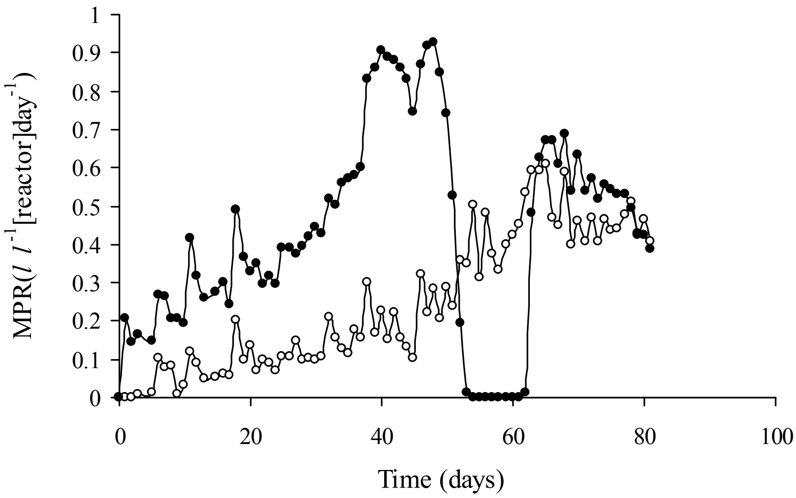


Fig.5.1.3. Methane production rate at the second run: ○, MPR at 40^{o}C; ●, MPR at 50^{o}C. Note: An interruption in the heating system at 50^{o}C took place from day 49 to day 62

Methane production during the stabilisation period

The results of methane yield from the mixed liquor remaining after the second run samples taken at different reactor heights are shown in Fig. 5.1.4,a and b. At 50 ^{o}C, no significant difference of the accumulated methane was found for the lower layers, *i.e.* below 40% of the reactor height. The higher layers increasingly gave a higher methane yield, which can obviously be attributed to the availability of substrate (Fig. 5.1.6) and to the presence of high concentrations of methanogenic bacteria. On the other hand, at 40^{o}C higher methane yields are found for each higher layer except for the top layer. Although the substrate concentration of the top layer is high in this case the lag phase lasts for a long period of about

25 days, likely due to the low content of methanogenic bacteria in the sludge biomass of this layer. Comparing the results of the top layers at both temperatures, one can say that either the high growth rate or the high motility (via *e.g.* diffusion or the mixing resulted from gas production) of methanogens at 50°C might be the main reason for the differences. In the experiment conducted at 40°C, the methane accumulated at heights of 0.2 to 0.8 of the reactor exceeds that found for the comparable heights in the experiment conducted at 50°C. This can be attributed to the availability of substrate.

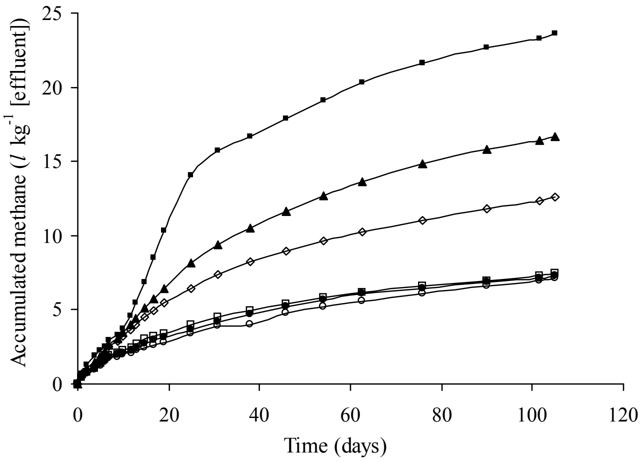


Fig. 5.1.4,a. Accumulated methane from batch bottles at 50°C: ■, reactor top; ▲, 0.8 of reactor height; ◊, 0.6 of reactor height; ○, 0.4 of reactor height; ●, 0.2 of reactor height; □, reactor bottom

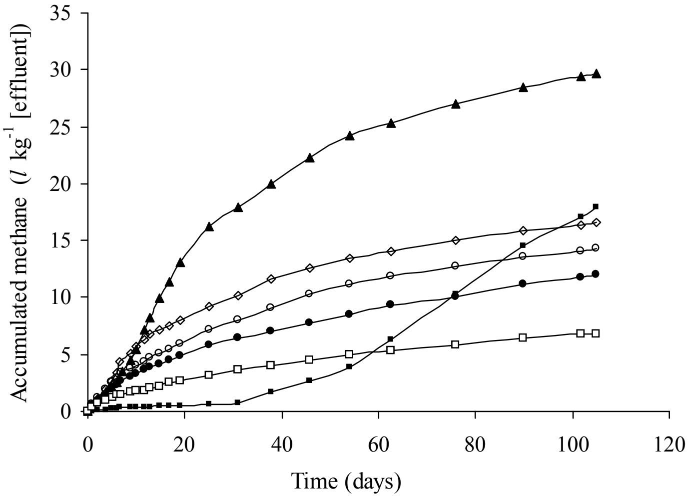


Fig. 5.1.4,b. Accumulated methane from batch bottles at 40°C: ■, reactor top; ▲, 0.8 of reactor height; ◊, 0.6 of reactor height; ○, 0.4 of reactor height; ●, 0.2 of reactor height; □, reactor bottom

5.1.3.2. Stratification of intermediates components

Stratification of intermediates components in Ac systems

As mentioned above, in the operation of the unmixed AC system two different zones can be distinguished, *i.e.* the inoculum zone and the substrate zone. Figure 5.1.5 shows the concentration of VFA and COD_{dis} over the AC system height as assessed during the first run. From this Figure it is clear that the lowest concentration of both VFA and COD_{dis} is present in the bottom layer, which obviously can be attributed to a combination of the long period of contact with the inoculum and the higher methanogenic activity of the sludge of this lower layers compared to that of the upper layers. According to Zeeman (1991) the reason for the observed VFA accumulation at the end of filling time found in treatment of liquid manure in an AC system at 15^{o}C, is the insufficient methanogenic capacity of the system. Moreover, although the retention of the higher layers is lower, the production of VFA and soluble COD starts immediately as a results of the presence of fermentative bacteria, which already cover and attack the particles within a few hours from the starting up of the digestion, even when the amount of bacteria present is not optimal (Ten Brummeler, 1993). The period needed for sufficient enzyme production is believed to be very short compared to the total digestion time of complex wastes (Hobson, 1987). Even in presence of high concentrations of VFA the methanogenesis process still proceeds, which may be attributed to either the predominance of *Methanosarcina sp* at high organic acid concentrations or the existence of different zones of substrate and inoculum (Ten Brummeler 1993).

Besides operational factors like temperature and HRT, reactor mixing is a main factor (*e.g.* De Baere, 2000) in the performance of the anaerobic process. Mixing improves the efficiency of the reactor, it avoids stratification of the substrate and temperature gradients. However, the gradient of stratification depends strongly on the moisture content of the substrate. Figure 5.1.6 shows the concentration of both COD_{dis} and VFA in the second run for both reactors and it is clear that up to 60% of the reactor height the concentrations of both these components are very similar. This obviously can be attributed to better transport of the different components between the layers as a result of the better mixing by the produced biogas production under conditions of higher moisture contents. The results of experiments and simulations made by Veeken and Hamelers (2000) on the solid state digestion of a biowaste in batch reactors revealed that the reactor performance could be improved by applying leachate recirculation. According to their insights the transport of VFA from the acidogenic pocket (fresh biowaste) to methanogenic pockets (seeding material) can only take place through the liquid phase. According to Ten Brummeler, (1993), leachate recirculation is essential to obtain a high digestion rate.

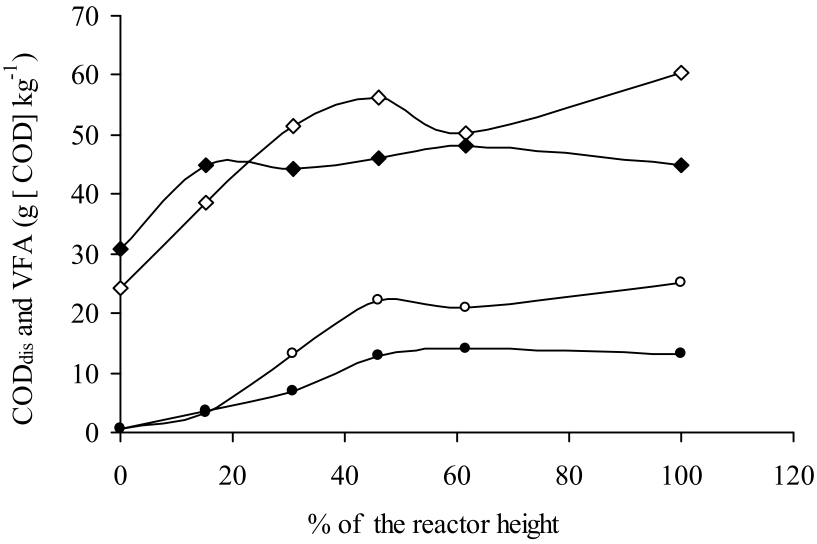


Fig.5.1.5. COD_{dis} and VFA concentrations over the reactor height in the first run: ◊, COD_{dis} at 40^{o}C; ♦, COD_{dis} at 50^{o}C; ○, VFA at 40^{o}C; ●, VFA at 50^{o}C

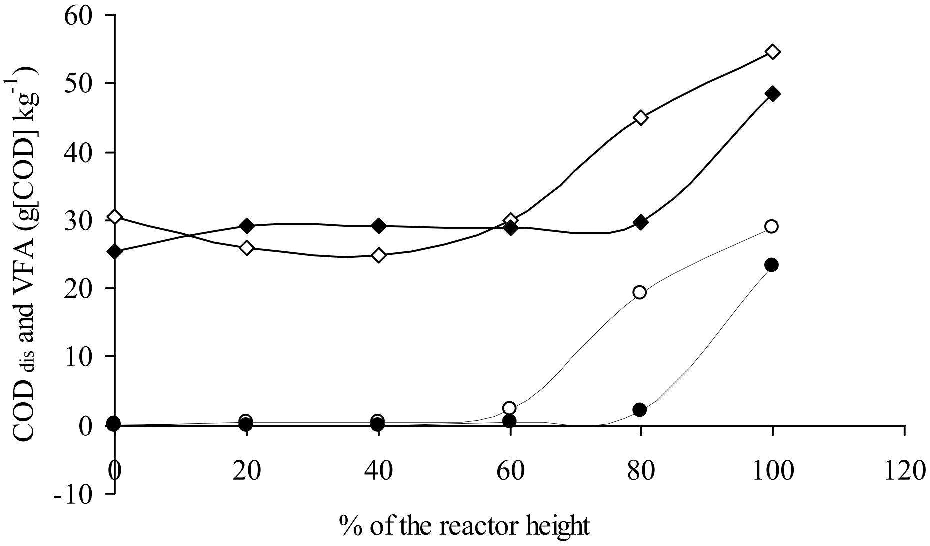


Fig.5.1.6. COD_{dis} and VFA concentrations over the reactor height in the second run: ◊, COD_{dis} at 40°C; ♦, COD_{dis} at 50°C; ○, VFA at 40°C; ●, VFA at 50°C

Stratification of intermediate components in batch bottles (stabilisation experiments)

Table 5.1.2 summarises the results of measurements of the COD_{dis} and VFA concentrations made in the batch bottles after 104 days of additional batch digestion. These results clearly demonstrate that the concentrations of both components is lower for the sludge collected from the lower part of the reactors at both studied temperatures and the vice versa. The average VFA concentrations after 104 days were 1.75 and 1.42 g kg^{-1} at 40°C and 50°C respectively. This means that after a total digestion time of 164 days there is still accumulated VFA, especially in the top layer. This supports the idea of applying methods such as leachate recirculation or supply of seed material (inoculum) in different doses with the feed as an option in order to reduce the digestion time for accomplishing a high degree of stabilisation of the manure. The results of applying these methods will be presented in *chapter* 5.2. The concentration of COD_{dis} is almost constant (about 32 g kg^{-1}) over 80% of the reactor height and the top layer has the highest concentration. These results indicate that the inert soluble part is about 32 g kg^{-1}.

Table 5.1.2. Concentrations of COD_{dis} and VFA in the batch bottles after 104 days.

% of the reactor height	*COD_{dis} (g kg^{-1})*		*VFA (g[COD] kg^{-1})*	
	40°C	*50°C*	*40°C*	*50°C*
0	31.9	33.9	0.00	0.00
20	33.9	34.0	0.002	0.01
60	29.8	29.0	0.22	0.12
80	31.2	30.1	0.12	0.00
100	51.3	49.3	8.41	7.00
Average over the 80% of the reactor height	31.7	31.7	0.085	0.033
Average over the whole height	35.6	35.3	1.8	1.4

Figure 5.1.7 shows the results of the calculations of a total mass balance for the second experimental rum after the AC system and after the batch experiments. Even after 184 days (the digestion time in the AC system + the batch experiments time), the total methane production is still lower at 40^{o}C compared to 50^{o}C. As the concentrations of COD_{dis} and VFA are almost the same at both temperatures (Table 5.1.2 and Fig. 5.1.7), it can be concluded that the particulate COD at 40^{o}C should be still higher compared to that in the system operated at 50^{o}C, and consequently that the rate of hydrolysis is lower at 40^{o}C compared with that at 50^{o}C.

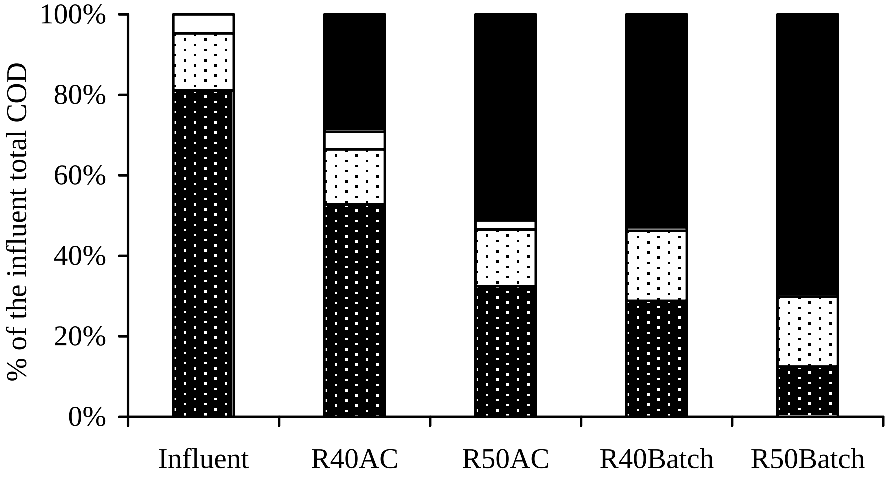


Fig. 5.1.7. A total mass balance for the second experimental rum: ▓, particulate; ░, non acidified COD_{dis};□, VFA; █, CH_4

5.1.3.3. System performance

It can be seen from Table 5.1.3 that the average total VFA concentrations, prevailing during the first run, were higher in the system operated at 40^{o}C (R_{40AC}) compared to that at 50^{o}C (R_{50AC}). After having operated the reactors in batch-mode (R_{50Batc} and R_{40Batc}), the VFA concentrations had decreased sharply. The results, of the second run (Table 5.1.4), also show distinct higher VFA concentration at R_{40AC} compared to R_{50AC}, while higher values for COD_{dis} were found for AC system operated at 40^{o}C compared with 50^{o}C (Tables 5.1.3, 5.1.4). The data presented in Tables 5.1.3 and 5.1.4 show that there is no accumulation of propionate in both experimental runs. The results of Zeeman (1991) dealing with the digestion of liquid animal waste in an AC demonstrated a negative effect of mixing on the breakdown of propionic acid, particularly at low degree of inoculation and at low temperature.

From Tables 5.1.3 and 5.1.4, it can be seen that in both reactors the ammonia concentration was high. Regarding the satisfactory performance, it can be concluded that apparently it will be possible to apply anaerobic digestion under thermophilic conditions satisfactorily on solid animal wastes, despite the prevailing high ammonia concentrations of about 4 g kg^{-1}. Although there exists a clear relation between the NH^{+}_{4}-N concentration and the effluent VFA concentration in CSTR-systems, Zeeman (1991) found that that such relation did not manifest for the digestion in the AC system. According to Zeeman (1991), the accumulation system behaves completely different than a CSTR, and even the methanogenic population might differ.

Furthermore the assessed percentages of hydrolysis, acidogenesis and methanogenesis were higher at R_{50AC} and $R_{50Batch}$ compared to the values found in R_{40AC} and $R_{40Batch}$. From the data presented in Table 5.1.3, it can also be concluded that methanogenesis is the rate-limiting step in the AC system, while it is the hydrolysis step in the batch digestion. The latter can be attributed to the improved contact with the inoculum in the second step. The calculated percentages in the second run (R_{50ACs} and R_{40ACs}) are higher than that those found in the first run (R_{50AC} and R_{40AC}) for the reasons mentioned above. Apparently (Fig 5.1.6 and Table 5.1.4) hydrolysis is the rate limiting step in R_{40ACs} and R_{50ACs} especially for the lower layers (*ca* 60% of the height).

Table 5.1.3. Concentrations of different parameters and system performance after anaerobic digestion of solid cow manure in an accumulation system followed by batch digestion (first run).

Parameters	*AC (after 60 days)*		*Batch (after 110 days)*	
	R_{40AC}	R_{50AC}	$R_{40Batch}$	$R_{50Batch}$
TS (g kg^{-1})	215.4 (64.1)*	213.1(13.2)	201.1(15.7)	192.3 (1.8)
VS (g kg^{-1})	160.7 (45.5)	156.9 (20.6)	124.4 (10.6)	116.7 (2.7)
C_2 (g [COD]kg^{-1})	6.3 (4.4)	2.15 (1.0)	1.2 (0.8)	0.6 (0.1)
C_3 (g [COD]kg^{-1})	4.1 (3.3)	3.6 (2.3)	1.4 (0.7)	0.5 (0.7)
i-C_4 (g [COD]kg^{-1})	0.9 (0.8)	0.7 (0.5)	0.0 (0.0)	0.0 (0.0)
n-C_4 (g [COD]kg^{-1})	1.3 (1.3)	0.9 (1.0)	1.7 (1.6)	0.0 (0.0)
b-C_5 (g [COD]kg^{-1})	1.6 (1.3)	1.1 (0.9)	0.2 (0.2)	0.0 (0.0)
n-C_5 (g [COD]kg^{-1})	0.1 (0.2)	0.2 (0.2)	0.2 (0.2)	0.0 (0.0)
VFA (g [COD]kg^{-1})	14.2 (10.4)	8.6 (5.7)	4.6 (3.5)	1.1 (0.8)
COD_{dis} (g kg^{-1})	46.8 (13.3)	43.2 (6.2)	43.3 (3.3)	46.5 (4.6)
Nkj (g kg^{-1})	7.0 (0.6)	6.9 (0.6)	6.2 (0.1)	6.4 (0.5)
NH_4^+N (g kg^{-1})	4.3 (0.8)	3.9 (0.9)	3.6 (0.2)	3.8 (0.5)
Accumulated CH_4(l kg^{-1} [manure])	16.3	18.3	18.5	20.1
Accumulated CH_4(l kg^{-1} [TS added])	65.0	73.0	74.1	80.3
MPR (l l^{-1}[reactor]day^{-1})	0.3 (0.1)	0.3 (0.2)	0.3 (0.1)	0.4 (0.2)
H (%)	29.6	30.3	15.6	19.2
A(%)	19.2	19.3	13.7	15.8
M (%)	14.7	16.5	16.8	18.2

*Standard deviations are shown between brackets.

Table 5.1.4. Concentrations of different parameters and system performance in the second run (after 80 days).

Parameters	*R_{40ACs}*	*R_{50ACs}*
TS ($g\ kg^{-1}$)	153.6 (25.9)*	145.8 (19.5)
VS ($g\ kg^{-1}$)	117.1 (25.5)	101.5 (23.3)
C_2 (g [COD]kg^{-1})	4.6 (6.7)	1.5 (2.9)
C_3 (g [COD]kg^{-1})	2.0 (2.9)	1.6 (3.4)
i-C_4 (g [COD]kg^{-1})	0.2 (0.3	0.2 (0.5)
n-C_4 (g [COD]kg^{-1})	1.1 (1.7)	0.7 (1.7)
b-C_5 (g [COD]kg^{-1})	0.6 (0.6)	0.3 (0.7)
n-C_5 (g [COD]kg^{-1})	0.2 (0.3)	0.1 (0.2)
VFA (g [COD]kg^{-1})	8.5 (12.4)	4.4 (9.3)
COD_{dis} ($g\ kg^{-1}$)	35.2 (12)	31.8 (8.3)
Nkj ($g\ kg^{-1}$)	7.5 (0.6)	7.3 (0.6)
NH_4^+N ($g\ kg^{-1}$)	3.7 (0.4)	3.7 (0.6)
Accumulated CH_4($l\ kg^{-1}$ [manure])	19.9	35.0
Accumulated CH_4($l\ kg^{-1}$ [TS added])	121.0	212.3
MPR ($l\ l^{-1}$[reactor]day^{-1})	0.3 (0.2)	0.4 (0.3)
H (%)	47.2	67.6
A(%)	33.6	53.4
M (%)	29.2	51.2

*Standard deviations are shown between brackets.

5.1.4. Conclusions

1- At seed material percentages of 10% (V/V) and lower, the contact between the substrate and the inoculum is clearly the limiting factor with respect to the process performance. Stratification of different components like VFA and COD_{dis} then occurs due to:

a- The long period of contact between the lower layer(s) and the inoculum.

b- The much higher methanogenic activity in the lower layers compared to the upper ones.

2 - During the digestion of solid cow manure (25% TS) in an AC system at filling time of 60 days, followed by a 50 day period of batch post-digestion a total hydrolysis, acidification and methanogenesis of 45; 33 and 32% of the total COD

added occurred respectively at a digestion temperature of 40^{o}C, while at a digestion temperature of 50^{o}C, those percentages were 50; 35 and 35% of the total COD added respectively.

3- During the digestion of solid cow manure (16% TS) in an AC system, at 60 days filling time followed by a feedless period of 20 days a total hydrolysis, acidification and methanogenesis of 47; 34 and 29% occurred respectively at 40^{o}C digestion temperature and 67; 53 and 51% occurred at 50^{o}C respectively.

4- Using manure of a high moisture content, the stratification is less pronounced due to the better mixing (due to biogas production) of both the methanogenic and the fresh waste pockets.

5- The moisture content comprises a crucial parameter affecting the methane production: the higher the moisture content the higher the methane production. It affects also the magnitude of both hydrolysis and acidogenesis.

6- It is well possible to attain a satisfactory anaerobic digestion on solid cattle manure at high ammonia concentrations up to about 4 g kg^{-1}.

7- For improving the system performance, leachate recirculation (Veeken and Hamelers, 2000) or addition of the same inoculum amount at different doses with the feed looks attractive and therefore will be investigated in more detail.

5.2. Effect of Inoculum Addition Modes and Leachate Recirculation on Anaerobic Digestion of Solid Cattle Manure in an Accumulation System

Abstract

The effect of both leachate recirculation (at 40^oC and 50^oC) and the mode of inoculum addition (at 50^oC) on the performance of a non-mixed accumulation (*i.e.* fed batch) system treating solid cattle wastes was investigated, using laboratory scale reactors at a filling time of 60 days. A relatively high methane production rate (MPR) and low stratification of intermediates occur with leachate recirculation. The leachate recirculation volume and methane production increase at increasing the temperature from 40^oC to 50^oC. The average MPR was 0.31 and 0.7 l [CH_4] l^{-1} [reactor] day^{-1} at 40 and 50^oC respectively. The increased MPR at higher temperature is at one hand caused by the increase of microbial activity, at the other hand by the increased leachate recirculation volume resulting from the lower viscosity at higher temperature. Dividing the inoculum in equal doses and distributing them with the feed positively affects the system behaviour as compared to adding the same inoculum amount at the reactor bottom at the start only. Without addition of inoculum a very poor system performance was observed. The average MPR was 0.2; 0.4 and 0.5 l [CH_4] l^{-1} [reactor] day^{-1} for respectively the reactor without inoculum; inoculum addition at the reactor bottom and inoculum addition in different equal doses.

5.2.1. Introduction

The choice of an anaerobic treatment system strongly depends on the substrate characteristics, the simplicity of the design and the operation (Lettinga, 2001) and on economical and technical aspects. Callaghan *et al.* (1999) mentioned that it is difficult to mix systems with total solid concentrations above 10% by conventional mixing methods. As the total solid content of manure depends on the bedding material (Hobson *et al.,* 1981), the application of the digestion system depends on the farm breeding system. Compared with conventional slurry digestion systems (*e.g.* plug flow or CSTR), digestion at high solids concentrations in systems like batch digesters has many advantages (Ten Brummeler, 1993). High solids digestion limits the need for extensive mixing, addition of water, high energy need for heating and also limits the need of effluent dewatering.

The accumulation system (AC) is suitable for on farm application for both storage and digestion of manure (Wellinger and Kaufmann, 1982; Zeeman, 1991). According to Zeeman (1991) a stable digestion of liquid slurry in AC systems is practically feasible, provided enough inoculum is present to prevent VFA accumulation at the end of the filling time. Earlier results (*chapter* 5.1) obtained from experiments during digestion of high solid cattle wastes (*ca* 25% TS) using an AC system with addition of 10% (V/V) inoculum at the reactor bottom, showed a pronounced stratification of COD_{dis} and VFA over the reactor height. The lowest concentrations of intermediate compounds were found in the bottom layers where the methanogenesis is the highest (Ten Brummeler, 1993). So for improvement of the digestion in an AC system, other operation strategies should be applied.

For the dry anaerobic digestion of vegetable and yard wastes in a pilot batch reactor (BIOCEL), Ten Brummeler (1993) studied the effect of leachate recirculation on the digestion rate. The results showed a higher digestion rate with a leachate recirculation rate of 0.3 $m^3m^{-3}.day^{-1}$. According to Veeken and Hamelers (2000), the transport of VFA from the acidogenic to the methanogenic pockets can take place only through the leachate. According to Chan *et al.* (2002) leachate recirculation was effective in enhancing the degradation rate (*i.e.* reducing stabilisation time) and biogas production from landfill co-disposal of municipal solid waste, sewage sludge and marine sediment. Veeken and Hamelers (1999) mentioned that the performance of dry batch digestion of biowastes can be improved by recirculation of leachate. At the start -up of the reactor, a low leachate flow prevents the irreversible acidification of the methanogenic pockets (*i.e.* seeding material). After the start up the methanogenic population will increase and the leachate flow can be increased thus preventing inhibition of hydrolysis in the acidogenic pockets (*i.e.* fresh biowaste). Veeken and Hamelers (1999) mentioned also that leachate recirculation should be controlled as a too large transport of VFA from biowaste to seed via leachate can result in irreversible acidification of the seeds having low methanogenic activity. According to Viéitez and Ghosh (1999) the inhibition of hydrolysis and acidification during solid state digestion by accumulated VFA and lower pH can be alleviated by recycling of the leachate through a separate methanogenic reactor and conveying methanogenic effluent to the solid bed. Increasing the leachate recirculation rate and improving mixing of biowaste and seed result in a higher biowaste conversion rate and consequently shorter solids retention times (Veeken and Hamelers, 2000).

From the literature mentioned above, the leachate recirculation could be an option to improve the performance of a stratified AC system seeded with inoculum at the reactor bottom. Another option to improve such AC system performance could be the addition of the inoculum with the feed. So the objectives of the present study are:

1- To study the effect of leachate recirculation on the performance of the digestion of solid cattle manure (%TS) in AC system at 40°C and 50°C.

2- To study the effect of different inoculum addition modes on the process performance at 50°C. Besides no inoculum addition and the addition of the inoculum in the reactor bottom, another addition mode is considered in which the same amount of inoculum, used in the reactor bottom, is divided into equal doses and added with the feed.

5.2.2. Material and methods

5.2.2.1. Substrate

The substrate used in the present study is solid cattle waste originating from fattening cows. It consisted of feces, urine, and bedding material. The animals are fed concentrated, antibiotics free diets. The manure was analysed for its composition then refrigerated (4°C) over the experimental course. No pre-treatment was applied for the manure. The chemical characteristics of the substrate used in the experiments are mentioned in Table 5.2.1.

Table 5.2.1. Substrate characteristics, standard deviations are between brackets

Parameters	*Leachate recirculation experiments*	*Inoculum addition experiments*
TS (g kg^{-1})	217.3 (1.6)	256.0 (7.6)
VS (g kg^{-1})	186.4 (1.2)	205.1 (6.8)
Total COD (g kg^{-1})	245.9 (7.5)	240.5(25.5)
C_2 (g [COD]kg^{-1})	3.1 (1.0)	0.8 (0.5)
C_3 (g [COD]kg^{-1})	2.5 (0.7)	0.7 (0.3)
i-C_4 (g [COD]kg^{-1})	0.01 (0.0)	0.0 (0.0)
n-C_4 (g [COD]kg^{-1})	0.8 (0.4)	0.3 (0.1)
b-C_5 (g [COD]kg^{-1})	0.3 (0.0)	0.00 (0.0)
n-C_5 (g [COD]kg^{-1})	0.0 (0.0)	0.0 (0.0)
VFA (g [COD]kg^{-1})	6.6 (2.1)	1.8 (0.9)
COD_{dis} (g kg^{-1})	26.5 (4.5)	26.6 (1.0)
Nkj (g kg^{-1})	5.8 (0.1)	8.4 (1.1)
NH_4^+N (g kg^{-1})	1.9 (0.4)	1.2 (0.2)

5.2.2.2. Experimental reactors and feed procedures

To study the effect of recirculation of leachate, the same reactors and the gas measurements used in our previous study (*chapter* 5.1) were also used in the current one. Some modifications were made for the reactors by making perforated bottoms to collect the leachate after them. For the reactors used for the inoculum addition modes, two reactor types were used. For the reactor without inoculum addition and the reactor with addition of inoculum on different doses, the same reactors used in our earlier study (*chapter* 5.1) were also used. For the reactor used with the inoculum at the bottom, multiple bottles (8 bottles) reactor (Sanders, 2001) was used (see *chapter* 5.3).

5.2.2.3. Experimental set up

The effect of leachate recirculation and the effect of inoculum addition modes were studied in two different experimental runs at 60 days filling time. For leachate recirculation, one reactor was kept at 40°C and another at 50°C. The reactors started with a 10% (V/V) digested manure taken from an AC system treating solid cattle waste (16% TS) at 40 and 50°C and at filling time of 60 days followed by another 20 days without feeding. In the present study, the leachate was collected manually before the feeding (*i.e.* weekly bases), then its volume was measured and mixed with the new feed to assure an equivalent distribution of the leachate and the substrate. The leachate recirculation started after the first 11 days.

For the inoculum addition modes, three different reactors were incubated at 50°C at 60 days filling time. In the first reactor no inoculum was added. The second reactor was inoculated (10% (V/V). This inoculum was equally divided and added in different doses with the feed. The third reactor is a multiple bottle reactor (see *chapter* 5.3) inoculated with 10%

(V/V) at the reactor bottom. The inoculum used in the three experiments was taken from the effluent of the reactor operated at 50°C with leachate recirculation.

5.2.2.4. Sampling and analysis

Samples were taken from different reactor heights (see Figs 5.2.2 and 5.2.7) as described in *chapter* 5.1. The analyses of TS, VS, $NH^{+}{}_4N$, N-Kj, VFA, total COD and COD_{dis} were carried out as described in *chapter* 5.1. In the leachate recirculation experiments, the VFA of the leachate was measured weekly after the first 11 days.

5.2.2.5. Calculations

Hydrolysis, acidogenesis, and methanogenesis were calculated as described in *chapter* 4.2. To quantify the effect of recirculation and inoculum addition on the profile of concentration of the intermediates (*i.e.* COD_{dis} and VFA), during the digestion of different substrate compositions, we proposed a Profile Extent Index (PEI) parameter. PEI is defined as the difference in the concentration of a particular intermediate between the reactor top (C_{top}) and the reactor bottom (C_{bottom}) divided by the concentration of COD_{dis} in the influent (COD_{dis}):

$$PEI = \left(\frac{C_{top} - C_{bottom}}{COD_{dis}}\right) \quad (5.2.1)$$

To calculate the total energy input to a well-insulated 10 m^3 AC system with an aspect ratio of 1.7, a simple energy balance model was set up (Equation 5.2.2). In this simple model the calculation of heat losses to the environment and the energy required for heating up of the feed is based on a constant temperature of both the ambient air and the feed of 25°C. The output energy production is based on the results presented in this study and on our earlier results using a methane calorific value of 37 MJ m^{-3} [CH_4] (Hill and Bolte, 2000).

$$E_T = (1/\eta)\begin{bmatrix} U(2A_c + AI_s + Ag_s)(T_r - T_{am})t + \\ + \sum_{N=1}^{60} UA_s(T_r - T_{am})(t - N*24*3600) + mCp(T_r - T_{am}) \end{bmatrix} \quad (5.2.2)$$

Where:

E_T = Total energy input to the system during the filling time, J
U = Overall heat transfer coefficient between the reactor and the environment, 0.3 W m^{-2} K^{-1}
A_c = Cross section area of the reactor, 2.9 m^2
AI_s = Reactor side area corresponds to the inoculum volume, 2.1 m^2
Ag_s = Reactor side area corresponds to the gas volume, 0.7 m^2
A_s = Reactor side area corresponds to the daily added feed, 0.3 m^2
T_r = Reactor operation temperature, K
T_{am} = Ambient temperature, K
t = Filling time, s
m = Mass of daily feed, 150 kg
N= Number of days before inserting a certain feed, day
Cp = Specific heat of the manure, 4 000 J kg^{-1} K^{-1}
η = Heater efficiency, 70%.

5.2.3. Results and discussion

5.2.3.1. Effect of leachate recirculation

Methane production

Figure 5.2.1 shows the measured methane production rate (MPR) at both studied temperatures (40°C and 50°C). Between both temperatures a lag phase of about 10 days can be observed. Such 'long lag' phase may be attributed to the long digestion time (*ca* 80 days) in the previous run from which inoculum was taken for this run. As soon as the methane was started at both temperatures, as expected, a noticeable higher methane production rate is observed at 50°C. This may be attributed to the higher hydrolysis rate and/or growth rate of methanogenic bacteria at 50°C compared with that at 40°C. However, the decay rate is also higher at the higher temperature. Another reason for such difference may be the larger amount of leachate recirculation at 50°C compared with that at 40°C (Fig. 5.2.3).

Concentrations of intermediates

As expected, the leachate recirculation caused a dramatic decrease in the profile extent of both VFA and COD_{dis}, compared with what we found in comparable experiments without leachate recirculation (*chapter* 5.1), specially at 50°C reactor (Fig. 5.2.2). At 50°C, a higher leachate amount could be collected compared with that at 40°C (Fig. 5.2.3). The increase of the leachate amount at 50°C could mainly be attributed to the lower viscosity at 50°C. Also the higher degradation rate 50°C may affect the viscosity. From Fig. 5.2.3 it can be observed that the leachate amount (*l* m^{-3}[reactor]day^{-1}) increases pronouncedly with time at 50°C. At 40°C, some increase of leachate is shown after 45 days of digestion. The amount of the leachate highly depends on the accumulated amount of substrate, the total solids content and the field capacity. The gravitational drainage of leachate occurs when the moisture content of a waste is above the field capacity (Jang *et al.,* 2002). Unfortunately, we did not measure the field capacity of the manure used in the presented experiments. For vegetable fruit and yard wastes digestion, Ten Brummeler (1993) revealed that total solids concentration (TS) in a reactor must be low enough in order to have a certain amount of free liquid, which is available for recycling. He mentioned also that at initial TS of 30%, the maximum possible recycle flow is *ca* 0.3 $m^{-3}m^{-3}day^{-1}$. According to Ten Brummeler (1993), leachate recirculation is not possible during the digestion of substrates having total solids exceeding 35% TS. This is due to the lack of free moving water.

The positive effect of the leachate recirculation on the process performance may be elucidated by one or all of three explanations: the first is that leachate brings the VFA from the top layers (*i.e.* freshly added manure) to the bottom layers (*i.e.* methanogenic seeding material). Veeken and Hamelers (2000) revealed this explanation during the solid state digestion of biowaste in batch reactors. The second explanation is that leachate recirculation may cause some mixing of the substrate with inoculum (Ten Brummeler, 1993). According to Torres-Castillo *et al.* (1995), the degree of substrate degradation is affected by the distribution of recirculation leachate. It acts directly on the contact between the substrate and micro-organisms. The third explanation is that leachate recirculation may contain some inoculum which is mixed with the freshly added manure. This explanation was reviewed by O'Keefe and Chynoweth (2000). They revealed that leachate recirculation between a landfill cell and either anaerobic digester or 'mature' landfill cell would provide inoculum to establish a balanced acidogenic and methanogenic population.

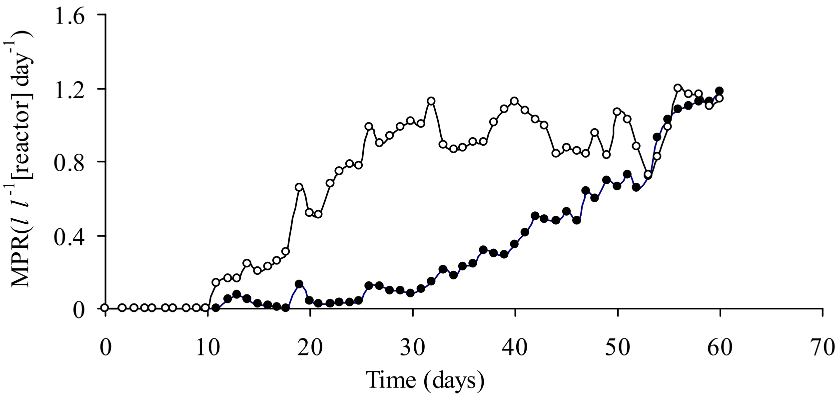


Fig.5.2.1. Methane production rate during the leachate recirculation experimental run: ○, 50°C; ●, 40°C

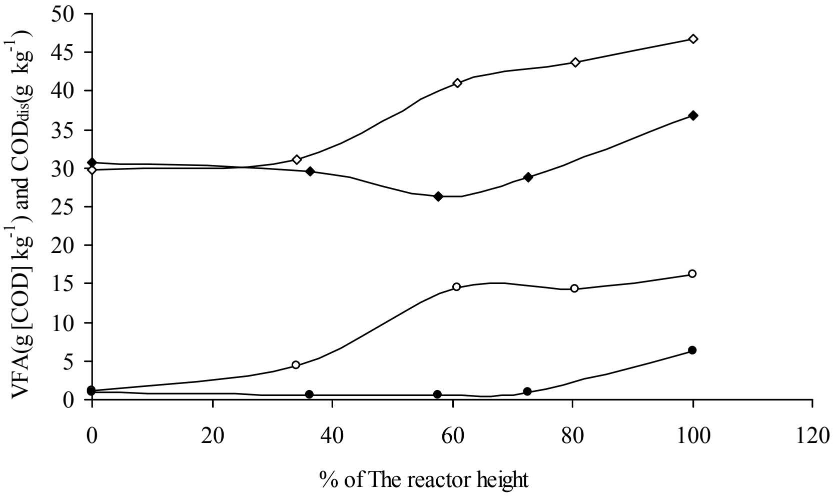


Fig.5.2.2. Profile of the intermediates concentrations at the end of the leachate recirculation experimental run: ●, VFA at 50°C; ○, VFA at 40°C; ◊, COD_{dis} at 50°C; ♦, COD_{dis} at 40°C

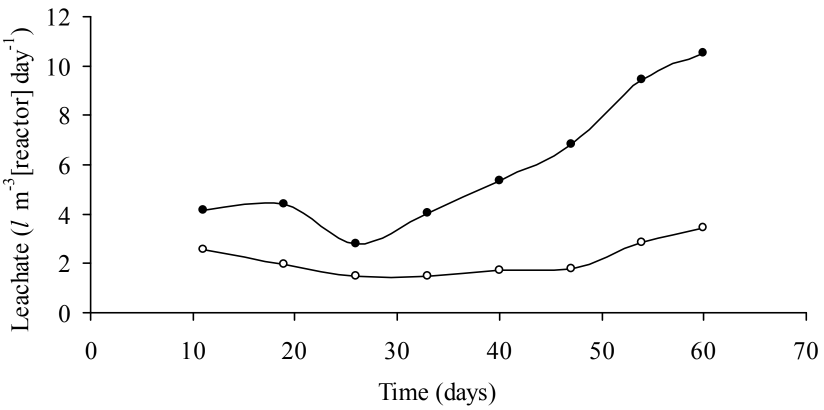


Fig.5.2.3. Average leachate recirculation rate:●, 50°C;○, 40°C

Figure 5.2.4 shows the VFA concentration of the leachate at both temperatures. The leachate from the reactor operated at 50°C has a very low and almost constant concentration of VFA along the filling period. The VFA concentrations in the leachate at 40°C started at high level of *ca* 1.2 g [COD] l^{-1} and subsequently decreased. Such decrease of the VFA is reflected on the pronounced methane production rate (see Fig. 5.2.1).

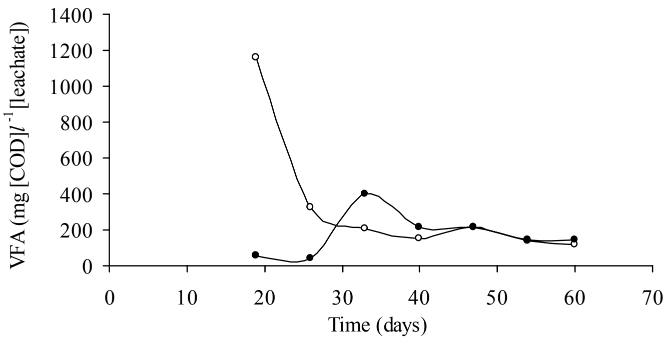


Fig.5.2.4. VFA concentrations in the leachate at both studied temperatures over the experimental course:●, 50°C;○, 40°C.

Table 5.2.2 shows the average concentrations of diffent parameters in the effluent and the percentages of hydrolysis; acidogenesis and methanogenesis. From this Table it can be concluded that a much better performance is achieved at 50°C as compared to 40°C. Besides the positive effect of the higher leachate recirculation rate and higher temperature on methanogenesis, there is also a positive effect on hydrolysis and acidogenesis. The data presented in Table 5.2.2 show that methanogenesis is likely the rate limiting step at 40°C while hydrolysis is the rate limiting step at 50°C. A non-acidified COD_{dis} part is almost equal for 40°C and 50°C. This can be considered as an inert COD_{dis} (Zeeman, 1991). It can be noticed (Table 5.2.2) that acetate and propionate represent the major VFA constuents at both temperatures. Other VFA's are presented in very small portions.

Table 5.2.2. Average concentrations of different parameters at the end of the leachate recirculation experiment with standard deviations as shown between the brackets.

Parameters	R_{40AC}	R_{50AC}
C_2 (g [COD] kg^{-1})	4.8 (3.7)	0.8 (0.3)
C_3 (g [COD] kg^{-1})	4.0 (3)	0.9 (2)
i-C_4 (g [COD] kg^{-1})	0.2 (0.2)	0.1 (0.1)
n-C_4 (g [COD] kg^{-1})	0.7 (0.8)	0.00 (0.0)
b-C_5 (g [COD] kg^{-1})	0.3 (0.2)	0.1 (0.1)
n-C_5 (g [COD] kg^{-1})	0.2 (0.2)	0.1 (0.1)
VFA (g [COD] kg^{-1})	10.1 (6.8)	1.9 (2.5)
COD_{dis} (g kg^{-1})	38.5 (7.6)	30.5 (3.9)
Nkj (g kg^{-1})	6.8 (1.2)	7.3 (0.9)
NH_4^+N (g kg^{-1})	2.5 (0.4)	2.8 (0.4)
Accumulated CH_4(l kg $^{-1}$[manure])	18.7	39.2
Accumulated CH_4(l kg^{-1} [TS])	85.9	180.4
MPR (l l^{-1}[reactor] day^{-1})	0.31 (0.4)	0.7 (0.4)
Hydrolysis (%)	37.3	57.8
Acidogenesis (%)	25.8	46.2
Methanogenesis (%)	21.6	45.4

Net energy production

Figure 5.2.5 shows the input energy, output energy and net energy production from the simulated 10 m^3 reactors operated with leachate recirculation (the present study) and without leachate recirculation (*chapter* 5.1). The total energy input is the summation of the total energy input during a filling time of 60 days. The output energy is calculated based on the accumulated methane production during the filling time. Higher specific net energy production can be realised at 50°C in spite of higher energy losses to the environment. From the results presented in Fig. 5.2.5 and keeping in mind the hygienic quality of the effluent, it is clear that the operation at 50°C is more attractive compared with the operation at 40°C. The experiments with the inoculum addition mode were therefore carried out at 50°C only.

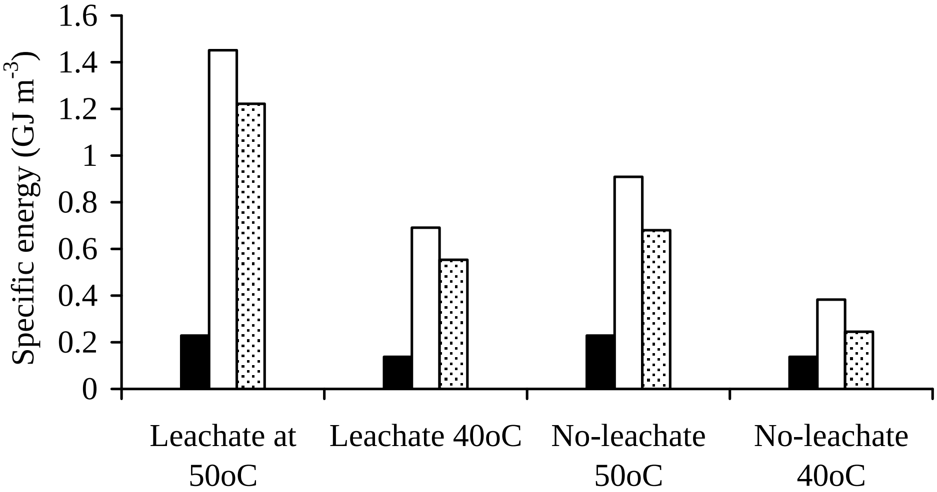


Fig.5.2.5. Specific energy input; output and net energy production from a 10m^3 AC system during a filling time of 60 days: █, input energy; □, output energy; ░, net energy

5.2.3.2. Effect of inoculum addition mode

Methane production rate

Figure 5.2.6 shows MPR over the filling time for the three different inoculum addition modes. The first is operated without inoculum addition (WI). The second reactor is operated with adding an inoculum volume of 10% (V/V of the reactor volume) at the reactor bottom (IB) and the third reactor is operated with adding the same amount of inoculum (10% V/V) in equal doses with the feed (ID). As expected, ID reactor does have the highest MPR compared with the two other reactors. This definitely is due to the presence of the methanogenic bacteria with the substrate along the reactor height. Without addition of inoculum, methane production occurs at a very low rate. According to Hobson (1985), the faecal bacteria and bacteria picked up from the environment, provide the inoculum from which the active digester flora develops, but a large proportion of these bacteria does not have a major role in the digester reactions. Unlike the experiments with leachate recirculation, no lag phase can be noticed (Fig. 5.2.6) even at the experiment without adding inoculum. It can be recognised that the amount of active bacteria in the raw manure changes from one batch to another and possibly depends on the original ambient temperature. It should be mentioned that the manure used in the leachate recirculation and inoculum addition mode experiments were collected in February (with an average monthly ambient temperature of about 4^{o}C) and July (*i.e.* average monthly ambient temperature about 17^{o}C) respectively.

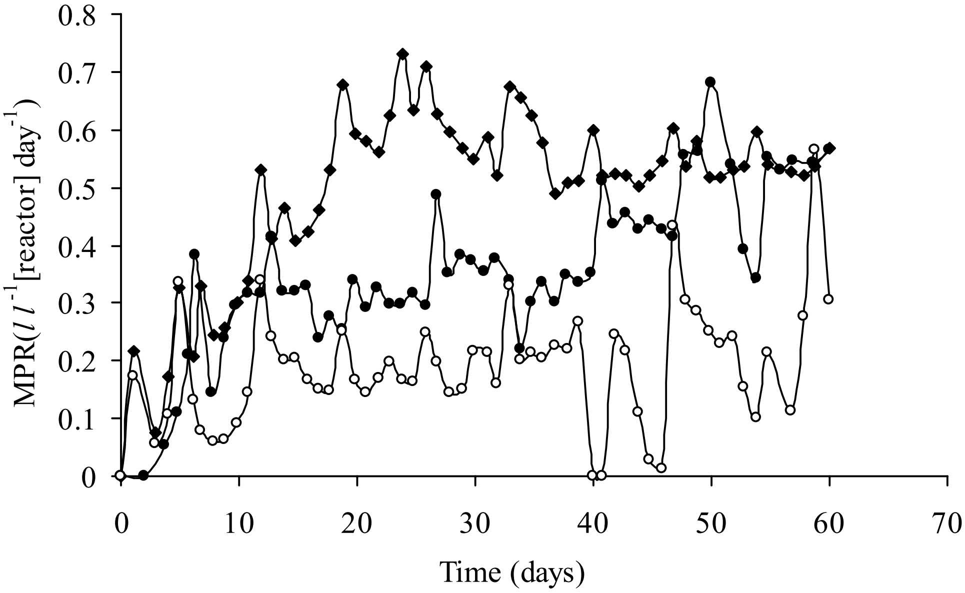


Fig.5.2.6. Experimental methane production rate for different inoculum addition modes: ♦, inoculum in equal doses; ●, inoculum at the reactor bottom; ○, no inoculum

Concentrations of intermediates

Figure 5.2.7 shows the concentration of VFA and COD_{dis} along the reactor height at the end of the filling time. The reactor operated without inoculum addition (WI) has the highest concentrations of both VFA and COD_{dis} compared with that operated at equal doses mode. It should be mentioned that Fig. 5.2.7 does not contain such profile for IB reactor as the sampling procedures are slightly different from that for the other two reactors (see *chapter* 5.3).

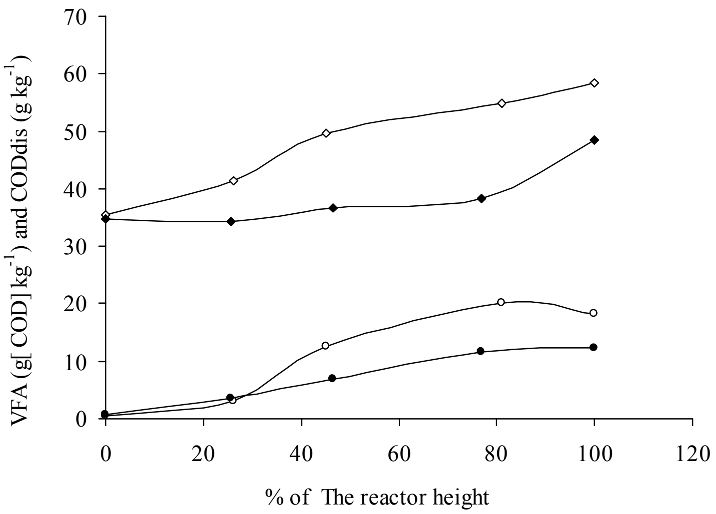


Fig.5.2.7. Profile of the intermediates concentrations at the end of inoculum addition mode experiments: ●, VFA at 50^{o}C with inoculum added in equal doses; ○, VFA at 50^{o}C without inoculum; ♦, COD_{dis} at 50^{o}C with inoculum added in equal doses; ◊, COD_{dis} at 50^{o}C without inoculum

The data in Table 5.2.3 show significantly higher percentages of hydrolysis; acedogenesis and methanogenesis occur in the ID reactor compared with those at both the WI and IB reactor. From this Table it can be concluded that significant improved system performance (*i.e.* higher hydrolysis ; acidogenesis and methanogenesis) can be realised with adding the inoculum in different doses. From the data presented in Table 5.2.3 it can be realised that methanogenesis is likely the rate limiting step in the experimets without inoculum or even with adding inocuum at different doses. It can be noticed that acetate and propionate represent the larger VFAs constituents in all studied reactors. Other VFAs are present in very small portions.

Table 5.2.3. Average concentrations of different parameters at the end (*i.e.* after 60 days) of the fed batch digestion of cow manure at different inoculation modes with standard deviations as shown between the brackets

Parameters	*Addition of inoculum in equal doses*	*With inoculum on the bottom*	*Without inoculum*
C_2 (g [COD] kg^{-1})	1.9 (0.4)	4.2 (6.0)	4.6 (3.1)
C_3 (g [COD] kg^{-1})	3 (2.2)	1.2 (1.1)	3.4 (3.2)
i-C_4 (g [COD] kg^{-1})	0.5 (0.4)	0.4 (0.5)	0.7 (0.8)
n-C_4 (g [COD] kg^{-1})	0.5 (0.7)	0.7 (1.1)	0.8 (1.0)
b-C_5 (g [COD] kg^{-1})	0.9 (0.9)	0.4 (0.7)	1.2 (1.2)
n-C_5 (g [COD] kg^{-1})	0.2 (0.2)	0.1 (0.0)	0.1 (0.2)
VFA (g [COD] kg^{-1})	7.0 (5.1)	6.9 (9.2)	10.9 (8.8)
COD_{dis} (g kg^{-1})	38.6 (5.8)	43.4 (9.8)	48.0 (9.4)
Nkj (g kg^{-1})	8.3 (0.4)	8.4 (0.6)	7.8 (0.7)
NH_4^+N (g kg^{-1})	3.4 (0.3)	3.6 (0.2)	3.5 (0.2)
Accumulated CH_4(l kg $^{-1}$[manure])	29.8	21.2	11.3
Accumulated CH_4(l kg^{-1} [TS])	116.6	82.9	44.1
MPR (l l^{-1}[reactor] day^{-1})	0.5 (0.1)	0.4 (0.1)	0.2 (0.1)
Hydrolysis (%)	51.4	43.2	33.33
Acidogenesis (%)	38.3	28.0	17.9
Methanogenesis (%)	35.4	25.2	13.4

5.2.4. General discussion

The experiment with leachate recirculation, with 10%(V/V) inoculation at the reactor bottom, reveals a pronounced methane production compared with other experiments: methanogenesis is 45%. Leachate recirculation can therefore be considered as operation strategy for improvement of the process performance. As mentioned above, the amount of leachate depends on the characteristics of the substrate. In case of high solids manure, extra water can be added. Yet such addition will affect the cost of the system, as a larger reactor volume is needed. However, such addition of extra water may help in the heating of the reactor content as a poor heat conductivity between layers exists at high solid concentrations, which decreases the efficiency of a heat exchanger installed at the reactor bottom (see *chapter* 5.4).

Based on the experimental data, the calculated PEI for VFA and COD_{dis} are shown in Table 5.2.4. The results show that the best operation occurs when leachate recirculation is applied at 50°C.

Table 5.2.4. Calculated PEI for VFA and COD_{dis}

Reactor operation	*PEI (VFA)*	*PEI (COD_{dis})*
Inoculum addition in different doses	0.44	0.65
Inoculum at the bottom	0.64	0.72
No inoculum added	0.67	0.99
Recirculation at 40°C	0.57	0.64
Recirculation at 50°C	0.20	0.23

Without adding inoculum a very poor system performance is recognised when only 60 days digestion time is applied, though the results show the possibility of starting up an AC system without inoculum at thermophilic conditions. To assure the presence of more active biomass in the manure, start up should be preferably made in summer. However, such start up is not recommended, as a long digestion time is required to achieve the same performance as compared to inoculated start up. The results of Zeeman (1991) indicated that the start up of a psychrophilic (≤ 15°C) AC system treating liquid manure is not possible within 5 months without seed.

The results of the experiments with inoculum addition in different doses with the influent showed better performance (*i.e.* higher MPR and lower PEI) compared with starting the system without inoculum or adding the inoculum at the reactor bottom. However, in practice, the preservation of the activity of the inoculum till the end of the filling time should be guaranteed. Moreover, a 10% extra reactor volume is required to store the inoculum. The inoculum could be kept in another batch digester provided that enough substrate is present.

In fact, dividing and addition of inoculum with the feed could be considered as multiple batch reactors with different digestion times: every added inoculum and manure mixture represents one batch reactor. To improve the system performance, the inoculum percentage could be increased. However, the increase of the inoculum percentages increases the reactor volume. In dry anaerobic batch digestion of vegetable fruit and yard waste at 35°C, Ten Brummeler (1993) found that at an inoculum/substrate ratio of 0.55, a retention time of 30 days is required with leachate recirculation. More research is required to study the effect of adding different inoculum percentages with the feed on the AC performance with and without leachate recirculation.

The results of the present and earlier (*chapter* 5.1) performed research, illustrate that a filling time of 60 days is not enough for complete degradation of VFA especially in the reactor top. To improve the system performance, either increase of the filling time or the use of a second reactor is possible. When using two reactors the content of the reactor after filling time can be kept for another 60 days of batch digestion. Another option is to apply aerobic composting as a post treatment. The last option could be attractive as the digested manure from the AC system still has a high moisture content, which causes high transport costs. Aerobic composting could produce a stabilised easy-transferable useful end product (*i.e.* compost). Ten Brummeler (1993) suggested this post treatment step for the effluent of the BIOCEL process after adding support material like wood chips and sawdust.

5.2.5. Conclusions

The effects of leachate recirculation and different inoculum addition modes on the performance of the AC system were studied for a filling time of 60 days. The following conclusions can be drawn:

1- Leachate recirculation during fed batch digestion of solid manure improves the contact between biomass and substrate and therefore increases the system performance (*i.e.* methane production).

2- Increase of the temperature from 40^{o}C to 50^{o}C increases the leachate recirculation volume and methane production.

3- An operation temperature of 50^{o}C can be recommended from the energetic and biotechnological point of view rather than the operation at 40^{o}C.

4- Addition of inoculum in different equal doses with the feed enhances the system performance compared with adding the same amount of inoculum at the beginning of the filling time, at the reactor bottom.

5.3. A Model for Anaerobic Digestion of Solid Cattle Wastes in a Stratified Thermophilic Accumulation System

Abstract

Based on the available models in literature, a dynamic model has been developed to describe the three biochemical steps (*i.e.* hydrolysis, acidogenesis, and methanogenesis) involved in the anaerobic digestion. The model was used to simulate an accumulation system (AC) treating solid cattle waste. Different system layers, added in time intervals, were modelled by using the dispersion of different components between layers. To calibrate the model, an experiment was carried out at lab scale AC at 50°C. The experiment was started using 10% (V/V) of the reactor volume inoculum on the reactor bottom. Every week a new layer of solid manure was added. The main result of the model, *i.e.* methane production shows a very good agreement with the experimental data. A very high determination coefficient (*i.e.* R^2= 0.998) between the predicted and measured data was calculated. However less agreement is evident for the intermediates (*i.e.* COD_{dis} and VFA). To validate the model, two other experimental data sets, at 50°C, were used. In the first data set no seed material was used in the experiments. In the second data set 10% (V/V) seed material was equally distributed with the feed. The model shows a very good agreement with the experimental methane production for both data sets. R^2 values of 0.973 and 0.987 can be calculated for the first and the second data set respectively. After model validation, the model was applied to study the effect of different aspect ratios on the system performance. An optimum aspect ratio of 2-3 could be recommended based on the model results.

5.3.1. Introduction

Many models have been published during the last four decades dealing with the biochemical description of the anaerobic digestion process (*e.g.* Andrews and Pearson 1965; Hill and Brath, 1977; Hill, 1983a; Angelidaki *et al.,* 1999; Batstone *et al.,* 2002; *Vavilin et al.,* 2002 a and b) for different systems and different substrates. According to Hobson (1985) there are various objectives of microbial growth and fermentation models, *e.g.* models derived to optimise or to predict the conditions of digester failure. According to Hill and Nordstedt (1980), the development and verification of a mathematical model would represent a useful tool for improving the basic understanding of complicated biological systems.

Many studies have been conducted to model livestock waste digestion process. Most of these models were dedicated to batch or Continuos Stirred Tank Reactor (CSTR) systems. Hill and Brath (1977) and Hill (1983a) presented dynamic models for animal waste digestion using CSTR system. Hill and Cobb (1996) presented a simulation for steady state operation of a CSTR systems. They used the nitrogen ratio (*i.e.* the ratio between total Kjeldahl nitrogen (Nkj) entering an anaerobic reactor and the Nkj leaving the reactor) as criteria for predicting the steady state operation. More recently, Angelidaki *et al.* (1999) presented a comprehensive dynamic model for the process for describing the hydrolysis and fermentation process of 19 different chemical compounds. Their model also includes inhibition functions of both long chain fatty acids (LCFA) and free ammonia concentration for different consortia of biomass involved in the process. The model was validated with data from lab scale CSTR and full scale reactors operated at 55°C.

Different process parameters are reported in literature. According to Hobson (1985), while the overall concepts of a model may be applicable from one feedstock to another, the values of the various parameters in the model will vary with the type of feedstock. The same animal unit with different fodder feeds gives distinct differences in the manure composition and particles size distribution.

The accumulation system (AC) looks a quite suitable system for on farm application, both for storage and for digestion of animal slurry (Wellinger and Kaufmann, 1982; Zeeman, 1991). So far there exists very limited information about modelling of the AC system. Recently, Zeeman *et al.* (2000) presented model results of sewage and swill digestion in a well mixed AC system. The use of high solids content substrates results in stratification of intermediates along the reactor height (*chapter* 5.1), due to difficulties in mixing of systems with solids levels above 10 % by conventional methods (Callaghan *et al.,* 1999). A model might represent a helpful tool in the design and optimisation of such system.

The objective of the present study is to optimise the methane production of an accumulation system treating solid cattle waste using the aspect ratio as parameters. For this purpose, a stratified model was developed, including dispersion-based transport mechanism (Perry *et al.,* 1997) of different components between the system layers. The model was calibrated and validated using the results from lab scale AC systems experiments, while it also was used to asses the effect of some design parameters like different aspect ratios on the methane production.

5.3.2. Materials and methods

5.3.2.1. Substrate

Table 5.3.1 shows the composition of the feed used in the experiments. The collection and storage of the feed were carried out as described previously (*chapter* 5.1).

Table 5.3.1. Substrate composition, standard deviations are between brackets.

Component	*unit*	*Value*
Total solids (TS)	g kg^{-1}	256.0 (7.6)
Volatile solids (VS)	g kg^{-1}	205.1 (6.8)
Total COD	g kg^{-1}	240.5 (25.5)
Volatile Fatty Acids (VFA)	g kg^{-1}	1.8 (0.9)
COD_{dis}	g kg^{-1}	26.6 (1.0)
Kjeldahl-nitrogen (Nkj)	g kg^{-1}	8.4 (1.1)
Total ammonia (AM)	g kg^{-1}	1.2 (0.2)

5.3.2.2. Experimental set up and measuring methods

An experimental run was carried out at 50^{o}C and at a filling time of 60 day. The reactor used in this study was a multiple bottle reactor (Sanders, 2001) in order to enable different analysis over the filling time. Eight bottles each of 5 *l* as effective volume (height = 0.26 m and diameter = 0.16 m) were used to represent one whole reactor. All bottles were started with an amount of feed for the first four days and with 10% (V/V) digested solid manure as seed material (see *chapter* 4.4). Then, the bottles were flushed with nitrogen for 3 minutes. One of these bottles was kept closed, using a gas tight valve, over the experiment for gas measurements. The feed was added weekly. The feed was added manually after opening the bottles, except for the gas-measuring bottle, where the feed was added via the gas tight valve. After feeding, the bottles were flushed with nitrogen for 3 minutes. Each week, the content of one of the bottles was analysed. Samples were taken from three different heights: from the bottom; from around the middle of the accumulated manure height and from the top of the accumulated manure.

The methane produced was collected daily, using a 5 *l* gasbag. After the biogas passes a 15% NaOH solution to absorb CO_2, the amount of methane was measured by a wet gas meter. The gas volume was re-calculated for standard temperature and pressure (STP).

The analyses of the samples on TS, VS, NH^+_4N (AM), N-Kj, VFA, total COD and COD_{dis} were carried out as described in *chapter* 5.1. To follow the dynamics of each layer and to compare the measurements with the calculated values, the measurements were linearly interpolated.

5.3.3. Modelling

5.3.3.1. Model concept

As mentioned before, the system starts with seed material on the reactor bottom. On top of the seed material, a layer of fresh manure is added. It is assumed that each separate layer is a batch reactor having a homogeneous composition. On top of this, some interaction between the layers is incorporated. This interaction is approximated by dispersion, which is used in Fick's diffusion law with the empirical dispersion coefficient substituted for the diffusion coefficient (Perry et *al.,* 1997). According to Kirkham and Powers (1972), Scheidegger (1961) suggested the term dispersion to differentiate this spreading mechanism from that caused by diffusion. This distinction is made because diffusion is a result of the random motion of molecules, whereas dispersion is a result of the erratic flow of the fluids through complex porous media.

5.3.3.2. Model equations

The model presented is a modification of the standard batch model of Hill and Brath, (1977); Hill (1983a); Dughba *et al.* (1999); Veeken and Hamelers (2000); Vavilin *et al.* (2002 a and b). The model is based on the three sub-processes proceeding in anaerobic digestion of complex wastes namely: hydrolysis; acidogenic and methanogenic. Though in general SI units are preferred we used units generally used in literature in the subject enabling comparison of results.

Hydrolysis

Assuming first order kinetics for the hydrolysis step, the change in the biodegradable particulate COD (P) can be described by Equation (5.3.1), an approach used for different substrates used by other researchers (*e.g.* Veeken *et al.,* 2000; Vavilin *et al.,* 2002a and b). The rate of hydrolysis (r_h) can be calculated as follows:

$$r_h = k_h P \tag{5.3.1}$$

We used a hydrolysis rate constant (k_h) of 0.2 day^{-1} in all simulations in order to be able to fit the results adequately. Angelidaki *et al.* (1993) used a comparable value of 0.25 day^{-1} for liquid manure. All the symbols used in this paper and their units are listed in the notation.

Mass balance for soluble COD (S)

The change of the soluble COD content can be described by Equation (5.3.2), where the first term in the right hand side of the Equation represents dispersion of COD between the layers. An increase of soluble COD is caused by hydrolysis (r_h), a part of which is consumed for the growth of acidogenic biomass (Hill and Brath, 1977; Hill, 1983a).

$$\frac{\partial S}{\partial t} = D_s \frac{\partial^2 S}{\partial z^2} + r_h - \frac{\mu_a X_a}{Y_a} \tag{5.3.2}$$

z is the vertical coordinate of the AC reactor. The growth rate of acidogenic bacteria (μ_a) can be calculated from the maximum specific growth rate (μ_{max}) using Equation 5.3.3, which is based on Monod equation, but modified by incorporation of an inhibition term for VFA (Hill, 1983a; Dugba *et al.,* 1999):

$$\mu_a = \frac{\mu_{\max}}{1 + \frac{k_s}{S} + \frac{VFA}{k_{ia}}} \tag{5.3.3}$$

where k_s is the half velocity for the acidification (g l^{-1}) and k_{ia} is the growth inhibition coefficient for acidogenic biomass by VFA (g [COD] l^{-1}).

The maximum specific growth rate (μ_{max}) is temperature dependent as reflected in Equation 5.3.4, which was proposed by Hashimoto *et al.* (1981a). This equation has been used by other researchers (Hashimoto, 1984; Dugba *et al.,* 1999) for all bacteria species involved in the digestion process. The equation seems to be valid in the temperature range of 20 to 60^{o}C.

$$\mu_{\max} = 0.013\,\mathrm{T} - 0.129. \tag{5.3.4}$$

With T, the temperature in ^{o}C.

COD balance for VFA

The balance of VFA concentration as COD is represented by Equation (5.3.5), a modified equation based on the models of Hill (1983a) and Vavilin *et al.* (2002a and b). Similarly as for Equation (5.3.2) the first term of the right hand side of Equation (5.3.5) depicts the dispersion of VFA between subsequent layers, with D_{VFA} the empirical dispersion coefficient of VFA.

$$\frac{\partial VFA}{\partial t} = D_{VFA} \frac{\partial^2 VFA}{\partial z^2} + \frac{\mu_a X_a}{Y_a}(1 - Y_a) - \frac{\mu_m X_m}{Y_m} \tag{5.3.5}$$

The growth rate of methanogenic bacteria (μ_m) in Equation (5.3.6), can be calculated from the maximum specific growth rate (μ_{max}), using the Monod equation after incorporation of the inhibition terms of VFA (Dugba *et al.,* 1999) and total ammonia concentration (AM). As the pH is not included in the present model, total ammonia inhibition is used as inhibitory components instead of free ammonia (Münch *et al.,* 1999), which only can be calculated when the pH is known.

$$\mu_m = \frac{\mu_{\max}}{1 + \frac{k_{sm}}{VFA} + \frac{VFA}{k_{im}} + \frac{AM}{k_{iam}}} \tag{5.3.6}$$

Where k_{sm} is the half velocity of VFA metabolism (g l^{-1}); k_{im} is the growth inhibition coefficient for methanogenic biomass by VFA (g [COD] l^{-1}) and k_{iam} is the inhibition coefficient of ammonia (g l^{-1}).

COD balance for acidogens and methanogens

The changes of both amounts of acidogenic (X_a) and methanogenic (X_m) viable biomass are presented by two terms (Equations 5.3.7 and 5.3.8): the dispersion term which is similar to the diffusion term used by Vavilin *et al.* (2002a and b) and the resultant of both the growth and decay first order term (Hill *et al.,* 1977; Hill, 1983a; Dugba *et al.,* 1999).

$$\frac{\partial X_a}{\partial t} = D_a \frac{\partial^2 X_a}{\partial z^2} + (\mu_a - kd_a)X_a \tag{5.3.7}$$

$$\frac{\partial X_m}{\partial t} = D_m \frac{\partial^2 X_m}{\partial z^2} + (\mu_m - kd_m)X_m \tag{5.3.8}$$

The specific death rate of acidogens (kd_a) and methanogens (kd_m) are calculated with Equations 5.3.9 and 5.3.10 proposed by Hill *et al.* (1983) and Dugba *et al.* (1999). In these two equations, the maximum specific death rate (kd_{max}) of viable biomass is assumed to be equal to one-tenth of maximum specific growth rate (μ_{max}), an approximation used by various researchers, *e.g.* Thomas and Nordstedt, (1993); Dugba *et al.* (1999).

$$Kd_a = \frac{kd_{\max}}{1 + \frac{kid_a}{VFA}} \quad (5.3.9)$$

$$Kd_m = \frac{kd_{\max}}{1 + \frac{kid_m}{VFA}} \quad (5.3.10)$$

where kid_a is death coefficient for acidogenic bacteria (g l^{-1}) and kid_m is death coefficient for methanogenic bacteria (g l^{-1}).

COD balance for methane

The accumulation rate of the methane production (Equation 5.3.11) is based on the equation of Hill (1983a). It depends on the yield coefficient of methanogenesis (Y_m), the growth rate of methanogenic bacteria (μ_m) and the methanogenic biomass concentration (X_m):

$$\frac{\mathrm{d}M}{\mathrm{d}t} = \frac{(1 - Y_m)}{Y_m}(\mu_m X_m) \quad (5.3.11)$$

Ammonia balance

Equation 5.3.12 represents the mass balance of ammonia (AM) concentration (g l^{-1}). The first term in the right hand side represents the dispersion of ammonia between layers, *i.e.* similarly as in the model of VFA balance presented by Valvilin *et al.* (2002). The last two terms in the right hand side of equation 5.3.12 represent the model of Hill and Cobb (1996) for a batch digester, which predicts the ammonia balance. The second term ($\mu_a X_a Y_{AM}$) stands for the biological conversion of organic nitrogen to NH_4^+-N (AM) by acidogenic bacteria and the third (total negative term) for the uptake of ammonia during growth and lysis of acidogenesis and methanogenesis.

$$\frac{\partial AM}{\mathrm{d}t} = D_{AM}\frac{\partial^2 AM}{\partial z^2} + \mu_a X_a Y_{AM} - N_{bacteria}\left(\frac{\partial X_a}{\partial t} + \frac{\partial X_m}{\partial t}\right) \quad (5.3.12)$$

Hill and Cobb (1996) used the empirical formula ($C_5H_7NO_2$) of Loehr (1977) to calculate the bacterial nitrogen content ($N_{bacteria}$), resulting in a value of 0.0873 g [N] g^{-1}bacteria [COD], when assuming 1 g of viable biomass equals 1.42 g [COD] (Münch *et al.,* 1999).

Initial conditions; model parameters and boundary conditions

The model initial conditions are shown in Table 5.3.2. The used values used for the model parameters are presented in Table 5.3.3. Some of the model parameters are taken from the literature and others were obtained on the bases of visual calibration of the model (Vavilin *et al.,* 2002 a and b). For the dispersion terms, the boundary conditions are:

$$\frac{\partial C_i}{\partial z} = 0 \qquad \text{at } z = 0 \text{ (\textit{i.e.} at reactor bottom).}$$

It is assumed that at the top of the highest layer, the boundary is a virtual layer (as the system has a moving boundary), which has the same concentration of the influent till the moment of inserting the next layer, it then becomes the new boundary, *i.e.* at z =z, $C_i = C_{i0}$, where C_i is the concentration of component i (*i.e.* COD_{dis}; VFA; ammonia, acidogenesis and methanogenesis) and C_{i0} is the initial concentration of the specific component i.

Table 5.3.2. Initial concentrations used in the model

Variables and initial conditions	*Unit*	*Value*
Biodegradable particulate COD	g l^{-1}	128.50
Biodegradable non acidified COD_{dis}	g l^{-1}	5.30
Volatile Fatty Acids (VFA) concentrations	g [COD]l^{-1}	1.84
Ammonia concentration (AM)	g l^{-1}	1.20
Acidogenic bacteria in seed material	g l^{-1}	3.90
Methanogenic bacteria in seed material	g l^{-1}	7.81
Acidogenic bacteria in manure	g l^{-1}	1.79
Methanogenic bacteria in manure	g l^{-1}	0.36

The initial concentration of active biomass was taken as a portion of volatile solids (VS) concentration of the seed material and of the manure (Keshtkar *et al.,* 2001). The proper way of defining the viable biomass in the model is still open (Noykova *et al.,* 2002). Hobson (1985) used an arbitrary size of inoculum in his model, which in fact makes the whole model rather questionable. He justified this to the fact that the number of different groups of bacteria in a reactor is unknown. It should be mentioned that the ratio between acidogenic and total biomass in the seed material and in the fresh manure was taken to be 1/3 and 1/6 (Veeken and Hamelers, 2000), which also is very arbitrary. But these ratios are quite close to 1/5, which was used by Bernard (2001) and Sanchez *et al.* (1994).

5.3.3.3. Simulation model

Based on the formulated mass balances, a simulation was carried out using Matlab and Simulink software. The simulation model for the AC system consists of 9 blocks, where each block represents one individual layer (modelled as a batch reactor). For the seed material and the first layer, the simulation is started from the beginning. For the rest of the layers, the input for the integrator is set to zero until the insertion of that layer. From the moment the considered layer is added the integrator is activated. The dispersion term is calculated, in the Simulink, by using the central finite difference expression. For the boundary conditions term, the forward finite difference expression was applied. Since the methane accumulation is caused by the sum of the production in all the manure layers, it was calculated explicitly.

Table 5.3.3. Model parameters

Parameter	*Unit*	*Used value*	*Literature values*	*Temperature (^oC)*	*Reference*
k_h	d^{-1}	0.2	0.25;0.25; 0.7	30 ; 55; 35	Veeken and Hamelers (2000); Angelidaki *et al.* (1993); Salminen *et al.* (2000)
k_{iam}	$g\ l^{-1}$	0.267		50	Model calibration
K_{ia}	$g\ l^{-1}$	17.28	17.28; 43.2	22.5-60; 30	Hill (1983a);Veeken and Hamelers (2000)
K_{im}	$g\ l^{-1}$	8	8.64; 11.52	22.5-60; 30	Hill (1983a); Veeken and Hamelers (2000)
kid_a	$g\ l^{-1}$	23.04	23.04; 23.04	22.5-60;35 and 55	Hill *et al.* (1983); Dugba *et al.* (1999)
kid_m	$g\ l^{-1}$	23.04	23.04; 23.04	22.5-60;35 and 55	Hill *et al.* (1983); Dugba *et al.* (1999)
k_s	$g\ l^{-1}$	4	0.21; 12.6	25; 22.5-60	Hill and Brath (1977); Hill *et al.* (1983)
k_{sm}	$g\ l^{-1}$	2	0.036; 0.72; 2.88; 2.88	25; 30;22.5-60;30	Hill and Brath (1977); Vavilin *et al.* (2002b); Hill (1983a); Vavilin *et al.* (2001)
Y_a	g acidogenic bacteria $[COD]g^{-1}[COD_{dis}]$	0.1	0.1; 0.1	22.5-60;30	Hill (1983a); Veeken and Hamelers (2000)
Y_m	g methanogenic bacteria $[COD]g^{-1}VFA[COD]$	0.012	0.0049; 0.0493; 0.03185	22.5-60;30;25	Hill (1983a); Veeken and Hamelers (2000); Hill and Nordstedt (1980)
D_a	m^2d^{-1}	1.5 E^{-4}		50	Model calibration
D_m	m^2d^{-1}	1.5 E^{-4}	5 E^{-6}; 1.5 E^{-4}	30;30	Vavilin *et al.* (2001); Vavilin *et al.* (2002b)
Ds	m^2d^{-1}	0.3 E^{-4}		50	Model calibration
D_{VFA}	m^2d^{-1}	1.5 E^{-3}	7 E^{-3}; 5 E^{-5}; 1.5 E^{-3}	30; 30;30	Vavilin *et al.* (2001); Vavilin *et al.* (2001); Vavilin *et al.* (2002b)
D_{AM}	m^2d^{-1}	0.4 E^{-4}		50	Model calibration

5.3.4. Results and discussion

5.3.4.1. Experimental results assessed for the intermediates

The assessed average concentrations of VFA and COD_{dis} in the AC system over the filling time of the AC system are shown in Fig. 5.3.1. It should be mentioned that each data point shown in this Figure is the average of six measurements (*i.e.* three different samples, taken from three different reactor heights, in duplicate). It should also be mentioned that the aspect ratio of this reactor was 1.66. Figure 5.3.1 illustrates that both fractions increased in concentration till about day 25 and then the concentrations levelled off. This likely indicates that before day 25 the rate of methanogenesis is lower than the rate of both hydrolysis and acidogenesis. After day 25, the rate of methanogenesis apparently becomes almost equal to the rates of both hydrolysis and acidogenesis. Figure 5.3.2 shows the average ammonia concentrations over the filling time. The data shown again are the average of six samples (similar to VFA and COD_{dis}). The average ammonia concentration also increases till about day 25 and then it remains more or less constant. The measured accumulation and rate of methane production over time are shown in Fig. 5.3.3a and b. More explanation about the measured accumulation and rate of methane production can be found in *chapter* 5.2.

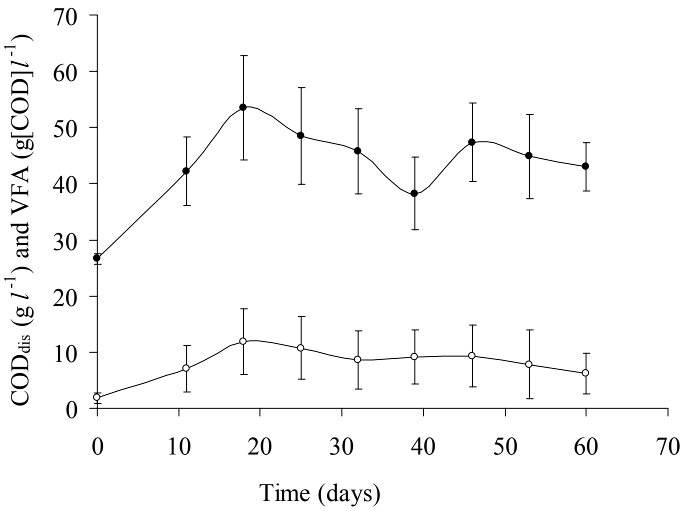


Fig.5.3.1. The assessed values of average VFA (○) and COD_{dis} (●) concentrations over the experimental filling time (vertical error bars are standard deviation values)

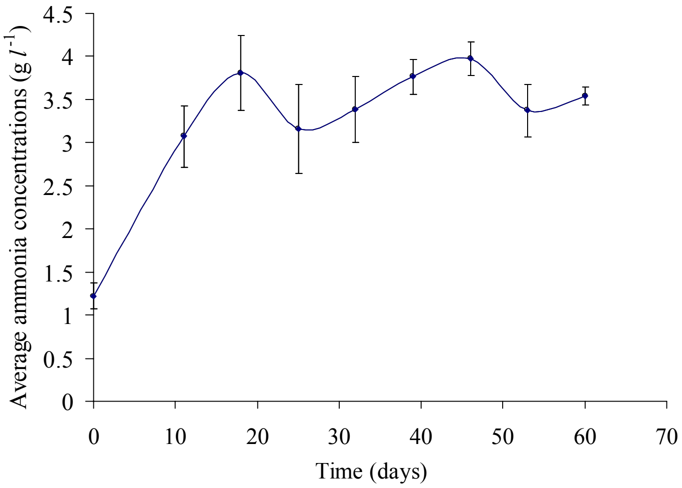


Fig.5.3.2. The assessed values of average ammonia concentrations over the experimental filling time (vertical error bars are standard deviation values)

5.3.4.2. Results of model calculations

It should be mentioned that in the model, where the empirical dispersion coefficient was not incorporated (see model equations section), it was assumed that every layer is behaving independently from the others. By taking this as a starting point, we carried out a model run with the parameters shown in Table 5.3.3. The results of that run show a production of methane of 8.22 *l*[CH4] l^{-1}[manure] within 60 days which represents only half of the experimentally achieved methane production. Therefore we decided to include the dispersion as an interaction mechanism between different layers.

Methane production

Comparison of the simulated and measurement values for Methane Production Rate (MPR) and accumulated methane production are shown in Fig. 5.3.3 a and b. A good agreement between the simulated values and the measured values of accumulated methane can be observed. In order to quantify the relevance of the model fitting, the predicted values were plotted against the measured ones. Ideally the regression line should pass through zero and the determination coefficient (R^2), *i.e.* square of correlation coefficient should be equal to unity (Dinopoulou *et al.,* 1988). The evaluated R^2 value for the accumulated methane production amounted to 0.998 indicating that the dispersion-based model indeed described the situation quite accurately. It therefore can be concluded that the dispersion mechanism is important so it is incorporated in all model runs.

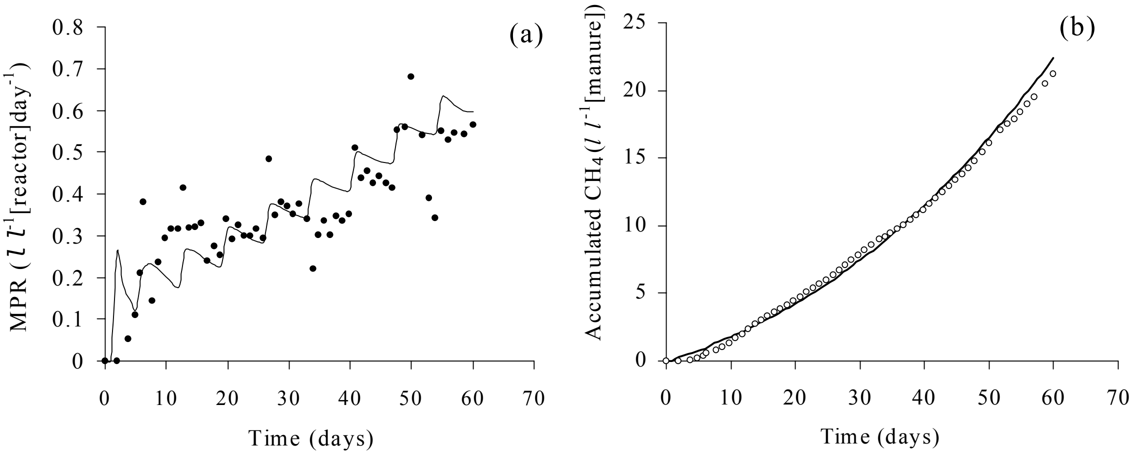


Fig.5.3.3 a and b. Experimental (o) and the model values (—) of MPR (a) and accumulated methane (b)

Experimentally, it was not possible to follow the methane production from each layer, the model was used to predict that. Figure 5.3.4 shows the simulated MPR from each separate layer. The data shown in Figure 5.3.4 are indeed calculated values for MPR which were derived from the fitting results for the separate layers. After inserting a specific layer, a higher MPR can be noticed. Then a more or less constant level is shown. It can be observed that the nearer the layer to the seed material (*i.e.* the bottom) the higher MPR. The exception is of course the seed material layer itself, wherein the availability of substrate is significantly less.

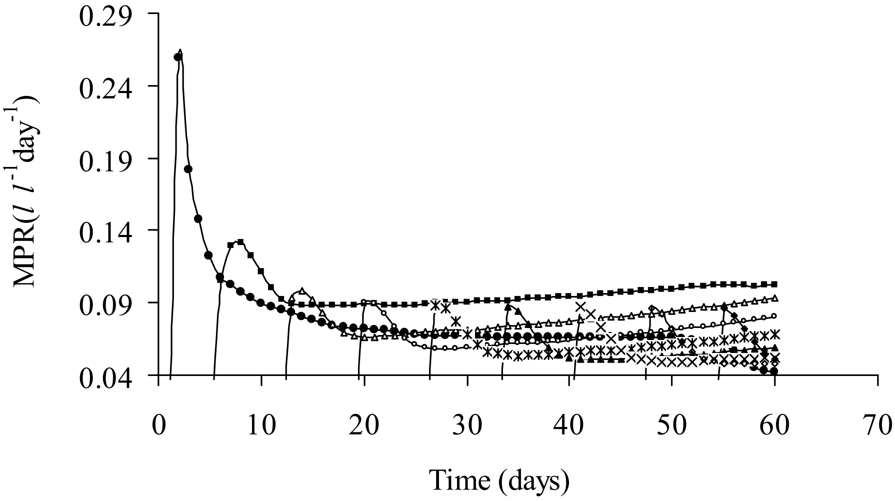


Fig.5.3.4. Simulated MPR for each separate layer over the complete filling time.

Intermediates

Figures 5.3.5 and 5.3.6 show the measured and simulated VFA and ammonia concentrations for some selected layers over the filling time. As can be seen the model only qualitatively (R^2 = 0.4-0.8) predicts the VFA and ammonia concentrations. The model prediction becomes less satisfactory at increasing effective reactor height (*i.e.* more added manure layers). Very poor correlation values (data not shown) between the simulated and measured concentrations of COD_{dis} can be noticed (Fig. 5.3.7), which may suggest that some other mechanisms for the transport of VFA and COD_{dis} may take place in practice, which are not included in the model. Also the biological parameters could be chosen wrongly. In their model, Vavilin *et al.* (2002a) mentioned that their model was not accurately in predicting the VFA concentrations. They attributed this to the model concept, wherein only the total VFA concentrations and not the VFA constituents were included. This means that the model was inadequate.

It should be emphasised here that calculated negative values of R^2 were obtained for COD_{dis} (data not shown), due to the fact that the regression line was forced to go through zero. By this forcing, the data are not normally distributed around the regression line hence the summation squares of residues is higher than those of the data points.

As the objective of the model is to predict accurately the methane production, the model parameters were tuned to get the best fit of the accumulated methane production. So some reduction in the correctness of fit of the other variables (COD_{dis} and VFA) would be expected (Hill, 1983a). In a comparable study, Hill (1983a) used literature data from a CSTR treating swine manure to validate his model at steady state conditions. The difference between the calculated and measured values for MPR in some reactors only amounted to 3-6% of the measured values. However for the same reactors, the difference between the measured and calculated values of volatile solids (VS) reduction was 70%-122.1% of the measured values.

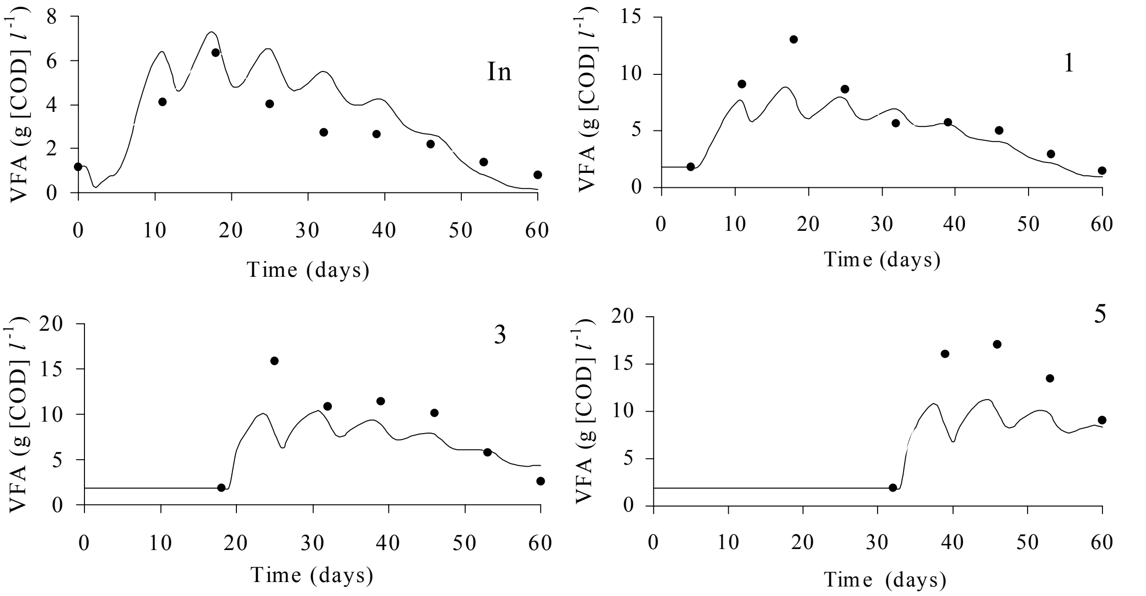


Fig.5.3.5. Measured and calculated VFA concentrations for some selected layers (In, seed material layer; 1, first layer; 3, third layer; 5, fifth layer): ●, measured value; —, calculated value

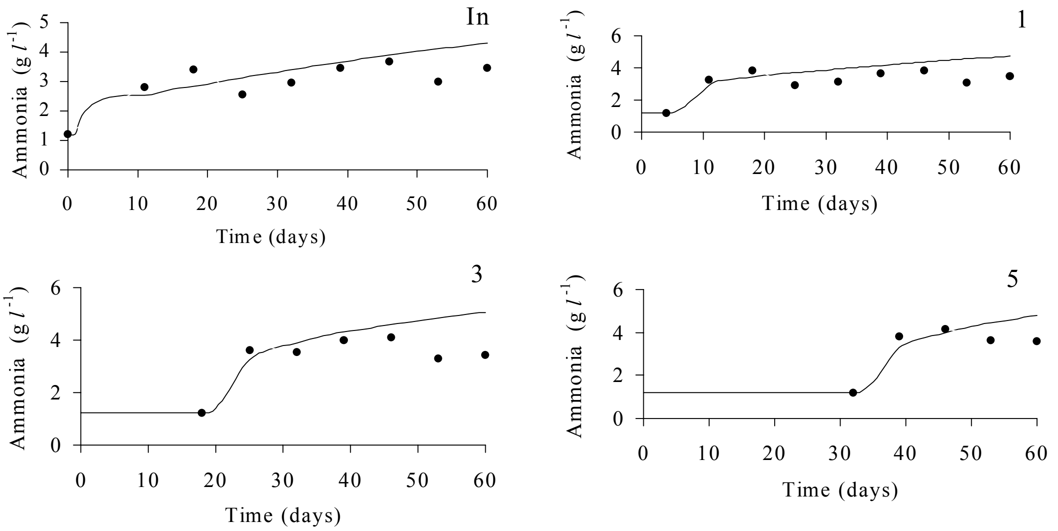


Fig.5.3.6. Measured and calculated ammonia concentrations for some selected layers (In, seed material layer; 1, first layer; 3, third layer; 5, fifth layer): ●, measured value; —, calculated value

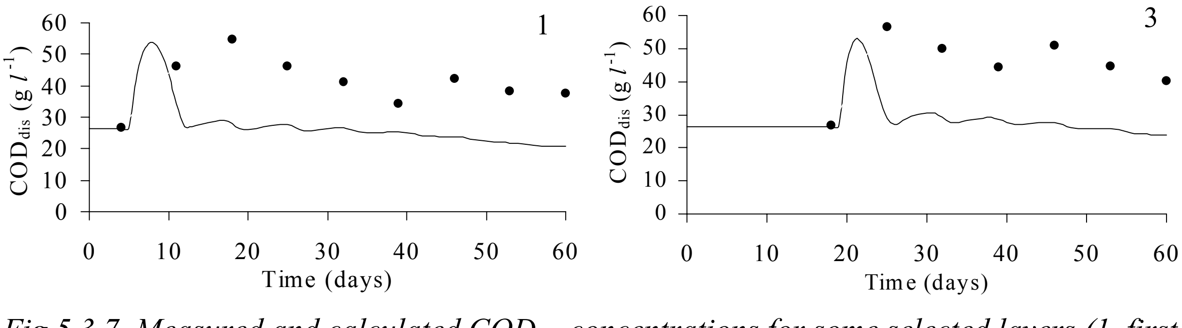


Fig.5.3.7. Measured and calculated COD_{dis} concentrations for some selected layers (1, first layer; 3, third layer): ●, measured value; —, calculated value

5.3.4.3. Model validation

The results of the methane production in the other two experimental runs with the same substrate (*chapter* 5.2) were used for model validation. In these two runs, the reactors (30 *l* each with an aspect ratio of 1.62) were also operated at 50^{o}C. In the first experiment, no seed material was used at all. In the second experiment, seed material of 10% (V/V) was used equally distributed in the feed.

For the experiments without seed material, a model run was carried out where the seed material volume was set at zero, while the viable biomass concentration originally present in the manure was set at the value presented in Table 5.3.2. Figure 5.3.8a shows a plot of the simulated against experimental values of the accumulated methane. A reasonable fitting (R^2 = 0.97) can be observed. Another model run was carried out to estimate the time required for conversion of the biodegradable COD into methane. The results (data not shown) of the latter run shows that even after one year only about 60 % of the biodegradable COD was converted into methane. From these model prediction it can be concluded that an AC for solid manure digestion should always be inoculated.

Figure 5.3.8b shows the experimental and the model values of accumulated methane for the experiments with seed material. The seed material (Table 5.3.2) was distributed homogeneously over the feed. A very good fitting (R^2 = 0.987) of the calculated values of accumulated methane against the measured values was obtained. The time required for the complete conversion of the biodegradable COD to methane was calculated at 95 days. This means that another 35 days digestion is required after the experimental filling time. In the case of the same amount of seed material is added at the reactor bottom, an additional digestion time of 55 days is required (*i.e.* a total of 115 days) to convert the biodegradable COD to methane.

Unfortunately, the concentrations of the intermediates of these two experimental runs were only measured at the end of the experiments, consequently the fitting of these experimental data with the calculated model results was impossible.

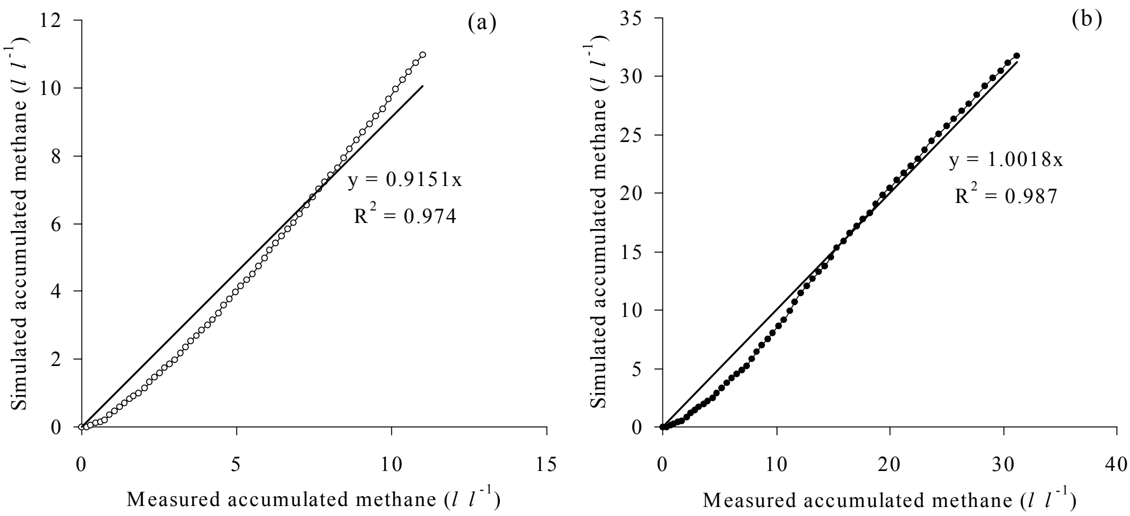


Fig.5.3.8a. Simulated and measured accumulated methane from the experiment without seed material. Fig.5.3.8b. Simulated and measured accumulated methane from the experiment with seed material in different doses.

5.3.4.4. Model application

The model was also applied to demonstrate the effect of different aspect ratios on the MPR of AC systems, conducted with added seed material (10%V/V) on the reactor bottom. Figure 5.3.9 shows the calculated specific accumulated methane production (*l* [CH_4] l^{-1} [manure]) after 60 days filling time at different aspect ratios, and Figures 5.3.10 and 5.3.11 show the detailed performance of AC systems with an aspect ratio of 3 and 0.6 respectively. The results in Figure 5.3.9 shows that the calculated specific accumulated methane production is 'optimal' at an aspect ratio of about 2. A further increase of the aspect ratio gives a reduction of specific accumulated methane production. This may be attributed to the relative small and large exchange area for dispersion of VFA to the seed material at the high and low aspect ratios respectively (see Fig.5.3.11b and Fig.5.3.12b). In their model, Vavilin *et al.* (2002 b) mentioned that with increase of the diffusion coefficient of VFA, in batch digestion, the lag phase of methane production increases. This is due to the high concentration of VFA, which causes inhibition to methanogenesis. Although they considered that diffusion coefficient can be changed, we are the opinion that the coefficients they used are some kind of pseudo-diffusion coefficients, because diffusion coefficient is a physical property which has specific values under different temperatures.

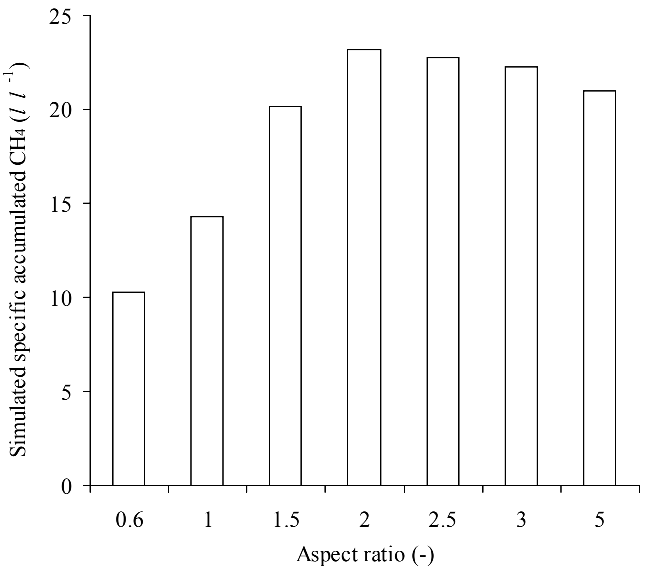


Fig.5.3.9. Simulated specific accumulated methane after 60 days for AC system with different aspect ratios

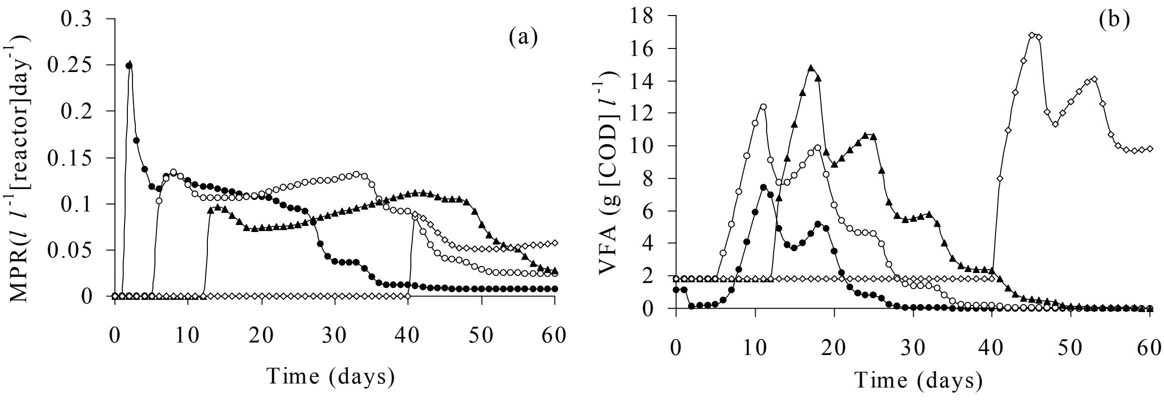


Fig.5.3.10. Simulation results for MPR (a) and VFA concentration (b) for some selected layers (●*,* seed material layer; ○*, 1*st *layer;* ▲*, 2*nd *layer;* ◊*, 7*th *layer) of an AC system with an aspect ratio of 3 over the complete filling time*

At an aspect ratio of 0.6 a high accumulation of VFA can be obtained from day 40 and onwards (Fig. 5.3.11b) coinciding with very low MPR (Fig.5.3.11a). Inspection of the results shown in Fig.5.3.11b indicates that incredibly high accumulation of VFA (about 90 g [COD] l^{-1}) occurs for the first layers at the end of the filling time. At a VFA concentration of about 60 g [COD] l^{-1}, the methane production is negligible (Fig.5.3.11b). During the batch digestion of the organic fraction of municipal solid waste, Ten Brummeler (1993) observed a very high VFA concentration (40-60 g [COD] l^{-1}), which caused a drop of the pH to values of 5.1-5.4. It is quite clear that the MPR at such extremely overloaded conditions was extremely low. In our model pH was not included.

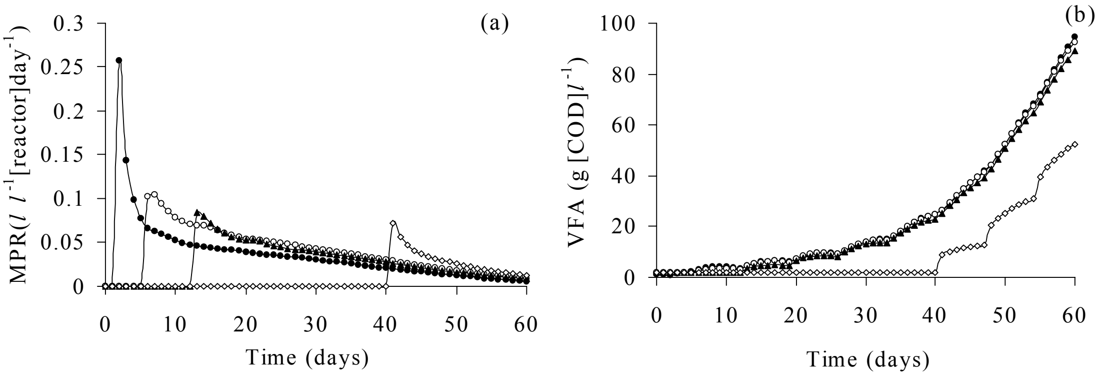


Fig.5.3.11. Simulation results for MPR (a) and VFA concentration (b) for some selected layers (●, seed material layer; ○, *1st layer;* ▲, *2nd layer;* ◊, *7th layer) of an AC system with an aspect ratio of 0.6 over the complete filling time. Note that there is overlapping of* seed material layer, *1st and 2nd in Fig.5.3.11b*

5.3.5. General discussion and conclusion

Dispersion looks an appropriate approach to model interaction between the layers. The dispersion-based model presented here fits well the methane production for the three different digesters operated with three different seed material addition modes. The model results show that the initial viable biomass concentration affects the system performance. This is contrary to the results of Dugba *et al.* (1999), who found that for the dynamic model the initial concentrations of biomass does not affect the final output as long as those concentrations are not initialised at zero.

The model predicts the VFA and ammonia concentrations only qualitatively but this certainly is not true for the soluble COD, which possibly can be attributed to the lack of sharp borders between layers due to the complex nature of the substrate.

According to Buhr and Andrews (1977), the simulation results may or may not be quantitatively correct, depending on the inherent accuracy of the model and process parameters employed. Our model although still in preliminary stage, provides an indication of process trends.

The results of the present study clearly indicate that more experimental data are needed, from different reactors with different aspect ratios, for the further validation of the model. In such experiments, viable biomass and dispersion coefficients can be measured in-situ.

Concluding, the dynamic model described in this study gives a good description of methane production from AC systems under different seed material addition modes. The model can predict the digestion time required for the conversion of all biodegradable COD into methane. However, it only can qualitatively predict the intermediates concentrations, suggesting that extra mechanisms need to be involved. Apparently, model results for methane not so sensitive for intermediate concentrations. A more detailed study is needed to evaluate the effect of each parameter on the methane production.

Notation

AM	Total ammonia, g l^{-1}
D_a	Empirical dispersion coefficient of acidogenic bacteria, m^2 day^{-1}
D_{AM}	Empirical dispersion coefficient of ammonia, m^2 day^{-1}
D_m	Empirical dispersion coefficient of methanogenic bacteria, m^2 day^{-1}
Ds	Empirical dispersion coefficient of soluble COD, m^2 day^{-1}
D_{VFA}	Empirical dispersion coefficient of VFA, m^2 day^{-1}
Kd_a	Specific death rate of acidogenic bacteria, d^{-1}
Kd_m	Specific death rate of methanogenic bacteria, d^{-1}
k_h	Hydrolysis constant, d^{-1}
K_{ia}	Growth inhibition coefficient for acidogenic bacteria by VFA, g VFA[COD] l^{-1}
kid_a	Death rate coefficient of acidogenic bacteria, g l^{-1}
kid_m	Death rate coefficient of methanogenic bacteria, g l^{-1}
k_{iam}	Inhibition coefficient of methanogenic bacteria by ammonia, g l^{-1}
K_{im}	Growth inhibition coefficient of methanogenic bacteria by VFA, g VFA[COD] l^{-1}
k_s	Half velocity constant of soluble COD metabolism, g l^{-1}
k_{sm}	Half velocity constant of VFA metabolism , g VFA [COD] l^{-1}
$N_{bacteria}$	Bacterial nitrogen content, g[N] g^{-1}bacteria [COD]
P	Biodegradable particulate COD, g l^{-1}
r_h	Hydrolysis rate, g l^{-1} d^{-1}
S	Soluble COD, g l^{-1}
T	Temperature, ^oC
t	Time, day
X_a	Concentration of viable acidogenic bacteria, g [COD] l^{-1}
X_m	Concentration of viable methanogenic bacteria, g [COD] l^{-1}
Y_a	Yield coefficient of acidogens, g acidogenic bacteria [COD]g^{-1}[COD_{dis}]
Y_{AM}	Yield of ammonia from organic nitrogen by acidogenic bacteria , g [N]g^{-1} organisms[COD]
Y_m	Yield coefficient of methanogens, g methanogenic bacteria [COD]g^{-1}VFA[COD]
z	Vertical coordinate, m
μ_a	Specific growth rate of acidogensis, d^{-1}
μ_m	Specific growth rate of methanogenic bacteria, d^{-1}
$\mu_{\max}$	Maximum specific growth rate, d^{-1}

5.4. Design of A Layered Accumulation System for Thermophilic Anaerobic Digestion of Solid Manure Heated with Solar Energy

Abstract

This paper concerns the modelling and simulation of the temperature in a stratified non-mixed accumulation system treating solid cattle manure. Every day a new layer is added on top of the older layers. The system is heated with a heat exchanger near the bottom of the reactor, which is connected with a flat plat solar collector mounted on the reactor roof. A mathematical model was developed based on heat balance to describe the temperature profile for the different layers along the system height. The simulation was carried out to study the heat exchange between the layers related to both different insulation materials and different aspect ratios of a 10 m^3 reactor. Moreover the interaction between the available solar energy from the solar heating system under Egyptian conditions and the temperature profile of the different layers has been simulated for two different periods (winter and summer) of 60 days each, aiming an average reactor temperature of 50^oC. The simulation results show that a minimum reactor temperature of 44.5 and 47.6 ^oC could be achieved during winter and summer filling periods respectively with a reactor aspect ration of 0.6 and heat transfer coefficient of the insulation material of 0.3 $Wm^{-2}K^{-1}$. Moreover, the simulation shows that the heat added via the heat exchanger together with adding preheated manure can compensate the heat losses.

5.4.1. Introduction

Anaerobic digestion is an attractive technology for disposal of liquid and solid cattle manure. It produces stabilised fertiliser and renewable energy in the form of methane. Many systems are commonly used for the treatment of animal manure. Accumulation system (AC) is a simple system for on farm application for both storage and digestion of cattle waste (Zeeman, 1991). Wellinger and Kaufmann (1982) showed, for the first time, the operation of an accumulation system (AC) for the digestion of liquid animal manure in practice. According to Zeeman (1991) an AC and completely stirred tank reactor (CSTR) systems are both continuously fed system, but while the effluent from a CSTR is continuously removed, the effluent in an accumulation system is removed only once, at the end of the filling period. The CSTR has a constant digestion volume, while that of the AC-system is increasing in time. In the operation of the accumulation system a fraction of the reactor volume is always filled with inoculum, to provide enough methanogenic activity.

According to Hobson *et al.* (1981) the faeces plus urine slurry from dairy cows consists of 12-14% total solids (TS). The total solid contents increase by using bedding material such as straw or sawdust (*i.e.* producing solid manure). Callaghan *et al.* (1999) mentioned that, due to the high viscosity, it is difficult to mix systems with solids levels of above 10 % by conventional mixing methods. The difficulties of mixing of high solids substrates lead to the stratification of both the content and the temperature over the reactor height. The stratification extent strongly depends on the moisture content of the substrate.

To obtain more hygienic stabilised fertiliser and high gas production, the digestion process could be applied under thermophilic condition (Van Lier, 1995; De Baere *et al.* 1985). To maintain such high temperatures (>45^oC), more energy input is required compared to mesophilic conditions (25-40^{o}C). This may lead to the reduction of the net energy production under thermophilic conditions.

To increase the energy efficiency and the sustainability of the system, other renewable energy sources (*e.g.* solar energy) can be used for the system operation. The interaction between the available solar energy and the temperature profile in the reactor is important from the microbial and energetic points of view. Modelling of the reactor temperature is a useful tool to assess the system behaviour. Simulation is a reliable tool for prediction the system performance under various environmental conditions and under different control strategies (Yaghoubi *et al.,* 2003).

In early investigations (*chapters* 4.4 and 4.5), we studied the modelling and simulation of solar energy incorporation for heating a CSTR system treating liquid cattle manure. Literature investigation showed that no attempts to study such integration on the behaviour of AC system treating solid manure have been reported. So the interaction between the seasonal variation of solar energy under subtropical areas, like the Egyptian situation, and the temperature profile along the reactor height is under investigation.

The objective of the present study is to enable the combination of small-farm scale thermophilic AC system and solar heating system. To do so a mathematical model is developed to describe the temperature profile of a layered non-mixed AC system. In this model, the interaction between the incorporation of solar energy as a heating source and the temperature profile in the AC system treating solid cattle manure (*e.g.* 25% TS) is included in order to study the system behaviour and controllability of the layered system. In this way the feasibility of the combination can be estimated.

5.4.2. Methodology

5.4.2.1. System operation

The AC system starts with a certain volume of inoculum (*ca* 10% V/V). Every day a new layer of fresh manure is added till the system is filled. After complete filling the system is emptied at once leaving a certain percentage of the reactor volume as an inoculum for the next filling period. In the present study, the filling time is chosen to be 60 days, based on the maximum period needed to store manure under Mediterranean conditions.

5.4.2.2. System configuration

Figure 5.4.1 shows the main components of the studied system. It consists of an AC system; preheater; solar heating system; two heat exchangers for the AC and for the preheater and control system. The AC system has a floating lid to maintain a constant and small gas volume to reduce the heat losses during the early stages of the filling time. The heat exchanger of both the reactor and the preheater is designed at heat exchange area equal to the half of the cross section area of the AC system (Beuger, 2002). The reactor heat exchanger is installed in the reactor bottom (*i.e.* within the inoculum volume). The preheater is used to raise the raw manure temperature to the reactor operating temperature as the heat is transferred from the bottom layers to the upper ones merely via heat conduction between the conjunct layers.

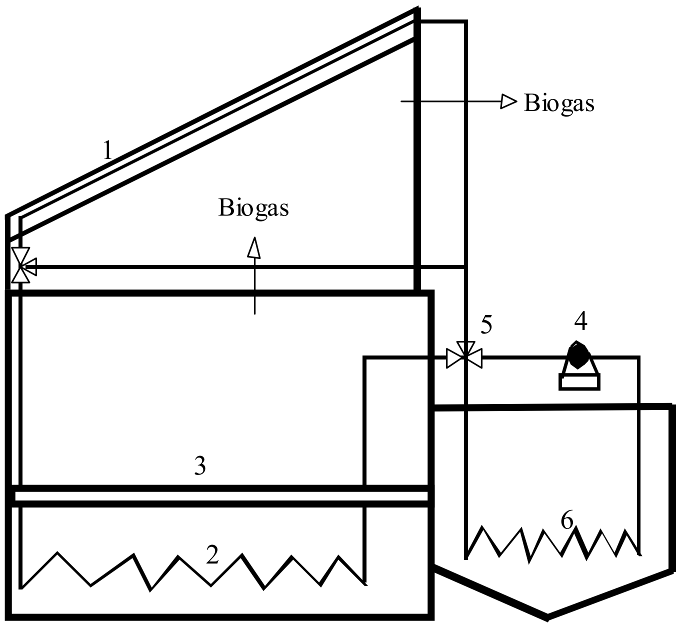


Fig.5.4.1. A scheme of the studied system: 1, solar collector; 2, reactor heat exchanger; 3, flotation lid; 4, pump for the solar heating system; 5, control system; 6, preheater heat exchanger

5.4.2.3. Mathematical model

The preheater

The preheater (Fig.5.4.1) has a capacity for the daily added manure. The preheater is operated batch wise as modelled in *chapter* 4.4. In the morning (9 h), the manure is placed in the preheater. Then the preheated manure is conveyed at 16 h to the AC via a screw conveyor.

The reactor

A 10 m^3 AC system (see Fig.5.4.1) is modelled with different aspect ratios (height/diameter): 0.6, 1 and 2. Different insulation materials with different overall heat transfer coefficients (U) of 0.3, 0.5, 1 and 2 $Wm^{-2}K^{-1}$ were applied for the reactor and the preheater. The system is starting with the inoculum and the first manure layer and the biogas layer (Fig 5.4.2a). Figure 5.4.2b shows the total model with more layers added. As can be seen the top layer is in contact with the biogas layer. When a new layer is inserted, this layer will be the new top layer and hence be in contact with the biogas layer. It is assumed that every layer has a homogeneous temperature (*i.e.* completely mixed). For simplicity, it is assumed that heat is transferred between layers merely by conduction and there is no mixing between the conjunct layers. The mathematical model of the system can be divided into three heat balances:

The inoculum layer

The system is heated by a fraction of the heat, which can be extracted from the solar heating system (Q_{us}). The other part of the heat gained from the solar heating system is added to the preheater. A part of the heat added to the inoculum (*i.e.* the system) is transferred by conduction (Q_l) to the first layer. Another part is lost to the environment (Q_e) through the reactor bottom and the sides. The metabolic heat from the digestion bacteria is very small and can usually be neglected (Hobson *et al.,* 1981).

$$V_{in} C\mathrm{p}_{\mathrm{m}} \rho_m \frac{\mathrm{d}T_{in}}{\mathrm{d}t} = Q_{us} - Q_e - Q_l \tag{5.4.1}$$

The Q_{us} is calculated based on the heat capacity of the hot water and the inlet (Tf_{in}) and outlet (Tf_{out}) temperature to and from the reactor. The latter temperature (Tf_{out}) was calculated based on the temperature of the inoculum layer (T_{in}); the heat exchanger surface area and the overall heat transfer coefficient between the heat exchanger and the inoculum (Axaopoulos *et al.,* 2001):

$$Tf_{out} = Tf_{in} + (T_{in} - Tf_{in})(1 - e^{\left(\frac{-U\, A_e}{mCp_w}\right)}) \tag{5.4.2}$$

Manure layer (l)

The manure layer (i) is in contact with the previous layer ($Q_{l\,(i-1)}$) and next layer ($Q_{l\,(i+1)}$). For the lowest layer this is inoculum (Fig. 5.4.2a and 5.4.2b). The top layer (n) is in contact with the biogas layer (Q_{lg}). The manure layer (i) loses heat ($Q_{le\,(i)}$) to the environment through the reactor walls.

$$V_l C\mathrm{p}_{\mathrm{m}} \rho_m \frac{\mathrm{d}T_{l(i)}}{\mathrm{d}t} = Q_{l(i-1)} - Q_{l(i+1)} + Q_{\mathrm{lg}} - Q_{le(i)} \tag{5.4.3}$$

Biogas layer

The biogas is in contact with the last inserted manure layer ($Q_{lg\,(n)}$). Heat is lost from the biogas volume to the environment (Q_{ge}) through the reactor walls and through the floating lid.

$$V_g C\mathrm{p}_{\mathrm{g}} \rho_g \frac{\mathrm{d}T_g}{\mathrm{d}t} = Q_{\mathrm{lg}(n)} - Q_{ge} \tag{5.4.4}$$

It should be reminded that the side area used for heat loss calculations in the previous equations is the area corresponding to the relevant volume: inoculum, manure or biogas. As the heat capacity of the biogas volume is smaller than that for the manure, a small time constant can be calculated for the biogas compared with that of the layers. As a result it is assumed that biogas is at quasi steady state and its temperature was calculated explicity by solving the equation of the biogas layer. The equations for calculating each term of heat flows (Q) in the previous Equations (5.4.1, 5.4.3 and 5.4.4) are explained by Beuger (2002). As the various heat flows (Q) are a function of the local temperature differences, the above equations can be solved numerically to calculate the local temperatures.

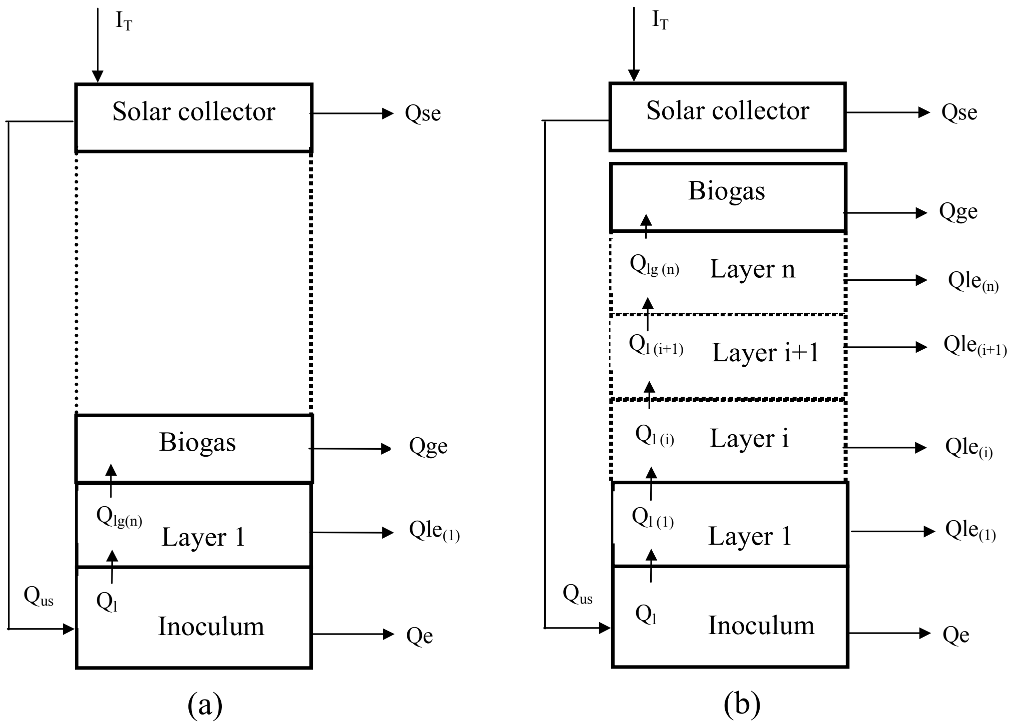


Fig.5.4.2. Overall heat balance diagram including temperatures and heat flows, the solid block is the inserted layer (activated in the simulation), while the dashed are the layers inserted later: (a) is the system for the first day and (b) is the system after putting n layers

5.4.2.4. The control system

An on/off differential controller is proposed to control the system, because it is simple and adequate as mentioned by Van Straten and Van Boxtel (1996). In the present study, the control system can be divided into two subsystems:

A- *Control of the solar collector*

The solar collector pump starts operating when the heat gain is positive.

B-Control of the reactor and the preheater

Figure 5.4.3 shows a schematic diagram of the control strategy. Valve (1) opens to permit the flow through the AC when the outlet temperature from the solar collector is higher than the AC temperature and the temperature of the inoculum is below 52^{o}C. Then the outlet temperature from the AC system passes through valve (2). As long as manure is present in the preheater (*i.e.* between 9 and 16 h) and the manure temperature is below 50^{o}C the manure is heated. Then the outlet temperature from the preheater is passed to the solar collector. If there is no manure loaded in the preheater or the temperature of the preheated manure is 50^{o}C (*i.e.* set point), the flow is directly bypassed to the solar collector. Valve (2) is opened also if the outlet water temperature from the solar collector is less than the AC temperature and there is manure loaded in the preheater.

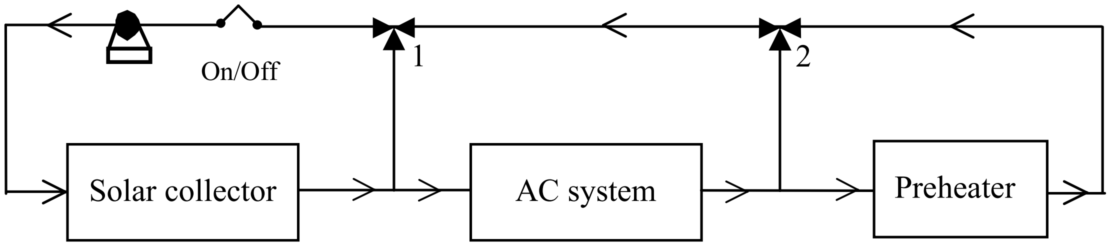


Fig.5.4.3. Control strategy of the system: 1 and 2 are two control valves

5.4.2.5. Measurements

The manure density, specific heat and thermal conductivity are calculated based on the manure moisture content (Chen, 1983). The measurements and further calculations of both solar energy and ambient temperature were carried out as described in *chapters* 4.4 and 4.5.

5.4.2.6. Simulation model

Based on the formulated heat balances a simulation was carried out using Matlab and Simulink software. The simulation model for the AC system consists of 60 blocks. Each block represents one individual layer. For the inoculum and the first layers, the simulation is started from the beginning. The rest of the layers, the input for the integrator is set to zero. From the moment the considered layer is added, the integrator is activated. As stated above the manure layer is in contact with the biogas layer until inserting a new one. In the simulation the new layer is inserted at 17 h every day.

As the preheater is operated batch wise, the simulation is set to zero before and after the presence of the manure *i.e.* before 9 h and after 16 h. For each layer, the electrical power of the screw is assumed to be added as a heat to the input for the simulation at 16 h. A power of 0.8 kW for the conveyor screw was estimated according to the regression equation of Barrington *et al.* (2002). For this estimation it is assumed that the screw inclination angle is 40^{o}.

The input parameters for the model are the hourly solar energy absorbed on the collector absorber plate; the hourly ambient air temperature and the initial temperature of the manure to the preheater. The later is assumed to be the same as the ambient air temperature at 9 h in the morning. The initial condition of the inoculum layer was set at 50^{o}C as for each filling period, an inoculum amount is left from the previous filling period. The data for ambient temperature and solar radiation are taken from our previous study (*chapter* 4.4). Table 5.4.1 shows the parameters used in the simulation. The simulation was carried out for two different periods: winter period (during January and February) and summer filling period (during July and August).

Table 5.4.1. Design parameters of the system

Parameter	*Unit*	*Value*
Reactor volume	m^3	10
Filling time	days	60
Volume of the inoculum	m^3	1
Height of the biogas layer	m	0.3
Heat transfer coefficient between the heat exchanger and the inoculum	$Wm^{-2}\,K^{-1}$	100
Preheater volume	m^3	0.15
Overall heat transfer coefficient for the heater installed in the preheater	$Wm^{-2}\,K^{-1}$	250

5.4.3. Results and discussion

5.4.3.1. Temperature gradient over the height of the layered system

The results of studying the effect of the combination of the aspect ratio and the insulation material on the system performance showed that the best combination is an aspect ratio of 0.6 and with an overall heat transfer coefficient of the insulation of 0.3 $Wm^{-2}K^{-1}$. The system performance of this combination is presented in sections 5.4.3.1, 5.4.3.2 and 5.4.3.3. Detailed explanations for this choice are mentioned in section 5.4.3.4. Figure 5.4.4 a and b shows the relation between the temperature and the height of the reactors for two periods (*i.e.* winter and summer) at different time intervals. The top of the inoculum is the reference for the height. Because heat is added from bottom (*i.e.* heat exchanger) and top (*i.e.* preheated manure), for all profiles it can be observed that a temperature minimum occurs at half of the filled height. Due to side wall losses this temperature minimum becomes deeper at increasing filling height, which corresponds with increasing time. A minimum temperature of 50°C could only be achieved for the first accumulated 20 layers and 30 layers for the winter and summer respectively. The reasons behind this are explained in section 5.4.3.3.

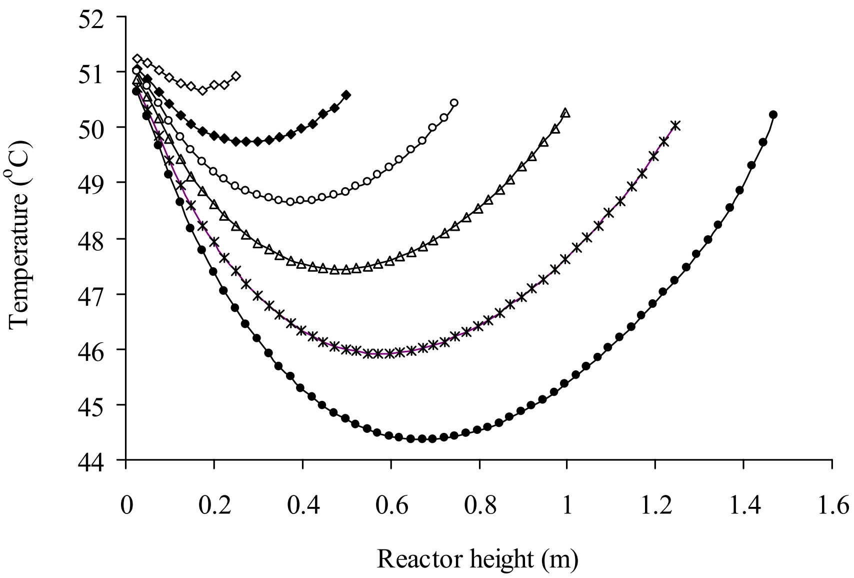


Fig.5.4.4, a. Temperature profile along the reactor height during the winter period: ◊, 10 days; ♦, 20 days; ○, 30 days; Δ, 40 days; ✳, 50 days; ●, 60 days

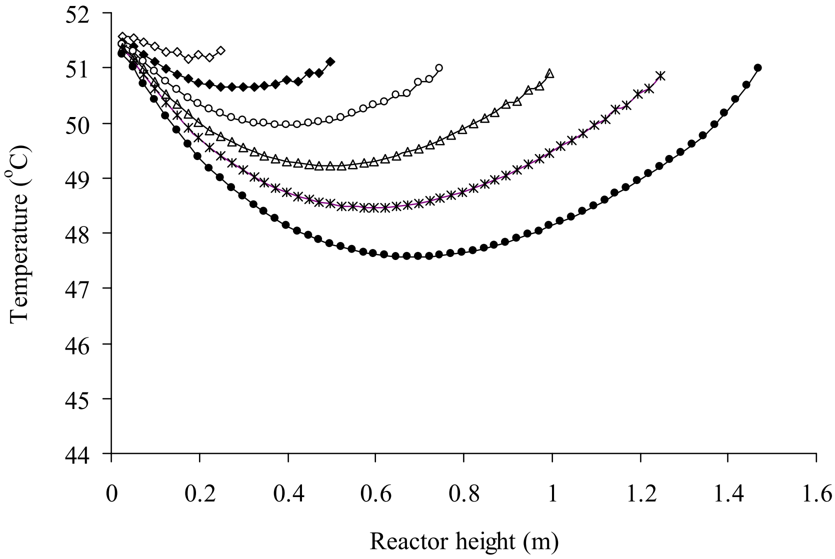


Fig.5.4.4, b. Temperature profile along the reactor height during the summer period: ◊, 10 days; ♦, 20 days; ○, 30 days; Δ, 40 days; ✳, 50 days; ●, 60 days

5.4.3.2. Performance of the preheater and general temperature profile of the reactor

Figure 5.4.5 shows the preheated manure temperature for a representative day in winter period and summer period. The Figure illustrates that while the maximum temperature of the preheated manure during the winter filling period reaches about 49^{o}C at 16 h, the desired temperature for manure preheating (*i.e.* 50^{o}C) is reached around 14 h during the summer period. This obviously can be attributed to the higher initial temperature of the manure and the higher solar flux in summer compared to the winter filling period.

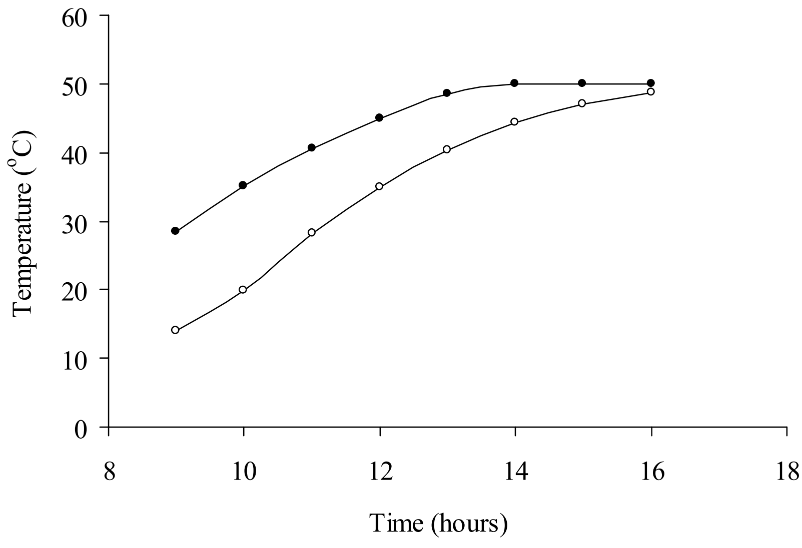


Fig.5.4.5. The preheated manure temperature: ○, January; ●, July

Figure 5.4.6 shows the temperature-time relationship for each layer during the summer filling periods. It is shown that the number of lines increases by one line (new added layer) every day. The temperature of each layer increases slightly for a short period (24 hours) because every layer remains in contact with the biogas, which has a slightly higher temperature (Fig.5.4.7) for such period before inserting the new layer of preheated manure. As can be deduced from Fig. 5.4.6 and Table 5.4.2 the minimum temperature in the reactor is about 47.6°C during the summer filling period. A similar Figure can also be obtained from the simulation for the winter period. The minimum temperature in the reactor is about 44.5°C during the winter filling period (Table 5.4.3).

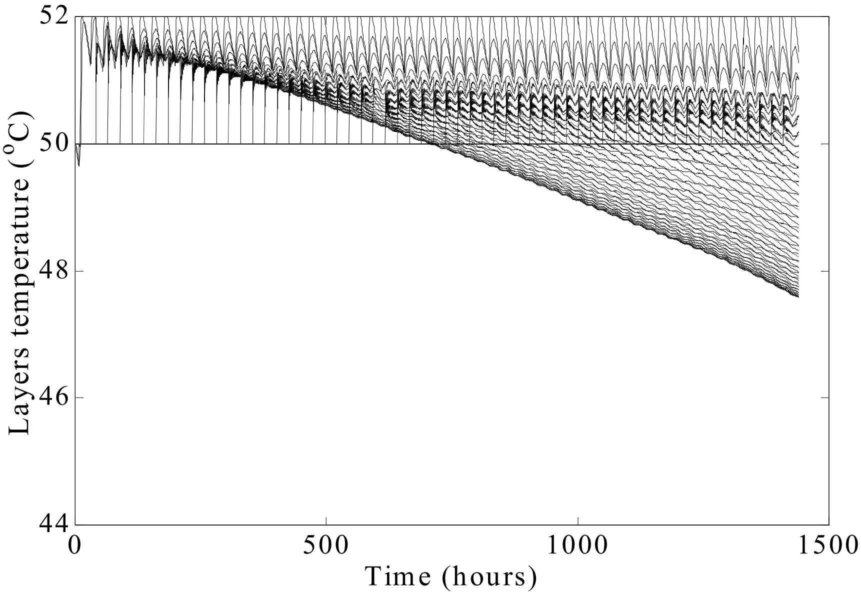


Fig.5.4.6. Temperature profile of all layers during the summer filling period. Note that every line represents a new daily added layer

5.4.3.3. Detailed performance of the reactor

Figure 5.4.7 shows the temperature profile of the biogas layer and the inoculum layer over the winter filling period. As mentioned before, the inoculum layer is the layer in direct contact with the heat exchanger. So it is expected that the inoculum has the highest and more constant temperature compared to the other layers. The temperature of the inoculum is not constant due to the heat losses to environment and there is no auxiliary heat is added during night times. Figure 5.4.7 and Table 5.4.2 show that the minimum inoculum temperature is 48.2°C in winter. While the minimum temperature of the inoculum in summer is 49.6°C (Table 5.4.3). The biogas layer is in contact with the preheated fresh manure layer so also is at high temperature.

Figure 5.4.8, a and b shows the temperature profile for some selected layers (5th; 10th; 15th; 20th; 30th; 40th; 50th layer) during the two studied filling periods. The ultimate temperature (at the end of filling time) of any selected layer depends on the position of this layer and on the time elapsed from the insertion of such layer to the end of the filling time. For example, the 5th layer remains 55 days in the reactor and its temperature at the end of the filling time is still higher than that for the 10th or 15th layer. This means that for the 5th layer the heat transferred from the heat exchanger is higher than the heat loss to the environment compared to both the 10th and 15th layers which are staying for 50 and 45 days respectively. For the upper layers (higher than 20th layer), the heat losses to the environment govern the magnitude of the ultimate layer temperature. So for these upper layers, the longer the elapsed time from the insertion of a certain layer to the end of the filling time the lower the ultimate temperature of such layer.

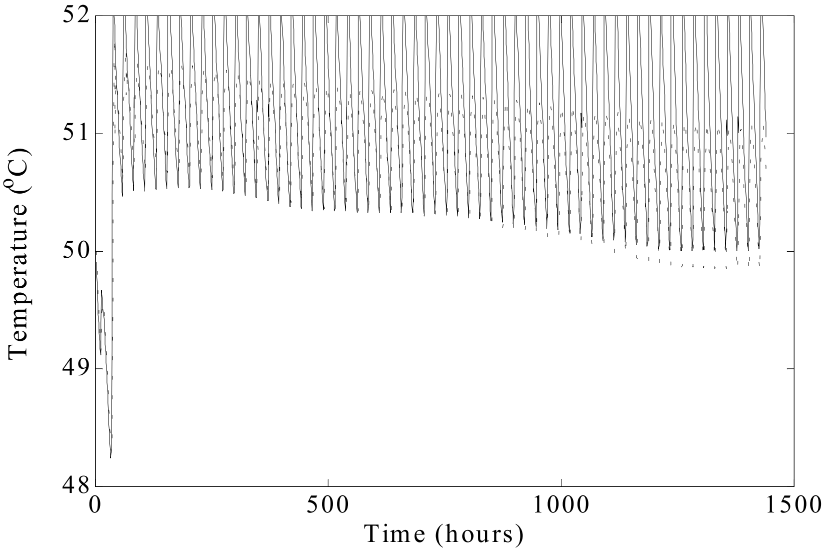


Fig.5.4.7. Temperature profile of inoculum and biogas layers during the winter filling period: —, inoculum;….., biogas

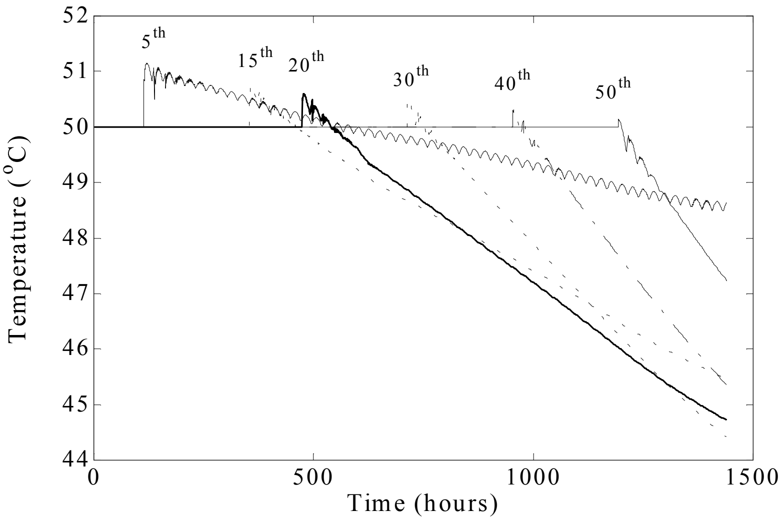


Fig.5.4.8, a. Temperature profile of some selected layers during the winter filling period

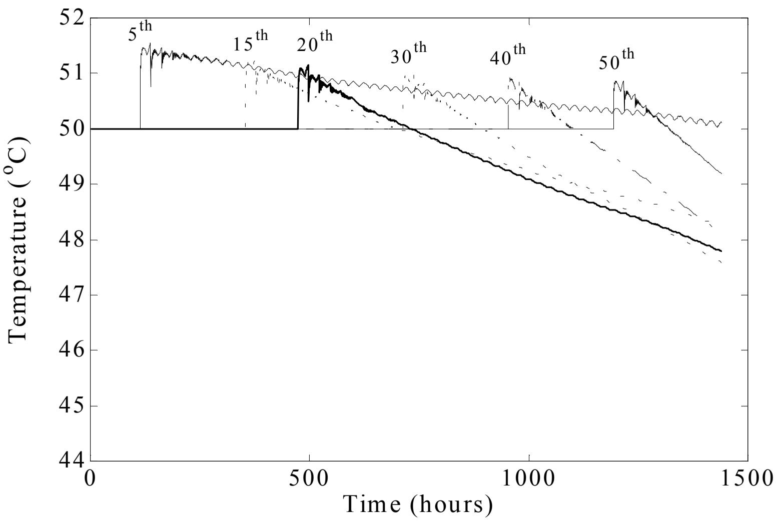


Fig.5.4.8, b. Temperature profile of some selected layers during the summer filling period

5.4.3.4. Effect of the aspect ratio and the insulation material on the system performance

Tables 5.4.2 and 5.4.3 show the effect of the interaction between the aspect ratio and the insulation material on the average, minimum reactor temperature during the winter and summer filling periods. It should be mentioned that the system performance for all aspect ratios and insulation materials is based on flat plat solar collectors of total area of 6 m^2. The solar collector was set at a fixed area in order to have a consistent comparison between different reactor designs. The solar collectors are facing south and fixed at a tilt angle of 30.1^o.

Table 5.4.2. Effect of aspect ratio and insulation material on the system performance during winter filling period

Aspect ratio	*U ($Wm^{-2}K^{-1}$)*	*Reactor temperature (^oC)*		*Inoculum temperature (^oC)*		*Input energy reactor (GJ)*	*Input energy preheater (GJ)*
		Min.	*Average*	*Min.*	*Average*		
0.6	2	21.3	40.4	33.0	39.1	2.29	1.14
	1	32.2	47.8	43.5	48.6	1.71	1.40
	0.5	40.3	48.2	46.8	50.6	1.62	1.41
	0.3	44.4	49.2	48.2	51.2	1.56	1.42
1	2	17.8	39.5	35.5	41.2	2.05	1.25
	1	26.9	44.4	44.73	49.6	1.59	1.44
	0.5	35.8	47.1	47.5	50.8	1.53	1.47
	0.3	41.1	48.5	48.7	51.3	1.49	1.47
2	2	14.5	37.8	38.1	43.1	1.77	1.38
	1	20.36	42.1	45.6	50.1	1.4	1.55
	0.5	29.3	45.4	47.9	51.0	1.35	1.56
	0.3	35.8	47.2	48.9	51.4	1.34	1.55

Table 5.4.3. Effect of aspect ratio and insulation material on the system performance during summer filling period

Aspect ratio	*U ($Wm^{-2}K^{-1}$)*	*Reactor temperature (^oC)*		*Inoculum temperature (^oC)*		*Input energy reactor (GJ)*	*Input energy preheater (GJ)*
		Min.	*Average*	*Min.*	*Average*		
0.6	2	35.7	46.4	46.4	49.7	3.69	1.23
	1	40.9	48.2	48.8	50.8	3.62	1.25
	0.5	45.3	49.4	49.4	51.4	3.60	1.26
	0.3	47.6	50.0	49.6	51.7	3.59	1.26
1	2	32.6	45.2	47.2	50.0	3.44	1.37
	1	37.4	47.2	49.0	51.0	3.39	1.38
	0.5	42.5	48.7	49.5	51.5	3.37	1.39
	0.3	45.6	49.5	49.7	51.7	3.36	1.39
2	2	30.1	43.7	47.9	50.3	3.02	1.62
	1	33.4	45.7	49.2	51.2	2.98	1.64
	0.5	38.6	47.6	49.58	51.6	2.96	1.64
	0.3	42.4	48.7	49.8	51.8	2.96	1.64

Naturally, in both winter and summer filling periods (Tables 5.4.2 and 5.4.3) the small heat transfer coefficient of the insulation material (*i.e.* good insulation) gives better system performance: higher average inoculum and reactor temperatures with less fluctuation. Interestingly, for the same insulation material, increase of the aspect ratio results in poor performance of the systems at summer and winter conditions with respect to average temperatures of both inoculum layer and reactor content. This is due to increasing external surface area in relation to internal surface areas with increasing aspect ratio (Beuger, 2002).

Higher average reactor temperatures can be obtained during the summer, which is attributed to the higher ambient temperatures (*chapter 4.4*) and higher energy input (*i.e.* higher solar fluxes) in summer (Tables 5.4.2 and 5.4.3). It should be mentioned that the amount of energy input (Tables 5.4.2 and 5.4.3) not only depends on the available solar energy and heat losses in both filling periods, but also on the temperature deviation of the inoculum with respect to the set point of the controller. The latter is the reason for the decrease of energy input with the increase of the aspect ratio. Less energy can be transferred to the upper layers in the reactors having larger aspect ratio ensuring an inoculum temperature close to the set point. It is also the reason for the higher average temperature of the inoculum at increasing the aspect ratio for the same heat transfer coefficient of the insulation (U). On the other hand, Tables 5.4.2 and 5.4.3 show that there is an inverse relation between the energy input to the reactor and that to the preheater. The lower the energy input to the reactor the more energy is left for the preheater.

From the model calculation, an aspect ratio of 0.6 combined with insulation material of U= 0.3 $Wm^{-2}K^{-1}$ is recommended. In that way the feasibility of combining solar energy with an AC system is achieved without auxiliary heating or additional heat exchanger equipment.

5.4.4. General discussion

The results of the present study demonstrate that it is possible to achieve thermophilic conditions (temperature > 45^oC) in a stratified non- mixed accumulation system treating solid cattle manure with a flat plate solar collector mounted on the reactor roof as a heating source. The results are based on a fixed heat exchanger on the reactor bottom and the heat is transferred merely by conduction between layers.

Based on the results presented, it can be postulated that the aspect ratio of 0.6 can be recommended from technological viewpoint because it possess a large cross section area for heat transfer between layers.

Although there is temperature stratification between layers, the maximum temperature difference between layers is *ca* 7 and 4^oC during winter and summer respectively. Based on results of earlier research on the effect of daily temperature fluctuation (*chapter* 4.2) and on the effect of stepwise temperature decrease from 55 to 51, 46 and 40^oC (Angelidaki and Ahring (1994), it can be expected that the temperature variation found in the present study will not seriously affect the activity of the microflora involved in the process.

Although the model results show a satisfactory temperature profile for thermophilic bacteria (45-52^oC), some deviations from the simulation results could take place in practice due to the thermal convection between the produced biogas from the bottom layers and the upper manure layers and the mixing between manure layers via biogas production. Generally, the strength of such mixing depends strongly on the substrate moisture content. With high heat transfer the gradient will be less deep but the energy input rise. Unlike the model, wherein we assumed equal distribution of the manure over the reactor cross section area, in practice the newly added manure could shape a heap in the top of old added manure in the reactor. This could be expected when there is no effective method to obtain an equal distribution of the newly added manure over the whole reactor cross section area. The height of such heap indeed depends on the manure angle of repose and the number of newly added manure layers. According to Malgeryd and Wetterberg (1996) there is no clear relationship between the active angle of repose and the total solid content of the solid manure. However after some layers a contact shape can be expected (Hasan, 2003).

The system efficiency based on the energy production at the different studied aspect ratios is not presented. This is due to the lack of available information on such issue. However, the earlier results (*chapter* 5.1) on a lab scale AC system with an aspect ratio of *ca* 1.7 showed that an average Methane Production Rate (MPR) of 264 and 302 l[CH4]m^{-3}[reactor].day^{-1} at 40 and 50^{o}C respectively was obtained at 60 days filling time. Based on a methane calorific value of 37 MJm^{-3} [CH_4] (Hill and Bolte, 2000), an energy production of 9.8 and 11.2 MJ m^{-3}[reactor].day^{-1} can be calculated at 40 and 50^{o}C respectively. The MPR will increase in time as the number of layers (*i.e.* reactor working volume) increases. Moreover, a higher methane production rate from reactors with small aspect ratio could be expected due to the increase contact between the inoculum layer and the other system layers. The effect of different aspect ratios on the biological conversion of organic material to methane is being studied.

It should be mentioned that another system operation regime could be applied. In such regime the same inoculum amount is added in different equal doses mixed with the feed and not in the reactor bottom. However, the heat balance model, which is presented in this study, will not change. But instead of starting with the inoculum volume (10% of the volume) the system should start with 10% of the reactor volume of a mixture of feed and inoculum.

5.4.5. Conclusions

The results of the present study show that:

1- A combination of an AC system and solar energy input is feasible. From the design study it can be concluded that an aspect ratio of 0.6 and insulation material with an overall heat transfer coefficient of 0.3 Wm^{-2}K^{-1} can be applied to give the smallest temperature gradient between the different layers.

2- A system with this combination can be operated with an on/off control strategy with a satisfactory thermophilic temperature range (45-52^{o}C).

3- The model can be applied successfully for simulation of the temperature profile along the reactor height in interaction with the seasonal variations of the solar energy and ambient conditions.

4- The simulation results show that the heat added via the heat exchanger affects the temperature of the lower layers, while the temperature of the upper layers is strongly affected by the heat losses to the environment.

5- It can be expected that temperature variations found in the present study will not affect the activity of the microflora involved in the process.

Notation

A_e	Surface area of the reactor heat exchanger, m^2
Cp_g	specific heat of the biogas, J kg^{-1} K^{-1}
Cp_m	specific heat of manure, J kg^{-1} K^{-1}
Cp_w	specific heat of water, J kg^{-1} K^{-1}
I_T	Solar flux absorbed in the absorber plate, W
m	flow rate of water inside the solar collector, kg s^{-1}
Q_{us}	Heat added to the reactor from solar collector, W
Q_e	heat loss to environment from inoculum, W
Q_l	heat transferred by conduction between layers, W
Q_{le}	heat loss to environment from every layer, W
Q_{ge}	heat losses from the gas volume to ambient, W
Q_{lg}	heat transferred form the top manure layer to the biogas, W
Q_{se}	Heat losses from the solar collector, W
U	Overall heat transfer coefficient between inoculum and the heat exchanger , $Wm^{-2}K^{-1}$
t	time, s
T_{in}	temperature of the inoculum layer, ^oC
Tf_{in}	water inlet temperature to the reactor, ^oC
T_l	Temperature of manure layer, ^oC
Tf_{out}	water outlet temperature from the reactor, ^oC
T_g	biogas temperature, ^oC
V_{in}	inoculum volume, m^3
V_l	volume of the manure layer, m^3
V_g	biogas volume, m^3
ρ_m	manure density, kg m^{-3}
ρ_g	biogas density, kg m^{-3}

CHAPTER 6: GENERAL DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

6. General Discussion, Conclusions and Recommendations

This *chapter* contains the most important results from this thesis together with a comparison with relevant literature, and it provides an evaluation of the improved sustainability that can be achieved with the Solar Thermophilic Anaerobic Reactor (STAR) compared with conventionally heated reactors. The *chapter* ends up with some practical recommendations.

The main objective of this research was maximising the net energy production from agricultural wastes with production of a hygienic organic fertiliser as a by-product.

6.1. Reuse potential of agricultural wastes in Egypt

Chapter 2 starts with an overview of different streams of agricultural wastes. The possible technologies for using agricultural wastes, as a source of bio-energy and valuable products, are discussed related to their applicability at small (on farm) scale in Egypt. Cattle wastes and rice straw represent the major streams in 2001 (FAO, 2001). For selecting a treatment technology, besides the material properties and the environmental benefits, low cost and low-tech technology are proposed as criteria for choice. It was concluded that controlled burning of rice straw and anaerobic digestion of cattle wastes followed by composting of the effluent mixed with rice straw are two options, which could meet the criteria. However, since burning does not conserve organic material, only a combination of anaerobic digestion of cattle manure with composting the mix of effluent and rice straw can be recommended. This combination will improve the quality of life in villages; and has economic benefits as it reduces the effluent transportation costs and chemical fertilisers usage. Based on the arguments presented in *chapter* 2*,* it was decided to focus on the thermophilic digestion of liquid and solid manure as a core process to achieve the goal of this thesis. Because the digestate can be used as a by-product and the composting can improve its quality as organic fertiliser some theoretical attention is given (*chapter* 2 and section 6.4 of this *chapter*) to the composting process. The features and potentials of the composting process were recently thoroughly discussed by Hamelers (2001).

6.2. Effect of ammonia

Chapter 3.2 deals with the roll of ammonia in the anaerobic digestion process. Unlike the importance of nitrogen for bacterial growth, high ammonia concentrations are inhibitory or even toxic for the anaerobic microflora, especially at thermophilic conditions (Van Velsen and Lettinga, 1980; Wiegant and Zeeman, 1986; Zeeman, 1991; Angelidaki and Ahring, 1993). Free ammonia is considered as the main inhibitory component for methanogenesis: likely the bacterial cell wall is far more permeable for un-dissociated molecules than for ions (Van Velsen and Lettinga, 1980). The mechanism of the inhibition effect of ammonia on methanogenesis has also been elucidated. According to Wiegant and Zeeman (1986) acetoclastic methanogens can be negatively affected by high ammonia concentrations either directly or indirectly (*i.e.* via accumulation of propionic acid). So far only few reports have been published about the negative effect of ammonia on hydrolysis (*e.g.* Van Velsen, 1981; Zeeman, 1991), but the mechanism of that detrimental effect is still not completely clear, and consequently requires more experimental research to become elucidated. Microflora adaptation is important to obtain successful digestion at high ammonia concentrations of about 1700 mg l^{-1} and higher (*e.g.* Van Velsen and Lettinga, 1981). The adaptation period depends on the applied ammonia concentration and organic loading rate.

To optimise the methane production, all process steps should be considered. The effect of ammonia on hydrolysis under thermophilic conditions was studied experimentally in batch reactors (*chapter* 4.3). The results of these experiments show a strong negative effect of the presence of high NH_3 concentration in the range of 0.08 to 0.36 g l^{-1} on the first order hydrolysis constant at thermophilic batch digestion (50 and 60^{o}C). The experiments were carried out at NH^+_4-N range of 1.06 to 3.77 g l^{-1} with an inoculum adapted to the lowest NH^+_4-N concentration (*i.e.*1.1 g l^{-1}). Whether or not the same results would have been achieved by using a seed sludge (inoculum) adapted to the highest concentration is still unclear. On the other hand, also in 'steady state' mesophilic digestion systems (CSTR) with sludge adapted to high NH^+_4-N concentrations, similar strong effects on hydrolysis were observed by Zeeman (1991) and Van Velsen (1981). From our results obtained at 'steady state' in a thermophilic (50 and 60^{o}C) CSTR (*chapter* 4.2), it was also found that the high free ammonia concentrations not only affected the acetate-utilising bacteria but also the hydrolysis and acidification steps. For application in practice the effect of NH^+_4-N on the hydrolysis constant is of utmost importance, as lower gas yields will be obtained when the detention time is not adjusted. The results of the batch experiments show that the hydrolysis of cow manure can be described by first order kinetics (values of R^2 are at least 0.7). Our results reveal that the rate-limiting step is seriously affected by both the imposed digestion temperature and ammonia concentration. These findings are in accordance with those of Speece (1983) and Pavlostathis and Giraldo-Gomez (1991).

6.3. Treatment of liquid manure: Effect of temperature and solar energy incorporation

In this section many aspects considering the treatment of liquid cattle manure and the design of STAR are elaborated. Rheological properties of liquid manure are important in designing mixing and pumping equipment during the anaerobic digestion. It is well known that temperature has a major influence on the viscosity of liquids. The results described in *chapter* 4.1 concern the viscosity of liquid manure at different shear rates and temperatures. The results show that manure has non-Newtonian flow properties, as the viscosity strongly depends on the applied shear rate, and also that manure has plastic behaviour. Moreover, the results show that the Arrhenius-type model fits very well the temperature effect on manure viscosity ($R^2 \geq 0.95$) with calculated activation energy of 17.0 ± 0.3 kJ mol^{-1} which is comparable to that of sieved beef-cattle manure (Chen, 1986).

To overcome the high energy (*i.e.* fossil or biogas) consumption during thermophilic digestion, a STAR can be applied, especially in countries with high solar incident like Egypt. To keep the STAR as simple as possible, the system is designed without external heat storage or auxiliary heating during nights. This obviously will impose some temperature fluctuations between day (*i.e.* where solar energy can be added) and night time on the system. According to Speece (1983) the anaerobic digestion process would be rather sensitive to sudden changes of environmental conditions, but according to Kroeker *et al.* (1979) this would not be the case for diurnal temperature fluctuations. The experimental results presented in *chapter* 4.2 concern the influences of temperature (50 and 60^{o}C) and temperature fluctuations (downward and upward regime) on the performance of completely stirred tank reactors (CSTR's) treating liquid cattle manure at two Hydraulic Retention Times (HRT's) of 10 and 20 days. The results show that the methane production rate at 60^{o}C is lower than that at 50^{o}C in almost all the experiments. The results illustrate that imposed upward temperature fluctuations more severely affect the maximum specific methanogenic activity as compared to imposed downward temperature fluctuations, *viz.* quite similarly as observed by Lau and Fang (1997). In practice, temperature fluctuations may not reach the extent as in the studied conditions. So the results obtained demonstrate the possibility of using available solar energy at daytime to heat up the reactor (s) without the need of auxiliary heating during nights and also without the jeopardising of the overheating especially for the digestion at 50^{o}C and 20 days HRT. Therefore it can be concluded, that the application of STAR is possible from a biological point of view.

Based on the biological evaluation of the effect of temperature fluctuations (*chapter* 4.2), a model has been developed (*chapter* 4.4) to calculate the specific net thermal energy production (SNTEP). SNTEP is defined as net energy production per cubic metre reactor volume: it is the caloric value of the produced methane minus the sum of the total energy needed for heating the feed and the total heat losses to the environment. The interaction between different reactor volumes and different insulation materials was studied in relation to the SNTEP. Moreover, the expected increase in SNTEP for STAR was evaluated. The results show that a maximum overall heat transfer coefficient of 1 $Wm^{-2}K^{-1}$ is needed for reaching at least 50% energy efficiency. Furthermore, adding a solar energy system on the roof of the reactor (*i.e.* STAR) improves the efficiency for large (> 100 m^3) reactors only slightly, while for small reactors (*e.g.* 10 m^3) a large improvement is achieved due to the relative large roof area. An energy efficiency of 90% can be achieved.

In *chapter* 4.5, the system dynamics related to the environmental disturbances (*e.g.* variations of ambient air temperature and solar energy flux) was studied using a simulation model for a 10 m^3 STAR. A simulation model has been developed of two system configurations, including a heat recovery unit to heat up the feed by extracting some heat from the effluent. The first configuration is simple and the second more complex (*i.e.* an integrated system), which includes an extra chamber for the pumps and the heat recovery unit. Total energy input to both systems, including the electrical energy used for pumping and agitation, was estimated. Both systems were controlled using a simple on/off strategy. An auxiliary heater, operated with the produced biogas, can be used during cold months. The simulation results show that by using a heat recovery unit, the feed temperature can be increased by about 10-20^{o}C, depending on raw manure temperature and/or ambient temperature. The integrated system can be recommended from the process technology and energy points of view. A daily temperature fluctuation of less than 1 K could be realised. Based on the results presented in *chapter* 4.2, it was demonstrated that such a system could be operated without harm for the microbial activity. A maximum annual temperature variation of about 5 K can be realised in both systems. The results of Angelidaki and Ahring (1994) showed that a stepwise temperature decrease, during a few months of operation, from 55 to 51, 46 and 40^{o}C did not affect significantly the reactor performance. They revealed also that after each change in the temperature the biogas production was soon re-established at the same level as at 55^{o}C. So it can be concluded that the seasonal variations in reactor temperature can be tolerated. The simulation results show also that an overall energy efficiency of 95% could be achieved.

6.4. Treatment of solid manure: Effect of temperature and solar energy incorporation

Many (small) farms, all over the world, still produce solid manure, i.e. depending on the food composition and the bedding material applied (Hobson *et al.,* 1981). Callaghan *et al.* (1999) mentioned that it is difficult to mix systems with total solid concentrations above 10% by conventional mixing methods. So the CSTR can not be easily applied for treatment of solid manure. The non-mixed accumulation system (AC) is proposed as an alternative for the treatment of such material. According to Wellinger and Kaufmann (1982) and Zeeman (1991) the AC system is the simplest system for on farm practice as it combines storage and digestion. In *chapter* 5.1, experiments have been carried out to assess the effect of temperature (40-50^{o}C) on the performance of an AC system treating solid cattle waste (16-25% TS) at a filling time of 60 days. The systems were started up using 10% (V/V) seed material (inoculum) disposed at the reactor bottom. Every week a new layer of manure is added on the top of the previously added layers. Due to the step-wise supply procedure of the fresh manure and the poor mixing conditions, a certain stratification occurs in the system, *viz.* the prevailing concentration of intermediates (VFA and COD_{dis}) largely depend on the reactor height. Moreover there exist two different zones: the seed sludge zone and the substrate zone (Ten Brummeler, 1993; Veeken and Hamelers, 2000). As expected, the methane production rate at 50^{o}C is distinctly higher than that at 40^{o}C. The results show also that at higher moisture content, the methane production is higher, while the extent of the stratification profiles are lower. The positive effect of a lower solid content can be explained on basis of the observations of Ten Brummeler (1993). He attributed the poor performance at higher total solids content to: (1) a lower water availability for the micro-organisms; (2) the higher concentration of inhibiting compounds such as NH^{+}_{4}-N and (3) insufficient mixing of substrate and bacteria due to high viscosity.

To improve the system performance at high solid content two operation strategies were separately studied in *chapter* 5.2, comprising (a) leachate recirculation and (b) distribution of the seed sludge with the feed. A very high methane production rate (MPR) and simultaneously a less pronounced stratification of the intermediates were observed at 50^{o}C compared with that at 40^{o}C, under conditions of leachate recirculation. This likely can be attributed to either the effect of high temperature on the process performance or the increased amount of leachate recirculation due to the lower viscosity at higher temperature. Veeken and Hamelers (2000) demonstrated the improvement of solid state batchwise digestion of biowaste by transporting VFA to the biomass via leachate recirculation. The results of our present research show also that a better system performance (*i.e.* a higher methane production rate with less pronounced profiles of the intermediates) can be achieved by distributing the seed material over the reactor height by adding it to the feed than by adding the same amount of seed sludge at the reactor bottom. A much better system performance can be expected by combining leachate recirculation with distribution of the seed sludge with the feed. The profiles of the intermediate concentrations were quantified by using the so called Profile Extent Index (PEI) parameter, which is defined as the difference in the concentration of a particular intermediate between the reactor top and the reactor bottom divided by the concentration of COD_{dis} in the influent.

In *chapter* 5.3, a mechanistic model was presented, describing the biological process, for a stratified AC system. The model, based on the available models in literature (*e.g.* Hill and Brath, 1977; Hill, 1983; Dughba *et al.,* 1999; Veeken and Hamelers, 2000; Vavilin *et al.,* 2002 a and b), includes all three well known process steps of the digestion process, i.e.

hydrolysis, acidogenesis and methanogenesis. A dispersion factor of different intermediates and bacteria species between the system layers is included in the model, and in this way a significantly better description of data is found than without using the dispersion phenomenon. The model was calibrated with experimental data from the AC system started with 10% (V/V) seed sludge at the reactor bottom and validated with the experimental data obtained in *chapter* 5.2. The model prediction of methane production is in agreement with the experimental data, but the concentration of intermediates only was described qualitatively, since the model parameters in fact were tuned to get the best fit of the accumulated methane production. As a consequence the rather poor fitting of other variables (*e.g.* COD_{dis} and VFA) could be expected (Hill, 1983). The model was also applied to estimate the optimum aspect ratio of the system. According to the results obtained, the optimal aspect ratio (height / diameter) would be about 2 when the seed sludge is added at the bottom of the reactor. The experimental results clearly showed that the better performance was achieved by distributing the seed sludge with the feed. In that case the aspect ratio would not influence the biological performance of the system.

The results presented in *chapter* 5.4 concern those of the mathematical and simulation model for a 10 m^3 STAR treating solid manure (*i.e.* AC concept). Different from the results presented in *chapter* 4.4, where we concluded implementation of a preheater is not necessary for liquid manure in a CSTR, a preheater is important when treating solid manure because of the bad heat transfer between manure layers. The effect of different aspect ratios on the temperature gradient over the reactor height was also evaluated. The STAR-system is preceeded with a solar energy driven preheater in order to raise the temperature of the influent to the digestion temperature (*i.e.* 50^{o}C) during day time. The interaction between the available solar energy under Egyptian conditions and the temperature profile of the different layers has been simulated for two different periods (winter and summer). The simulation results show that a minimum reactor temperature of 44.5 and 47.6^{o}C could be achieved during winter and summer filling periods respectively, using a reactor aspect ratio of 0.6 and heat transfer coefficient of the insulation material of 0.3 $Wm^{-2}K^{-1}$. So the optimum aspect ratio of 0.6 based on the energetic analysis differs from that of 2-3 based on the biological analysis. By adding the seed sludge with the feed, the aspect ratio does not severely affect the biological processes any more. So it can be concluded that the best combination of design and operation of the AC system is using an aspect ratio of 0.6 with distribution of 10% (V/V) of inoculum with the feed.

Although the goal of the present study was achieved, there still remain some aspects to be considered for future research, while some other experiments are required mainly for verification of the different models:

1- The models of solar energy incorporation, in CSTR and AC systems, should be validated with experimental data.

2- The effect of the interaction between the inoculum distribution with the feed and the leachate recalculation on the system performance should be experimentally assessed. Further validation of the AC system model with more experimental data and the leachate recirculation should be considered.

6.5. System evaluation: Emergy analysis of the STAR

The incorporation of a solar heating system in the anaerobic digestion will, definitely, increase the installation costs. However, a cost analysis cannot provide the sustainability benefits of such system. According to Brown and Ulgiati (2002) an evaluation of sustainability should include net energy, environmental effects, and production emissions (greenhouse gases) that must be treated and recycled by the environment. The "sustainability" concept, stands for the idea that the present and coming generations should preserve resources, energy and a balanced healthy life environment for the future generations (Brundtland Commission, 1987). Analyses that do not regard human labour, environmental work and quality differences between different places and time are not sufficient to rely on when discussing ecological sustainability on large time and spatial scale (Bjorklund *et al.,* 2001).

EMERGY is a concept closely related to energy, but it includes the indirect forms of energy added to the system as well. EMERGY analysis of a system, a technique of quantitative analysis, determines the values of non-moneyed and moneyed resources, services and commodities in common units of the solar energy, which are used to produce it (Brown and Herendeen, 1996). Unit: *solar emergy Joules, abbreviated seJ.*

As an example, a comparison between two 10 m^3 CSTR systems treating animal manure was carried out. The first system is operated with a conventional heat source and the second is operated with solar energy (see *chapter*s 4.4 and 4.5). Both systems are preceded with a heat recovery unit. Moreover, the sustainability of these two systems is discussed based on the emergy-based indices. Figure 6.1 shows the energy diagram of the studied systems. It is essential that the system should be diagrammed and understood as completely as possible prior to the evaluation. The detailed methodology of emergy analysis has been reported by various researchers (*e.g.* Brown and Herendeen, 1996). The methane production rate, which is used in this analysis, is the rate obtained in *chapter* 4.4.

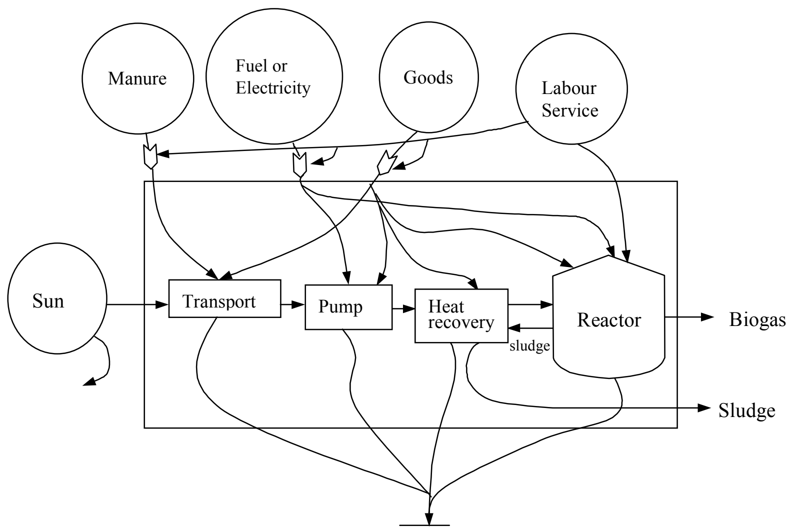


Fig.6.1. The energy diagram of the studied system: symbols are shown in appendix (A)

Table 6.3 summarises the preliminary results obtained from the emergy analysis. It can be seen from this table that emergy yield for the conventional heated system is higher than that for the solar heated system. Consequently, the transformity in the first system is higher than that for the second one. The transformity is a measure of the amount of work required, directly or indirectly through the economic system in order to generate a service or a product (Lagerberg, 2000). Some of the calculations of EMERGY analysis are presented in Appendix (B).

The higher the transformity, the larger is the potential environmental impact resulting from its use (Lagerberg, 2000). In addition, the Emergy yield ratio for the conventional heating system is higher than that for the solar heated system, indicating a high emergy content of the resources invested from outside in the second system. This is due to the extra equipment needed for the solar system installations.

Table 6.3. Emergy analysis and its indices for methane production

Parameters	*Unit*	*Conventional heated*	*Solar heated*
Renewable sources (R)	seJ year^{-1}	4.09E+10	5.46E+10
Purchased input other than fuel (F)	seJ year^{-1}	1.38 E+15	1.45 E+15
Non renewable source (N)	seJ year^{-1}	1.19 E+15	4.89E+14
Emergy Yield = R+ F+ N	seJ year^{-1}	2.57 E+15	1.94 E+15
Emergy Yield ratio =Emergy Yield/F	----	1.86	1.34
Total energy produced	J year^{-1}	1.14E+11	1.14E+11
Transformity	seJ J^{-1}	2.26E+04	1.71E+04

In conclusion it can be stated that:

1. These preliminary results show that the transformity of methane production was $2.26E^{+04}$ and $1.71E^{+04}$ seJ J^{-1} for conventional and solar heating system respectively.
2. The incorporation of solar energy system has a more beneficial impact from a sustainability point of view. About 20% better performance could be achieved by STAR.

6.6. Practical application

Our results demonstrate that the STAR option is feasible both for liquid and solid manure. Although the incorporation of solar energy in such system would increase the costs of the system construction, our preliminary results based on EMERGY analysis show that such incorporation has a positive effect on the transformity (*i.e.* seJ J^{-1} [produced]) compared to using conventional heating sources.

The produced methane (*i.e.* biogas) can be used for heating; lighting and cooking in villages. According to a survey of the World Energy Council (1993), about 39.5% of rural households in Egypt use burning of dry biomass for cooking, while 30% of rural households use it for heating. Especially the replacement of this biomass is useful. The survey also shows that, while the consumption of electricity and liquid petroleum per household increases with income, biomass use varies inversely to income. According to El-Shimi (1994), the demand for both cooking and lighting in rural Egypt had been estimated to be 0.6-0.7 m^3 [biogas] per capita per day. Based on this estimation it can be calculated that a volume of 1 m^3 STAR reactor, operated at 50^{o}C and 20 days HRT using liquid manure with 10% TS as feed, can cover the energy demand of approximately 2 persons. On the other hand, the average methane production rate from 1 m^3 of AC system, operated at 50^{o}C at a filling time of 60 days with seed sludge distribution with the feed, could cover the energy demand for approximately 1 person. It should be mentioned that one of the drawbacks of the AC system is the fluctuating daily methane production rate over the filling time (Zeeman, 1991). Naturally, the economic production of biogas depends on the reactor volume and insulation.

In Egypt, the mixed crop-livestock system is the most important cattle production system, *i.e.* representing over 70% of all cattle, together with large numbers of buffaloes and some sheep and goats (Tabana, 2000). On mixed farms digested manure, in general, can be used as fertiliser on the fields, therefore decentralised biogas production can be attractive. Moreover the distance between the reactor and the place where biogas is used, is highly important. In case of difficulties to match the produced methane with home energy need, it could be used for on farm pasteurisation or cooling of milk. Under Egyptian conditions the milk is commonly transferred from small farms to dairy factories or consumers without pasteurisation or cooling. This can add another benefit for biogas technology application via increasing the quality of milk especially during summer.

Production of biogas as energy source from manure preserves the organic matter (and nutrients), which is 'otherwise' burnt directly as a source of energy. Moreover, it increases the quality of life in villages as a result of better hygienic conditions. Table 6.4 shows the emission factors of different greenhouse gases for different fuels used for cooking in developing countries (Bhattacharya and Abdul Salam, 2002). The data in this table show that biogas stoves have the lowest CH_4 emission factor compared to other biomass stoves. Compared to non-renewable sources (*e.g.* Kerosene), the closed CO_2- cycle of biomass is to be preferred.

Like many other countries, Egypt has signed the Koyoto Protocol for climate change. According to Egyptian New and Renewable Energy Authority (2000), it is expected that the application of biogas technology can contribute to the fulfilment of Egyptian future commitments under the climate convention.

Table 6.4. Emission factors from different fuel types (Bhattacharya and Abdul Salam, 2002)

Cooking options	*Stove efficiency (%)*	*Emission factor (kg TJ^{-1})*		
		CO_2	CH_4	N_2O
Traditional stoves (wood)	11	-----	519.6	3.74
Traditional stoves (residues)	10.2	-----	300	4
Traditional stoves (charcoal)	19	-----	253.6	1
Traditional stoves (dung)	10.6	-----	300	4
Improved stoves (wood)	24	-----	408	4.83
Improved stoves (residues)	21	-----	131.8	4
Improved stoves (charcoal)	27	-----	200	1
Improved stoves (dung)	19	-----	300	4
Biogas stoves	55	-----	57.8	5.2
Natural gas	55	90402	20.65	1.84
Liquefied Petroleum Gas (LPG)	55	106900	21.11	1.88
Kerosene	45	155500	28.05	4.18

A part from energy source, the effluent of the anaerobic digestor can be used as a high value fertiliser. This is because the anaerobic treatment preserves the nutrients contained in the raw manure with a mineralization of a large fraction of the organic nitrogen to the inorganic form (ammonia) which is easy to uptake by the plant. Yet the application of the effluent, which has higher ammonia concentrations than untreated manure might cause a high emission of ammonia. However, According to Sommer and Hutchings (2001), ammonia emission from application of anaerobically digested slurry was similar to that from application of untreated slurry. Ammonia volatilisation can be reduced by taking a variety of measures (Sommer and Hutchings, 2001) such as injection of the slurry into the cultivated soil; application of the manure in the coldest part of the day between plants rows and reducing the manure viscosity. The effluent can also be used to produce an easy transferable fertiliser (compost) by mixing it with other available materials like rice straw. On one hand, this will be a good option for the disposal of rice straw in a friendly way for the environment. On the other hand, by this mixing the proper C/N ratio and the moisture content for composting the rice straw (high solid content and high C/N ratio) and the digestate (low solid content and low C/N ratio) could be achieved. The proper mixtures to obtain a successful composting with achieving sufficient temperature to get hygienic compost should be studied in detail.

It can be concluded that the direct using of the effluent as a fertiliser and/or after composting with rice straw offer at least two economical benefits besides the environmental benefits, *viz.*:

1- Improving the soil structure and fertility as compared to a method like direct burning of these residues. Therefore the crop quantity especially for the newly reclimated soils is expected to increase.

2- Less dependency on chemical fertilisers, which in turn saves energy otherwise used for the production of chemical fertilisers.

6.7. Recommendations and most important conclusions

Based on the results obtained in this PhD-research some recommendations and most important conclusions can be formulated:

1- The incorporation of solar energy in thermophilic digestion of cattle manure has been proven to be applicable from an energetic and microbial point of view. This incorporation increases the system sustainability significantly.

2- From energetic and process stability point of view, it can be recommended that the STAR should be operated at 20 days HRT and 50^{o}C.

3- The operation of an AC system for digestion of solid manure at 60 days filling time and 50^{o}C particularly looks well feasible when the seed sludge (10% V/V) is distributed with the feed, and by combining this with leachate recirculation the performance could even be further improved. Further enhancement could also be obtained by an integrative solar heating system.

4- The incorporation of a composting process for a mixture of the effluent of the anaerobic digester and rice straw looks highly attractive in order to produce a high quality easy transferable organic fertiliser.

REFERENCES

References

Abd Elaty, B.S.A. (1985). Bioenergy from Organic Residues for Rural Egypt. Ph.D. Thesis, Faculty of Agriculture Ain Shams University, Egypt

Achkari-Begdouri, A. and Goodrich, P.R. (1992). Bulk density and thermal properties of Moroccan dairy cattle manure. Biores. Technol. **40**: 225-233

Agote, I.; Odriozola, A.; Gutierrez, M.; Santamaria, A.; Quintanilla, J.; Coupelle, P. and Soares, J. (2001). Rheological study of waste porcelain feedstocks for injection moulding. J. Europ. Ceramic Soc. **21:** 2843-2853

Ahring, B.K. (1994). Status on science application of thermophilic anaerobic digestion. Wat. Sci. Technol. **30** (12): 241-250

Ahring, B.K. (1995). Methanogenesis in thermophilic biogas reactors. Antonie van Leeuwenhoek **67**: 91-102

Ahring, B.K.; Ibrahim, A.A. and Mladenovska, Z. (2001). Effect of temperature increase from 55 to 65^oC on performance and microbial population dynamics of an anaerobic reactor treating cattle manure. Wat. Res. **35** (10): 2446-2452

Al Seadi, T. (2001). Good practice in quality management of AD residues from biogas production. International energy agency. http://websrv5.sdu.dk/bio/pdf/manage.pdf

Albertson, O. E. (1961). Ammonia nitrogen and the anaerobic environment. J. Wat. Poll. Contr. Fed. **33**(9): 978-995

Al-Ismaily, H.A. and Probert, S.D. (1995). Solar-desalination prospects for the sultanate of Oman. Appl. Energy **52**: 341-368

Alkhamis, T.M.; El-Khazali, R.; Kablan, M.M. and Alhusein, M.A. (2000). Heating of a biogas reactor using a solar energy system with temperature control unit. Solar Energy **69** (3): 239-247

Allan, D.; Katovich, E. and Nelson, C. (2003). Fertiliser value and weed seed destruction potential of digested manure. Paper presented at A National Summit "Anaerobic Digestion Technology Applications in Animal Agriculture". 2-4 June, Raleigh, North Carolina, USA

Anaerobic Lab Work (1992). International course on anaerobic waste water treatment. Wageningen University and IHE Delft, The Netherlands

Andrews, J.F. (1968). A mathematical model for the continuos culture of microorganisms utilising inhibiting substrates. Biotechnol. Bioeng. **10**: 707-723

Andrews, J.F. and Pearson, E.A. (1965). Kinetics and characteristics of volatile acid production in anaerobic fermentation processes. Int. J. Air. Wat. Poll **9**: 439-461

Angelidaki, I. and Ahring, B.K. (1993a). Thermophilic anaerobic digestion of livestock: the effect of ammonia. APPl. Microbiol. Biotechnol. **38** (4): 560-564

Angelidaki, I. and Ahring, B.K. (1993b). Effect of the clay mineral bentonite on ammonia inhibition of anaerobic thermophilic reactors degrading animal waste. Biodegradation **3**: 409-414

Angelidaki, I. and Ahring, B.K. (1994). Anaerobic thermophilic digestion of manure at different ammonia loads: the effect of temperature. Wat. Res. **28** (3): 727-731

Angelidaki, I.; Ellegaard, L. and Ahring, B.K. (1993). A mathematical model for dynamic simulation of anaerobic digestion of complex substrates: Focusing on ammonia inhibition. Biotechnol. Bioeng. **42** (2): 159-166

Angelidaki, I.; Ellegaard, L. and Ahring, B.K. (1999). A comprehensive model of anaerobic bioconversion of complex substrates to biogas. Biotechnol. Bioeng. **63** (3): 363-372

APHA (1992). In Standard Methods for the Examination of Water and Wastewater, 18th Ed. American Public Health Association, Washington, DC, USA

Axaopoulos, P.; Panagakis, P.; Tsavdaris, A. and Georgakakis, D. (2001). Simulation and experimental performance of a solar-heated anaerobic digester. Solar Energy **70** (2): 155-164

Barrington, S.; Nieuwenhof, P.; Vigneault, C.; Choinie`re, D. and Clarke, S. (2002). A computer program to size agricultural standby power units and electrical service entrances. Comp. Electr. Agric. **36**: 79-86

Bartlett, H.D.; Persson, S.P. and Regan, R.W. (1980). Energy production potential of a $100m^3$ biogas generator. Agricultural Energy, Vol. 2. Biomass Energy Crop Production. Selected papers and abstracts from the 1980 ASAE national energy symposium. American Society of Agricultural Engineers, USA

Bastianoni, S.; Marchettini, N.; Panzieri, M. and Tiezzi, E. (2001). Sustainability assessment of a farm in the Chianti area (Italy). J. Cleaner Prod. **9**: 365-373

Batstone, D.J.; Keller, J.; Angelidaki, I.; Kalyuzhnui, S.V.; Pavlostanthis, S.G.; Rozzi, A.; Sanders, W.T.M.; Siegrist, H. and Vavilin, V.A. (2002). Anaerobic digestion model No.1. IWA task group for mathematical modelling of anaerobic digestion processes. IWA publishing

Beek, W.J. and Muttzall, K.M.K. (1975). Transport Phenomena. John Wiley & sons, London, UK

Bendixen, H.J. (1994). Safeguards against pathogens in Danish biogas plants. Wat. Sci. Technol. **30** (12): 171-180

Benjamin, M.M.; Woods, S.L. and Ferguson, J.F. (1984). Anaerobic toxicity and biodegradability of pulp mill waste constituents. Wat. Res. **18** (5): 601-607

Bernard, O.; Hadj-Sadok, Z.; Dochain, D.; Genovesi, A.; Steyer, J. (2001). Dynamical model development and parameter identification for an anaerobic wastewater treatment process. Biotechnol. Bioeng. **75** (4): 424-438

Beuger, A.L. (2002). Modelling and temperature control of a solar powered anaerobic digestion unit. MSc. Thesis, Wageningen University, Wageningen, The Netherlands

Bhandari, B.; D'Arcy, B. and Chow, S. (1999). Rheology of selected Australian honeys. J. Food Engin. **41:** 65-68

Bhattacharya, S. K. and Parkin, G.F. (1989). The effect of ammonia fermentation processes. J. Wat. Poll. Contr. Fed. **61** (1): 55-59

Bhattacharya, S.C. and Abdul Salam, P. (2002). Low greenhouse gas biomass options for cooking in developing countries. Biom. Bioeng. **22**: 305-317

Bhumibhamon, O.; Chaiyapol, K. and Sirisansaneeyakul, S. (1988). Studies on chemical and environmental changes during composting. Recent Advances in Biotechnology and Applied Biology. Proceedings of Eighth International Conference on Global Impacts of Applied Microbiology, August 1985, Hong Kong (pp 587-594)

Bitton, G. (1994). Wastewater Microbiology. Weley-Liss, New York, USA

Bjorklund, J.; Gerber, U. and Rydberg, T. (2001). Emergy analysis of municipal wastewater treatment and generation of electricity by digestion sewage sludge. Res. Conserv. Recycl. **31**: 293-316

Borja, R.; Sānchez, E. and Weiland, P. (1996). Influence of ammonia concentration on thermophilic anaerobic digestion of cattle manure in upflow anaerobic sludge blanket (UASAB) reactors. Proc. Biochem. **31** (5): 477-483

Braun, R.; Huber, P. and Meyrath, J. (1981). Ammonia toxicity in liquid piggery manure digestion. Biotechnol. Lett. **3**: 159-164

Brown, M.T. and Herendeen, R.A. (1996). Embodied energy analysis and EMERGY analysis: a comparative view. Ecol. Econ. **19**: 219-235

Brown, M.T. and Ulgiati, S. (2002). Emergy evaluations and environmental loading of electricity production systems. J. Cleaner Prod. **10**: 321-334

Brundtland Commission (1987). World Commission on Environment and Development: Our Common Future. Oxford University Press, UK

Buhr, H.O. and Andrews, J.F. (1977). The thermophilic anaerobic digestion process. Review paper. Wat. Res. **11**: 129-143

Butler, J.N. (1964). Ionic Equilibria, A Mathematical Approach. Addison-Wesley Pub.CO., Menlo Park, California

Buzàs, J.; Farkas, I.; Biró, A. and Németh, R. (1998). Modeling and simulation of a solar thermal system. Math. Comp. Simul. **48**: 33-46

Callaghan, F.J.; Wase, D.A.J.; Thayanithy, K. and Forster, C.F. (1999). Co-digestion of waste organic solids :batch studies. Biores. Technol. **67**: 117-122

Chamy, R.; Poirrier, P.; Schiappacasse M.C.; Alkalay, D. and Guerrero, L. (1998). Effect of ammonia content in the biodegradability of the salmon industry wastes. Bioproc. Engin. **19** (1): 1-5

Chan, G.Y.S.; Chu, L.M. and Wong, M.H. (2002). Effects of leachate recirculation on biogas production from landfill co-disposal of municipal solid waste, sewage sludge and marine sediment. Environ. Poll. **118**: 393 –399

Chandler, J.A.; Jewell, W.J.; Gossett, J.M.; Soest, P.J.van and Robertson, J.B. (1980). Predicting methane fermentation biodegradability. Biotechnol. Bioeng. Symp. **10**: 93-107

Chang, C.S.; Lai, F.S. and Miller, B.S. (1980). Composting of grain dust. Transactions of the ASAE May/June **23** (3): 709-711

Chen, Y.R. (1983). Thermal properties of beef cattle manure. Agric. Wast. **6**: 13-29

Chen, Y.R. (1986). Rheological properties of sieved beef-cattle manure slurry: rheological model and effects of temperature and solids concentration. Agric. Wast. **15**: 17-33

Chen, Y.R. and Hashimoto, A.G. (1976). Rheological properties of aerated poultry waste slurries. Transactions of the ASAE **19** (1): 128-133

Chen, Y.R. and Hashimoto, A.G. (1981). Energy requirements for anaerobic fermentation of livestock wastes. In: Smith, R.J. (Ed.), Livestock waste: A Renewable Resource. ASAE publication No. 2-81, ASAE, St. Joseph, MI 49085, USA

Chen,Y.R.; Varel, V.H. and Hashimoto, A.G. (1980). Effect of temperature on methane fermentation kinetics of beef-cattle manure. Biotechnol. Bioeng. Symp.No.**10**: 325-339

Chynoweth, D.P.; Owens, J.M and Legrand, R. (2001). Renewable methane from anaerobic digestion of biomass. Ren. Energy **22**: 1-8

Cintoli, R.; Di Sabatino, B; Galeotti, L. and Bruno, G. (1995). Ammonium uptake by zeolite and treatment in UASB reactor of piggery wastewater. Wat. Sci. Technol. **32** (12): 73-81

Claassen, P.A.M.; Lier, J.B. van; Lopez-Contreras, A.M.; Niel, E.W.J.; Sijtsma, L.; Stams, A.J.M.; Vries, S.S. de and Weusthusi, R.A. (1999). Utilisation of biomass for the supply of energy carriers. Appl. Microbiol. BioTechnol. **52**: 741-755

CLAC (1997). Central Laboratory for Agricultural Climate, Egypt. http://www.calc. edu.eg/

Cobb, S.A. and Hill, D.T. (1990a). Maximum specific methane production of animal wastes and the effect of non-steady-sate conditions on anaerobic fermenters. In: Agricultural and Food Processing Wastes. Proceedings of the Sixth International Symposium on Agricultural and Food Processing Wastes, December 17-18, 1990, Hyatt Regency Chicago in Illinois Centre, Chicago, Illinois, USA

Cobb, S.A. and Hill, D.T. (1990b). Using nitrogen ratio as an indicator of biomass retention and steady-state in anaerobic fermentation. Transactions of the ASAE **33** (1): 282-287

Coulson, J.M. and Richardson, J.F. (1964). Chemical Engineering. Volume one, fluid flow, heat transfer and mass transfer. Pergamon press. Oxford, UK

Cuevas, V. (1993). Rapid composting fits rice farmers. ILEIA. **9** (2): 11-12
Dagnall, S.; Hill, J. and Pegg, D. (2000). Resource mapping and analysis of farm livestock manures assessing the opportunities for biomass-to energy schemes. Biores. Technol. **71**: 225-234
Dahl, S.D. and Davidson, J.H. (1995). Comparison of natural convection heat exchangers for solar water heating. Proceedings of Solar 95, The 1995 American Solar Energy Society Annual Conference, July 15-20, Minneapolis, Minnesota, USA (pp 288-293)
Dayton, D.C.; Jenkins, B.M.; Bakker, R.R.; Williams, R.B.; Bell, O.D. and Hill, L.M. (1999). Release of inorganic constituents from leached biomass during thermal conversion. Energy and Fuels **13** (4): 860-870
De Baere, L. (2000). Anaerobic digestion of solid waste: state-of-the-art. Wat. Sci. Technol. **41**(3): 283-290
De Baere, L.; Verdonck, O. and Verstraete, W. (1985). High rate anaerobic composting process for the organic fraction of solid wastes. Biotechnol. Bioeng. Symp. No. **15**: 321-330
De Baere, L.A.; Devocht, M.; Van Assche, P. and Verstrate, W. (1984). Influence of high NaCl and NH_4Cl salt levels on methanogenic associations. Wat. Res. **1** (5): 543-548
Devêvre, O.C. and Horwáth, W.R. (2000).Decomposition of rice straw and microbial carbon use efficiency under different soil temperatures and moistures. Soil Biol. & Biochem. **32**: 1773-1785
Di-Blasi, C.; Portoricco, G.; Borrelli, M. and Branca, C. (1999). Oxidative degradation and ignition of loose-packed straw beds. Fuel **78** (13): 1591-1598
Dinopoulou, G.; Sterritt, R.M. and Lester, J.N. (1988). Anaerobic acidogenesis of a complex wastewater: II kinetics of growth, inhibition, and product formation. Biotechnol. Bioeng. **31**: 869-877
Dohne, E. (1980). Biogas storage and utilisation. In: Stafford, D.A.; Wheatley, B.I. and Hughes, D.E. (Eds.), Anaerobic Digestion. Applied Science Publishers Ltd, London, UK
Duffie, J.A. and Beckman, W.A. (1974). Solar Energy Thermal Processes. John Wiley & Sons, New York, USA
Duffie, J.A. and Beckman, W.A. (1991). Solar Engineering of Thermal Processes, Second Edition. Wiley, New York, USA
Dugba, P.N. and Zhang, R. (1999). Treatment of dairy wastewater with two-stage anaerobic sequencing batch reactor systems- thermophilic versus mesophilic operations. Biores. Technol. **68**: 225-233
Dugba, P.N.; Zhang, R.H.; Rumsey, T.R. and Ellis, T.G. (1999). Computer simulation of a two-stage anaerobic sequencing batch reactor system for animal wastewater treatment. Transactions of the ASAE **42** (2): 471-477
Duran, M. and Speece, R.E. (1997). Temperature staged anaerobic processes. Environ. Technol. **18**: 747-754
Eastman, J.A. and Ferguson, J.F. (1981). Solubilization of particulate organic carbon during the acid phase of anaerobic digestion. J. Wat. Poll. Contr. Fed. **53**: 253-266
Egyptian New and Renewable Energy Authority (2000). Implementation of renewable energy technologies (RETs) project opportunities & barriers, Egypt country study. Final report to UNEP collaborating centre on energy and environment, Risø National Laboratory, Denmark
El-Hadidi, Y.M. (1998). Biogas Technology. Proceedings of Anaerobic Treatment of Solid Wastes Workshop, 4 May 1998, Mansoura University, Egypt (pp 6-32) [In Arabic]
El-Mashad, H.M.; Zeeman, G. and Lettinga, G. (2001). Thermophilic anaerobic digestion of cow manure. Effect of temperature on hydrolysis. In: Van Velsen, A.F.M. and Verstraete, W.H. (Eds.). Proceedings of the 9th World Conference of Anaerobic Digestion, September 2-6, Antwerp, Belgium (part 2, pp505-507)

Elmitwalli, T.A. (2000). Anaerobic treatment of domestic sewage at low temperature. Ph.D. Thesis, Wageningen University, Wageningen, The Netherlands

El-shimi, S. and Arafa, S. (1998). Biogas technology transfer to rural communities in Egypt. http: //www.virtualcentre.org/en/dec/toolbox/Tech/EL_S0291.pdf

El-Shimi, S.A. (1994). Biogas production and utilization in rural Egypt. Activities of agricultural research centre. Egyptian-French Seminar on Biological N-Fix Associated with Cereal Crops (Sep. 26-28). Giza, Egypt

FAO (2001). Production yearbook. Food and Agricultural Organisation of the United Nations

Fischer, J. R.; Iannotti, E.L.; Proter, J. H. and Garcia, A. (1979). Production methane gas from swine manure in a pilot-size digester. Transactions of the ASAE **22** (2): 370-374

Fischer, J.R.; Iannotti, E.L. and Durand, J. (1986). Anaerobic digestion of animal manure. In: Goswami, I. and Yogi, D. (Eds.), Alternative energy in agriculture, Volume 2, Agriculture and Energy. CRC Press, Inc, Florida, USA

Florides, G.A.; Kalogirou, S.A.; Tassou, S.A. and Wrobel, L.C. (2002). Modelling and simulation of an absorption solar cooling system for Cyprus. Solar Energy **72** (1): 43-51

Forrest, L.; Collin, I.; Eaton, M.; Holtzer, R.; Lundberg, B.; Maben, L.; Merz, J.; Parsons, G.; Waite, W. and Williams, J. (1997). Report of the advisory committee on alternatives to rice straw burning. California air resources board, California department of food and agriculture, USA

Fujishima, S.; Miyahara, T. and Noike, T. (2000). Effect of moisture content on anaerobic digestion of dewatered sludge: ammonia inhibition to carbohydrate removal and methane production. Wat. Sci. Technol. **41** (3): 119-127

Gallert, C. and Winter, J. (1997). Mesophilic and thermophilic anaerobic digestion of source-stored organic wastes: effect of ammonia on glucose degradations and methane production. Appl. Microbiol. Biotechnol. **48**: 405-410

Gaskell, D.R. (1992). An Introduction to Transport Phenomena in Materials Engineering. Macmillan Publishing Company, New York, USA

Geber, U. and Björklund, J. (2001). The relationship between ecosystem services and purchased input in Swedish wastewater treatment systems- a case study. Ecol. Engin. **18**: 39-59

Georgacakis, D.; Sievers, D.M. and Iannotti, E.L., (1982). Buffer stability in manure digesters. Agric. Wast. **4**: 427-441

Ghosh, A. and Bhattacharyya, B.C. (1999). Biomethanation of white rotted and brown rotted rice straw. Bioproc. Engin. **20**: 297-302

Ghosh, S. (1986). Methane production from farm wastes. In: El-Halwagi, M.M. (Ed.), Biogas Technology, Transfer and Diffusion. Proceedings of the International Conference, held at the National Research Centre, Cairo, Egypt, Elsevier Applied Science Publishers, London, UK (pp 372-380)

Ghosh, S. and Lall, U. (1988). Kinetics of anaerobic digestion of solid substrates. In: Hall, E.R. and Hobson, P.N. (Eds.), Anaerobic Digestion 1988. Proceeding of the 5th International Symposium on Anaerobic Digestion, Bologna, Italy, 22-26 May 1988, Pergamon press, Oxford, UK

Goss, J.R. and Jain, K.A. (2000). Determination of reactor scaling factors for throttles rice husk gasifier. Biom. Bioen. **18**: 249-256

Grady, C.P.L. and Lim, H.C. (1980). Biological Wastewater Treatment: Theory and Applications. Marcel Dekker, New York, USA

Guerrero, L.; Omil, F.; Mèndez, R. and Lema, J.M. (1997). Treatment of saline wastewaters from fishmeal factories in an anaerobic filter under extreme ammonia concentrations. Biores. Technol. **61** (1): 67-78

Guerrero, L.; Omil, F.; Mèndez, R. and Lema, J.M. (1999). Anaerobic hydrolysis and acidogenesis of wastewaters from food industries with high content of organic solids and protein. Wast. Res. **33** (15): 3281-3290

Haga, K. (1990). Production of Compost from Organic Wastes. Extension Bulletin No 311. Taipei City, Republic of China on Taiwan

Hamdi, M. (1991). Effects of agitation and pretreatment on the batch anaerobic digestion of olive mill wastewater. Biores. Technol. **36**: 173-178

Hamdy, Y.A. (1998). The Current Situation of Egyptian Agricultural Wastes. Proceedings of Anaerobic Treatment of Solid Wastes Workshop, 4 May 1998, Mansoura University, Mansoura, Egypt (pp 1-5) [In Arabic]

Hamelers, H.V.M. (2001). A Mathematical Model for Composting Kinetics. Ph.D. Thesis, Wageningen University, Wageningen, The Netherlands

Hanaki, K.; Hirunmasuwan, S. and Matsuo, T. (1994). Protection of methanogenic bacteria from low pH and toxic materials by immobilisation using polyvinyl alcohol. Wat. Res. **28** (4): 877-885

Hansen, K. H.; Angelidaki, I. and Ahring, B. K. (1998). Anaerobic digestion of swine manure inhibition by ammonia. Wat. Res. **23** (1): 5-12

Hansen, K.H.; Angelidaki, I. and Ahring, B.K. (1999). Improving thermophilic anaerobic digestion of swine manure. Wat. Res. **33**(8): 1805-1810

Harada, Y. (1990). Composting and Application of Animal Wastes. Extension Bulletin No 311. Taipei City, Republic of China on Taiwan

Hartmann, D. and Kaltschmitt, M. (1999). Electricity generation from solid biomass via co-combustion with coal; energy and emission balances from a German case study. Biom. Bioen. **16**: 397-406

Hasan, M. (2003). Deposition and shaking of dry granular piles. A granular dynamics model for reversible transitions between stick and slip contact. Ph.D. Thesis, Wageningen University, Wageningen, The Netherlands

Hashimoto, A.G. (1982). Methane from cattle waste: Effect of temperature, hydraulic retention time and influent substrate concentration on kinetic parameter (K). Biotechnol. Bioeng. **24**: 2039-2052

Hashimoto, A.G. (1983). Thermophilic and mesophilic anaerobic fermentation of swine manure. Agric. Wast. **6**: 175-191

Hashimoto, A.G. (1984). Methane from swine manure: effect of temperature and influent substrate concentration on kinetic parameter (K). Agric. Wast. **9**: 299-308

Hashimoto, A.G. (1986). Ammonia inhibition of methanogenesis from cattle wastes. Agric. Was. **17**: 241-261

Hashimoto, A.G. and Chen, Y.R. (1976). Rheology of livestock waste slurries. Transactions of the ASAE **19** (1): 930-934

Hashimoto, A.G.; Chen, Y.R. and Varel, V.H. (1981a). Theoretical aspects of methane production: State of the art. In: Livestock Waste: A renewable Resource, Proceedings of 4th Annual International Symposium on livestock wastes, Transaction of ASAE, USA (pp 86-91)

Hashimoto, A.G.; Varel, V.H. and Chen, Y.R. (1981b). Ultimate methane yield from beef cattle manure: effect of temperature, constituents, antibiotics and manure age. Agric Wast. **3**: 241-256

Hauserman, W. (1995). From fundamental gasification research to commercial energy production: engineering and economic aspects. In: Chartier, A.A.; Beenackers, C.M. and Grassi, G. (Eds.), Biomass for Energy, Environment, Agriculture and Industry. Proceedings of the 8th European Biomass Conference, Vienna, Austria, 3-5 October 1994. Pergamon, Oxford, UK (pp 1836-1841)

Hawkes, D.L. (1980). Factors affecting net energy production from mesophilic anaerobic digestion. In: Stafford, D.A.; Wheatley, B.I. and Hughes, D.E. (Eds.), Anaerobic Digestion. Applied Science Publishers Ltd, London, UK

Hill, D.J. (1980). Methane Gas production from dairy manure at high solids concentration. Transactions of the ASAE: 122-126

Hill, D.T. (1982). A comprehensive dynamic model for animal waste methanogenesis. Transactions of the ASAE **25** (5): 1374-1380

Hill, D.T. (1983a). Simplified Monod kinetics of methane fermentation of animal wastes. Agric. Wast. **5**: 1-16

Hill, D.T. (1983b). Energy consumption relationships for mesophilic and thermophilic digestion of animal manures. Transaction of the ASAE **26** (3): 841-848

Hill, D.T. (1985). Practical and theoretical aspects of engineering modelling of anaerobic digestion for livestock waste utilisation systems. Transactions of the ASAE: 599-605

Hill, D.T. and Barth, C.L. (1977). Simulation of animal waste digestion. J. Wat. Poll. Contr. Fed. **49**: 2129-2143

Hill, D.T. and Bolte, J.P. (1987). Modeling fatty acid relationships in animal waste anaerobic digesters. Transactions of the ASAE **30** (2): 502-508

Hill, D.T. and Bolte, J.P. (2000). Methane production from low solid concentration liquid swine waste using conventional anaerobic fermentation. Biores. Technol. **74**: 241-247

Hill, D.T. and Cobb, S.A. (1996). Simulation of process steady state in livestock waste methanogenesis. Transactions of the ASAE **39** (2): 565-573

Hill, D.T. and Nordstedt, R.A. (1980). Modelling techniques and computer simulation of agricultural waste treatment processes. Agric. Wast. **2**: 135-156

Hill, D.T.; Cobb, S.A. and Bolte, J.P. (1987). Using volatile fatty acid relationships to predict anaerobic digester failure. Transactions of the ASAE **30** (2): 496-501

Hill, D.T.; Taylor, S.E. and Grift, T.E. (2001). Simulation of low temperature anaerobic digestion of dairy and swine manure. Biores. Technol. **78**: 127-131

Hill, D.T.; Tollner, E.W. and Holmberg, R.D. (1983). The kinetics of inhibition in methane fermentation of swine manure. Agric. Wast. **5**: 105-123

Hills, D.J. and Roberts, D.W. (1981). Anaerobic digestion of dairy manure and field crop residues. Agric. Wast. **3**: 179-189

Hills, D.J. and Stephens, J.R. (1980). Solar energy heating of dairy-manure anaerobic digesters. Agric. Wast. **2**: 103-118

Hobson, P.N. (1983). The kinetics of anaerobic digestion of farm wastes. J. Chem. Technol. Biotechnol. **33B**: 1-20

Hobson, P.N. (1985). A model of anaerobic bacterial degradation of solid substrates in a batch digester. Agric. Wast. **14**: 255-274

Hobson, P.N. (1987). A model of some aspects of microbial degradation of particulate substrates. J. Ferment. Technol. **65**: 431-439

Hobson, P.N. and Richardson, A.J. (1983). The microbiology of anaerobic digestion. In: Pain, B.F. and Hepherd, R.Q. (Eds.), Anaerobic Digestion of Farm Waste. Technical Bulletin 7. The national institute for research in dairying, Reading, England

Hobson, P.N. and Shaw, B.G. (1971). The role of strict anaerobes in the digestion of organic material. In: Sykes, G. and Skinner, F.A. (Eds.), Microbial Aspects of Pollution. Academic press, London. New York

Hobson, P.N. and Shaw, B.G. (1976). Inhibition of methane production by *Methanobacterium Formicicum*. Wat. Res. **10**: 849-852

Hobson, P.N.; Bousfield, S. and Summers, R. (1981). Methane Production from Agricultural and Domestic wastes. Applied Science publishers ltd, London, UK

Hulshoff Pol, L. (2000). Wastewater analysis and characterisation. International short course on anaerobic treatment of industrial wastewater, May 29-Jun 9. Wageningen UR and IHE Delft, The Netherlands

Hunik, J.H.; Hamelers, H.V.M. and Koster, I.W. (1990). Growth rate inhibition of acetolastic methanogens by ammonia in poultry manure digestion. Biolog. Wast. **32**: 285-297

Husain, A. (1998). Mathematical models of the kinetics of anaerobic digestion- a selected review. Biom. Bioen. **14** (5/6): 561-571

IEA (2000). International Energy Agency.http://www.fe.doe.gov/international /egyptover .html

IEA Bioenergy (2001). Biogas upgrading and utilisation. International energy agency. http://www.novaenergie.ch/iea-bioenergy-task37/Dokumente/Biogas%20upgrading.pdf

Jang, Y.S.; Kim, Y.W. and Lee, S.I. (2002). Hydraulic properties and leachate level analysis of kimpo metropolitan landfill, Korea. Waste Manag. **22**: 261-267

Jelinek, T. (1977). Collection, storage and transportation of swine wastes. In: Taiganides, E.P. (Ed.), Animal Wastes. Applied Science Publishers, London, UK

Jenkins, B.M. (1991). Reaction kinetics for the combustion and gasification of rice straw in a circulating fluidised bed reactor system. Agricultural Engineering Department, University of California at Davis, USA

Jenkins, B.M. and Bhatnagar, A.P. (1991). On the electric power potential from paddy straw in the Punjab and the optimal size of the power generation station. Biores. Technol. **37**: 35-41

Jenkins, B.M. and Knutson, G. (1984). Energy balances in biomass handling systems: net energy analysis of electricity from straw. Pap-Am-Soc-Agric-Eng-Microfiche-Collect. Winter 1984. American Society of Agricultural Engineers, USA (pp 3584-3593)

Jenkins, B.M. and Rumsey, T.R. (1985). Field drying of biomass for enhanced performance of renewable energy systems. Agricultural Engineering Department, University of California at Davis, USA

Jenkins, B.M. and Sumner, H.R. (1986). Harvesting and handling agricultural residues for energy. Transactions of ASAE 27: 824-834

Jenkins, B.M.; Bakker, R.R.; Baxter, L.L.; Gilmer, J.H. and Wei, J.B. (1997). Combustion characteristics of leached biomass. In: Bridgwater, A.V. and Boocock, D.G.B. (Eds.), Developments in Thermochemical Biomass Conversion. Blackie Academic & Professional, London (Volume 2, pp 1316-1330)

Jetten, M.S.M; Strous, M.; Pas-Schoonen, K.T.Van de; Schalk, J.; Dongen, U.G.J.M. Van; Graaf, A.A. Van de; Logemann, S.; Muyzer, G.; Loosdrecht, M.C.M. Van; Kuenen, G.J. (1999). The anaerobic oxidation of ammonium. FEMS Microbiol. Rev. **22**: 421-437

Jirka, A. and Carter, M.J. (1975). Micro semi-automated analysis of surface and wastewaters for chemical oxygen demand. Analy. Chem. **47**: 1397-1401

Jothi, G.; Pugalendhi, S.; Poornima, K.; Rajendran, G. (2003). Management of root-knot nematode in tomato Lycopersicon esculentum, Mill., with biogas slurry. Biores. Technol. **89** (2): 169 –170

Kadam, K.; Forrest, L.H. and Jacobson, W.A. (2000). Rice straw as a lignocellulosic resource: collection, processing, transportation, and environmental aspects. Biom. Bioen. **18**: 369-389

Kakezawa, M.; Mimura, A. and Takahara, Y. (1992). Application of two-step composting process to rice straw compost. Soil Sci. Plant Nut. **38** (1): 43-50

Kaupp, A. (1982). Myths and facts about gas producer engine system. Paper presented at first international producer gas conference, 8-12 November 1982, Colombo, Sri Lanka, *cited* from Rajvanshi (1986)

Kaya, A. and Belibağli, K.B. (2002). Rheology of solid Gaziantep Pekmes. J. Food Engineering **54**: 221-226
Kayhanian, M. (1994). Performance of a high-solids anaerobic digestion process under various ammonia concentrations. J.Chem.Technol. Biotechnol. **59**: 349-352
Kelleher, B.P.; Leahy, J.J.; Henihan, A.M.; O'Dwyer, T.F.; Sutton, D. and Leahy, M.J. (2002). Advances in poultry litter disposal technology: A review. Biores. Technol. **83**: 27-36
Keshtkar, A.; Ghaforian, H.; Abolhamd, G. and Meyssami, B. (2001). Dynamic simulation of cyclic batch anaerobic digestion of cattle manure. Biores. Technol. **80**: 9-17
Keshtkar, A.; Meyssami, B.; Abolhamd, G.; Ghaforian, H.; and Khalagi Asadi, M. (2003). Mathematical modelling of non-ideal mixing continuos flow reactors for anaerobic digestion of cattle manure. Biores. Technol. **87**: 113-124
Kirkham, D. and Powers, W.L. (1972). Advanced Soil Physics. John Wiley & Sons, Inc, New York, USA
Kofoed Nielsen, H. and Nielsen, H. (1983). Experiments with Gas Scrubbers as Heat Exchangers in Straw Furnaces. In: Strub, A.; Chartier, P. and Schleser, G. (Eds.), Energy from Biomass. Proceedings of Energy from Biomass, 2^{nd} E.C. Conference, 20-23 September 1983, Berlin, Germany. Applied Science Publishers, London (pp 479-483)
Kofoed Nielsen, H.; Nielsen, H. and Berthelsen, L. (1982). The use of gas scrubber for heat extraction from straw furnaces. In: Grassi, G. and Palz, W. (Eds.), Energy from Biomass. Proceeding of the EC Contractors Meeting, 5-7 May 1982, Brussels. D. Reidel Publishing Company, London, UK (pp 165-169)
Korenaga, T.; Liu, X. and Huang, Z. (2001). The influence of moisture content on polycyclic aromatic hydrocarbons emission during rice straw burning. Chemosphere-Global Change Science **3**: 117-122
Koster, I. W. (1986). Characteristics of the pH-influenced adaptation of methanogenic sludge to ammonia toxicity. J. Chem. Technol. Biotechnol. **36**: 445-455
Koster, I. W. (1989). Toxicity in anaerobic digestion with emphasis on the effect of ammonia, sulfide and long-chain fatty acids on methanogenesis. Ph.D. Thesis. Wageningen University. The Netherlands
Koster, I.W. and Koomen, E. (1988). Ammonia inhibition of the maximum growth rate (μ_m) of hydrogenotrophic methanogens at various pH-levels and temperatures. Appl. Microbiol. Biotechnol. **28**: 500-505
Koster, I.W. and Lettinga, G. (1984). The influence of ammonia-nitrogen on the specific activity of pelletized methanogenic sludge. Agric Wast. **9**: 205-216
Koster, I.W. and Lettinga, G. (1988). Anaerobic digestion at extreme ammonia concentrations. Biol. Wast. **25**: 51-59
Kroeker, E.J.; Schulte, D.D.; Sparling, A.B. and Lapp, H.M. (1979). Anaerobic treatment process stability. J. Wat. Poll. Contr. Fed. **51** (40): 718-727
Krylova, N.I; Khabiboulline, R.E.; Naumova, R.P. and Nagel, M.A. (1997). The influence of ammonia and methods for removal during the anaerobic treatment of poultry manure. J.Chem.Technol.Biotechnol.**70**: 99-105
Kumar, M.; Bartlett, H.D. and Mohsenin, N.N. (1972). Flow properties of animal slurries. Transactions of the ASAE **15** (4): 718-722
Lagerberg, C. (2000). Evaluation of resource flows of tomato production systems under glass accounting to the method of emergy analysis. In: Challa, H; Monteiro, A.A; Heuvelink, E. and Aguiar Pinto, A. (Eds.). Proceedings of the XXV International Horticultural Congress part 9, 2-7 August 1998, Brussels, Belgium
Lagerberg, C. and Brown, M.T. (1999). Improving agricultural sustainability: the case of Swedish greenhouse tomatoes. J. Cleaner Production **7** (6): 421-434

Larsen, H.E.; Munch, B. and Schlundt, J. (1994). Use of indicators for monitoring the reduction of pathogens in animal waste treated in biogas plants. Zentralblatt Fur Hygiene Und Umweltmedizin = Internat. J. Hygiene Environ. Medicine, **195** (5-6): 544-555
Lau, I.W.C. and Fang, H.H.P. (1997). Effect of temperature shock to thermophilic granules. Wat. Res. **31** (10): 2626-2632
Lay, J.J.; Li, Y.Y.; Noike, T.; Endo, J. and Ishimoto, S. (1997). Analysis of environmental factors affecting methane production from high-Solids organic waste. Wat. Sci. Technol. **36** (6-7): 493-500
Lee, S.R.; Cho, N.K. and Maeng, W.J. (1995). Using the pressure of biogas created during anaerobic digestion as the source of mixing power. J. Ferment. Bioeng. **80** (4): 415-417
Lepori, W.A.; Lalk, T.R. and Craig, J.D. (1980). Fluidised bed combustion and gasification of biomass. Agricultural Energy, Vol. 2. Biomass Energy Crop Production. Selected papers and abstracts from the 1980 ASAE National Energy Symposium. American Society of Agricultural Engineers, USA
Lettinga, G. (1996). Sustainable integrated biological wastewater treatment. Wat. Sci. Technol. **33**: 85-98
Lettinga, G. (2001). Digestion and degradation, air for life. Wat. Sci. Technol. **44** (8): 157–176
Liao, P.H.; Chen, A. and Lo, K.V. (1995). Removal of nitrogen from swine manure wastewater by ammonia stripping. Biores. Technol. **54**:17-20
Liliedah, T.; Henrik, K.; Rosen, C. and Sjostron, K. (1999). Analysing fluidised bed sintering through multivariate methods. Dep. of Chem. Eng. & Tech., the Royal Institute of Technology, Se-10044, Stockholm, Sweden
Loehr, R.C. (1977). Pollution Control for Agriculture. Academic Press, New York, USA
Lund, B.; Jensen, V.F.; Have, P. and Ahring, B.K. (1995). Inactivation of virus during anaerobic digestion of manure in laboratory scale biogas reactors. Proceedings of International Meeting on Anaerobic Processes for Bioenergy and Environment, 25-27 January 1995, Copenhagen, Denmark
Mackie, R.I. and Bryant, M.P. (1995). Anaerobic digestion of cattle waste at mesophilic and thermophilic temperatures. Appl. Microbiol. Biotechnol. **43**: 346-350
Mahmoud, N.J.A.H. (2002). Anaerobic pre-treatment of sewage under low temperature (15^{o}C) conditions in an integrated UASB-digester system. Ph.D. Thesis, Wageningen University, Wageningen, The Netherlands
Maibaum, C. and Kuehn, V. (1999). Thermophilic and mesophilic operation of an anaerobic treatment of chicken slurry together with organic residual substances. Wat. Sci. Technol. **41** (1): 231–236
Makaly Biey, E.; Mortier, H. and Verstraete, W. (2000). Nitrogen transfer from grey municipal solid waste to high quality compost. Biores. Technol. **73**: 47-52
Malgeryd, J. and Wetterberg, C. (1996). Physical properties of solid and liquid manures and their effects on the performance of spreading machines. J. Agric. Engng. Res. **64**: 289-298
Marcotte, M., Taherian Hoshahili, A.R. and Ramaswamy, H.S. (2001). Rheological properties of selected hydrocolloids as a function of concentration and temperature. Food Res. Internat. **34**: 695-703
Maynard, A.A. (1991). Intensive vegetable production using composted animal manures. Bulletin 894, The Connecticut Agricultural Experiment Station, New Haven, USA
McCarty, P.L. (1964). Anaerobic waste treatment fundamentals. –Part 3 Toxic materials and their controls. Pub. Works Nov., 91

McCarty, P.L. (2001). The development of anaerobic treatment and its future. In: Anaerobic Digestion for Sustainable Development. Papers of the Farewell Seminar of Prof. Dr. Ir Gatze Lettinga. March 29 and 30, 2001,Wageningen, The Netherlands

McCarty, P.L. and McKinney, R.E. (1961). Salt toxicity in anaerobic digestion. J. Wat. Poll. Contr. Fed. **33**: 399-415

McQueen, A. and Bailey, J.E. (1991). Growth inhibition of hybridoma cells by ammonium ion: correlation with effects on intracellular pH. Bioproc. Engin. **6**: 49-61

Mehta, V.; Gupta, J.K. and Kaushal, S.C. (1990). Cultivation of pleurotus Florida mushroom on rice straw and biogas production from the spent straw. World J. Microbiol. Biotechnol. **6**: 366-370

Melbinger, N.R. and Donnellon, J. (1971). Toxic effects of ammonia nitrogen in high rate digestion. J. Wat. Poll. Contr. Fed. **43** (8): 1658-1668

Metcalf and Eddy, Inc. (2003). Wastewater Engineering, Treatment and Reuse. MC Graw Hill, New York, USA

Mink, G. (2000). Earth Construction Handbook. The Building Material Earth in Modern Architecture. WIT Press, Southampton, UK

Moeller, G. and Torres, L.G. (1997). Rheological characterisation of primary and secondary sludges treated by both aerobic and anaerobic digestion. Biores. Technol. **61**: 207-211

Münch, E.V; Keller, J.; Lant, P. and Newell, R. (1999). Mathematical modelling of prefermenters. I Model development and verification. Wat. Res. **33** (12): 2757-2768

Natarajan, E.; Ohman, M.; Gabra, M.; Nordin, A.; Liliedahl, T. and Roa, A.N. (1998). Experimental determination of bed agglomeration tendencies of some common agricultural residues in fluidised bed combustion and gasification. Biom. Bioen. **15** (2): 163-169

Nilsson, C. (1981). Heat From Wood-Products and Straw. Department of farm buildings, Swedish University of Agricultural Sciences, ISSN 0348-0259, No. (18), Sweden

Noykova, N.; Müller, T.G.; Gyllenberg, M.; Timmer, J. (2002). Quantitative analysis of anaerobic wastewater treatment processes: Identifiability and parameter estimation. Biotechnol. Bioeng. **78** (1): 89-103

O'Keefe, D.M. and Chynoweth, D.P. (2000). Influence of phase separation, leachate recycle and aeration on treatment of municipal sold waste in simulated landfill cells. Biores. Technol. **72** (1): 55-66

Odum, H.T. (1996). Environmental Accounting Emergy and Environmental Decision Making. John Wiley & Sons, INC, New York, US

Odum, H.T. and Peterson, N. (1996). Simulation and evaluation with energy systems blocks. Ecol. Model. **93**: 155-173

Omil, F.; Mendez, R. and Lema, J.M. (1995). Anaerobic treatment of saline wastewaters under high sulfide ammonia content. Biores. Technol. **54**: 269-278

Orth, H.W.; Wilkens, D. and Meyer-Bothling, D. (1983). Investigations of a straw burning furnace. In: Strub, A.; Chartier, P. and Schleser, G. (Eds.), Energy from Biomass. Proceedings of the 2nd E.C. Conference, 20-23 September 1983, Berlin, Germany. Applied Science Publishers, London, UK (pp 465-469)

Ouden, F.W.C. den (1995). Physico-chemical stability of tomato products. Ph.D. Thesis, Wageningen University, Wageningen, The Netherlands

Pathak, B.S.; Jain, A.K. and Dev, D.S. (1985). Biogasification of cattle dung and cattle dung-rice straw mixture at different solid concentrations. Agric. Wast. **13**: 251-259

Pavlostathis, S.G. and Giraldo-Gomez, E. (1991). Kinetics of anaerobic treatment: A critical review. Critical. Rev. Environ. Cont. **21** (5/6): 411-490

Perry, R.H. and Chilton, C.H. (1973). Chemical engineers handbook 5th Ed. McGraw-Hill, New York, USA

Perry, R.H.; Green, D.W. and Maloney, J.O. (1997). Perry's Chemical Engineers' Handbbok Seventh Edition. MaGraw-Hill, New York, USA
Poggi-Varaldo, H. M.; Rodríguez-Vázquez, R.; Fernández-Villagómez, G. and Esparza-García, F. (1997). Inhibition of mesophilic solid-substrate anaerobic digestion by ammonia nitrogen. Appl. Microbiol. Biotechnol. **47**: 284-291
Poggi-varaldo, H.M.; Tingley, J. and Oleszkiewicz, J.A. (1991). Inhibition of growth and acetate uptake by ammonia in batch anaerobic digestion. J. Chem. Technol. Biotechnol. **52**: 135-143
Rajvanshi, A.K. (1986). Biomass gasification. In: Goswami, D.Y. (Ed), Alternative Energy in Agriculture. CRC Press, Inc. Boca Raton, Florida, USA (Vol. 2, pp 83-102)
Rick, S.C.; Nisbet, D.J. and Maciorowski, K.G. (1997). Batch culture growth responses of poultry SALMONELLA TYPHIMURIUM isolate to ammonium salts. Biores. Technol. **60**: 107-111
Robbins, J.E.; Gerhardt, S.A. and Kappel, T.J. (1989). Effect of total ammonia on anaerobic digestion and an example of digestor performance from cattle manure-protein mixtures. Biol. Wast. **27**: 1-14
Robertson, A.W.; Burnett, G.A.; Hobson, P.N.; Bousfield, S. and Summers, R. (1975). Bioengineering aspects of anaerobic digestion of piggery waste. In: Managing Livestock Wastes. Proceedings of 3rd International Symposium ASAE. St. Joseph, MI 49085 (pp 544-548)
Rodale, J.I. (1971). The Complete Book of Composting. Rodale Books, Inc., Emmaus, Pennsylvania, USA
Rollon, A.P. (1999). Anaerobic digestion of fish processing wastewater with special emphasis on hydrolysis of suspended solids. Ph.D. Thesis, Wageningen University, Wageningen, The Netherlands
Sahlström, L. (2003). A review of survival of pathogenic bacteria in organic waste used in biogas plants. Biores. Technol. **87**: 161-166
Salminen, E.; Rintala, J.; Lokshina, L.Ya and Vavilin, V.A. (2000). Anaerobic batch degradation of solid poultry slaughterhouse waste. Wat. Sci. Technol. **41** (3): 33-41
Sánchez, E.; Borja, R.; Weiland, P.; Travieso, L. and Martín, A. (2000). Effect of temperature and pH on the kinetics of methane production, organic nitrogen and phosphorus removal in the batch anaerobic digestion process of cattle manure. Bioproc. Engin. **22**: 247-252
Sanchez, J.; Arijo, S; Muňoz, M.; Moriňigo, M. and Boirrego, J. (1994). Microbial colonisation of different support materials used to enhance the methanogenic process. Appl. Microbiol. Biotechnol. **41**: 480-486
Sanders, W.T.M. (2001). Anaerobic hydrolysis during digestion of complex substrates. Ph.D. Thesis, Wageningen University, Wageningen, The Netherlands
Scheidegger, A.E. (1961). General theory of dispersion in porous media. J. Geophys. Res. **66**: 3273-3278
Siegrist, H. (1996). Nitrogen removal from digester supernatant-comparison of chemical and biological methods. Wat. Sci. Technol. **34** (1-2): 399-406
Siegrist, H. and Batstone, D. (2001). Free ammonia and pH inhibition of acetotrophic methanogenesis at meso and thermophilic conditions. In: Van Velsen, A.F.M. and Verstraete, W.H. (Eds.). Proceedings of the 9th World Conference of Anaerobic Digestion, September 2-6, Antwerp, Belgium
Sievers, D.M. and Brune, D.E. (1978). Carbon/Nitrogen ratio and anaerobic digestion of swine waste. Transactions of the ASAE **21**: 537-541
Singh, R.P. (1978). Energy accounting in food process operations. Food Technol. **32** (4): 40-46

Skea, J. (1995). Technological and policy instruments to mitigate causes and adverse impacts of global environmental change. http://www.nerc.ac.uk/ukgeroff/globe26.htm

Smith, E. M. (1997). Thermal Design of Heat Exchangers, A Numerical Approach, Direct Sizing & Stepwise Rating. John Wiley & Sons, Chichester, UK

Sobotka, M.; Votruba, J.; Havlik, I. and Minkevich, I.G. (1983). The mass energy balance of anaerobic methane production. Folia Microbial. **28**: 195-204

Somayaji, D. and Khanna, S. (1994). Biomethanation of rice and wheat straw. World J. Microbiol. Biotechnol. **6**: 366-370

Sommer, S.G. and Hutchings, N.J. (2001). Ammonia emission from field applied manure and its reduction invited paper. European J. Agronomy **15**: 1-15

Soto, M.; Mèndez, R. and Lema, J.M. (1991). Biodegradability and toxicity in the anaerobic treatment of fish canning wastewaters. Environ. Technol. **12**: 669-677

Speece, R.E. (1983). Anaerobic biotechnology for the industrial wastewater treatment. Environ. Sci. Technol. **17**: 416-427

Sprott, G.D. and Patel, G.B. (1986). Ammonia toxicity in pure cultures of methanogenic bacteria. System. Appl. Microbiol. Biotechnol. **7**: 558-563

Steenari, B.M. and Lindqvist, O. (1998). High temperature reactions of straw ash and the anti-sintering additives kaolin & dolomite. Biom. Bioen. **14** (1): 67-76

Sterling, M.C.; Lacey, R.E.; Engler, C.R. and Ricke, S.C. (2001). Effects of ammonia nitrogen on H_2 and CH_4 production during anaerobic digestion of dairy cattle manure. Biores. Technol. **77**: 9-18

Stevens, M.A. and Schulte, D.D. (1979). Low temperature anaerobic digestion of swine manure. J. Env. Engr. Div, ASCE, **105**: 33-42

Streher, A. (1980). Energy from straw: a comparison of some straw-burning furnaces. Agric. Wast. **2**: 241-252

Stroot, P.G.; McMahon, K.D.; Mackie, R.I. and Raskin, L. (2001). Anaerobic codigestion of municipal solid waste and biosolids under various mixing conditions. I. Digester performance. Wat. Res. **35** (7): 1804-1816

Sukhatme, S. P. (1997). Solar energy principles of thermal collection and storage 2^{th} edition. Tata McGraw-Hill publishing company limited. New Delhi, India

Sung, S. and Liu, T. (2001). Ammonia inhibition on thermophilic aceticlastic methanogens. In: Van Velsen, A.F.M. and Verstraete, W.H. (Eds.). Proceedings of the 9^{th} World Conference of Anaerobic Digestion, September 2-6, Antwerp, Belgium

Tabana, A. (2000). Development of a decision support system for individual dairy farms in mixed irrigated farming systems in the Nile delta. Ph.D. Thesis, Wageningen University, Wageningen, The Netherlands

Tafdrup, S. (1995). Viable energy production and waste recycling from anaerobic digestion of manure and other biomass materials. Biom. Bioen. **9** (1-5): 303-314

Taiganides, E.P. (1977). Composting of feedlot wastes. In: Taiganides, E.P. (Ed.), Animal Wastes (pp 241-251). Applied Science Publishers, London, UK

Ten Brummeler, E. (1993). Dry anaerobic Digestion of the Organic Fraction of Municipal Solid Waste. Ph.D. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands

Ten Brummeler, E. (1999). Full scale experience with the BIOCEL process. In: Meta-Alvarez, J.; Tilche, A. and Cecchi, F. (Eds.). Proceedings of II International Symposium on Anaerobic Digestion of Solid Waste, 15-17 June, Barcelona, Spain (pp308-314)

Thomas, M.V. and Noedstedt, R.A. (1993). Generic anaerobic digestion model for the simulation of various reactor types and substrates. Transactions of the ASAE **36** (2): 537-544

Thomas, R.M.; Baxter, L.L.; Richard, W.B. and Jenkins, B.M. (1995). Alkali deposits found in biomass power plants. A Report for National Renewable Energy Laboratory, NREL Subcontract TZ-2-11226-1

Torres-Castillo, R.; Llabrés-Luengo, P. and Mata-Alvarez, J. (1995). Temperature effect on anaerobic digestion of bedding straw in a one-phase system at different inoculum concentration. Agric., Ecosys. Environ. **54**: 55-66

Tripathi, A.K.; Iyer, P.V.R. and Kandpal, T.C. (1998). A techno-economic evaluation of biomass brquetting in India. Biom. Bioen. **14** (5/6): 479-488

Van Doorn, J.; Bruijn, P.; Vermeij, P.; Kos, B. and Hanse, J. (1995). Combined combustion of biomass, municipal sewage sludge and coal in an atmospheric fluidised bed installation. ECN (Netherlands Energy Research Foundation) report number: C-- 95-096, Petten, The Netherlands

Van Haandel, A. and Lettinga, G. (1994). Anaerobic Sewage Treatment- A Practical Guide for Regions with Hot Climate. John Wiley & Sons. Chichester, UK

Van Lier, J.B. (1995). Thermophilic anaerobic wastewater treatment; temperature aspects and process stability. Ph.D. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands

Van Lier, J.B.; Martin, J.L.S. and Lettinga, G. (1996). Effect of temperature on the anaerobic thermophilic conversion of volatile fatty acids by dispersed and granular sludge. Wat. Res. **30** (1): 199-207

Van Straten, G. and Boxtel, A.J.B. (1996). Progress in process operation by goal oriented advanced control. Annual Rev. Cont. **20**: 209-223

Van Velsen, A.F.M. (1979a). Anaerobic digestion of piggery waste. 2. Start up procedure. Neth. J. Agric. Sci. **27**: 142-152

Van Velsen, A.F.M. (1979b). Adaptation of methanogenic sludge to high ammonia-nitrogen concentrations. Wat. Res. **13**: 995-999

Van Velsen, A.F.M. (1981). Anaerobic digestion of piggery waste. Ph.D. Thesis. Wageningen University. The Netherlands

Van Velsen, A.F.M. and Lettinga, G. (1980). Effect of feed composition on digester performance. In: Stafford, D.A.; Wheatley, B.I. and Hughes, D.E. (Eds.), Anaerobic Digestion. Applied Science Publishers Ltd, London, UK

Varel, V.H.; Hashimoto, A.G. and Chen, Y.R. (1980). Effect of temperature and retention time on methane production from beef cattle waste. Appl. Environ. Microbiol. **40** (2): 217-222

Varel, V.H.; Isaacson, H.R. and Bryant, M.P. (1977). Thermophilic methane production from cattle waste. Appl. Environ. Microbiol. **33** (2): 298-307

Vavilin, V.A.; Rytov, S.V. and Losshina, L.Y.A. (1996). Description of hydrolysis kinetics in anaerobic degradation of particulate organic matter. Biores. Technol. **56**: 229-237

Vavilin, V.A.; Rytov, S.V.; Pavlostathis, S.G.; Jokela, J. and Rintala, J. (2002a). A distributed model of solid waste anaerobic digestion: sensitivity analysis. Proceedings of 3rd International Symposium "Anaerobic Digestion of Solid Wastes", September 18-20, Munich, Germany

Vavilin, V.A.; Shchelkanov, M.Y. and Rytov, S.V. (2002b). Effect of mass transfer on concentration wave propagation during anaerobic digestion of solid waste. Wat. Res. **36**: 2405-2409

Vavilin, V.A.; Shchelkanov, M.Yu.; Lokshina, L.Ya.; Rytov, S.V.; Jokela, J.; Salminen, E. and Rintala, J. (2001). A compartive analysis of a balance between the rates of polymer hydrolysis and acetoclastic methanogenesis during anaerobic digestion of solid waste. In: Van Velsen, A.F.M. and Verstraete, W.H. (Eds.). Proceedings of the 9th World Conference of Anaerobic Digestion, September 2-6, Antwerp, Belgium (part 1, pp191-196)

Veeken, A. and Hamelers, B. (1999). Effect of temperature on hydrolysis rates of selected biowaste components. Biores. Technol. **69:** 249-254

Veeken, A.; Kalyuzhnyi, S.; Scharff, H. and Hamelers, B. (2000). Effect of pH and VFA on hydrolysis of organic solid waste. J. Environ. Engin. **December**: 1076-1081

Veeken, A.H.M. and Hamelers, B.V.M. (2000). Effect of substrate-seed mixing and leachate recirculation on solid state digestion of biowaste. Wat. Sci. Technol. **41** (3): 255-262

Verhoff, F.H.; Tenney, M.W. and Echelberger, W.F. (1974). Mixing in anaerobic digestion. Biotechnol. Bioeng. **XVI**: 757-770

Vidal, G.;Carvalho, A.; Mèndez, R. and Lema, J.M. (2000). Influence of the content in fats and proteins on the anaerobic biodegradability of dairy wastewaters. Biores. Technol. **74**: 231-239

Viéitez, E.R. and Ghosh, S. (1999). Biogasification of solid wastes by two-phase anaerobic fermentation. Biom. Bioen. **16** (5): 299-309

Viesturs, U.; Teliseva, G.; Dobele, G. and Dizbite, T. (1995). Energy production from biomass: World experience. Proceedings of the Latvian Academy of Science. Section B, No 9 /10 (578/579), The Latvian Academy of Science, Latvia (pp 97-112)

Vijil, J.; Amand, L.E.; Leckner, B. and Ljungstrom, E. (1984). Fluidised bed combustion: a comparison between biomass and coal. Proceedings of BIOENERGY 84 World Conference, Gothenburg, Sweden (Vol. IV, pp 113-118)

Visser, A.; Gao, Y. and Lettinga, G. (1993). Effects of short-term temperature increases on the thermophilic anaerobic breakdown of sulfate containing synthetic wastewater. Wat. Res. **27** (4): 541-550

Warnecke, R. (2000). Gasification of biomass: comparison of fixed bed and fluidised bed gasifier. Biom. Bioen. **18**: 489-497

Watanabe, I. (1984). Anaerobic Decomposition of Organic Matter in Flooded Rice Soils. In: Organic Matter and Rice, International Rice Research Institute, Los Banos, Laguna, Philippines (pp 237-258)

Webb, A.R. and Hawkes, F.R. (1985). The anaerobic digestion of poultry manure: variation of gas yield with influent concentration and ammonia-nitrogen levels. Agric. Wast. **14**: 135-156

Weber, S.; Lueders, T.; Friedrich, M.W. and Conrad, R. (2001). Methanogenic populations involved in the degradation of rice straw in anoxic paddy soil. FEMS Microbiol. Ecol. **38**: 11-20

Wellinger A. and Kaufmann R. (1982). Biogasproduktion aus Schweingülle in nicht beheizten Anlagen. *Blätter für Landtechnik*, **198**: 1-12 [in German]

Wellinger, A. (1984). Anaerobic digestion: A review comparison with two types of aerobic system for manure treatment and energy production on the small farm. Agric. Wast. **10**: 117-133

Wiegant, W.M. (1986). Thermophilic anaerobic digestion for waste and wastewater treatment. Ph.D. Thesis, Department of Environment Technology, Agricultural University, Wageningen, The Netherlands

Wiegant, W.M. and Zeeman, G. (1986). The mechanism of ammonia inhibition in the thermophilic digestion of livestock wastes. Agric. Wast. **16**: 243-253

Wilen, C. and Rautalin, A. (1995). Handling and feeding of biomass to pressurised reactors: safety engineering. Biores. Technol. **46** (1/2): 77-85

World Energy Council (1993). http://www.worldenergy.org/wecgeis/publications/reports/rural/case_studies/annII_egypt.asp

Wunderground (2000). www. wunderground.com

Yaghoubi, M.; Azizian, K. and Kenary, A. (2003). Simulation of Shiraz solar power plant for optimal assessment. Ren. Energy **28**: 1985-1998

Yang, Y. and Speece, R.E. (1985). Effects of engineering controls on methane fermentation toxicity response. J. Wat. Poll. Contr. Fed. **57** (12): 1134-1141

Yang, Z.; Niimi, H.; Kanda, K. and Suga, Y. (2003). Measurement of ammonia volatilisation from a field in upland Japan, spread with cattle slurry. Environ. Poll. **121**: 463-467

Zeeman, G. (1991). Mesophilic and psychrophilic digestion of liquid manure. Ph.D. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands

Zeeman, G. (1994). Methane production/emission in storages for animal manure. Fert. Res. **37**: 207-211

Zeeman, G., and Sanders, W. (2001). Potentials of anaerobic digestion of complex waste (water). Papers of the farewell seminar of Prof. Dr. Ir. Gatze Lettinga. March 29 - 30,Wageningen, The Netherlands

Zeeman, G.; Koster-Treffers, M.E. and Halm, H.D. (1983). Anaerobic digestion of dairy cow manure. In: Van den Brink, W.J. (Ed.). Proceedings of the European Symposium on Anaerobic Wastewater Treatment. TNO corporate communication department, The Hague, The Netherlands

Zeeman, G.; Koster-Treffers, M.E. and Halm, H.D. (1985a). Laboratory and farm scale anaerobic digestion in the Netherlands. In: Pain, B.F. and Hepherd, R.Q. (Eds.), Anaerobic Digestion of Farm Waste, Technical Bulletin 7. The national institute for research in dairying, Reading, UK

Zeeman, G.; Sanders, W. and Lettinga, G. (2000). Feasibility of the on-site treatment of sewage and swill in large buildings. Wat. Sci. Technol. **41** (1): 9-16

Zeeman, G.; Wiegant, W.M.; Koster-Treffers, M.E. and Lettinga, G. (1985b). The influence of the total ammonia concentration on the thermophilic digestion of cow manure. Agric. Wast. **14**: 19-35

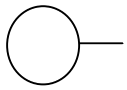
Zhang, R. and Zhang, Z. (1999). Biogasification of rice straw with an anaerobic-phase solids digester system. Biores. Technol. **68**: 235-245

Zinder, S.H.; Anguish, T. and Cardwell, S.C. (1984). Effect of temperature on methanogenesis in a thermophilic (58^{o}C) anaerobic digestor. Appl. Environ. Microbiol. **Apr**: 808-813

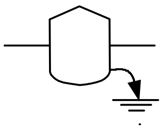
APPENDICES

Appendix A: Some symbols used in EMERGY analysis (Odum and Peterson, 1996)

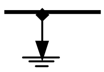
Figure A.1 shows energy system symbols and definitions (Odum and Peterson, 1996)



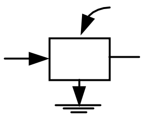
Source. Outside source of energy delivering forces according to a program controlled from outside; a forcing function.



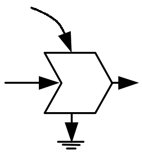
Tank. A compartment of energy storage within the system storing a quantity as the balance of inflows and outflows; a state variable.



Heat sink. Dispersion of potential energy into heat that accompanies all real transformation processes and storages, loss of potential energy from further use by the system.



Box. Miscellaneous symbol to use for whatever unit or function is labelled.



Interaction. Interactive interaction of two pathways coupled to produce an outflow in proportion to a function of both.

Fig. A.1. Energy system symbols and definitions (Odum and Peterson, 1996)

Appendix B: Some calculations of EMERGY analysis

Table B.1. Emergy analysis of 10 m^3 CSTR system with conventional heating system*.

Input	*Unit*	*Unit year^{-1}*	*Transformity (seJ unit^{-1})*	*Reference for transformity*	*Solar Emergy (seJ year^{-1})*
Solar	J	4.1 E+10	1	4	4.1 E+10
Concrete	kg	259.3	6.21 E+11	1 and 2	1.6 E+14
Insulation	kg	6.8	1.67 E+12	1 and 2	1.1 E+13
Heat exchanger (Steel)	kg	0.3	2.77 E+12	1	8.9 E+11
Recovery unit (steel)	kg	4.6	2.77 E+12	1	1.3 E+13
Insulation for heat recovery	kg	0.3	1.67 E+12	1 and 2	4.7 E+11
Connecting pipes	kg	2	2.77 E+12	1	5.4 E+12
Insulation for connecting pipes	kg	0.3	1.67 E+12	1 and 2	5.2 E+11
Pumps and valves	kg	0.9	2.77 E+12	1	2.4 E+12
Agitator	kg	1.2	2.77 E+12	1	3.3 E+12
Heater	kg	20	2.77 E+12	1	5.5 E+13
Human Labour	J	1.4 E+08	7.38 E+06	3	1.1 E+15
Agitation	J	1.5 E+09	2.00 E+05	3	3.0 E+14
Pumping	J	6.1 E+08	2.00 E+05	3	1.2 E+14
Heating including start up	J	1.6 E+10	4.80 E+04	4	7.6 E+14
Maintenance		----	-----		6.6 E+13
Transformity (seJ J^{-1})					2.26 E+04

(1) Brown and Ulgiati (2002); (2) Bjorklund *et al.*, (2001); (3) Bastianoni *et al.*, (2001); (4) Odum (1996)

* The lifetime of the system components is assumed to be 25 years.

Table B.2. Emergy analysis of 10 m^3 STAR*

Input	*Unit*	*Unit year^{-1}*	*Transformity (seJ unit^{-1})*	*Reference for transformity*	*Solar Emergy (seJ year^{-1})*
Concrete	kg	259.3	6.21 E+11	1 and 2	1.6 E+14
Insulation	kg	6.8	1.67 E+12	1 and 2	1.1 E+13
Heat exchanger (Steel)	kg	0.3	2.77 E+12	1	8.9 E+11
Recovery unit (steel)	kg	4.6	2.77 E+12	1	1.9 E+13
Insulation for heat recovery	kg	0.3	1.67 E+12	1 and 2	4.7 E+11
Connecting pipes	kg	2	2.77 E+12	1	5.4 E+12
Insulation for connecting pipes	kg	0.3	1.67 E+12	1 and 2	5.2 E+11
Pumps and valves	kg	0.9	2.77 E+12	1	2.4 E+12
Agitator	kg	1.2	2.77 E+12	1	3.3 E+12
Agitation	J	1.5 E+09	2.00 E+05	3	3.0 E+14
Pumping	J	6.1 E+08	2.00 E+05	3	1.2 E+14
Aluminium	kg	1.7	1.77 E+13	5	3.1 E+13
Copper pipes	kg	0.9	6.80 E+13	6	6.1 E+13
Glass	kg	4.8	6.43 E+09	7	3.1 E+10
Wood	kg	34.6	4.04 E+11	3	1.4 E+13
Collector insulation	kg	1.1	1.67 E+12	1 and 2	1.8 E+12
Auxiliary Heater	kg	5.0	2.77 E+12	1	1.4 E+13
Conventional heating (auxiliary + start up)	J	1.3 E+09	4.80 E+04	4	6.3 E+13
Heating emergy (solar)	J	5.5 E+10	1	4	5.5 E+10
Human Labour	J	1.4 E+08	7.38 E+06	3	1.1 E+15
Maintenance	5 %	----	-----		6.9 E+13
Transformity (seJ J^{-1})					1.71 E+04

(1) Brown and Ulgiati (2002); (2) Bjorklund *et al.*, (2001); (3) Bastianoni *et al.*, (2001); (4) Odum (1996); (5) Lagerberg and Brown(1999);(6) Geber and Björklund (2001);(7)Lagerberg (2000).

* The lifetime of the system components is assumed to be 25 years.

Summary

Summary

From the studies presented in this thesis, it is clear that cattle waste represents one of major waste flows in Egypt. Traditionally, most of this waste is used as fertiliser or as fuel (by direct burning after drying), but a large portion is lost in the handling. This leads to environmental pollution problems and losses of organic matter. So a suitable technology (economic and easy for application) enabling the production of energy with preservation of the non biodegradable organic matter and nutrients should be applied for the disposal of cattle waste. Anaerobic digestion (AD) looks an attractive option (Lettinga, 2001), because this method represents one of the renewable energy production technologies commonly used for animal wastes. It has many benefits from the sustainability point of view (Lettinga, 2001), because besides the production of renewable energy in the form of biogas a high quality organic fertiliser can be obtained, especially also under thermophilic conditions. However, the application of thermophilic digestion of animal waste may suffer from high-energy demands as compared to mesophilic digestion systems, while in addition, the process may be more vulnerable for inhibitory/toxic compounds such as high concentrations of ammonia, a compound normally present in high concentrations in animal waste. Ammonia may affect not only methanogenesis but also the hydrolysis step (Zeeman, 1991).

The research presented in this thesis concerns the design of a Solar Thermophilic Anaerobic Reactor (STAR) aiming at maximising the net energy production from the thermophilic digestion of liquid and solid cattle wastes. For this purpose experimental work is combined with modelling studies. In the experimental studies, the effect of temperature on the rheological properties of liquid cattle manure is elucidated. The effect of temperature and temperature fluctuations (downward and upward) on the performance of a completely stirred tank reactor (CSTR), treating liquid cattle manure is studied, while in addition emphasis is given to the assessment of the effect(s) of ammonia on anaerobic hydrolysis of liquid cattle manure. Solid manure is digested in another type of reactor. Each week a layer of fresh manure is added to the reactor, which becomes more filled. This is so called an accumulation system. In this layered system, the lower the layer the longer it is digesting in the reactor. The effects of temperature, leachate recirculation and different modes of addition of seed material (inoculum) on the performance of an accumulation system (AC) are investigated. In the modelling studies, the interaction between the environmental disturbances (*e.g.* available solar energy and ambient air temperature) under Egyptian climatic conditions and the STAR performance is evaluated. In addition, a model for the biological steps involved in the AD of solid cattle waste in an AC system is developed and calibrated with the experimental data.

Liquid manure

The results obtained in the assessment of the rheological properties of liquid manure reveal that manure has non-Newtonian flow properties. The results showed also that manure behaves like 'real plastic' material. The fitting of the experimental data to the power-law model shows that the magnitude of the consistency coefficient decreases with temperature increase. Moreover, the results show that the Arrhenius-type model fits very well the temperature effect on manure viscosity with calculated activation energy of 17.0 ± 0.3 kJ mol^{-1}.

The results obtained for the effect of temperature (50 and 60°C) and temperature fluctuations (downward and upward regime) on the performance of CSTR's at two HRT's (10 and 20 days) show that the methane production rate at 60°C is lower than that at 50°C at almost all experimental conditions. At 'steady state' conditions, hydrolysis is negatively affected by temperature increase in the temperature range of 50 to 60ºC. The maximum specific methanogenic activity (SMA) of the digested manure becomes lower in reactors operated at shorter HRT and upward temperature fluctuations affect the SMA more severely than downward temperature fluctuations. With respect to the effect of ammonia, a high concentration of free ammonia not only negatively affects the acetate-utilising bacteria, but also the hydrolysis and acidification process. However, the reason(s) for the detrimental effect on hydrolysis is still not clear.

These experimental results indicate that indeed it might be attractive to use available solar energy under Egyptian climatic conditions as a heating source for a simple designed STAR (i.e. without the need for heat storage during night), because any detrimental effects on the activity of micro-organisms, especially for reactors operated at 50°C and 20 days HRT, can be prevented easily.

The effect of ammonia on hydrolysis of liquid cattle manure at thermophilic conditions (50 and 60°C) has been studied in batch experiments at 20 days digestion time. The experimental rate of hydrolysis of cow manure can be well fitted by first order kinetics. The rate-limiting step is seriously affected by the imposed digestion temperature and ammonia concentration. At each of the studied temperatures the calculated first hydrolysis constant (k_h) decreases with an increase of both the total ammonia and the free ammonia concentrations, and apparently more or less linearly. These results are in accordance with those of other researchers (*e.g.* Van Velsen, 1981; Zeeman, 1991) who found a decrease of the hydrolysis of both swine and cattle manure with the increase of total and free ammonia concentrations.

A modelling study has been carried out to study the effect of adding a preheater to the CSTR system on the energy efficiency of the system. The results show that the additional preheater can not be recommended as it results in a drop of the energy efficiency. The same model shows that a better insulation of the system results in a higher energy efficiency. Moreover, to obtain a thermal efficiency of 50%, a maximum overall heat transfer coefficient of 1 $Wm^{-2}K^{-1}$ is needed. The implementation of a solar energy system mounted on the reactor roof only slightly improves the efficiency for large reactors, but for small *(≤ ca* 10 m^3) reactors the improvement is significant. A thermal energy efficiency of 90% can be obtained for the STAR system.

The dynamics of a 10 m^3 STAR in relation to variations of ambient air temperature and solar energy flux has been studied in a simulation model, consisting of two system configurations: the first configuration is a simple one and the second is an integrated system. The latter includes an extra chamber for the pumps and the heat recovery unit. Heat recovery from the effluent to heat the influent is included in the model. The simulation results show that the influent temperature increases about 10-20°C by using the heat recovery unit. A daily temperature fluctuation of less than 1 K and a seasonal temperature reduction of 5K are realised. Based on the experimental results presented in this study and those of Angelidaki and Ahring (1994), it can be demonstrated that such reactor can be operated without harming the microbial activity. The application of an integrated system is recommended from both process technological and energetical point of view. Moreover, our simulation results also show that an overall energy efficiency (i.e. thermal and electrical) of the integrated STAR of 95% can be achieved.

Solid manure

In a non-mixed AC system treating solid cattle wastes, a higher methane production rate was found at an operational temperature of 50^oC compared to 40^oC. A pronounced stratification of substrate and intermediate products (VFA and COD_{dis}) manifests along the reactor height, which mainly can be due to the presence of two different zones: the inoculum zone and the substrate zone (Ten Brummeler, 1993; Veeken and Hamelers, 2000). This stratification also results from the manure adding at time intervals. The extent of this stratification remains lower at higher moisture content of the mixture, and then also the methane production is higher.

The effects of both leachate recirculation and different addition modes of the seed material (inoculum) on the AC performance have been assessed. Leachate recirculation improves significantly the methane production rate and stratification of the intermediates remains significantly lower. The positive effect of leachate recirculation also has been demonstrated by various other researchers, *e.g.* Veeken and Hamelers (2000). In case seed sludge addition is omitted the system performance remains very poor, but by distributing 10% (V/V) of seed material with the feed a pronounced higher methane production rate is found while profile of the intermediates is distinctly less pronounced.

The model calculations for a stratified AC system are in good agreement with the experimental data for methane production. However the model does not fit accurately the all phenomena included in the model, such as the course of the concentrations of the intermediates (*i.e.* COD_{dis} and VFA).

The interaction between the available solar energy at Egyptian climatic conditions and the temperature in a 10 m^3 stratified AC system working with a flat plate solar collector (STAR) has been simulated, *i.e.* the temperature profile of the different layers during winter and summer period. The simulation shows that for a well-insulated AC reactor (i.e. heat transfer coefficient of the insulation material of 0.3 $Wm^{-2}K^{-1}$), a minimum reactor temperature of 44.5 during winter and 47.6^oC during summer is achieved, which is within the range to provide thermophilic biomethanation.

System application and evaluation

The results obtained in this study lead to the recommendation to apply a solar heating system for biogas production under thermophilic conditions instead of a conventional heating system. Decentralised and small-scale systems are recommended in order to reduce the transport costs of the slurry. The produced biogas can be used in villages for heating purposes. The daily produced methane from a 1 m^3 reactor could cover the daily energy requirements for one person, which amounts in Egyptian rural regions to about 0.65 m^3 of biogas (El-Shimi, 1994). Moreover, the effluent which is hygienically reliable, can be used either directly as a fertiliser or can be used as a feedstock for composting process by mixing it with a high C/N ratio material like rice straw, which represents one of the major agricultural wastes in Egypt. This composting process will solve the pollution problems of the direct burning of rice straw in the fields, as applied generally nowadays, while at the same time an easy-transferable organic fertiliser (i.e. compost) is produced.

Economically, the STAR system will be more costly in its construction than the conventional heated system. The EMERGY concept is applied to evaluate the system sustainability (*e.g.* Brown and Herendeen, 1996; Brown and Ulgiati, 2002). Based on our preliminary results, the STAR system has a 20% better transformity than the conventional heated system, which proves a higher sustainability of the system. The transformity is defined as a measure for the amount of direct or indirect environmental work required to generate a service or product (Lagerberg, 2000).

Concluding, the STAR can be recommended from the point of view of energy economics as well as in the light sustainability criteria. Moreover, the operation of an AC system for solid manure treatment is a quite well feasible option when the seed material (inoculum) is distributed with the feed or by applying leachate recirculation as well. Of course the abundance of solar energy during the year in Egypt is an important success factor for STAR.

Samenvatting:

Zonnebiogasreactor voor duurzame energieproductie

Volgens dit proefschrift is koeienmest een van de voornaamste afvalstromen in Egypte. Het grootste deel wordt traditioneel gebruikt als bemesting of (in gedroogde vorm) als brandstof. Echter een groot deel gaat tijdens het verwerken verloren. Dit leidt tot milieuvervuiling en verlies van organische stoffen. Betere technologieën zijn nodig voor hergebruik van koeienmest, zowel in de vorm van brandstof als in de vorm van mest. Een veelgebruikte methode om duurzaam energie uit dierlijke afval te produceren is anaërobe vergisting. Deze methode is duurzaam omdat het naast hernieuwbare energie in de vorm van biogas, ook organische mest van hoge kwaliteit oplevert (Lettinga, 2001). Dit laatste gebeurt echter onder thermofiele omstandigheden, hetgeen relatief veel energie kost. Daarbij is het vergistingsproces onder hoge temperaturen ook gevoeliger voor hoge ammonia concentraties met een remmende werking. Ammonia wordt in het algemeen snel in hoge concentraties in urine gevormd. Behalve op de methanogenese kan het ook een negatieve invloed hebben op de hydrolyse (Zeeman, 1991).

In dit proefschrift worden laatstgenoemde problemen ondervangen door een ontwerp van een anaërobe, thermofiele reactor, verwarmd met zonne-energie (Engelse afkorting STAR: Solar Thermophilic Anaerobic Reactor). De STAR maximaliseert de netto energieproductie van de thermofiele omzetting van vloeibare of vaste koeienmest. Het onderzoek bevat zowel experimenten als modelstudies. Experimenteel is eerst de invloed van de temperatuur op de rheologische eigenschappen van vloeibare mest onderzocht. Vloeibare mest wordt vergist in een goed geroerde tank reactor (CSTR), waar continu nieuwe mest (langzaam) instroomt en verwerkte mest langzaam weer uitstroomt. De invloed van temperatuur en temperatuurfluctuaties op het functioneren van de mestvergisting in een CSTR is ook experimenteel onderzocht. Daarbij is ook naar de invloed van ammonia op de anaërobe hydrolyse gekeken. Vaste mest wordt anders verwerkt: het wordt dagelijks toegevoerd aan de reactor, zodat deze steeds verder gevuld wordt. Dit is het zogenaamde accumulatiesysteem (AS). Zo ontstaat een gelaagd systeem, in verschillende stadia van omzetting. In het AS voor vaste mest worden de effecten van temperatuur, recirculatiewater en verschillende manieren van startcultuur toevoeging onderzocht op de mate van vergisting. In modelstudies wordt de werking van de STAR onder Egyptische klimatologische omstandigheden geëvalueerd. Vooral de beschikbare zonnestraling en de omgevingstemperatuur zijn relevant. Tenslotte wordt een model voor de anaërobe omzetting van vaste mest ontwikkeld en geverifieerd met experimentele gegevens.

Vloeibare mest

Uit de experimenten voor de rheologische eigenschappen blijkt vloeibare mest niet Newtoniaans gedrag te vertonen: het vertoont plastisch gedrag. De consistentie coëfficiënt, die uit de metingen volgde, is lager bij hogere temperaturen. Verder blijkt de Arrhenius vergelijking goed te kloppen met het experimentele temperatuureffect op de viscositeit van de mest: de activeringsenergie is 17.0 ± 0.3 kJ mol^{-1}.

Uit de experimenten met vloeibare mest in CSTR's (met verblijftijden van 10 en 20 dagen) blijkt bijna steeds, dat de methaanproductiesnelheid bij 50^oC hoger is dan bij 60^oC. Onder stationaire omstandigheden wordt de hydrolyse negatief beïnvloed door een

temperatuurtoename van 50 naar 60°C. De maximale specifieke methanogene activiteit van de vergiste biomassa is lager in reactoren met kortere verblijftijd. Dit effect was sterker aanwezig bij opwaartse dan bij neerwaartse temperatuurfluctuaties. Nader onderzoek naar het effect van ammonia wees uit, dat een hoge concentratie van vrij ammonia niet alleen de acetaatverbruikende bacteriën, maar ook de hydrolyse en acidificatie negatief beïnvloedt. De oorzaak van de slechtere hydrolyse is echter nog niet duidelijk.

Onder de klimatologische omstandigheden van Egypte is het inderdaad aantrekkelijk om zonne-energie voor de verwarming van de reactor te gebruiken. Ook zonder warmteopslag gedurende de nacht kan een redelijk eenvoudige STAR goed functioneren volgens de modelberekeningen. De kleine neerwaartse temperatuurfluctuaties verminderen de activiteit van de micro-organismen nauwelijks. Vooral als de reactor op 50°C met een verblijftijd van 20 dagen wordt gebruikt, voldoet het systeem goed.

Het effect van ammonia op de hydrolyse van vloeibare mest is bestudeerd voor thermofiele (50 en 60°C) omstandigheden in batch experimenten gedurende 20 dagen. De hydrolyse van de koeienmest kan goed worden gemodelleerd met een eerste orde reactie. De belangrijkste invloeden op de reactiesnelheid zijn de (opgelegde) temperatuur en de ammonia concentratie. Bij elke temperatuur nam de berekende hydrolyse constante (k_h) min of meer lineair af met zowel toenemende totale als toenemende vrije ammonia concentratie. Dit komt goed overeen met bevindingen van b.v. Van Velsen (1981) en Zeeman (1991), die een zelfde afname van hydrolyse snelheid vonden.

Het effect van het voorverwarmen van de ingaande meststroom van de CSTR is met een model geëvalueerd. Het bleek meer energie te kosten dan op te leveren. Met hetzelfde model is ook aangetoond dat een hogere isolatiewaarde van de reactor tot een hogere energie-efficiëntie leidt. Een totale warmtedoorgangscoëfficiënt van maximaal 1 $Wm^{-2}K^{-1}$ is nodig om 50% rendement te halen. Als een STAR wordt gebruikt, door een vlakke plaat zonnecollector op het dak van de reactor te monteren, vergroot dat het energierendement. Voor grote reactors is de verbetering minimaal door het relatief kleine dakoppervlak, maar voor kleine reactoren ($\leq$ 10 m^3) is de verbetering aanzienlijk. Een maximaal rendement van 90% kan met zo'n STAR worden bereikt.

De veranderingen van luchttemperatuur en zonnestraling, gekoppeld aan de dynamiek van de reactor zijn ook gemodelleerd. Er is uitgegaan van een STAR van 10 m^3 met losse componenten. Een tweede model is gemaakt met alle onderdelen geïntegreerd, zodat zoveel mogelijk afvalwarmte in het systeem blijft. Vooral de warmteterugwinning uit de uitgaande verwerkte mest blijkt erg voordelig te zijn, omdat hiermee de ingaande stroom mest kan worden voorverwarmd met 10-20°C. De dagelijkse temperratuur fluctuatie in de reactor wordt zo teruggebracht tot minder dan 1 K en de jaarlijkse zomer-winter fluctuatie tot ongeveer 5 K. Volgens het onderzoek van Angelidaki en Ahring (1994) hebben zulke kleine fluctuaties een verwaarloosbare invloed op de activiteit van de micro-organismen. Het geïntegreerde systeem werkt zowel vanuit de energiebehoefte als vanuit de biologische activiteit beter dan de losse componenten: uit de simulaties blijkt zelfs een jaarlijks energie rendement van 95% mogelijk.

Vaste mest

In de gelaagde accumulatiereactor voor vaste koeienmest, is bij een reactortemperatuur van 50°C een hogere methaanproductie gevonden dan bij 40°C. De gelaagdheid bleek ook uit de grote verschillen in concentratie over de hoogte van tussenproducten als VFA and COD_{dis}. Ook de grote verschillen in beginconcentratie van de startcultuur in de onderste laag in vergelijking met de later aangebrachte lagen zorgt voor de gelaagdheid (Ten Brummeler, 1993; Veeken and Hamelers, 2000). Verder is de gelaagdheid het gevolg van de verschillende tijdstippen, waarin de verschillende lagen zijn toegevoegd aan de reactor. Een langere verblijftijd in de reactor geeft natuurlijk een hogere totale omzetting. Het blijkt dat naarmate de vaste mest natter is, de gelaagdheid afneemt en de methaanproductie hoger wordt.

Het lekwater, met de daarin opgeloste stoffen kan weer aan de bovenzijde van de reactor worden toegevoegd. Het effect van deze recirculatie is experimenteel bepaald. De methaanproductie was bij lekwater recirculatie aanzienlijk hoger dan zonder recirculatie. Dit is in overeenstemming met de bevindingen van bijvoorbeeld Veeken and Hamelers (2000). Ook de invloed van de startcultuur is experimenteel bepaald. Zonder startcultuur kwam de methaanproductie nauwelijks op gang. Het mengen van 10% (V/V) startcultuur bij elke nieuwe toegevoegde laag geeft nog betere resultaten dan alleen startcultuur op de bodem van de reactor: de methaanproductie is veel hoger, hetgeen veel minder gelaagdheid geeft in de profielen van tussenproducten.

Het gelaagde accumulatiesysteem is ook gemodelleerd. Het model kan goed de methaanproductie voorspellen. Echter het modelleren van de tussenstappen is nogal moeizaam: de gemeten en berekende concentraties van de tussenproducten (i.e. COD_{dis} en VFA) komen slechts kwalitatief overeen.

Onder Egyptische klimatologische omstandigheden is de temperatuurverdeling in een gelaagd accumulatiesysteem van 10 m^3 met zonnecollector gesimuleerd. In deze STAR worden de temperatuurprofielen gedurende zomer en winter doorgerekend. Hieruit blijkt dat een goed geïsoleerd reactor, met een warmtedoorgangscoëfficiënt van 0.3 $Wm^{-2}K^{-1}$, een minimum temperatuur van 44.5 ^oC in de winter en 47.6^oC in de zomer te kunnen bereiken, hetgeen ruim voldoende is voor een goede methaanproductie.

Toepassingen en evaluatie

Het is zonneklaar geworden dat zonne-energie goed toegepast kan worden om biogas te produceren onder thermofiele omstandigheden. Gedecentraliseerde, kleinschalige systemen worden aanbevolen om de transportkosten van de mest zo laag mogelijk te houden. Het geproduceerde biogas (vooral methaan) kan in de dorpen gebruikt worden voor verwarming of koken. De dagproductie methaan van een reactor van 1 m^3 reactor is voldoende voor de dagelijkse energiebehoefte van één persoon, hetgeen op het Egyptische platteland overeen komt met ongeveer 0.65 m^3 biogas (El-Shimi, 1994). Daarbij is de vergiste koeienmest een hygiënische meststof, die direct op het land kan worden toegepast. Ook is het mogelijk om de vergiste koeienmest met rijststro te mengen en vervolgens te composteren. De compost heeft dan een betere C/N verhouding dan de mest en is ook verder met minder (stank-)problemen te verwerken. Daarbij wordt rijststro op een betere manier gebruikt dan de traditionele, milieuvervuilende verbranding op het veld.

De bouwkosten van een STAR zullen in het algemeen hoger zijn dan die van een conventioneel verwarmde reactor, maar de STAR zal op het gebied van duurzaamheid beter scoren. Het zogenaamde EMERGY concept is gebruikt om de mate van duurzaamheid te evalueren (b.v. Brown en Herendeen, 1996; Brown en Ulgiati, 2002). Een grove berekening volgens dit principe wijst uit dat de STAR een 20% hogere transformiteit heeft dan een conventioneel verwarmde reactor. De transformiteit is een maat voor alle directe of indirecte energie die nodig is om een bepaalde dienst of product te leveren (Lagerberg, 2000).

Samenvattend kan het STAR concept worden aanbevolen, zowel vanuit energieopbrengst als vanuit duurzaamheid. Zelfs vaste mest kan goed worden verwerkt in een accumulatiesysteem, mits lekwater recirculatie en een verdeelde startcultuur wordt toegepast. Natuurlijk is de overvloed aan zonne-energie gedurende het hele jaar in Egypte een belangrijke succesfactor van de STAR.

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Curriculum vitae

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