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WAGENINGEN UR

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Fotokatalytische oxidatie op TiO_2 van methaan uit stallen en drijfmestopslagen

R.W. Melse
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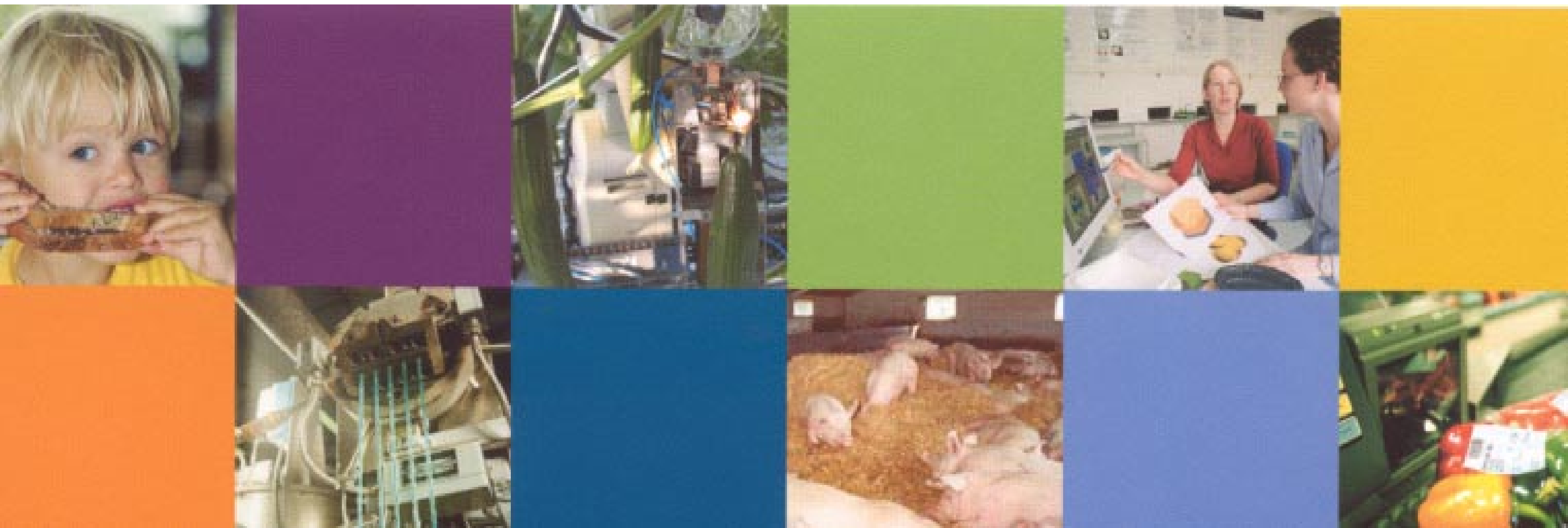
Report 011



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Colophon

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Abstract

The aim of this research was to develop a laboratory scale photocatalytic air filter installation for the oxidation of methane (CH_4) at room temperature and atmospheric pressure, in order to reduce the emission of methane from animal houses and liquid manure storages. Experiments on titanium dioxide (TiO_2) coated glass wool, exposed to 365 nm radiation [CH_4 = 80 -125 ppm], were not successful because of 'ageing'. On TiO_2 coated quartz fibres degradation of methane [CH_4 = 250 ppm] was about 20 times faster. In literature higher degradation rates are mentioned, which may be caused by differences in methane concentration and the use of different TiO_2-minerals. However, with respect to commercial application of an air treatment installation, the reported methane degradation rates are still too low for cost effective emission reduction. Further research is necessary to increase this rate, which may imply the development of new (mixtures of) catalysts and dopants.

Keywords: photocatalysis, methane oxidation, titanium dioxide, manure, rumen, room temperature, methanol, n-hexane.

Contents

1 Introduction

1.1 Problem definition

Livestock in the Netherlands is responsible for a large emission of greenhouse gases. This emission mainly consists of methane (CH_4) and equals an emission of 10 Mton CO_2-eq. 80% of this CH_4-emission (8 Mton CO_2-eq.) originates from enteric fermentation that takes place in ruminants (mainly cattle) and 20% (2 Mton CO_2-eq.) originates from fermentation processes that take place in liquid manure storage's (in- and outdoors) (RIVM & CBS, 2001). So cleaning of exhaust air from animal houses (i.e. emissions from the animals and from indoor manure storage) and from outdoor manure storages has a large potential for reduction of emission of greenhouse gases. Yet at this moment no methane filters are available commercially.
If during the air purification process (part of) the methane is converted to CO_2, there is still a reduction of the emission of greenhouse gases because methane is a much more potent greenhouse gas than CO_2 (1). Every molecule of CO_2 that may be produced from methane during the air treatment comes from organic matter (i.e. manure) that was produced by photosynthesis at the time the feed of the animals was grown. Because this CO_2 is a part of the short carbon cycle it does not contribute to the enhanced greenhouse effect.

1.2 Previous experiences

Air from liquid manure storages and air from animal houses has a temperature range from 15 to 25 °C and is at atmospheric pressure. From literature we know that photocatalytic conversion of methane is possible at this temperature and pressure (Grätzel *et al.*, 1989; Thampi *et al.*, 1988). That is why in the year 2000 preliminary tests were carried out by Agrotechnology & Food Innovations (A&F) in order to achieve photocatalytic oxidation of methane in biogas that originated from liquid cattle manure. For these experiment glass wool coated with TiO_2 was provided by Saint-Gobain Isover SA, a French company that produces glass wool products. In earlier experiments by Isover it had already been shown that this coated glass wool showed quick photocatalytic degradation of phenol (C_6H_5OH) and n-hexane (C_6H_{14}) under radiation of UV-365 nm (Saint-Gobain Isover SA, 2000). The tests that were carried out by A&F generated both negative (0% removal) and positive results (50-93% removal) (Hilhorst & Gijsel, 2000). As the reproducibility of the experiments was low and the experimental installation may have suffered from leakages it was not clear if the decrease of methane that was measured had been caused by photocatalytic oxidation.

1.3 Aim

The aim of this project was to study the photocatalytic conversion of methane on TiO_2 and to develop, design and test a laboratory scale photocatalytic air filter installation for removal of methane from air originating from animal housing systems and liquid manure storages. If this study would result in a working laboratory set-up, a plan will be made for the design and

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(1) Methane is a 21 times more potent greenhouse gas than CO_2 on a mass basis.

construction of a pilot-scale installation. The aim of the air filtration unit was to achieve a reduction of the emission of greenhouse gases from the air that was treated of at least 50%. The investment and exploitation costs of such an installation should be competitive to other techniques for reduction of the emission of greenhouse gases. At the time the subsidy application for this project was submitted, the investment costs for such an air filtration unit were estimated at about € 2,300 (*fl.* 5,000) per 100 fattening pig places.

1.4 Financing

This project was carried out by A&F in cooperation with Saint-Gobain Quartz SAS and Saint-Gobain Isover SA. The research was funded by Novem (Nederlandse Organisatie voor Energie en Milieu, Netherlands; project number: 375102/0020) and the Dutch Ministry of Agriculture, Nature and Food quality (LNV). The project started in January 2001 and was finished in November 2003.

2 Theory and background information

2.1 Principles of the photocatalytic process

The ingredients for photocatalytic processes are a catalyst, a light source, water and air. Under experimental conditions, usually a catalyst (e.g. TiO_2) is radiated with light from an ultraviolet (UV) source and brought into contact with the components that should be converted. Exposure to UV causes TiO_2 to release electrons (e^-). Simultaneously, positively charged holes are formed (h^+). The electrons and positive holes cause generation of super oxide (O_2^-) and hydroxy radicals (OH) from water and air, as is schematically shown below:

$$\begin{array}{lll} & \text{UV} & \\ TiO_2 & ==> & e^- + h^+ \\ O_2 + e^- & ==> & O_2^- \\ OH^- + h^+ & ==> & OH^\cdot \end{array}$$

These radicals may induce the conversion of present organic compounds, setting of a chain-reaction of radical formation and oxidation. If total oxidation takes place end-products are carbon dioxide and water. A schematic of the photocatalytic oxidation of an organic compound is given in Figure 1.

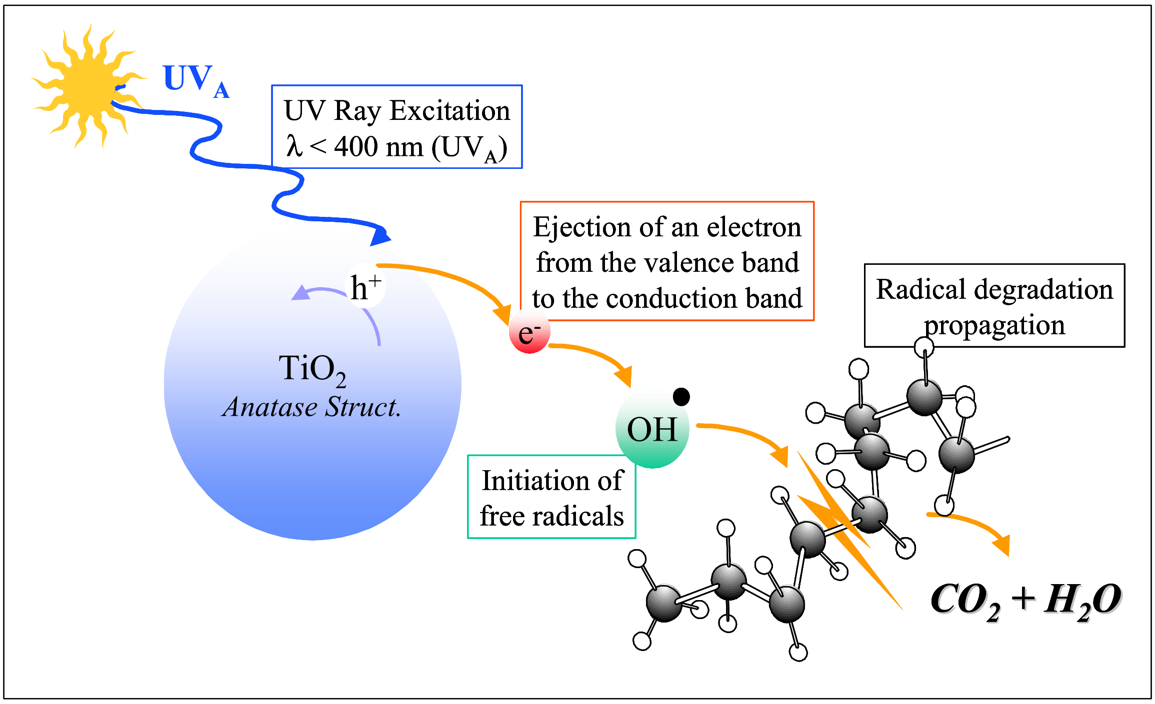


Figure 1 Schematic of photocatalytic oxidation of an organic compound (Source: Saint-Gobain Isover SA, 2000).

In the case of methane, the overall oxidation reaction is as follows:

$CH_4 + 2O_2 ==> CO_2 + 2 H_2O$

This means that 1 molecule of CH_4 is converted to 1 molecule of CO_2. Although both are greenhouse gases, a reduction of the global warming impact is achieved as CH_4 is a much stronger greenhouse gas than CO_2 (about 21 times stronger).

2.2 Process conditions of the photocatalytic conversion of methane

2.2.1 Temperature / Pressure

Like all chemical reactions, photocatalytic reactions run more fast at high temperature and pressure. Much research on photocatalytic reactions focuses on high temperatures (100-500°C) and high pressure. However, in literature it is demonstrated that photocatalytic converision of methane is possible at atmospheric pressure and at rather low temperatures (40-50°C) (Grätzel *et al.*, 1989; Thampi *et al.*, 1988). Although these authors conclude that methane conversion takes place at room temperature, the temperature of the air from animal houses and liquid manure storages we intend to treat eventually, has a much lower temperature (10-25°, see Table 1 and 2) than the temperature of 40-50° at which the experiments were carried out.

2.2.2 Humidity

In order to have formation of hydroxy radicals it is necessary to have water molecules that are in contact with the catalyst. If condensation takes place on the catalyst however, contact between catalyst and gaseous compounds may be hampered. In order to have optimal conditions for photocatalytic conversion it may be important to control humidity in the system.

2.2.3 Catalyst

Many catalysist for photocatalysis are known. Usually these compounds are oxides of one or more elements such as tungsten (W), titanium (Ti), indium (In), tantalum (Ta), molybdena (Mo), vanadium (V), niobium (Nb), or silicium (Si). Conversion of methane was reported using La with WO_3 (Noceti *et al.*, 1997; Taylor & Noceti, 2000), WO_3 (Kolmakov & Pak, 1999), TiO_2 with or without MoO_3 (Thampi *et al.*, 1988), TiO_2 with or without $SiW_{12}O_4$ (Grätzel *et al.*, 1989). TiO_2 is widely used as a catalyst; it is a cheap material. In the experiments that were carried out by Isover and A&F before this project started also TiO_2 was used (Saint-Gobain Isover SA, 2000; Hilhorst & Gijsel, 2000).

2.2.4 UV radiation

The wavelength of ultraviolet (UV) light ranges from 180 to 400 nm. The range from 315 to 400 nm is called UV-A, 280 to 315 nm is called UV-B and 180 to 280 nm is called UV-C. As energy content is reciprocal to wavelength UV-C has higher energy content than UV-B and UV-B has higher energy content than UV-A.

The experiments that were carried out by Isover and A&F before this project showed that UV-365 nm radiation (UV-A) provided sufficient energy to have photocatalytic conversion on TiO_2 (Saint-Gobain Isover SA, 2000; Hilhorst & Gijsel, 2000). Besides it is known from literature (e.g. Puichat *et al.*, 2000) that photocatalysis takes place on TiO_2 at this wave length. Apart from that, UV-A light is not harmful to human eyes or skin.

2.2.5 Discussion

We only know of very few research papers that prove that photocatalytic conversion of methane to CO_2 is possible at atmospheric pressure and moderate temperature (40-50°) (Thampi *et al.*, 1988; Grätzel *et al.*, 1989). In these two papers TiO_2 was used as a catalyst, sometimes combined with MoO_3 or $SiW_{12}O_4$. The catalyst (200 mg) was spread on the bottom of a flat pyrex glass cel of 20-24 mL which was equipped with sample and injection ports. Prior to the experiments the air in the cell was replaced with argon (Ar). For illumination a solar simulator (total output of 80 mW/cm^2) was used. In one of the experiments in which pure TiO_2 was used, 300 µL of O_2 and 2,000 µL of CH_4 was injected in the cell; at t= 0 this resulted in $[O_2]$ = 15,000 ppm, $[CH_4]$ = 100,000 ppm, and $[CO_2]$ = 0 ppm. After 10 hours of illumination all O_2 was consumed so that 300 µL of CO_2 was produced (15,000 ppm) from oxidation of 300 µL of CH_4 (remaining CH_4 concentration: 85,000 ppm) (Thampi *et al.*, 1988). Another experiment, which started with 3,000 µL of O_2 6,000 µL of CH_4 ($[CH_4]$ = 300,000 ppm), showed 50% conversion of CH_4 after 5.5 hours. As all experiments by Thampi *et al.* (1988) en Grätzel *et al.* (1989) were limited by low availability of O_2, no data are available of the photocatalytic activity at lower CH_4 concentrations. However, after a new injection of oxygen, methane photooxidation continues. Thampi *et al.* (1988) also show that, for oxidation of methane on a TiO_2/MoO3 catalyst, an increase of the reaction temperature from 42°C to 290° results in a doubling of the methane oxidation at t = 0 (at t = 0, $[CH_4]$ = 2,000 ppm and $[O_2]$ = 1,000 ppm).

Significant photocatalytic oxidation of methane under similar experimental conditions was also found by Kleinschmidt & Hesse (2002), $[CH_4]$ = about 2,000 - 20,000 ppm, and by Chen *et al.* (2000). The actual methane concentration of the latter was not reported.

2.3 Characteristics of air from animal houses and liquid manure storages

The ultimate goal of this project is to develop a treatment facility for air from animal houses and liquid manure storages. The characteristics of these air flows are described below.

2.3.1 Air from animal houses

In the past many measurements have been done on air in and exhaust air from animal houses. Measured concentrations may vary as they depend on animal species, housing system, ventilation rate and other management aspects. Housing facilities for pigs and cattle often have a storage pit for liquid manure that is situated underneath the barn and has an open connection with the barn itself. The air in the barn is a mixture of outside air and components that are emitted from the manure pit and from the animals. Table 1 shows some of the data that were collected in the past.

Table 1 Characteristics of exhaust air from animal houses (cattle and pigs)[1].

Component	Unit	Value
CH_4	ppm	10 - 160
NH_3	ppm	5 - 50; the Netherlands: 2 - 20
H_2S	ppm	0 - 100
CO_2	ppm	400 - 4,000
N_2O	ppm	0.3 - 3
Odour	Odour Unit/m^3 (OU$_E$/m^3)	1,000 - 5,000
Temperature	°C	15 - 25
Relative humidity	%	50 - 80

[1] From: Anderson *et al.*, 1987; Schulte, 1997; Guingand *et al.*, 1997; Groot Koerkamp, 1997; references from Meyer & Manbeck, 1986; Ogink & Lens, 2000.

Pig barns generally are closed rooms that are ventilated with outside air using a mechanical ventilation system. Ventilation rates vary from 20 - 240 $m^3.h^{-1}.sow^{-1}$ (average: 100 $m^3.h^{-1}.sow^{-1}$) to 10 - 90 $m^3.h^{-1}$.fattening pig^{-1} (average: 35 $m^3.h^{-1}$.fattening pig^{-1}) (Mol, 2003).
Cattle barns generally are partially open rooms that are ventilated naturally: outside air flows freely through the building under the influence of wind speed and direction. Ventilation rates are about 750 - 3,000 $m^3.h^{-1}.cow^{-1}$.

2.3.2 Air from outdoor liquid manure storages

If no sufficient manure storage is available underneath the barn, usually liquid manure is stored in an covered outdoor manure storage tank. In the Netherlands, manure storage facilities at farms usually have a capacity of the manure production of about 6 months, as manure may only be applied on the land from February through August. The size of liquid manure storage tanks usually varies from 500 to 1,500 m^3. Table 2 shows some concentrations that were measured in the headspace of some covered manure storage tanks.

Table 2 Characteristics of air in headspace of covered liquid manure storage tanks (cattle and pig manure). [1]

Component	Unit	Value
CH_4	ppm	200 - 33,000 [2]
NH_3	ppm	1 - 71
H_2S	ppm	0 - 4,100
CO_2	ppm	400 - 4,000
N_2O	ppm	100 - 150,000
N_2	vol.%	60 - 81
O_2	vol.%	15 - 22
Temperature	°C	10 - 16 [3]
Relative humidity	%	100

[1] From: Uenk *et al.*, 1993; Williams & Nigro, 1997.

[2] If ventilation is zero, methane concentration equals pure biogas, i.e. 66 %vol or 660,000 ppm.

[3] Equals average outside temperature.

In some studies not only concentrations but also emissions of methane from liquid manure storage tanks have been measured. Some of these results are shown in Table 3.

Table 3 Methane emission from manure storages at different temperatures (cattle and pig manure).

Source	Temperature	CH_4 emission ($g.m^{-3}.day^{-1}$)	
		Pigs	Cattle
Williams & Nigro, 1997:	4°C	6	18
	11°C	4	36
	18°C	46	61
Hansen, s.a.:	4°C	6	2.4
	11°C	16	6
	18°C	40	12
Husted, 1994:	seasonal variations	0.4 - 35.8	0.0 - 34.5

Besides temperature, emission of CH_4 from manure largely depends on organic matter content and age of manure.

3 Materials and methods

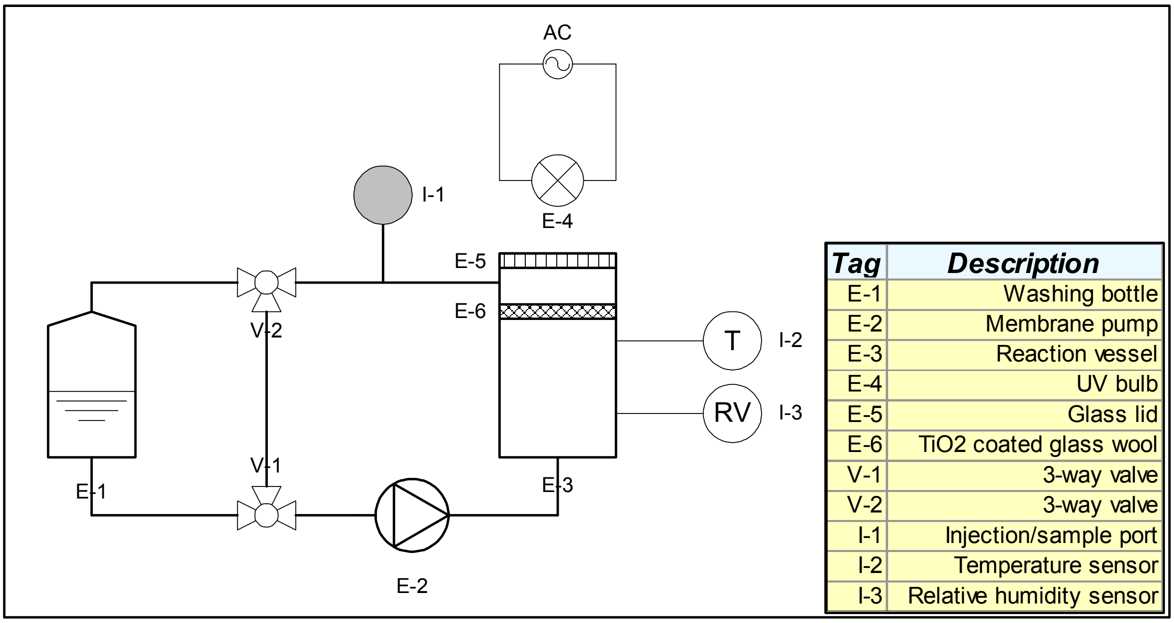
Part 1: Experiments using TiO_2 coated glass wool (carried out by A&F)

3.1 Description of laboratory installation

For Experiment 1 through 4, a cylindrical 5.6 L aluminium reaction vessel was used (length: 290 mm; diameter: 150 mm internal, 180 mm external). One side of the vessel is closed with a aluminium lid, the other side is closed with a glass lid (DURAN®: borosilicate glass 3.3, DIN ISO 3585; thickness: 5 mm). DURAN glass absorbs light of a wave length below 300 nm totally. One or more layers of glass wool (thickness: 0.7 mm; weight: 52 $g.m^{-2}$) coated with TiO_2 (100% anatase) are placed on top of each other in a ring shaped aluminium frame (inner diameter: 125 mm) and placed in the reaction vessel parallel to and at a distance of 35 mm from the inner side of the glass lid. As the glass wool is very porous, air can freely flow through it. A photograph of the glass wool layers and the aluminium frame is shown in Figure 2. The TiO_2 coated glass wool is supplied by Saint-Gobain Isover SA, France.

Figure 2 TiO_2 coated glass wool layers (left) and aluminium frame (right).

A UV light source (Philips HPW-125, Black Light High Pressure Mercury bulb) is placed at a distance of 70 mm from the outer glass surface so the TiO_2-coated glass wool is exposed to this radiation. According to specifications, 90% of the radiation of the bulb is emitted at the 365 nm band and no light is emitted at wavelenths < 320 nm. A membrane pump (KNF Laboport N 86 KT.18) is connected to the reaction vessel and circulates air through the system in a closed loop at a flow of 5.3 L/min. Tubing (internal diameter: 4.35 mm) is made of stainless steel; connections and valves were obtained from Swagelok®. Through an injection port in the tubing gases can be injected into the system and gas samples can be taken for analysis. A washing bottle filled with water can be used for humidification of the air or can be by-passed. A combined temperature/relative humidity probe (Rotronic Hygromer Serie 1200) is installed in the wall of the reaction vessel and is connected to a data logger that logs relative humidity and temperature every 5 minutes. A small household desktop fan (30 Watts) is used fro cooling the bulb and the glass lid. A schematic of the experimental setup is shown in Figure 3; a photograph of the laboratory installation is shown in Figure 4.



Tag	Description
E-1	Washing bottle
E-2	Membrane pump
E-3	Reaction vessel
E-4	UV bulb
E-5	Glass lid
E-6	TiO2 coated glass wool
V-1	3-way valve
V-2	3-way valve
I-1	Injection/sample port
I-2	Temperature sensor
I-3	Relative humidity sensor

Figure 3 Schematic of closed-loop laboratory installation at A&F for photocatalytic experiments.

3.2 Measurements

UV radiation

The intensity of UV-365 nm radiation is measured using a hand-held UV-365 light meter (Lutron UVA-365). The sensor in this meter has highest response at 355 nm (100%) and a slightly lower response (85%) at 365 nm. The sensor is calibrated at 365 nm and gives readings from 1 mW.m^{-2} to 0.1 W.m^{-2} at three different ranges.

Gaseous compounds

Methane, carbon dioxide, nitrous oxide, and sulfur hexafluoride were determined using a gas chromatograph (Interscience/Carbo Erba Instruments, GC 8000 Top; column: Molsieve 5A (CH_4, CO_2), Haysep Q (N_2O, SF_6); detector: CH_4: FID/HWD, N_2O: ECD/HWD, CO_2: HWD; SF_6: ECD). n-hexane was determined using gas detector tubes (Kitagawa 113SA, 113SC).

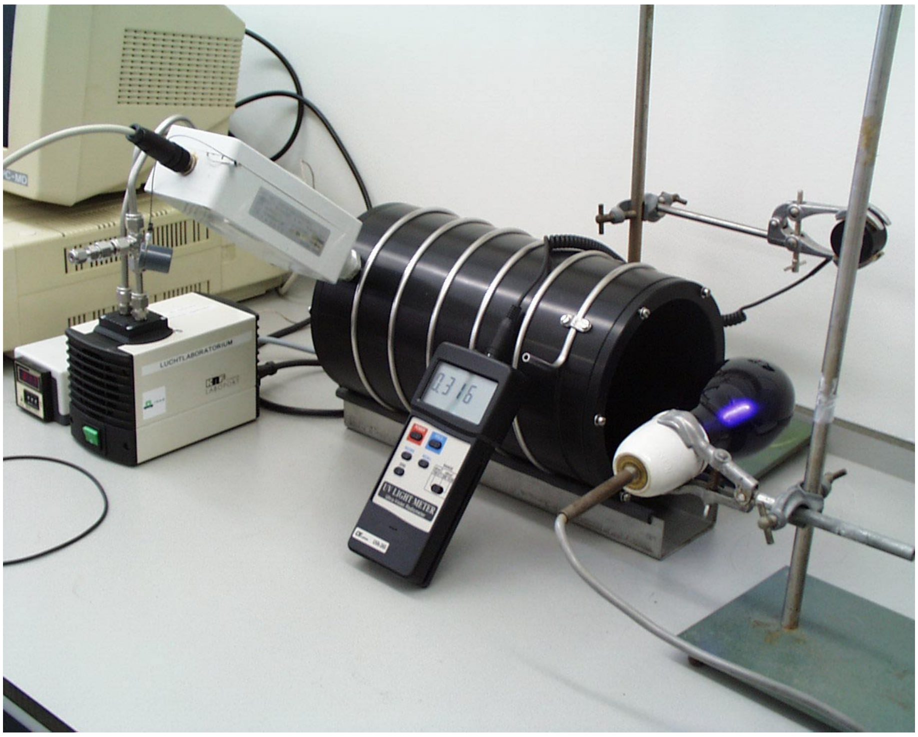


Figure 4 Photograph of laboratory installation at A&F for photocatalytic experiments.

3.3 Description of experiments

3.3.1 Experiment 1: Transmission of glass and glass wool layers

Aim:

The aim of the experiment is to measure the UV-365 nm radiation energy density (W.m-^{2}) the TiO_2-coated glass wool is exposed to and to find out what part of the energy is lost while passing through the glass lid and through up to three layers of glass wool.

Setup and measurements:

Several measurements are carried out:

a) Loss of energy by glass lid

Half an hour before starting the experiment the UV lamp is switched on as it takes some time before the lamp is at its operating temperature. The radiation energy density is measured at 9 spots in an imaginary circle (diameter: 125 mm) at a distance of 75 mm from the UV lamp as this is the distance between the lamp and the inner surface of the glass lid in the laboratory installation. Then the glass lid is placed at a distance of 70 mm from the UV lamp and the radiation energy density is measured after the glass lid at a distance of 75 mm from the UV lamp in the same way. The difference between the first and the second measurement is the amount of UV-365 radiation energy that is lost while passing through the glass lid.

b) Loss of energy by glass wool layers

Half an hour before starting the experiment the UV lamp is switched on as it takes some time before the lamp is at its operating temperature. The glass lid is placed at a distance of 70 mm from the UV lamp and the radiation energy density is measured after the glass lid at 9 spots in an imaginary circle (diameter: 125 mm) at a distance of 110 mm from the UV lamp as this is the distance between the lamp and the glass wool layer in the laboratory installation. Then the aluminium ring with one layer of glass wool is installed at distance of 110 mm from the UV lamp and the radiation energy density is measured after the glass wool layer in the same way as described above. This measurement is repeated with two and three layers of glass wool on top of each other respectively. The difference between the measurements tells what amount of UV-365 radiation energy is lost while passing through each glass wool layer.

3.3.2 Experiment 2: Photocatalytic conversion of methane (ambient humidity)

Aim:
The aim of the experiment is to find out if photocatalytic conversion of methane occurs at ambient conditions, i.e. without adjustment of the humidity level of the air.
Setup and measurements:
Half an hour before starting the experiment the UV lamp is switched on as it takes some time before the lamp is at its operating temperature. Three layers of TiO_2 coated glass wool (123 cm^2 each) are placed on top of each other in the aluminium ring and placed in the reaction vessel. The reaction vessel is tested for leakage by pressurizing the system at 0.5 atm and measuring pressure decrease in the system during half an hour. The washing bottle is disconnected and the pump is switched on. About 0.5 ml of pure CH_4 is injected into the reaction vessel to achieve a starting concentration of about 100 ppm methane, which is the upper range of the methane concentration of exhaust air from animal houses and the lower range of the air from the head space of liquid manure storages. After 5 minutes (t = 0) a gas sample is taken and the inside of the reaction vessel is exposed to the UV lamp. The experiment is continued for about 170 hours and at a regular basis gas samples are taken. The samples are analysed for its CH_4, CO_2, and N_2O content. Temperature and relative humidity in the system are measured continuously.
To check if the conversion is really caused by photocatalysis, three blank measurements can be carried out in which the UV lamp is switched on or off, with or without the presence of glass wool in the reaction vessel: 1) UV: no; glass wool: no; 2) UV: yes; glass wool: no; 3) UV: no; glass wool: yes.

3.3.3 Experiment 3: Photocatalytic conversion of methane (humidified air)

Aim:
The aim of the experiment is to find out if photocatalytic conversion of methane occurs at a high humidity level of the air.
Setup and measurements:
As we know that humidity may be a control parameter of photocatalytic conversion, in this experiment the measurements of Experiment 2 are repeated at a high humidity level. In this way we hope to achieve a higher photocatalytic conversion of methane. Half an hour before starting the experiment the UV lamp is switched on as it takes some time before the lamp is at its

operating temperature. Three layers of TiO_2 coated glass wool (123 cm^2 each) are placed on top of each other in the aluminium ring and placed in the reaction vessel. The reaction vessel is tested for leakage by pressurizing the system at 0.5 atm and measuring pressure decrease in the system during half an hour. The pump is switched on and the air is led through the washing bottle filled with water until relative humidity does not increase any more; then the washing bottle is disconnected. About 0.5 ml of pure CH_4 is injected into the reaction vessel to achieve a starting concentration of about 100 ppm methane, which is the upper range of the methane concentration of exhaust air from animal houses and the lower range of the air from the head space of liquid manure storages. About 10 ml of 15 ppm SF_6 is injected as a tracer gas to achieve a starting concentration of about 25 ppb. The concentration of SF_6 is assumed only to be influenced by leakage of the system. By following SF_6 concentration during time the courses of CH_4, CO_2, and N_2O concentrations can be corrected under assumption that occurring leakage is not compound specific. After 5 minutes (t = 0) a gas sample is taken and the interior of the reaction vessel is exposed to the UV lamp. The experiment is continued for about 1000 hours and at a regular basis gas samples are taken. The samples are analysed for its CH_4, CO_2, N_2O, and SF_6 content. Temperature and relative humidity in the system are measured continuously.
To check if the conversion is really caused by photocatalysis, three blank measurements can be carried out in which the UV lamp is switched on or off, with or without the presence of glass wool in the reaction vessel: 1) UV: no; glass wool: no; 2) UV: yes; glass wool: no; 3) UV: no; glass wool: yes.

3.3.4 Experiment 4: Photocatalytic conversion of n-hexane (ambient humidity)

Aim:

The aim of the experiment is to find out if photocatalytic conversion of n-hexane occurs in order to compare the results with previous experiments as carried out by Isover (Saint-Gobain Isover SA, 2000). The experiments by Isover were carried out at room temperature and without adjustment of humidity level of the air.

Setup and measurements:

Half an hour before starting the experiment the UV lamp is switched on as it takes some time before the lamp is at its operating temperature. The reaction vessel is equipped with the same layers of TiO_2 coated glass wool that had already been used in Experiment 3. The reaction vessel is tested for leakage by pressurizing the system at 0.5 atm and measuring pressure decrease in the system during half an hour. The washing bottle is disconnected and the pump is switched on. About 90 ml of n-hexane vapour (in equilibrium with liquid n-hexane) is injected to achieve a starting n-hexane concentration of about 2500 ppm. At the time of the experiment no SF_6 analyes could be carried out due to technical problems. Therefore it was decided to use CH_4 as tracer gas in this experiment. CH_4 is assumed to be suitable as a tracer for this experiment because Experiment 2, which was carried out under the same conditions and run for the same length of time, showed no decrease of methane. About 0.5 ml of pure CH_4 was injected to achieve a starting concentration in the reaction vessel of about 100 ppm. After 5 minutes (t = 0) a gas sample is taken and the interior of the reaction vessel is exposed to the UV lamp. The experiment is continued for about 330 hours and at a regular basis gas samples are taken. The samples are analysed for its CH_4, CO_2, and N_2O content. Temperature and relative humidity in the system are measured regularly.

To check if the conversion is really caused by photocatalysis, three blank measurements can be carried out in which the UV lamp is switched on or off, with or without the presence of glass wool in the reaction vessel: 1) UV: no; glass wool: no; 2) UV: yes; glass wool: no; 3) UV: no; glass wool: yes. In order to check if the presence of glass wool was necessary to have conversion of n-hexane, one blank measurement was carried out without glass wool in the reaction vessel while the UV lamp was switched on.

Part 2: Experiments using TiO_2 coated quartz fibres (carried out by Saint-Gobain Quartz SAS)

3.4 Description of experiments

3.4.1 Experiment 5: Photocatalytic conversion of methanol

Aim:

The aim of the experiment is find out if photocatalytic conversion takes place on TiO_2 coated quartz fibres, in contrast to the earlier experiments when TiO_2 coated glass wool was used.

Setup and measurements:

In this 8-hour-experiment a continuous-flow photocatalytic reactor was used that is schematically shown in Figure 5. Methanol (CH_3OH) is used as a model component to find out if photocatlytic conversion takes place. Gas from gas cylinder (E-1), containing 250 ppm methanol, enters the photocatalytic reactor (E-3) after opening valve V-1. The flow of the air stream is set to 62.5 ml/minute.

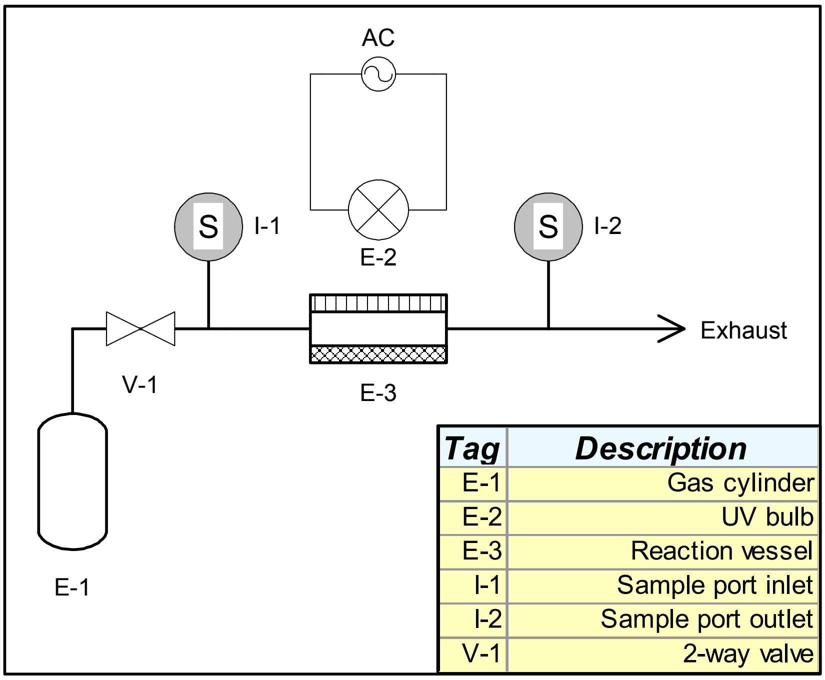
In Experiment 5A, the photocatalytic reaction vessel contains a disk (diameter: 47 mm) with a sheet of quartz fibres (Quartzel). The sheet has been needle-punched to increase the contact area of TiO_2 with air; the quartz fibres have been impregnated with TiO_2 (100% anatase) powder.

In Experiment 5B the reaction vessel contains a disk with the TiO_2 coated glass wool that had been used in Experiment 1 through 4.

The reaction vessel is closed with a glass lid and the contents are radiated by a high-pressure mercury vapor lamp (Philips HPK 125W) which has a spectrum from 190 - 700 nm and an energy maximum at 365 nm. The lamp that was used in Experiment 1 through 4 (see section 3.4.3) does not have any radiation below 320 nm. In Experiment 5 the radiation density of the lamp is changed from 8 to 48 mW/cm^2. Air samples are taken from the air inlet (I-1) and air outlet (I-2) two times per hour; the concentration of methanol in the samples is analyzed using gaschromatography. The experiment is carried out at ambient conditions (room temperature and humidity).

To eliminate the possibility that differences between the experimental or analytical setup of A&F (see Figure 3) and that of Saint-Gobain Quartz SAS (Figure 5) may have influenced the results that were found, Experiment 5B is carried out. Experiment 5B uses the experimental setup from

Saint-Gobain Quartz SAS that had been already used in Experiment 5A, together with the TiO_2 coated glass wool that had been used in Experiments 1 through 4 that were carried out by A&F.



Tag	Description
E-1	Gas cylinder
E-2	UV bulb
E-3	Reaction vessel
I-1	Sample port inlet
I-2	Sample port outlet
V-1	2-way valve

Figure 5 Schematic of continuous-flow photocatalytic reactor at Saint-Gobain Quartz SAS.

3.4.2 Experiment 6: Photocatalytic conversion of methane using TiO_2 coated quartz fibres

Aim:

The aim of the experiment is to find out if photocatalytic conversion of methane occurs on the TiO_2 coated quartz fibres at ambient conditions.

Setup and measurements:

At first the continuous-flow reactor from Experiment 5 (see Figure 5) was used for the photocatalytic conversion of methane in this experiment. For this purpose the gas cylinder containing methanol was replaced by a cylinder that contained 250 ppm methane. However, because after some days still no degradation of methane had been found, the reactor setup was changed from a continuous-flow to a closed vessel system in order to increase the residence time of methane in the system.

The experimental setup of this closed vessel or batch system consists of a closed cylindrically shaped reactor with a glass lid and a volume of 1.2 L. The reactor contains a disk (diameter: 47 mm; identical to Experiment 5) with a sheet of quartz fibres (Quartzel) that has been needle-punched to increase the contact area of TiO_2 with air; the quartz fibres have been impregnated with TiO_2 powder. At the bottom of the reactor a magnetic stirrer is placed. The reactor is flushed with a mixture of N_2 (50 mL/minute), which contains 350 ppm CH_4, and of O_2 (12.5 mL/minute); after some time the concentrations in the reactor are supposed to be stable and the flows are switched of. The reactor is irradiated with a high-pressure mercury vapor lamp (Philips HPK 125W). This lamp provides maximum energy at 365 nm (P = 48 mW/cm^2). Air samples (2 mL) are taken from the reactor at regular intervals during 2 days; the concentration of methane in the samples is analyzed using gaschromatography. The experiment is carried out at ambient conditions (room temperature and humidity).

4 Results and discussion

Part 1: Experiments using TiO_2 coated glass wool

4.1 Experiment 1: Transmission of glass and glass wool layers

The results of Experiment 1 are shown in Figure 6. Over 20% of the UV-365 nm radiation energy density is lost while passing through the glass lid. After passing through the first glass wool layer energy density is reduced to 26%; transmission after the third layer is only 3%. As 100% equals 2.0 mW.cm^{-2} the first layer of glass wool is exposed to a UV-365 nm radiation of 1.6 mW.cm^{-2}.

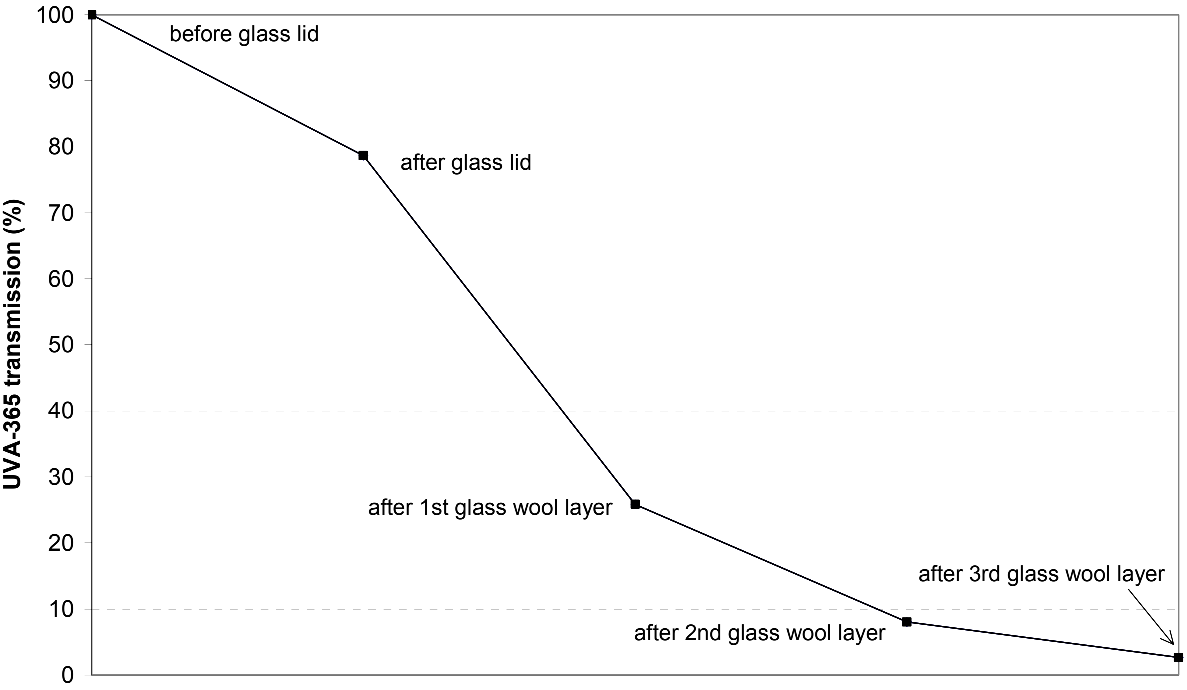


Figure 6 Transmission of glass lid and glass wool layers for UV-365 nm; 100% = 2.0 mW.cm^{-2}.

From these results it can be concluded that in order to have a maximum photocatalytic conversion capacity three layers of glass wool should be used on top of each other. As the transmission after the third layer is only 3% the photocatalytic conversion capacity is would not be significantly raised if more than three layers of glass wool were used. Therefore the setup with three layers of glass wool has been used in all experiments.

4.2 Experiment 2: Photocatalytic conversion of methane (ambient air)

The results of Experiment 2 are shown in Figure 7. The glass wool is exposed to 1.6 mW.cm^{-2} UV-365 nm radiation. Temperature varies from 21 to 31°C and relative humidity from 39 to 48% (see Appendix A). During the time of the experiment (170 hours) no reduction of CH_4 concentration is measured. In comparable experiments (same glass wool material, similar experimental setup) that were carried out by Isover (Saint-Gobain Isover SA, 2000) with n-hexane and phenol, large reductions of these components were already achieved in order of minutes, even at much lower radiation energy density (0.2 mW.cm^{-2}). N_2O concentration increases from 0.16 to 0.22 ppm (38% increase). This increase is probably caused by photocatalytic conversion of N_2 in the air. A large increase of CO_2 was measured. During the experiment the concentration increased from ambient conditions (500 ppm) to over 9,000 ppm. As the CO_2 increase is not caused by oxidation of CH_4 it must have another source.

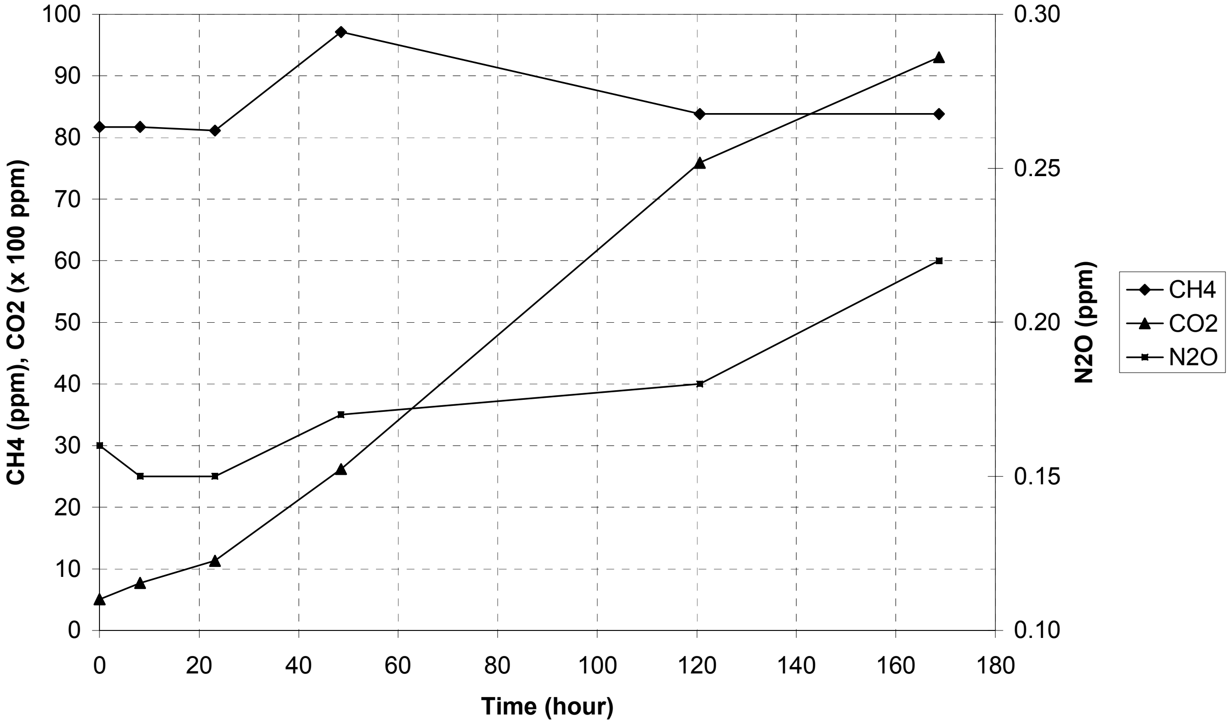


Figure 7 Development of methane, carbon dioxide and nitrous oxide concentration during irradiation in closed-loop reactor (TiO_2 coated glass wool, UV-365 nm); temperature: 21-31°C; relative humidity: 39-48%.

To find the source of CO_2 production the glass wool layers were taken out for further inspection. The glass wool layers were oven dried at 105°C (> 16 hours) followed by 4 hours in a furnace (550°C) to determine dry matter and ash content. The difference between dry matter and ash content is assumed to be organic matter. The organic matter content was 7% of the dry matter content. It can be calculated that if all organic material, assume composition as CH_2O, in the three glass wool layers was converted to CO_2, the CO_2 concentration in the system would have risen to 19,000 ppm CO_2. This means that the amount of organic matter that is present in the glass wool material is more than enough to be responsible for the rise of the CO_2 concentration. Therefore it is concluded that the measured increase in the CO_2 concentration is caused by photocatalytical oxidation of organic material present in the glass wool layer.

The organic compounds are probably incorporated into the glass wool material during its production process; a coupling agent with a carbonaceous chain is used for sticking the glass wool together.

Because of the unsatisfactory methane conversion that was found in this experiment no blank measurements were carried out.

4.3 Experiment 3: Photocatalytic conversion of methane (humidified air)

The results of Experiment 3 are shown in Figure 8. The concentrations in this figure have been corrected for tracer loss (SF_6) as described in 3.3. The glass wool is exposed to 1.6 $mW.cm^{-2}$ UV-365 nm radiation. Temperature varies from 22 to 31°C and relative humidity from 56 to 85% (see Appendix B) because of humidification of the air.

During the experiment we see a slight linear decrease of CH_4 from 125 ppm at the start to 105 ppm at 1,000 hours, i.e. a 15% decrease. In the first 170 hours of Experiment 3, with is the length of Experiment 2, the CH_4 concentration decreases with about 3.5 ppm or 3% of its initial concentration. This decrease is much higher than the decrease of the CH_4 concentration that was measured in Experiment 2 where no decrease was found in 170 hours. However, in comparison with the experiments carried out by Isover on n-hexane and phenol, (Saint-Gobain Isover SA, 2000), conversion of methane is still very low.

As was the case in the previous experiment, CO_2 concentration rises to high levels. The CO_2 production during the first 170 hours of Experiment 3 is similar to that in Experiment 2. Although the CO_2 concentration at the end of the experiment (1100 hours) may have risen further if the experiment had been continued, CO_2 seems to stabilize at a level of about 21,000 ppm. This value quite well corresponds to the estimate of 19,000 ppm that was calculated in section 4.2 based on the assumption that all organic content in the glass wool is converted to CO_2.

The N_2O concentration in Experiment 3 increases from ambient conditions (0.18 ppm) to 0.93 ppm (416% increase). The N_2O production rate ($ppm.hour^{-1}$) is about twice the production rate that was measured in Experiment 2; this increase is probably caused by photocatalytic conversion of N_2 that is present in the air to N_2O.

As both the conversion rate of methane and the production rate of nitrous oxide in Experiment 3 are much higher than in Experiment 2, it may be concluded that humidity is an important factor to influence and control the photocatalytic conversion process. However, the conversion rate of methane is still much too low for the development of a filter installation for treatment of air from manure storage facilities and animal housings, as is the aim of this research.

Because of the unsatisfactory methane conversion that was found in this experiment no blank measurements were carried out.

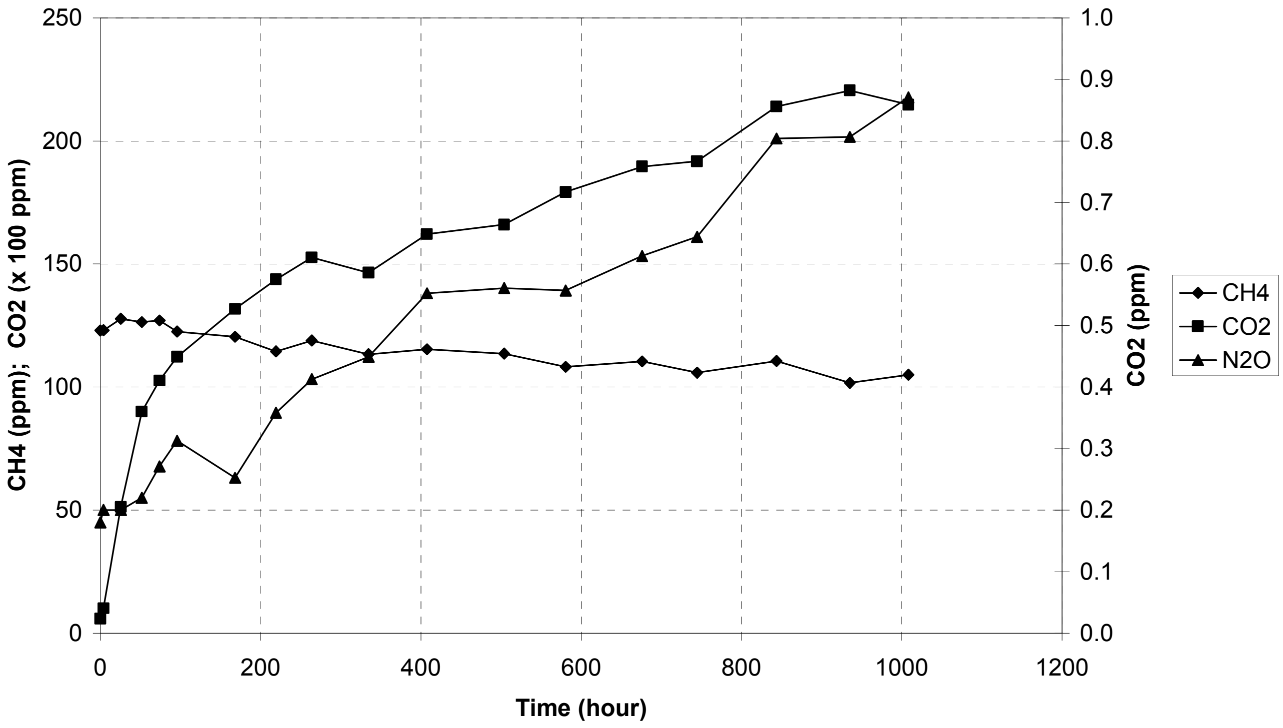


Figure 8 Development of methane, carbon dioxide and nitrous oxide concentration during irradiation in closed-loop reactor (TiO_2 coated glass wool; UV-365 nm); temperature: 22-31°C; relative humidity: 56-85% - corrected for tracer loss.

4.4 Experiment 4: Photocatalytic conversion of n-hexane (ambient air)

To find a reason for the low methane conversion rates that were measured in Experiment 2 and 3, it was decided to repeat the experiment on photocatalytic conversion of n-hexane that was initially carried out by Isover (Saint-Gobain Isover SA, 2000).

The results of Experiment 4 are shown in Figure 9 and 10, both for the measurements in presence of glass wool and for the blank measurements without glass wool. The concentrations in Figure 9 and 10 have been corrected for tracer loss as described in 3.3. The glass wool is exposed to 1.6 $mW.cm^{-2}$ UV-365 nm radiation. Temperature varies from 22 to 24°C and relative humidity from 33 to 57% (see Appendix C). During the experiment with glass wool it takes about 60 hours to decrease n-hexane concentration from 2500 ppm to 250 ppm (90% reduction, Figure 9). When the experiment is carried out in the absence of glass wool it takes about 220 hours to reach this concentration so the time needed for this degradation is reduced by 3 to 4 times. However, in similar experiments that were carried out by Isover (Saint-Gobain Isover SA, 2000) using similar coated glass wool layers 90% decrease of n-hexane had already been found after 10 minutes (i.e. 400 times faster) at a UV radiation density of 0.2 $mW.cm^{-2}$.

There is a possibility that the TiO_2 coated glass wool material that was used in Experiments 1 through 4 is subject to aging. This means that the photocatalytic activity of the material decreases in time and could explain the large differences in the rate of photocatalytic oxidation of n-hexane in Experiment 4 and the results of Isover (Saint-Gobain Isover SA, 2000). This subject is discussed further in section 4.5

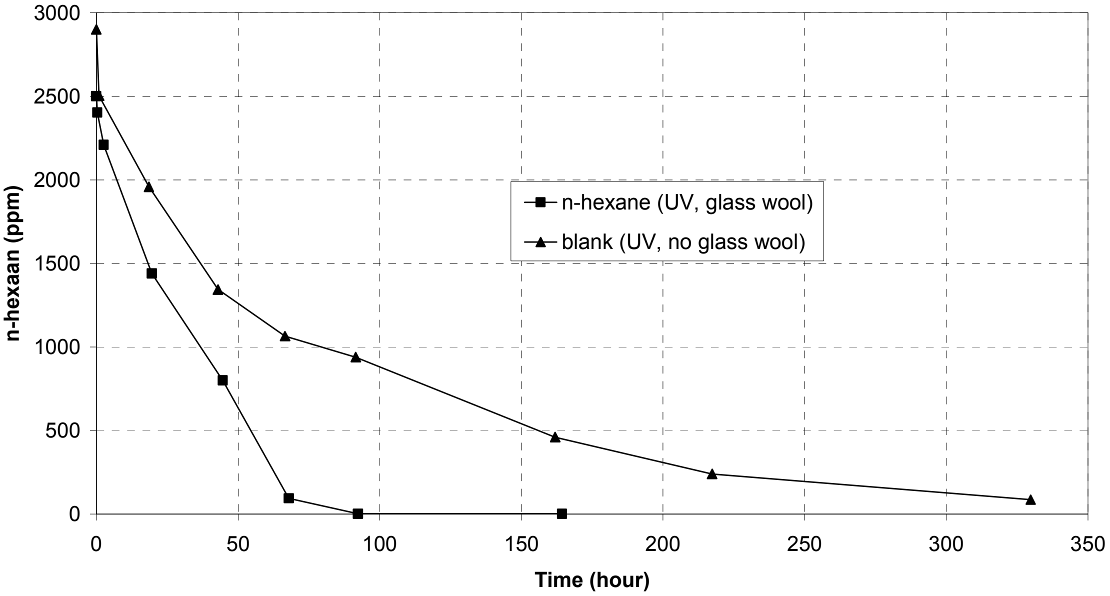


Figure 9 Development of n-hexane concentration during irradiation in closed-loop reactor (UV-365 nm) in presence or in absence of TiO_2 coated glass wool (blank measurement); temperature: 21-24°C; relative humidity: 33-57% - corrected for tracer loss.

During the blank measurement in the absence of glass wool no CO_2 is produced (Figure 10). This confirms the assumption that the large CO_2 increase in Experiment 2 and 3 was caused by degradation of compounds present in the glass wool layer. The N_2O concentrations that were measured in the situation with and without glass wool are similar.
Because of the unsatisfactory results of Experiment 2 through 4, no further experiments are carried out with the glass wool material.

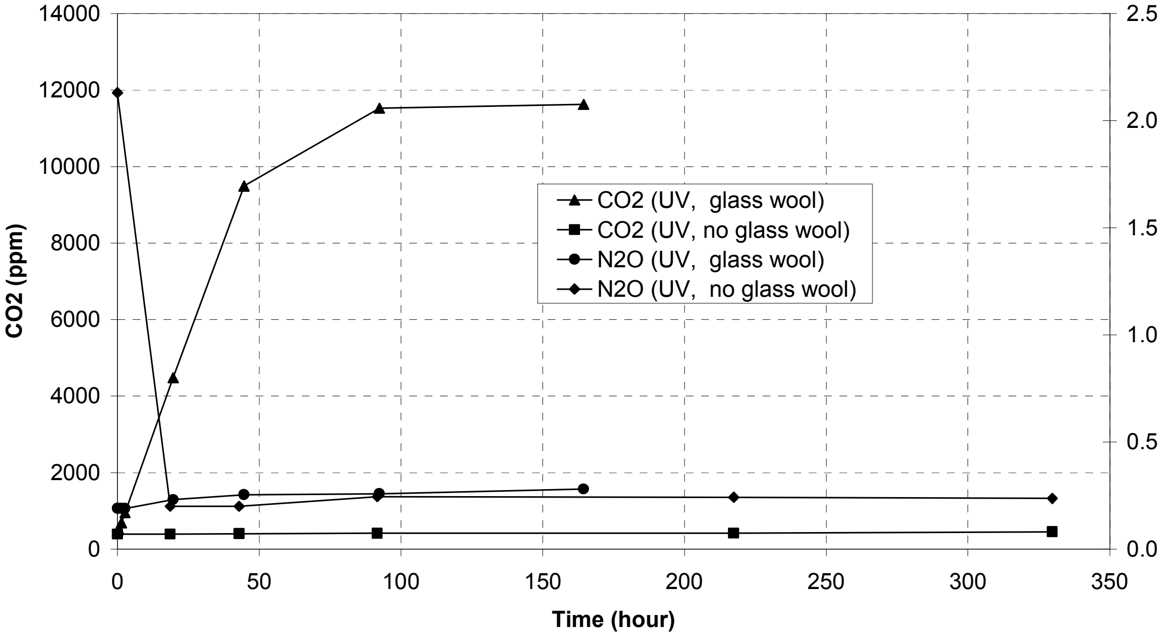


Figure 10 Development of carbon dioxide and nitrous oxide concentration during irradiation in closed-loop reactor (UV-365 nm) in presence or in absence of TiO_2 coated glass wool (blank measurement); temperature: 21-24°C; relative humidity: 33-57% - corrected for tracer loss

4.5 Ageing of TiO_2 coated glass wool

As stated in section 4.4, there is a possibility that the TiO_2 coated glass wool material that was used in Experiments 1 through 4 is subject to aging. This means that the photocatalytic activity of the material decreases in time and could explain the large differences in the rate of photocatalytic oxidation of n-hexane in Experiment 4 and the results of Isover (Saint-Gobain Isover SA, 2000).
Ageing of the material could occur in two ways:
1. *Loss of TiO_2.*
If the TiO_2 powder is not fixed very well to the glass wool, part of the TiO_2 powder could have been lost during the handling of the glass wool material, e.g. during transport, cutting and building the experimental set-up.
2. *Migration of ions from the glass wool to the TiO_2 crystal structure.*
It is known that some ions (e.g. Na) may migrate to the TiO_2 crystal structure and 'occupy' photoactive sites of the material. This results in lower photocatalytic activity of the material.

To find out if the glass wool really suffered from ageing, a sample of it was analyzed using X-Ray Fluorescence diffraction (XRF). The results of this analysis is shown in Table 4.

Table 4 Analysis of contents of TiO_2 coated glass wool using XRF. [1]

TiO_2 content (g TiO_2/kg coated glass wool)	Na content of TiO_2 [2] (g Na/kg TiO_2)
100 - 120	> 100

[1] X-Ray Fluorescence diffraction.

[2] TiO_2 powder was removed from the glass wool before analysis.

Table 4 shows that the amount of TiO_2 in the glass wool is still sufficient to show normal photocatalytic activity. The sodium (Na) content of the TiO_2 itself, however, is very high. This means that a substantial amount of Na has migrated from the glass wool to the cristal structure of TiO_2 causing low photocatalytic activity.
It is therefore concluded that the TiO_2 coated glass wool has been subjected to ageing and that this ageing may very well explain the low photocatalytic oxidation rate of n-hexane that was found in Experiment 4. Ageing may also have caused low oxidation rated of methane in Experiments 2 and 3.

In order to find out if photocatalytic oxidation of methane at a wavelength 365 nm occurs at a TiO_2 surface with a high photocatalytic activity, it is decided to replace the glass wool with another material that does not have the drawbacks of glass wool. An alternative for glass wool could be a quartz fibre as was developed by Saint-Gobain Quartz SAS, a sister company of Isover. If this quartz fibre (brand name 'Quartzel') is used for fixation of TiO_2 instead of glass wool, no migration of Na to the TiO_2 will occur as the quartz fibre does not contain Na. It was decided to carry out some new photocatalytic experiments with TiO_2 fixed to this Quartzel material; these experiments are described in section 4.6 and 4.7.

Part 2: Experiments using TiO_2 coated quartz fibres

4.6 Experiment 5: Photocatalytic conversion of methanol (continuous-flow reactor)

Experiment 5A
The results of the measurements of methanol degradation on TiO_2 coated Quartzel in the continuous-flow reactor are given in Figure 11. After switching in the UV lamp at a radiation density of 48 mW/cm^2 at t = 0, the outlet concentration instantly decreases from 250 ppm to 0 ppm, i.e. 100% degradation. When the radiation density is lowered, the methanol concentration starts to increases. At a radiation density of 8.22 mW/cm^2, the methanol outlet concentration stabilizes at 125 ppm after 24 hours (data not shown), i.e. the removal percentage is 50%.

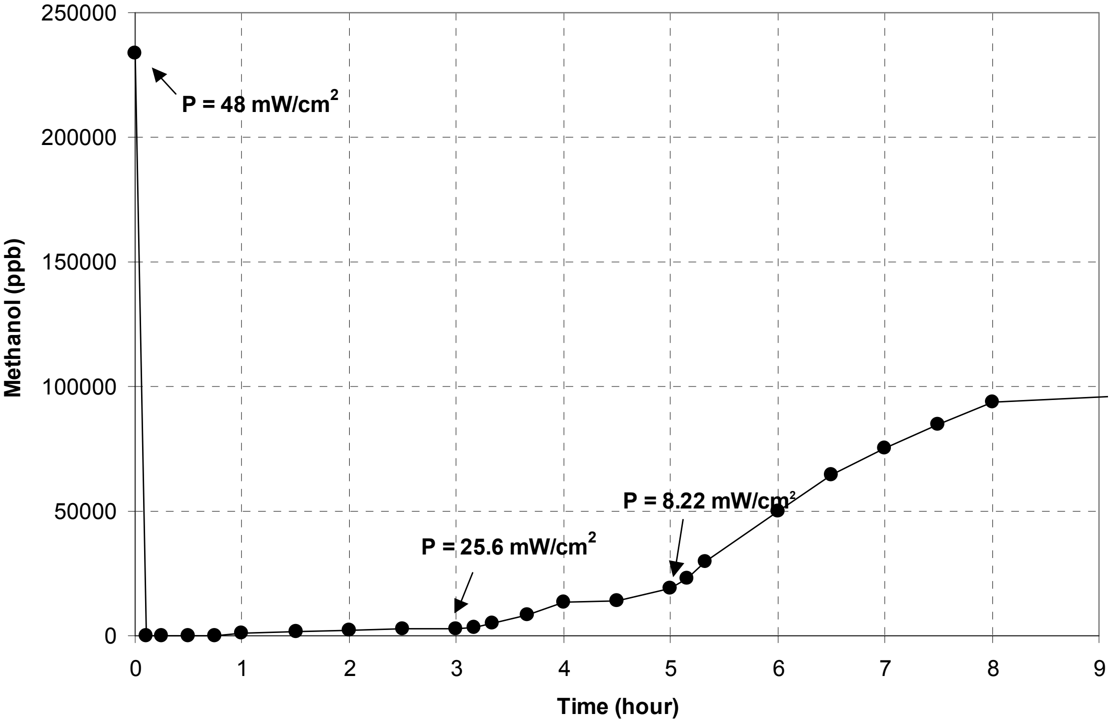


Figure 11 Methanol outlet concentration of continuous-flow photocatalytic reactor (190-700 nm; TiO_2 coated Quartzel) at methanol inlet concentration of 250 ppm at different radiation densities (P in mW/cm^2) (Saint-Gobain Quartz SAS, 2003).

Although the UV lamp has its energy maximum at 365 nm, that was used emits light with a wavelength from 190 - 700 nm. From an experiment with a filter in front of the lamp that blocks all wavelengths < 400 nm, it was found that still 30% methanol degradation takes place at P = 8.22 mW/cm^2, i.e. the methanol outlet concentration is 180 ppm at an inlet concentration of 250 ppm (data not shown).

Experiment 5B

In Figure 12 the methanol degradation is shown that is measured in the continuous-flow reactor after replacing the TiO_2 coated Quartzel (Experiment 5A) with the TiO_2 coated glass wool that had been used in Experiments 1 through 4. The methanol degradation that was found is about 20%, regardless of the radiation density. This degradation is much lower than the degradation that was found in Figure 11, where complete degradation occurred at high radiation density.

From Figure 11 and 12 it can be concluded that the Quartzel material shows a much higher photocatalytic activity than the glass wool material that had been coated with TiO_2 in the same way. This confirms the conclusion that the glass wool material has aged (see section 4.5). As the TiO_2 coated Quartzel material is not subject to the aging caused by migration of Na ions as the TiO_2 coated glass wool is (see section 4.5), the Quartzel material offers better possibilities for successful application of photocatalytic degradation than the glass wool material.

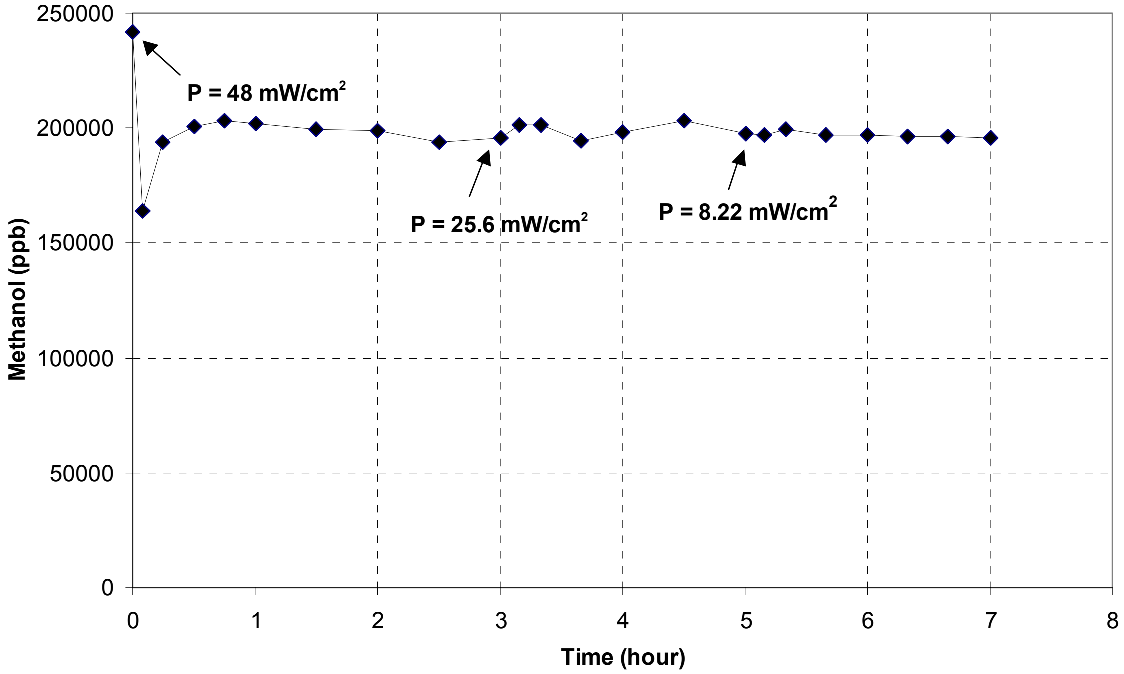


Figure 12 Methanol outlet concentration of continuous-flow photocatalytic reactor (190-700 nm; TiO_2 coated glass wool) at methanol inlet concentration of 250 ppm at different radiation densities (P in mW/cm^2) (Saint-Gobain Quartz SAS, 2003).

4.7 Experiment 6: Photocatalytic conversion of methane (batch reactor)

The results of the methane degradation on TiO_2 coated Quartzel in the batch reactor are given in Figure 13. Figure 13 shows that after 2 days the concentration of methane in the vessel has decreased about 15%. This means that hardly any degradation of methane takes place on the TiO_2 coated Quartzel, especially in comparison with methanol which was instantly removed under the same experimental conditions (see Figure 11).

It follows TiO_2 that coated Quartzel, which proved to be very successful in the photocatalytic conversion of other compounds (e.g. methanol), is not suitable for the degradation of methane under these experimental conditions.

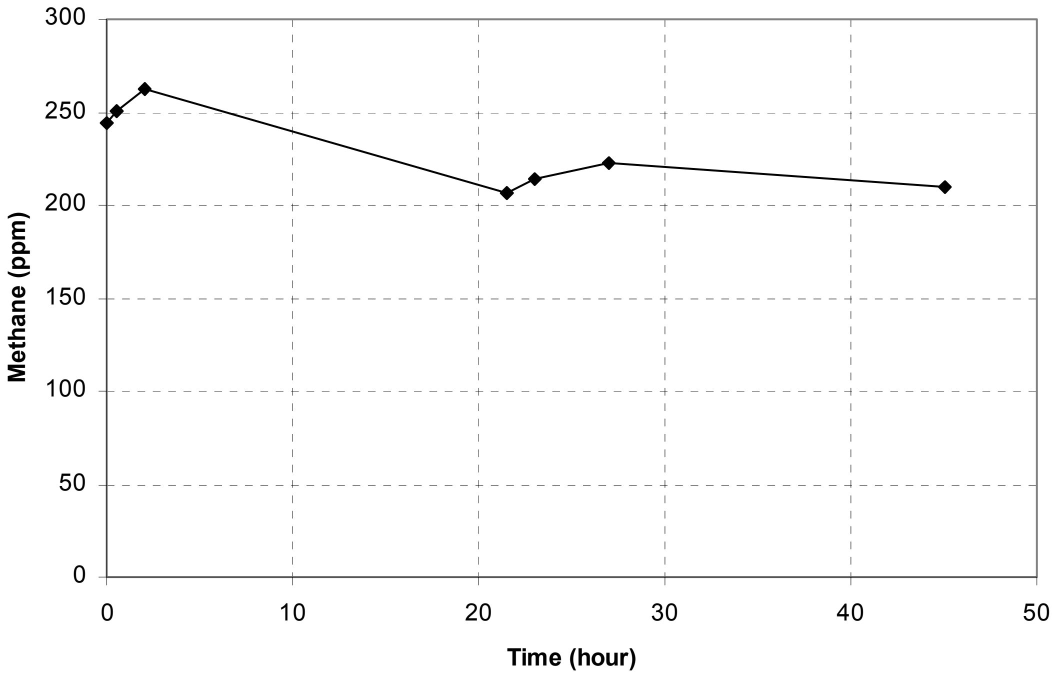


Figure 13 Methane concentration in batch photocatalytic reactor (UV-365 nm; TiO_2 coated Quartzel) (Saint-Gobain Quartz SAS, 2003).

4.8 Possible reasons for low methane degradation rate

In this research we were not able to show significant photocatalytic breakdown of methane at room temperature and atmospheric pressure in a methane concentration range from 80 to 250 ppm. These concentrations correspond to the upper range of the methane concentration of exhaust air from animal houses and to the lower range of the methane concentration in the head space of liquid manure storages. From this it follows that we were not able to meet the aim of the research until now (see section 1.3). Other organic compounds however (e.g. methanol and n-hexane), could be degraded at a much higher rate using the same laboratory installation and equipment. From literature only very few reports are known on successful photocatalytic oxidation of methane; these reports are discussed in section 2.2.5. Although the oxidation rates of methane that are reported are not very high in comparison with other organic compounds (e.g. methane degradation is 6 times as slow as propene degradation (Kleinschmidt & Hesse, 2002)), the oxidation rate is still much higher than the methane decrease we found in our experiments. We infer two possible explanations for the relatively low degradation of methane that we found in comparison with the literature discussed in section 2.2.5:

1) The experiments we know from literature (see section 2.2.5) were conducted at much higher methane concentrations than our experiments, viz 10 to 1000 times higher. If the concentration of methane is the rate-limiting factor in the photocatalytic process, a higher methane concentration will thus result in a higher methane conversion rate. This may (partly) explain the relatively low methane oxidation rates that were found in our experiments.

2) TiO_2 is a collective term for three different minerals: anatase, rutile, and brookite. Because these minerals have different spatial structure, their capacity for enhancing photocatalytic reactions may differ. In some experiments that were described in literature (see section 2.2.5) mixtures of different minerals where used whereas in our experiments 100% anatase was used. Therefore differences in the composition of the TiO_2 that is used may (partly) explain the different rates of methane oxidation that were found.

Another difference between our experiments and the experiments from literature (see section 2.2.5) is that our experiments were carried out at lower temperature (at 20 - 30°C); the experiments that were described in literature had been carried out at 40 - 50°C. In general, lower reaction temperatures result in a lower oxidation rate. As already has been mentioned in section 2.2.5, Thampi *et al.* (1988) showed for the photocatalytic oxidation of methane on a TiO_2/MoO_3 catalyst, that an increase of the reaction temperature of 150° resulted in a doubling of the methane oxidation rate. Therefore no large influence is expected from a temperature raise of 20 - 30°C so that the temperature aspect does not sufficiently explain the large differences in the measured methane oxidation rates.

However, on the basis of the current work it is not possible to conclude if these explanations are applicable to our experimental results. Further research is necessary.

5 Conclusions and recommendations

The aim of this research was to develop a laboratory scale photocatalytic air filter installation for removal of methane from air originating from animal houses and manure storages. This eventually should result in a cost effective air treatment technique for reducing methane emissions.

However, in our laboratory installation we were not able to realise a significant photocatalytic breakdown of methane at room temperature and atmospheric pressure in a methane concentration range from 80 to 250 ppm. Although some reports on photocatalytic oxidation of methane under mild conditions are known, the oxidation rate of methane that we found was much lower than in these reports.

We recognize three possible explanations for the relatively low degradation rate of methane that we found:

1) The experiments we conducted were carried out at much lower methane concentrations than the experiments we know from literature, viz 10 to 1000 times lower. If the concentration of methane is the rate-limiting factor in the photocatalytic process, a lower methane concentration will thus result in a lower methane conversion rate. This may (partly) explain the relatively low methane oxidation rates that we found.

2) TiO_2 is a collective term for three different minerals: anatase, rutile, and brookite. Because these minerals have different spatial structure, their capacity for enhancing photocatalytic reactions may differ. In some of the experiments that were reported in literature mixtures of different minerals where used whereas in our experiments 100% anatase was used. Therefore differences in the composition of the TiO_2 that is used may (partly) explain the different rates of methane oxidation that were found.

But even at degradation rates that are similar to the cited literature, the degradation rate is still too low to form the basis of an air filter installation that can be operated in a cost effective way. Therefore it is necessary to further increase the methane degradation rate. This would require further research on new (mixtures of) catalysts and dopants that could be used by photocatalysis in order to achieve higher methane degradation rates.

It is difficult to assess the extent of such research because until now little research effort has been put into the subject of photocatalytic oxidation (of methane) at room temperature and atmospheric pressure, in comparison with research on photocatalytic conversion processes at high temperatures and pressures.

References

Anderson GA., Smith RJ, Bundy DS, Hammond EG (1987) Model to predict gaseous contaminants in swine confinement buildings. J. Agric. Engng Res. 37, pp. 235-253 (reference 10-16).

Chen X, Li S (2000) Catalytic activities of MoO_3/TiO_2 and WO_3/TiO_2 for photocatalytic oxidation of CH_4 by O_2. Fenzi Cuihua, 14(4), p. 245-246.

Grätzel M, Thampi KR, Kiwi J (1989) Methane oxidation at room temperature and atmospheric pressure activated by light via polytungstate dispersed on titania. Journal of Physical Chemistry 93, pp. 4128-4132. 3.

Guingand N, Granier R, Massabie P (1997) Characterization of air extracted from pig housing: effects of the presence of slurry and the ventilation rate. In: Proceedings of the international symposium on ammonia and odour control from animal production facilities, pp. 49-55. October 6-10, 1997, Vinkeloord, Netherlands.

Groot Koerkamp PWG (1997) Climatic conditions and aerial pollutants in and emissions from commercial animal production systems in the Netherlands. In: Proceedings of the international symposium on ammonia and odour control from animal production facilities, pp. 139-144. October 6-10, 1997, Vinkeloord, Netherlands.

Hansen MN (s.a.) Danish Institute of Agricultural Sciences, Department of Agricultural Engineering, Denmark.

Hilhorst MA (2001) Projectvoorstel Fotokatalytisch luchtfilter voor methaan uit stallen en mestopslagen. Aanvraag subsidie. Besluit milieusubsidies. Subsidieregeling Reductie Overige Broeikasgassen (ROB) 2000 (in Dutch). IMAG, Wageningen, Netherlands.

Husted S (1994) Seasonal variation in methane emission from stored slurry and solid manures. Journal of Environmental Quality, 23: 3, pp. 585-592.

Hilhorst MA, Gijsel de P (2000) Unpublished results. IMAG, Wageningen, Netherlands.

Kleinschmidt O, Hesse D (2002) Kinetics of the photocatalytic total oxidation of different alkanes and alkenes on TiO_2 powder. The Canadian Journal of Chemical Engineering, vol. 80, pp. 71-78.

Kolmakov KA, Pak VN (1999) Photocatalytic oxidation of methane to formaldehyde on the tunsten oxide surface. Russian Journal of Applied Chemistry 73, 1, pp. 170-171. 4.

Meyer DJ, Manbeck HB (1986) Dust levels in mechanically ventilated swine barns. ASAE paper no. 86-4042. American Society of Agricultural Engineers, St. Joseph, MI, USA.

Mol G (2003) Personal communication. Figures originate from database of ventilation rates measured by IMAG (published in several reports). IMAG, Wageningen, Netherlands.

Noceti RP, Taylor CE, D'Este JR (1997) Photocatalytic conversion of methane. Catalysis Today 33, pp. 199-204.

Pichat P, Disdier J, Hoang-Van C, Mas D, Goutailler G, Gaysse C (2000) Purification/deodorization of indoor air and gaseous effluents by TiO_2 photocatalysis. Catalysis Today 63, pp. 363-369.

Ogink NWM, Lens PN (2000) Geuremissies uit de veehouderij (in Dutch). IMAG-nota V 2000-11, 36 pp. IMAG, Wageningen, Netherlands.

RIVM & CBS (2001) Milieucompendium 2000: het milieu in cijfers. Rijksinstituut voor Volksgezondheid en Milieu, Bilthoven, Netherlands.

Saint-Gobain Isover SA (2000) Unpublished results. Courbevoie, France.

Saint-Gobain Quartz SAS (2003) Unpublished results. Nemours, France.

Schulte DD (1997) Critical Parameters for Emissions. In: Proceedings of the international symposium on ammonia and odour control from animal production facilities, p. 23-34. October 6-10, 1997, Vinkeloord, Netherlands.

Thampi KR, Kiwi J, Grätzel M (1988) Room temperature photo-activation of methane on TiO2 supported molybdena. Catalysis Letters 1, pp. 109-116.

Uenk GH, Demmers TGM, Hissink MG (1993) Luchtsamenstelling onder de overkapping van mestsilo's vóór en na het mixen van de mest (in Dutch). Report 93-10. IMAG-DLO, Wageningen, Netherlands.

Taylor CE, Noceti RP (2000) New developments in the photocatalytic conversion of methane to methanol. Catalysis Today 55, pp. 259-267.

Williams AG, Nigro E (1997) Covering slurry stores and effects on emissions of ammonia and methane. In: Proceedings of the international symposium on ammonia and odour control from animal production facilities; pp. 421-428. October 6-10, 1997, Vinkeloord, Netherlands.

Summary

The methane (CH_4) emission from livestock farming in the Netherlands adds up to about 10 Mtonne CO_2-eq. per year. The aim of this research is to develop a laboratory scale photocatalytic air filter installation that is capable of reducing this emission by removing methane from air that is withdrawn from liquid manure storages and from exhaust air of animal houses. This eventually should result in a cost effective air treatment technique that is capable to remove 50% of the methane from the air that is treated.

A first series of photocatalytic experiments was carried out on laboratory scale using titanium dioxide (TiO_2) coated glass wool that is exposed to UV-A light of 365 nm and to an air/methane mixture of 80 - 125 ppm CH_4. As the foreseen practical application of such an air filter installation should be able to operate under moderate conditions, the experiments were carried out at room temperature and atmospheric pressure. Unfortunately we were not able to demonstrate significant photocatalytic breakdown of methane under these conditions, as the decrease was only 15% after 1,000 hours. However, under the same conditions we were able to show a much higher degradation rate of n-hexane (C_6H_{14}), viz. 90% removal after 60 hours. Regardless of the degradation that was found, all experiments showed a significant increase of the CO_2 concentration, from atmospheric concentration (500 ppm) up to 21,000 ppm after 1,000 hours. This CO_2 production is probably caused by the photocatalytic breakdown of an organic coupling agent that is present in the manufactured glass wool.

XRF analysis of the TiO_2 coating that was present on the glass wool showed that migration of sodium (Na) ions to the TiO_2 crystal structure ('aging') may be responsible for a low photocatalytic activity of the TiO_2 which may explain the low oxidation rate that was found for methane.

Therefore a second series of photocatalytic experiments was carried out on laboratory scale in which the TiO_2 coated glass wool had been replaced by TiO_2 coated quartz fibres, as the TiO_2 coated quartz is not subject to this aging process due to the absence of Na ions. Experiments with methanol in a continuous-flow reactor indeed showed that the photocatalytic degradation capacity at UV-365 nm for TiO_2 coated quartz is much higher than for TiO_2 coated glass wool. The methane degradation rate also seemed to increase with the use of quartz. In a batch experiment with TiO_2 coated quartz (at $t = 0$, $[CH_4] = 250$ ppm) the methane concentration decreased with 15% after 50 hours. However, with respect to the commercial application of an air treatment installation, the methane degradation rate is still too low for cost effective emission reduction.

Although only few reports on photocatalytic oxidation of methane under mild conditions are known, these reports mention higher oxidation rates than the rates we found. Possible explanations for this inconsistency are:

1) The experiments we conducted were carried out at much lower methane concentrations than the experiments we know from literature, viz 10 to 1000 times lower. If the concentration of methane is the rate-limiting factor in the photocatalytic process, a lower methane concentration will thus result in a lower methane conversion rate. This may (partly) explain the relatively low methane oxidation rates that we found.

2) TiO_2 is a collective term for different minerals, viz anatase, rutile, and brookite, that each have a different spatial structure so that the photocatalytic activity may differ for the different forms. In our experiments 100% anatase was used whereas in some of the experiments that were reported in literature mixtures of anatase, rutile, and brookite were used. This may (partly) explain the relative low methane oxidation rate that was found in this research.

Nevertheless, the methane degradation rates that can were found in literature, are still too low for the development of a cost effective air filter installation for reduction of methane emissions. Therefore it is necessary to further increase the methane degradation rate. This would require further research on new (mixtures of) catalysts and dopants that could be used to improve the photocatalysis process. With the current knowledge it is difficult to assess the extent of such research because until now little research effort has been put into the subject of photocatalytic oxidation (of methane) at room temperature and atmospheric pressure, in comparison with the research effort that has been put into the subject of photocatalytic conversion processes at high temperatures and pressures.

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Samenvatting

De Nederlandse veestapel is verantwoordelijk voor een emissie van methaan (CH_4) van circa 10 Mton CO_2-eq. Tachtig procent van deze emissie is afkomstig van pensvergisting in herkauwers (hoofdzakelijk koeien) en twintig procent is afkomstig van vergistingsprocessen die plaatsvinden gedurende mestopslag, zowel onder de stal als in opslagen buiten de stal. Reiniging van ventilatielucht van stallen, d.w.z. emissies uit de mestopslag onder de stal en rechtstreekse emissies uit het dier, en van ventilatielucht van externe mestopslagen heeft daarom een hoog potentieel voor reductie van de emissie van broeikasgassen. Op dit moment is er echter geen 'methaanfilter' commercieel beschikbaar.

Het doel van onderhavig onderzoek is het ontwikkelen van een fotokatalytisch luchtfilter op laboratorium-schaal dat in staat is methaan te verwijderen uit ventilatielucht van stallen en mestopslagen. Het te ontwikkelen luchtfilter moet in staat zijn om een methaanverwijdering van 50% te realiseren.

Een eerste serie laboratoriumexperimenten werd uitgevoerd in een afgesloten cilindervormig reactorvat van 5,6 liter waarvan één zijde was afgesloten met een glazen plaat. In de reactor bevonden zich één of meerdere doeken van glaswol waarop een coating van titaniumdioxide (TiO_2) was aangebracht. De reactor werd gevuld met een methaan/luchtmengsel (80 - 125 ppm CH_4) en blootgesteld aan UV-A straling (365 nm); de concentraties van methaan en kooldioxide (CO_2) in de reactor werden gemeten. De experimenten werden uitgevoerd bij kamertemperatuur en atmosferische druk, aangezien dit de condities zijn van de stallucht die uiteindelijk beoogd wordt te behandelen. Helaas waren we onder deze condities niet in staat om een significante afbraak van methaan te bereiken; de afbraak bedroeg slechts 15% na 1.000 uur. Onder dezelfde omstandigheden konden we echter wel een significante afbraak van n-hexaan (C_6H_{14}) aantonen, te weten 90% verwijdering na 60 uur. Onafhankelijk van de mate waarin afbraak werd gevonden, werd in alle experimenten een sterke toename van CO_2 gevonden; de CO_2 concentratie in de reactor nam toe van 500 ppm (atmosferische concentratie) tot 21.000 ppm na 1.000 uur. Deze CO_2 productie wordt waarschijnlijk veroorzaakt door fotokatalytische afbraak van organische bindmiddelen die aanwezig zijn in het glaswol als gevolg van het productieproces.

Analyses van de kristalstructuur van het TiO_2 dat zich op het glaswol bevond, wezen uit dat de kristalstructuur was vervuild met natrium-ionen die waarschijnlijk afkomstig zijn van het glaswol. Dit verklaart mogelijk de lage fotokatalytische activiteit van TiO_2 zoals die werd gevonden voor de oxidatie van methaan.

In een tweede serie laboratoriumexperimenten werd de glaswol in de reactor vervangen door kwartsvezels, aangezien er dan geen vervuiling van het TiO_2 kan plaatsvinden door natrium-ionen. Experimenten waarin een reactor continu werd doorstroomd met een luchtstroom met 250 ppm methanol (CH_3OH), wezen uit dat op deze manier een zeer snelle fotokatalytische afbraak van methanol plaatsvindt op de kwartsvezels met TiO_2 coating. Deze afbraak werd niet gevonden wanneer zich in de reactor glaswol bevond in plaats van kwartsvezels. In deze continu doorstroomde reactor werd echter geen afbraak van methaan waargenomen, ook al was de glaswol vervangen door kwartsvezels. Daarom werd tenslotte een experiment uitgevoerd in een gesloten reactor (1,2 liter) bij een methaanconcentratie van 250 ppm, om op deze manier de verblijftijd van methaan in de reactor te verhogen. Op deze manier werd een afname van de

methaanconcentratie gevonden van 15% na 50 uur, hetgeen een veel sterkere reductie van de methaanconcentratie is dan in eerdere experimenten. Voor de commerciële toepassing van het fotokatalytisch proces in een luchtwassysteem is deze afbraak echter nog veel te laag. De kosteneffectiviteit van de reductie van methaanemissies zou erg laag zijn in een dergelijk luchtwassysteem.

Uit de literatuur is weinig onderzoek bekend naar de fotokatalytische oxidatie van methaan onder milde omstandigheden, d.w.z. bij kamertemperatuur en onder atmosferische druk. In de bekende onderzoeken worden echter wel hogere oxidatiesnelheden gevonden voor methaan dan in onderhavig onderzoek. Drie mogelijke verklaringen hiervoor zijn:

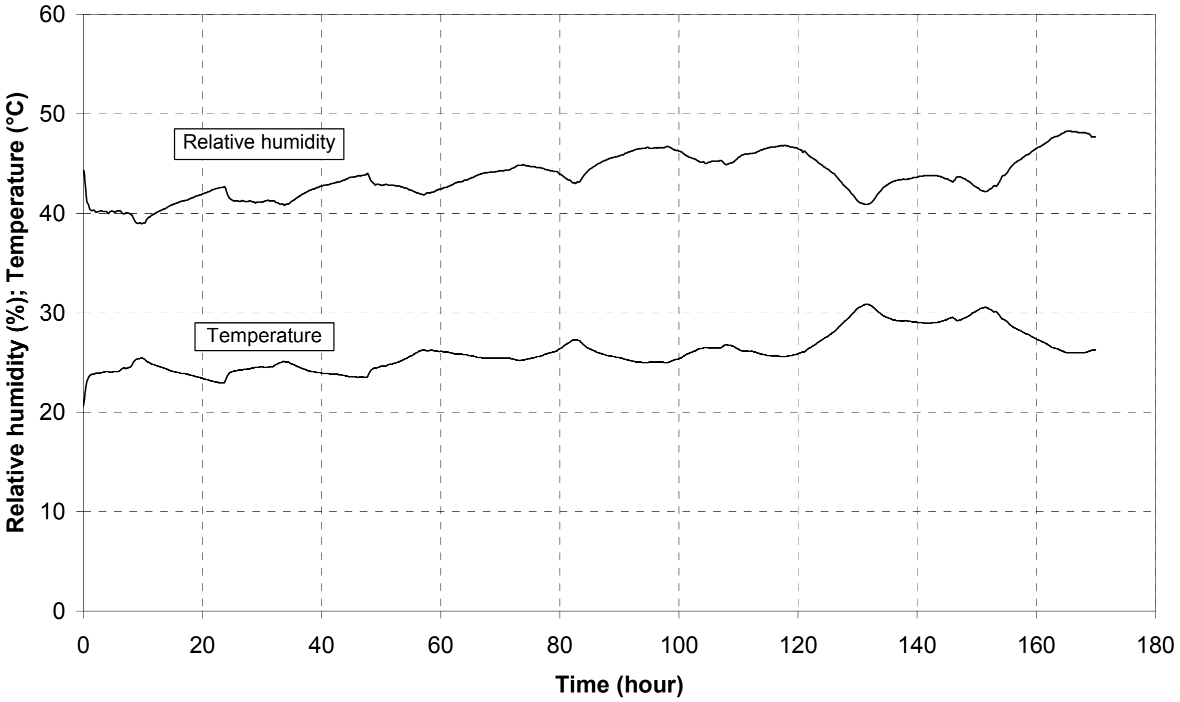
1) De experimenten in onderhavig onderzoek zijn uitgevoerd bij een methaanconcentratie die 10 tot 1.000 maal zo laag is als de uit de literatuur bekende onderzoeken. Wanneer de methaanconcentratie de snelheidsbeperkende factor is voor de methaanomzetting, zal een lagere methaanconcentratie resulteren in een lagere methaanomzettingssnelheid. Hiermee zou de relatief lage methaanoxidatiesnelheid in onderhavig onderzoek (deels) kunnen worden verklaard.

2) TiO_2 is een verzamelnaam voor verschillende mineralen, te weten anataas, rutiel en brookiet, die elk een verschillende ruimtelijke kristalstructuur hebben. Op grond hiervan wordt een verschillende fotokatalytische activiteit verwacht voor de verschillende mineralen. In de in dit rapport beschreven experimenten is gebruik gemaakt van 100% anatase terwijl in sommige uit de literatuur bekende onderzoeken mengsels van anataas, rutiel en brookiet werden gebruikt. De verschillen in samenstelling van TiO_2 tussen de onderzoeken zouden (deels) de relatief lage methaanoxidatiesnelheid in onderhavig onderzoek kunnen verklaren.

Desondanks zijn de hogere methaanafbraaksnelheden die in de literatuur worden gevonden nog steeds te laag voor de praktische toepassing van fotokatalyse in een luchtwassysteem op een kosteneffectieve wijze. Hiervoor is het noodzakelijk de methaanafbraaksnelheid verder te verhogen. Om de methaanafbraaksnelheid te verhogen is het noodzakelijk nader onderzoek te doen naar nieuwe (mengsels) van katalysatoren en toevoegstoffen die het proces van fotokatalyse kunnen verbeteren. Op grond van de huidige kennis is de omvang van dergelijk onderzoek moeilijk in te schatten, aangezien er tot op vandaag de dag weinig onderzoek is gedaan naar fotokatalytische omzettingsprocessen (van methaan) bij kamertemperatuur en onder atmosferische druk, in vergelijking met onderzoek naar fotokatalyse bij hoge temperatuur en druk.

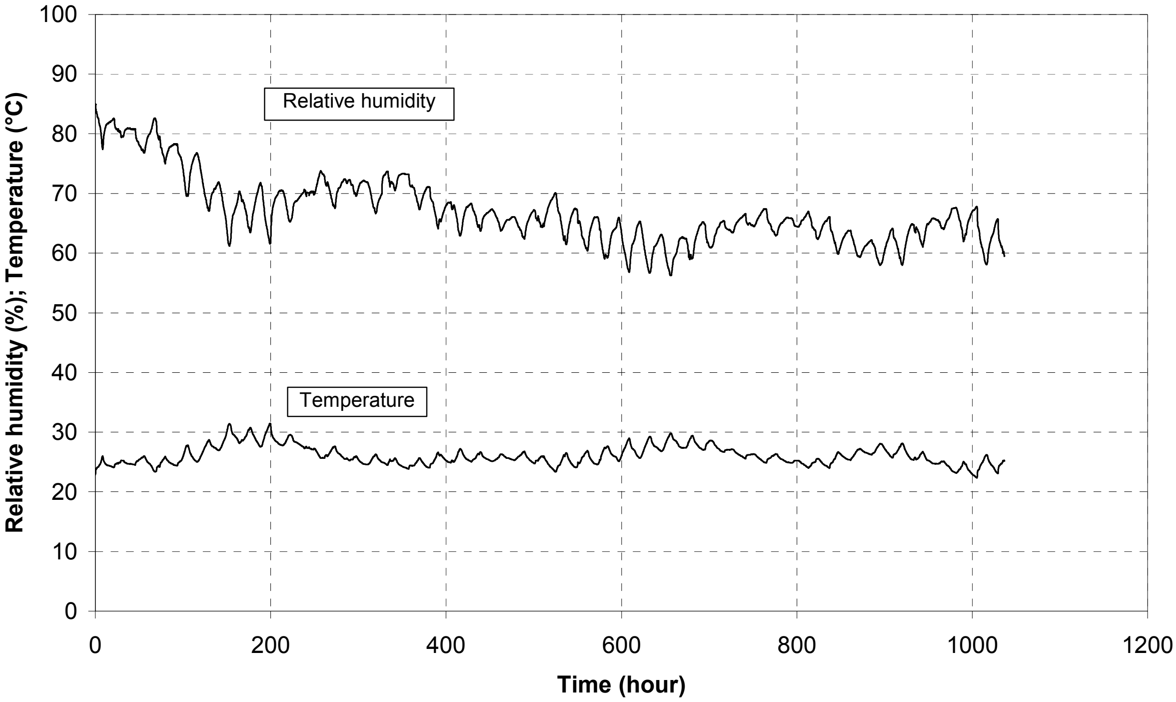
Het onderzoek is uitgevoerd door Agrotechnolgy & Food Innovations in samenwerking met Saint-Gobain Quartz SAS and Saint-Gobain Isover SA. De financiering van het project is afkomstig van Novem in het kader van het Besluit milieusubsidies Subsidieregeling Reductie Overige Broeikasgassen (ROB-AGRO projectnummer: 375102/0020) en van het Ministerie van Landbouw, Natuur en Voedselkwaliteit (Vrije ruimte programma 309, 'Gasvormige emissies in de veehouderij'). Het project is uitgevoerd in de periode van januari 2001 tot oktober 2003.

Appendix A



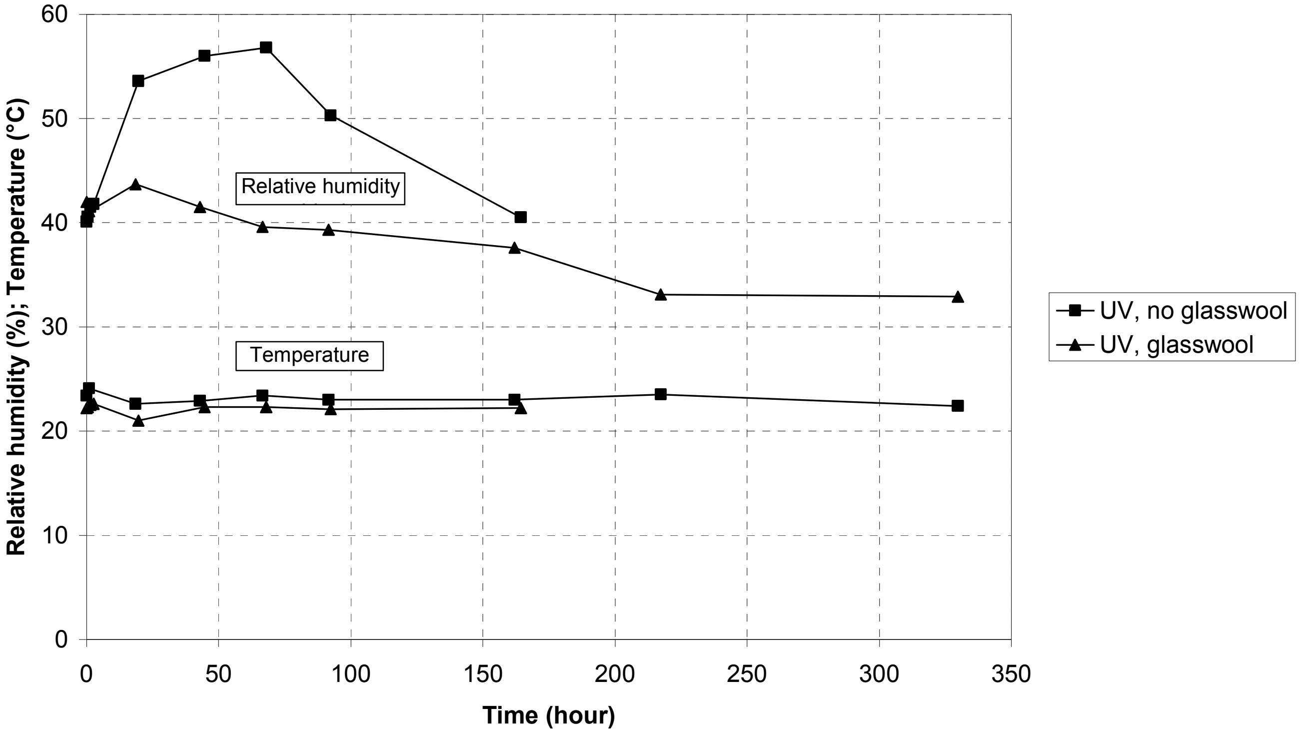
Experiment 2: Temperature and relative humidity

Appendix B



Experiment 3: Temperature and relative humidity.

Appendix C



Experiment 4: Temperature and relative humidity.