Thesis Biomass Refinery and Process Dynamics

# Membrane technology for the optimization of bioethanol production from coffee waste

Titus Galema

26-08-2014





WAGENINGEN UNIVERSITY AGROTECHNOLOGY AND FOOD SCIENCES



WAGENINGEN UR

# Membrane technology for the optimization of bioethanol production from coffee waste

Name course	:	Thesis project Biomass Refinery and Process
		Dynamics
Number	:	BRD-80436
Study load	•	36 ects
Date	•	26-08-2014
Student	:	Titus Galema
Registration numb	ber	: 821128249110
Study programme		: Master Biosystem Engineering (MAB)

Supervisor(s)	•	dr. ir.Ton van Boxtel		
Examiners	:	dr. ir.Ton van Boxtel, dr.ir. PM Puylaert-Slegers		
Group	:	Biomass Refinery and Process		
Address	•	Bornse Weilanden 9		
		6708 WG Wageningen		
		the Netherlands		
		Tel: +31 (317) 48 21 24		
		Fax: +31 (317) 48 49 57		



#### Preface

The production of bioethanol from coffee waste has my interest since I did my bachelor thesis at Colombia in 2006. There I worked with John Loke (renewable energy specialist at the International Centre for Tropical Agriculture) on a feasibility study on Jatropha for the Colombian agro-climatic situation. In the meanwhile, John was developing small scale bioethanol unit for the use of coffee waste using local construction materials. In the last seven years, several bioethanol units for this feedstock have been constructed and tested in Colombia and Central American countries. Later, during my work at the STRO foundation (a Netherlands based NGO that fosters rural development) I have been involved in the setup of one of these installations in Costa Rica at the Coopevictoria Cooperative. The willingness to find smart solutions for waste streams is the drive for this thesis. I would like to give special thanks to John Loke (Ecoenergy B.G. Ltda., Cali, Colombia), Peter Moers, Christina Santos (STRO). Many thanks to Winfried Rijssenbeek from FACT Foundation who gave me the opportunity to start working for FACT while starting this thesis work and supported with his knowledge on renewables and membrane technology. Also special thanks to Ton van Boxtel (Wageningen University) who saw an opportunity in this thesis work. I highly appreciate his flexibility and regular feedback sessions.

#### **Summary**

The coffee industry is a significant consumer of fossil energy and generates large amounts of organic waste streams, resulting in a pressure on the environment. Several initiatives exist in order to tackle both issues in a combined solution, implementing renewable energy solutions using industrial waste streams. An interesting technology is the production of ethanol from the waste streams depulping coffee berry. Currently the demand of energy of small scale bioethanol production is relatively high compared to large scale ethanol production.

This thesis aims to optimize the energy requirement for the production of bioethanol from coffee waste using membrane technology focussing on mucilage (honey water) from coffee berries as feedstock.

For this, current industrial processes for the production of ethanol have been analysed in terms of energy use. Promising alternative techniques like reverse osmosis and pervaporation were analysed in order to determine their potential for implementation in small scale bioethanol production. Several tests on the concentration of sugar before fermentation and tests on fermentation were carried out in order to determine the behaviour of these production steps in practice.

In the current ethanol production process distillation is the most energy demanding step especially when fermentation is done at a relative low concentration of sugar. Pervaporation seems to be an energy saving solution mainly for the azeotrope phase of the ethanol water separation. Reverse osmosis can contribute significantly to improve the energy efficiency of the current bioethanol production process by the concentration of sugars in the feedstock. Reverse osmosis will be implemented prior to the fermentation process in order to concentrate the sugars in the feedstock resulting in a higher ethanol concentration in the fermentate. Higher viscous substances do have lower fermentation efficiency, but energy savings can still be made.

This thesis was carried out driven by the motivation to improve local conditions for small coffee farmers. The effect of improved ethanol production from coffee waste on the livelihoods of farmers largely depends on many other factors among other adaptability of the technology and economic feasibility. Coffee waste contains other valuable elements like pectines and proteins that can be extracted for commercial purpose. The market opportunities for energy in rural areas are nevertheless higher than those for organic compounds.

### Abbreviations and acronyms

°C	Degree Celsius
BOD	Biological oxygen demand
CIAT	International Center for Tropical Agriculture
COD	Chemical oxygen demand
DM	Dry matter
E90	Ethanol at a concentration of 90% (v/v)
EtOH	Ethanol
FACT	FACT Foundation
GHG	Greenhouse gas
М	Molecular mass
MJ	Megajoule
Мра	Megapascal
MWCO	Molecular weight cut of
NER	Net energy ratio
Ра	Pascal
рН	Power of hydrogen
RE	Renewable energy
RO	Reverse osmosis
STP	Standard conditions for temperature and pressure
STRO	Social Trade Organization
wно	World Health Organization

### Contents

Preface .	
Summar	yiv
Abbrevia	tions and acronymsv
List of fig	uresviii
List of ta	blesix
Introd	uction1
1.1.	The global coffee industry
1.2.	Coffee berry and its products2
1.3.	The potential use of by products from coffee processing
1.4.	Membrane technology for ethanol production4
1.5.	Aim of this thesis 4
1.6.	Research Approach5
2. Pro	cess description of small scale coffee processing
2.1.	Introduction of small scale coffee processing
2.2.	Description of post-harvest activities
2.3.	Use of coffee waste streams
2.4.	Fermentation process of coffee waste9
2.5.	Distillation of the coffee waste broth10
3. Ene	rgy requirements of coffee and ethanol production processes
3.1.	Introduction11
3.2.	Energy requirements of fermentation reaction
3.3.	Energy requirement for the distillation process14
3.3.1.	Introduction14
3.3.2.	Calculating the energy requirement for distillation15
3.3.3.	Energy requirements in practice from pilot projects
3.4.	Other process energy requirements
3.5.	Total energy requirements of ethanol production18
3.6.	Hypothesis on current energy use
3.7.	Membranes as an energy saving alternative19
3.8.	Pervaporation19

	3.9.	Energy requirements of pervaporation	20
	3.10.	Reverse osmosis as an energy saving alternative	23
	3.11	Energy requirements of reverse osmosis	24
	3.12.	Experimental set up for concentrating sugar solutions using reverse osmosis	27
	3.12.1	Introduction of RO experiment	27
	3.12.2	Objective reverse osmosis experiment	28
	3.12.3	Material and methods	28
	3.12.2	Results of RO test	31
4	Effect	of the sugar content of the feedstock on the fermentation efficiency.	34
	4.1	Introduction	34
	4.2	Effect of concentrating feedstock	35
	4.3	Objective	35
	4.4	Experimental procedure	35
	4.4.1	Principles	35
	4.4.2	Materials Method	36
	4.5	Results of the fermentation experiment on fermentation efficiency	37
	4.6	Laboratory analysis	39
	4.7	Conclusions on fermentation experiment	41
5	Discus	sion	43
6	Conclu	isions	44
Ann	exes		45
١.	Compo	osition of coffee waste	45
١١.	Energy	for mucilage transport	48
III.	Ener	rgy requirement for pervaporation	49
IV.	Ener	rgy requirement for reverse osmosis	51
V.	Practic	al RO Test calculations	52
VI.	Set u	up for fermentation experiment	52

#### **List of figures**

Figure 1 Structure of the coffee berry Figure 2. Construction of ethanol plant in Costa Rica Figure 3 From left to right: submerging, reception, depulping and demucilaging Figure 4 From left to right: coffee pulp disposal, mucilage recollection and coffee bean storage Figure 5 Flow chart of coffee processing (percentages are in fresh weight%) Figure 6 Flow chart of mucilage and pulp for ethanol production (own elaboration) Figure 7 Continuous stirred batch fermentation reactors for coffee pulp in Colombia Figure 8 Small scale bioethanol plant designed for agricultural waste installed in Panama Figure 9 Potential energy release from the fermentation vessel Figure 10 Systematic drawing of liquid and vapour flows of distillation process Figure 11 Energy requirement of distillation process Figure 12 Comparison of energy requirement and release of ethanol production process Figure 13 Working principle of pervaporation (FACT outlook membrane technology) Figure 14 Schematic view of pervaporation system Figure 15 Place of pervaporation in process flow of coffee waste for ethanol Figure 16 Energy requirement for pervaporation Figure 17 Potential place of reverse osmosis in coffee waste processing for ethanol Figure 18 Schematic representation of reverse osmosis in a batch reactor Figure 19 Required energy for ethanol concentration using reverse osmosis Figure 20 Energy requirement for concentration sugar at 4x10<sup>6</sup> [Pa] and 6x10<sup>6</sup> [Pa] Figure 21 labcell Koch CF1 Figure 22 RO batch system Figure 23 cumulative permeate flow of RO sugar treatment Figure 24 cumulative permeate flow of RO sugar treatment at different pressures Figure 25 membrane resistance of 10% sugar/puree samples at different pressures. Figure 26 Energy savings when applying RO Figure 27 Flow chart for coffee waste processing using concentrated mucilage Figure 28 Fermentation efficiency of different sugar solutions based on weight measurements Figure 29 fermentation rate as a function of sugar concentration in puree samples Figure 30 fermentation rate as a function of sugar concentration in sugar solution samples Figure 31 Chromatogram of determination of components in test bottles 1-6 (puree) Figure 32 Chromatogram of determination of components in test bottles 7-12 (sugar solutions) Figure 33 Setup fermentation test

#### **List of tables**

Table 1 Weight of the different components of coffee berry (Bressani, 1979) Table 2 Composition of mucilage and pulp adapted from (Mazzafera, 2002) Table 3 Potential ethanol production from diluted mucilage Table 4 Gibbs energy of different components of the fermentation reaction Table 5 Potential temperature change of batch fermentation Table 6 Energy requirement for distillation Table 7 Energy requirement for distillation from empirical data Table 8 Data for energy requirement for pervaporation Table 9 Data for energy for RO ethanol concentration compared with distillation Table 10 Energy requirement for R.O. of ethanol at different pressures Table 11 set up of the samples of the RO experiment Table 12 comparison of Reverse Osmosis and distillation energy requirements Table 13 composition of used apple puree Table 14 Comparison between laboratory analysis of and measurements Table 15 Calculation of potential ethanol production from coffee mucilage Table 16 Composition of coffee pulp Table 17 Composition of coffee waste water Table 18 Energy for mucilage transport Table 19 Energy requirement for pervaporation Table 20 Energy requirement for reverse osmosis Table 21 Comparing energy for RO and mixing of Labcell CF 1 Table 22 Set up for fermentation experiment Table 23 List of materials for fermentation experiment

#### Introduction

Since fossil fuels are finite, alternatives have been developed in order to realize the energy transition from fossil fuels to renewable energy (e.g. biodiesel, bioethanol). Moreover with regard to climate change, alternative energy sources that reduce greenhouse gas emissions are gaining more attention. A promising alternative is bioethanol (Goettemoeller, 2008). It can (among other applications) be used as a transport fuel, mixed with gasoline or used for indoor cooking. For the latter application it has potential to contribute to reducing the pressure on forests for firewood use and reduce respiratory diseases due to indoor air pollution. Yearly over 4 million people die prematurely from illness attributable to the household air pollution from cooking with solid fuels (WHO, 2014).

Furthermore, many agricultural waste products with high BOD, low pH or high nitrogen levels, are released into the environment, causing environmental damage e.g. carbon dioxide and methane emissions and water contamination. Some of these agricultural waste products can instead be used as a feedstock for biorefinery processes like energy production. Currently only little attention is given to adequate treatment of residual production streams since individual quantities are relatively low, environmental legislation is lacking, laws are not enforced by local governments and no technological solutions are available. Waste streams can however be used in order to generate bio energy for on farm production processes, produce organic fertilizer and reduce environmental impact of coffee production.

Although the technical feasibility of bioethanol installations have been demonstrated, it was suggested from pilot experiences in Central America that operational costs could be reduced in order to reach economic feasibility. Since the technology is currently being optimized (according to strategic niche management (Schot & Geels, 2008) and in the phase of development and small scale pilot project), more research is required in order to make this technology widely applicable.

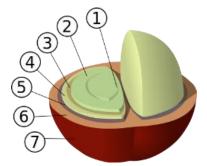


Figure 1. Structure of the coffee berry: 1, center cut; 2, bean (endosperm); 3, silver skin (testa, epidermis); 4, parchment (hull, endocarp); 5, pectin layer; 6, pulp (mesocarp); 7, outer skin (pericarp, exocarp (picture from Wikipedia).

#### 1.1. The global coffee industry

The worldwide coffee consumption is currently 2,25 billion cups per day (Ponte, 2002). The coffee production, trade and consumption is an enormous global industry that includes a production of 7,8 million tons of coffee beans per year. The world's main coffee producers are Brazil, Vietnam and Colombia ("FAOSTAT," 2009) while the biggest consumers are Finland (12 kg per capita annum), Norway (9,9 kg per capita per annum) and Iceland (9,0 kg per capita per annum) ("Chartbin," 2008). The energy requirement for one cup of coffee (100 ml) is 1,94 MJ (Humbert, Loerincik, Rossi, Margni, & Jolliet, 2009)

#### 1.2. Coffee berry and its products

Coffee beans grow as the seed of a berry on a shrub in (sub) tropical areas around the world. The bean (endosperm) consists of 39% of the total fresh weight of the coffee berry and is dried, roasted and grinded. The other 61% consists of pulp (43%), mucilage (12%), parchment, husk or silver skin (6%).

Component of the whole coffee fruit	Followed by the process step	Fresh weight [g]	Weight [%]	Moisture [%]	Dry weight [g]	Dry weigh t [%]
Coffee berry	Pulper	1.000	100	66	345	
Coffee pulp		432	43	77	99	29
Beans+mucilage+hull	Fermentation and washing	568	57	56	250	72
Mucilage					17	5
Beans+coffee hulls	Dehulling	450		50	225	
Coffee hulls		61	6	32	41	12
beans		389	39	51	191	55

#### Table 1. Weight of the different components of coffee berry (Bressani, 1979).

Table 1 presents the different processing steps and the related fresh weight, relative weights and percentages of the coffee berry's components.

At the smaller coffee processing units, the practice is that these by products are mainly considered as waste products and separated during the post-harvest processing. At the larger coffee processors the husk is used as a fuel for coffee drying and in some occasions, coffee pulp and mucilage is used in composting or feed or it is dumped locally.

	Mucilage		Р	ulp
Component	Fresh	Dry	Fresh	Dry
Unit	%	%	%	%
Water	92		77	13
Dry matter	8		23	87
Ether extract			0,5	2,5
Fiber			3	21
Protein (N x 6,25)		6	2	11
Ash		4	1,5	8
N free extract		1	15	44
рН	4			
Degree brix	9			
Reductive sugar		64		12
Total sugars		80		14
Total nitrogen		1,5		
Pectin	1	11		6,5

#### Table 2. Composition of mucilage and pulp adapted from (Mazzafera, 2002).

#### 1.3. The potential use of by products from coffee processing

The waste products from the coffee production process like pulp and mucilage, nevertheless, do contain valuable components that could be used or extracted in order to create an added value. The process wastewaters are rich in nutrients, pectines and sugars ("Cenicafe," 2006). The composition of mucilage and pulp is shown Table 2. The coffee pulp has potential to be used in animal feed, as a substrate for mushroom production, as a substrate for biogas or for the production of ethanol (Bressani, 1979). Mucilage is used for ethanol production due to its significant sugar levels (80% of its dry weight) or it can be used in order to isolate the unrefined pectines (Graziosi, 2005). In the mucilage brix levels (indicator of sugar content) between 2 and 16 degrees have been measured. This corresponds with sugar concentrations of maximum 2-16% (w/w). The coffee pulp also contain sugars (15% of the total available sugars in the waste streams), but preferably requires an extra processing step before its potential conversion to ethanol if compared to mucilage<sup>1</sup>.

<sup>&</sup>lt;sup>1</sup> It is also possible to collect mucilage and pulp together before fermentation (Ecoenergy B.G. Ltda. Colombia)



Figure 2. Construction of ethanol plant in Costa Rica (picture John Loke).

In Latin America, mainly in Colombia but also in Costa Rica, and Honduras, small scale bioethanol processing units using coffee waste as a feedstock, have been installed. The experiences so far are variable. The sugar level of the mucilage is depending on the amount of water used in the post-harvest process and the ripeness of the berry. It possibly also depending on the rainfall during the season, the variety of the coffee plant and the height of the production location. So far, there is not yet adequate information available on these variations. However the technical feasibility of ethanol production has been shown in production units of 500 liters of ethanol per day at an ethanol concentration of 60-80% (v/v). The actual experiences, nevertheless are hampered by a lack of interest of coffee research institutes, relatively high capital costs of the installation, the high energy requirements of the distillation process and the seasonal character of the availability of feedstock (J. Ferrell, 2012).

#### 1.4. Membrane technology for ethanol production

Membrane technology is generally used to separate substances based on the differences in properties like particle or molecular size, difference in phase (gas/liquid/solid), volatility and diffusion rate. Membrane technology is common in the food industry; reverse osmosis for example is used in concentrating whey proteins and fruit juices while pervaporation technology is used for dealcoholization and product improvement of aromas and flavors in the beverage industry (Nijhuis, 1993). It is claimed that the energy requirement for reverse osmosis is significantly less than for mechanical vapour compression (Jorge R. Lara, 2011) and may therefore be an interesting option for ethanol production as well. (Lipnizki, 2010) states that membrane technology as a highly selective and energy-saving unit operation has a great potential in the bioethanol industry of today and in the future. Hence, membrane technology can contribute to solving future energy and environmental problems.

#### **1.5. Aim of this thesis**

Although the technical feasibility of the production process of ethanol from mucilage has been shown, it is requested that improvements will be made to the process. The aim of the thesis is **to investigate the potential of membrane technology in the production of bioethanol from coffee** 

waste (mucilage) on the energy requirement of the process. The promising techniques and its effect on the process will be assessed in laboratory.

#### **1.6. Research Approach**

The aim of this thesis is divided in two sub questions.

• How can energy be saved by implementing membrane techniques in the current ethanol production process?

• And how will the improved production process of ethanol function in practice? In order to get these questions answered the approach is divided in different steps:

- The baseline technology for the ethanol production from mucilage is determined. This is done based on an existing examples of small scale ethanol in a rural setting in Latin America.
- 2. The energy needs of the overall process will be determined. This process will so be analysed in terms of energy use. Based on this, the bottlenecks of the process will be determined.
- 3. It is expected that membrane technology could play an important role in the improvement of the process. Therefore it is included in the energy calculations in order to quantify its potential effect on energy use.
- 4. Several experiments will be established in order to gain technical data from practice and get insight in the practical implementability of the technology.

The thesis does not assess the economic feasibility of the separation techniques, it is focussing on the energy requirements and its technical potential for implementation. It focusses on the ethanol purification process until 90% (v/v) and will not assess the optimization of the azeotrope purification process of ethanol water mixtures

The approach includes a **desk study** to describe and evaluate the production process of small scale bioethanol production from coffee waste and determine the energy requirements of the process steps. Furthermore, the different available membrane techniques for separation processes are described. The theoretical applicability of different separation technologies in the bioethanol production process are assessed by using **spreadsheet models**. Based on the findings of the desk study and the calculations, a **laboratory experiment** is designed with a similar substance as mucilage in order to investigate the practical applicability of membrane technology for separation processes in the production of bioethanol from coffee waste. Where energy requirement is expressed in joule per kilogram ethanol it is referring to ethanol of a maximum concentration of ninety percent (v/v).

Many studies on the feasibility of membrane technology for ethanol production do exist (Kaewkannetra, Chutinate, Moonamart, Kamsan, & Chiu, 2012) and (Kazi et al., 2010) but do mainly focus on the economic feasibility for larger scale ethanol industries (Lipnizki, 2010), (Wei et al., 2014). This thesis focusses specifically on the **technical and energy aspects of small scale ethanol installations (500 L/day) and low sugar containing feedstock (coffee waste).** 

#### 2. Process description of small scale coffee processing

#### 2.1. Introduction of small scale coffee processing

The global coffee production is dominated by small scale coffee farmer families summing over 25 million worldwide (America, 2005). In the following section an overview is given of current small/medium scale coffee post harvesting process.

#### 2.2. Description of post-harvest activities

As explained in section 1.2 the coffee berry consists of various components. In the post-harvest process the coffee bean is separated from the coffee pulp, the mucilage and the husk. This is done manually, biologically or mechanically. For this process various sizes of equipment are available on the market from low, appropriate technology to large industrial solutions. In general terms two different processes are distinguished: the wet process and the dry process. Wet processing is more expensive than the dry method and more care is taken right from harvesting to drying leading to a better quality coffee (Mutua, 2000). The process described below is based on coffee processing common in Central America.





After the (mainly manual) harvest, coffee berries are transported to the farm. There the berries are submerged in a reception tank filled with water. This is where selection takes place. The floating, green berries are manually removed. The reception basin is located above the depulping and demucilager in order to make feeding by gravity possible. In the depulping machine the pulp is removed from the rest of the berry **by friction** in the horizontal rotating cylinder and disposed. Next step is the separation of the mucilage by compression and washing in the vertically rotating cylinder using additional water. Current demucilaginators use minimum 1 L of water per kg of coffee beans (wet process). In some countries like Costa Rica, legislation allows 1 m<sup>3</sup> of water per fanega<sup>2</sup> of coffee (1,3 L/kg bean) for demucilaging. A more traditional way of demucilaging is by means of fermentation during 24 to 36 hours (dry process). This weakens contact between the mesocarp and the silverskin in the berry so it can be easily removed by using water. If fermentation is applied, more water is needed in the process.

<sup>&</sup>lt;sup>2</sup> A fanega is a unit of volume especially used for coffee, corresponding with 55,5 L.



Figure 4. From left to right: coffee pulp disposal, mucilage recollection and coffee bean storage.

The remaining beans (still containing the husk or silverskin) are dried to a humidity of 10%. Normally dried, starting from approximately 18% to 13% humidity after drying by sun, followed by mechanical drying until 10% humidity. Full mechanical drying is only done at very high relative humidity or place (area) restrictions. After drying, the husk is removed by using friction. This husk or silver skin represents 6% of the total dry fruit weight and is often used as a fuel for forced drying. The following step is roasting and grinding of the coffee bean (see Figure 5).

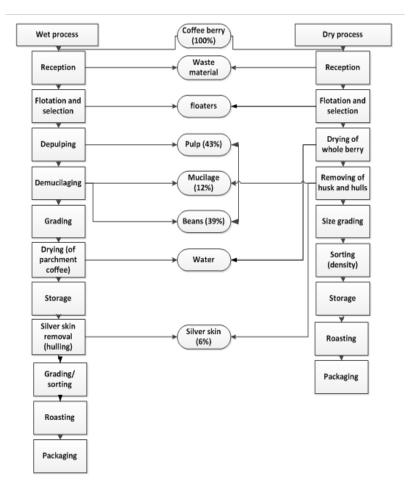
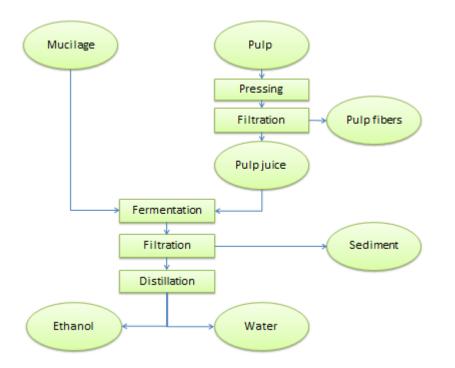


Figure 5. Flow chart of coffee processing (percentages are in fresh weight%) numbers from (Mazzafera, 2002) and (Mutua, 2000).

#### 2.3. Use of coffee waste streams

The main waste streams resulting from the coffee processing are pulp, mucilage, unripe berries, silver skin, wash water, other organic waste and dirt originating from the field during harvest. Although the highest amount of waste is represented by pulp (43% of the coffee berry), the main focus for ethanol production is on the use of mucilage because of its ease of mechanical displacement (pumping). Even though the pulp contains interesting amounts of sugars<sup>3</sup>, it is sometimes used as organic fertilizer in on farm composting processes. Moreover the use of pulp for ethanol production would require additional processing steps as shown in Figure 6.



#### Figure 6. Process scheme of mucilage and pulp for ethanol production (own elaboration).

The pulp first need to be pressed and filtered in order to separate the solid from the liquid fraction. The solid pulp fraction will be separated from the process and the liquid pulp fraction, containing the sugars, could be used for fermentation. As stated before, these steps have not been fully evaluated in practice.

In this thesis the focus is on the mucilage. Mucilage used for fermentation has been diluted with water during the separation of pulp from the seeds (beans)<sup>4</sup>. This results in lower sugar concentrations as compared to the original mucilage in the berry. Despite of the relatively low sugar levels several full scale processing plants exists.

<sup>&</sup>lt;sup>3</sup> 12,4% DM according to Paulo Mazzafera 2002 while mucilage contains of to 80% of its dry matter.

<sup>&</sup>lt;sup>4</sup> Approximately 1 liter of water is used for demucilaging per kg of dry coffee beans.

#### 2.4. Fermentation process of coffee waste

The separated mucilage is fermented. Fermentation is defined as the anaerobic conversion of sugars into ethanol and carbon dioxide by yeast. The fermentation process is described as follows:

 $C_6H_{12}O_6 \rightarrow 2.C_2H_5OH + 2CO_2$ 

For the fermentation, the yeast *Saccharomyces cerevisiae* is used. These fungi convert the sugars into ethanol and carbon dioxide.

Per mole of sugars, two moles of ethanol and 2 moles of carbon dioxide are formed. The molecular mass of sugar ( $M_{sugar}$ ) is 180 [g/mol] and the molecular mass of ethanol (MEtOH) is 46 [g/mol]. The conversion factor (Fc) used for sugars to ethanol is 2xMEtOH/ $M_{sugar}$ = 0,51 [-], meaning the production of 0,51 grams of ethanol per gram of sugar.

Description	Unit	Amount
Fresh mucilage	Grams	1.000
Total sugars	Grams	62,2
Additional water	Grams	1.500
Total sugars after dilution	Grams	24,9
Total ethanol after dilution	Grams	12,7

Table 3. Potential minimum ethanol production from diluted mucilage.

The sugar level in the ripe coffee berry is between 6 and 15% (w/w) (Valencia 2010). In this scenario we focus on the minimum value. Theoretical ethanol yield from mucilage calculated from fully diluted mucilage is around 12,7 grams in a total volume of approximately 2,5 liter. This results in an ethanol percentage of slightly more than 1%<sup>5</sup>. The amount of ethanol produced increases either by reducing the amount of water during the production process or by selecting coffee fruit with higher sugar levels. In general low-concentration fermentable sugars in the pre hydrolyzates and fermentation inhibitors lead to low ethanol concentrations, which in turn leads to high operational cost and energy consumption for subsequent purification steps (Wei et al., 2014). An example of continuous stirred batch fermentation in practice is shown in Figure 7.

<sup>&</sup>lt;sup>5</sup> The full calculation is shown in Annex I.



Figure 7. Continuous stirred batch fermentation reactors for different raw materials including mucilage and lixiviate of coffee pulp in Colombia (picture John Loke).

#### 2.5. Distillation of the coffee waste broth

In the current ethanol production process the broth from the fermented mucilage is concentrated by distillation (as indicated in Figure 6). The technology used is au bain-marie glycol, wood fired oven and a stainless steel multi stage distillation column using plates to facilitate liquid vapour phase change. Figure 8 is an example of small scale bioethanol production at Panama. There the technology is used for ethanol production from cassava waste streams.



Figure 8. Small scale bioethanol plant designed for agricultural waste (e.g. cassava) installed in Panama (picture Agro2).

#### 3. Energy requirements of coffee and ethanol production processes

#### **3.1. Introduction**

After having described the baseline technology for small scale bioethanol production from mucilage, the next section describes the energy requirements of the ethanol production process as it is currently practiced based on theoretical values and field gathered data. This gains insight in the overall energy demand of the ethanol production process and allows to indicate possible areas of improvement on energy efficiency of the process.

#### 3.2. Energy requirements of fermentation reaction

In order to determine the energy requirement or release of the fermentation process, the Gibbs energy<sup>6</sup> of the different component are stated:

Table 4. Gibbs energy of different components of the fermentation reaction.

Chemical substance	Gibbs energy [KJ/mole]
Glucose	-917
Ethanol	-182
Carbon dioxide	-394

The Gibbs energy of the reaction is described by:

 $\Delta_r G = \Delta_r G^{\theta} + RT Ln Q$  (Peter Atkins, 2009)

Where Q is the reaction quotient and is expressed by:

 $Q = \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad \text{(for the reaction } aA + bB \to cC + dD \quad or \quad C_6 H_{12} O_6 \to 2. C_2 H_5 OH + 2CO_2)$ 

$$Q = \frac{a_{EtOH}^{c} a_{CO2}^{d}}{a_{Sugar}^{a}} = \frac{1^{2} 1^{2}}{1^{1}} = 1$$

 $\Delta_r G^{\theta} = standard \ Gibbs \ energy \ of \ a \ reaction = \ \Sigma_v \Delta_f G^{\theta}(products) - \ \Sigma_v \Delta_f G^{\theta}(reactants)$ R= gas constant =8,314.10<sup>-3</sup> [KJ/mol.K]

T = temperature [K]

<sup>&</sup>lt;sup>6</sup> In thermodynamics, the Gibbs energy is a thermodynamic potential that measures the 'useful' or processinitiating work obtainable from an isothermal isobaric thermodynamic system (definition from <u>gibbsenergy.com</u>).

Using the data above the  $\Delta_r G$  or gibbs energy of the fermentation reaction is:

$$\Delta_r G^{\theta} = -364 - 788 + 917 = -235 \, KJ/mol$$

 $\Delta_r G = -235 + 8,31.10^{-3}.298.Ln(1) = -235$  KJ/mol (assuming a Temperature of 298K)

This means that 235 KJ of heat is released per mole of reactant. From this calculation one can also conclude that the reaction energy is not depending on the temperature in which the reaction takes place. In order to put the energy release of the reaction in perspective of significance, an example is given. The following circumstances are given:

- A system of 1 m<sup>3</sup> filled with broth
- A concentration of 5 [%m/m] of sugars in the reactant

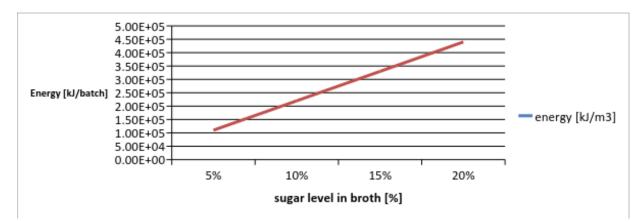
The amount of energy is released in this system and the expected temperature is calculated as follows:

ΔΤ =	E msystem*Cp	[K]
ΔΤ =	Change in Temperature	[K]
Q <sub>ferm</sub> =	Total energy release of fermentation	[KJ]
m <sub>system</sub> =	Mass of system	[kg]
Cp =	Specific heat of solution	[KJ/kg.K]

#### Table 5. Potential temperature change of batch fermentation.

Description	Symbol	Unit	Value
Mass of system	m <sub>system</sub>	kg	1.050
Volume system	V <sub>system</sub>	I	1.000
Density of solution	ρ	kg/l	1,05
Molecular mass sugar	$M_{sug}$	g/mole	180
Mass of sugar in system	m <sub>sug</sub>	kg/system	50
Moles of sugar in system	m <sub>sug</sub>	mole/system	278
Energy release	Q	KJ/mole	235
Energy release	Q	KJ/system	65.223
Energy release	Q	KJ/l mucilage	65
Specific heat	Cp	KJ/Kg.K	4,2
Change in temperature	ΔΤ	К	14,9

From Table 5 it is seen that the density of this fluid is 1,05 [kg/l] (sugar is dissolved), the molecular mass of sugar (glucose) is 180,15 [g/mole]. In the system 50 kg of sugar is present (5%) equal to 277,8 moles. Since 235 kJ per mole is released during the reaction this results in a total energy availability in heat of 65,3 MJ. The specific heat of the solution is 4,18 [KJ/Kg.°C] (excluding the effect of dissolved sugar) resulting in a potential temperature increase of 14,9°C of the complete barrel (1.000 l) in fully insulated conditions.<sup>7</sup> The energy release is thus 65 KJ/liter mucilage.



The potential to use this energy (heat) from the fermentation reaction highly depends on the conditions in order to capture (insulation and heat exchange) this energy.

## Figure 9. Potential energy release from the fermentation vessel during fermentation as a function of the sugar level in the broth.

The energy released is a direct function of sugar concentration: at double concentrations the released energy is also double. In order to make optimal use of the energy that is released from the biological fermentation process, different design measures could be taken;

- Improve insulation of the reaction vessel
- Reduction of the surface of the fermentation vessel. This could be done using round spherical shaped fermentation tanks with the highest volume/surface ratio.
- Use a heat exchanger

The reaction rate is needed in order to determine the potential use of this energy. If the energy is produced in a time span of several weeks, the potential use for it highly reduces compared to for example a reaction time of a few hours. Common fermentation times are 48 h for batch fermentation resulting in an energy release of 4.583 KJ/h in a 1 m<sup>3</sup> reactor with a sugar concentration of 10% at the start of fermentation.

In the next section the reaction rate and its factors of influence are worked out in more detail. In the fermentation process of the coffee residue the rate of the fermentation is important in order to determine the required fermentation capacity and to control the process from invasive organisms that may disturb the fermentation process.

<sup>&</sup>lt;sup>7</sup> in practise this will cause problems due to the increased decay rate of yeast at increased temperatures

The Monod equation is a mathematical expression for the specific growth rate of microorganisms. The amount of microorganisms is a direct function for the overall production rate. The equation is described as follows

$$\mu = \mu max \frac{S}{Ks + S}$$

The specific growth rate  $\boldsymbol{\mu}$  as a function of the substrate concentration S.

•	$\boldsymbol{\mu}$ is the specific growth rate of the Saccharomyces cerevisiae	[/hour]
---	--	---------

[/hour]

- μ<sub>max</sub> is the maximum specific growth rate
- S is the concentration of the limiting substrate for growth (sugar) [g/kg]

•  $K_s$  is the half saturation coefficient expressed by  $\mu/\mu_{max}=0.5$  [g/kg]

In the case of *Saccharomyces cerevisiae* the estimated values are:

S = 87	[g/kg]	(Mazzafera, 2002)
$K_{s} = 200$	[g/kg]	(see derivation from experiment)
$\mu_{max}$ = 0,35	[/hour]	(see derivation from experiment)
$\mu = 0,35. \frac{87}{200+87}$	,= 0.11	[/hour]

This results in a rate of substrate utilization  $(r_{su})$  of

 $r_{su} = -\mu X/Y$ 

X = total biomass = assuming average total biomass of 0,2% of total volume = 2 kg/1.000 L

Y= yield coefficient = 0,51 [g EtOH/g sugar]

*r*<sub>su</sub> = -0,11x2.000/0,51= 431 g/h

This results in a fermentation time of 2.000/431= 4,6 hours.

This means that 65,3 MJ<sup>8</sup> is released in a time span of 4,6 hours.

#### 3.3. Energy requirement for the distillation process

#### 3.3.1. Introduction

Distillation is the separation of two (or more) liquids by means of difference in volatility. Distillation of ethanol from fermented broth remains the dominant practice in ethanol separation in large and small ethanol production facilities (Madson, 2003). Thermal energy is applied in order to evaporate the liquid mixture. Evaporation and condensation of water and ethanol takes place

<sup>&</sup>lt;sup>8</sup> See table for the calculation

continuously in distillation columns. Columns usually contain stainless steel plates (or packing material like Raschig rings) this to provide the surface for the vapor to condensate. The most volatile fraction of the liquid mixture is removed from the top part of the columns while the water is separated at the bottoms of the columns.

#### 3.3.2. Calculating the energy requirement for distillation

The energy requirements for the distillation process can be calculated using the model in Figure 10 (Wesselingh, 2013) where the different flows in the distillation column are:

- The feed flow [F],
- The vapor flow [V],
- The distillate [D],
- The liquid flow [L] and
- The bottom flow [B] [all in moles/hour]

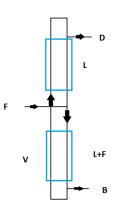


Figure 10 Systematic drawing of liquid and vapour flows of distillation process (Wesselingh, 2013)

The reflux is the liquid mixture that is recirculating in the distillation column. The applied reflux ratio is based on the ethanol concentration of the broth. The lower the ethanol percentage in the broth, the higher the reflux ratio (R) should be. The reflux ratio is set 20 for a feed containing 5% of ethanol according to the formula.

 $R = \frac{1}{EtOHi}$  (Where EtOHi is the initial ethanol percentage in the broth)

Within the distillation column the different flows, indicated by the capital letters will be determined in mole fluxes.

The feed flow [F] is determined by the amount of water removed from the broth (95% of broth is water and 10% of end product is water). Also the molecular flow of the distillate [D] is easily

determined based on the end product (the 5% EtOH in the broth including 10% water of its end product). Based on the distillate flow [D] the liquid flow [L] is determined:

[L] =R.[D] [mole/hour]

where R is the reflux ratio.

Then the vapor flow is calculated using:

[V]=(R+1).[D] [mole/hour]

Once the Vapor flow is determined the required amount of energy for distillation is calculated using;

 $Q_{net} = [V].\Delta H$  [KJ]

where  $\Delta H$  is [42 KJ/mol].

In practice energy losses will take place during the whole distillation process. Assuming an efficiency of the oven of 60% and a efficiency of 80% for the distillation column, the overall energy efficiency is 0,48 ( $\eta$ =48%). Then the total energy requirement for the distillation process is determined by:

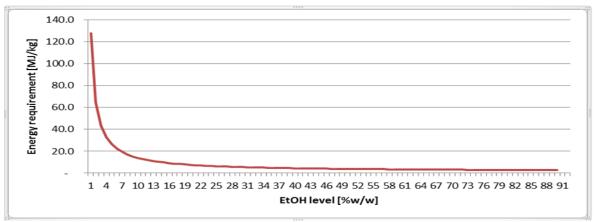
Total Q =  $Q_{net}/\eta$  [KJ]

This results in an energy requirement of 42/0.48 = 87.5 [KJ/mole] (of vapor flow [V]). The total energy requirement per kg of ethanol is shown in the table below.

#### Table 6. Energy requirement for distillation.

Description	Symbol	Unit	Amount
Ethanol level in end product	EtOH <sub>out</sub>	%	90%
Ethanol level in broth	EtOH <sub>in</sub>	%	5%
Reflux ratio	R	mole/hour	19
Molecular mass of EtOH water mixture	Μ	g/mole	43
Top product molecular flux	(Distillate=D)	mole/hour	381
Water outflow	(Bottoms=B)	mole/hour	776
Influx in the distiller	(Feed=F)	mole/hour	1.157
Liquid flow	(L)	mole/hour	7.470
Feed + liquid flow	(F+L)	mole/hour	8.627
Vapor flow	(F+L) - B	mole/hour	7.851
Energy requirement	Q	KJ/mol	42
Distillation efficiency	η	%	48%
Energy requirement for distillation	Q <sub>net</sub>	KJ/kg E90	26.100

Applying this method for the determination of the energy requirement for distillation of broth with higher ethanol levels, show a significant decrease in energy requirement (see Figure 11).





In general the energy requirement for distillation behaves as a reverse binominal function as shown in Figure 11 . This is confirmed by Mousdale who states in 'Biofuels' that the economics of the downstream processes are markedly affected by the concentration of the ethanol in the fermented broth; for example the steam required to produce an ethanol of 10% (v/v) solution of ethanol is only 58% of that required for a more dilute (5%, v/v) starting point, and pushing the ethanol concentration to 15% v/v reduces the required steam to approximately half that required for low conversion broth feeds. Since mucilage is currently diluted in the post-harvest process, the ethanol in the broth is in some cases around 1% resulting in extremely high energy demands for distillation<sup>9</sup>.

#### 3.3.3. Energy requirements in practice from pilot projects

It seems interesting to compare the calculated energy requirements with data gathered from field experiences. From empirical data, collected from existing small scale processing plants it is known that around 1,5 kilograms of wood (15 MJ/kg) are required in order to produce 1 liter of ethanol at 90% (v/v).

Assuming an energy content of 15.000 KJ/kg of dry wood, 22.500 KJ is required for 0,79 kg of ethanol (density is 0,79 kg/l). Per kilogram ethanol at 90% (v/v) the energy requirements are 25.600 KJ which is similar to the calculated amount of energy in Table 6 energy requirement for distillation above (26.100 KJ/kg E90).

Different statements exists on the energy use for small scale distillation units. In Panama (Agro2/FACT 2010) it is claimed to use 1 kg of wood (sun dry) per two litres ethanol (at 80% EtOH) resulting in approximately 7,5.10<sup>3</sup> KJ/L ethanol at 80% (v/v). In Costa Rica on the contrary

<sup>&</sup>lt;sup>9</sup> Energy can also be saved by direct using of hydrous ethanol in adapted engines. In this case the energy demanding anhydrous ethanol production (including the azeotrope phase) is avoided.

consumption is observed of 1 kg of (sun dry) wood per litre ethanol at 80% which is equivalent to  $15.10^3$  KJ/IE80 (Coopevictoria 2010)<sup>10</sup>.

The energy for biofuel production is often expressed in terms of Net Energy Ratio (NER). This is relates the energy required for the production of the biofuel and the energy it contains and is expressed as:

NER =  $Q_{out}/Q_{in}$ 

Ethanol itself contains around 40 [MJ] per liter (36 MJ/kg ethanol at 90% v/v). Using the energy requirements as calculated, this shows a net energy ratio (NER) of 1,6. The heat of vaporization of ethanol is 841 [KJ/kg], suspecting much lower energy requirements for evaporation. The higher energy demand in practice, is related to the high water amounts in the broth (approximately 95%) requiring 2.260 [KJ/kg] for its evaporation.

Description	Symbol	Unit	Amount
Production capacity	Р	l E90/day	500
Wood use	W	kg/IE90	1,5
Energy in wood	Qwood	KJ/kg	15.000
Density ethanol 99,6	r	kg/l	0,79
Energy in ethanol (90%)	Q <sub>E90</sub>	KJ/I	36.000
Net Energy Ratio	NR	rate	6
Heat of vaporization EtOH	Не	KJ/kg	8,4
Heat of vaporization $H_2O$	Н	KJ/kg	2.260
Total energy requirement	Q	KJ/kgE90	25.600

#### Table 7. Energy requirement for distillation from empirical data.

#### 3.4. Other process energy requirements

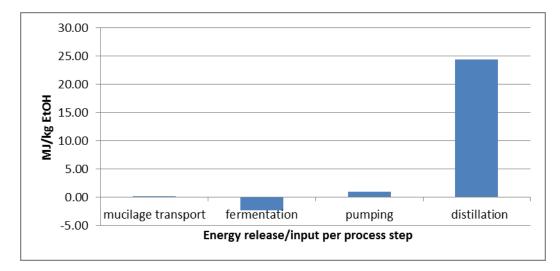
For the displacement of the broth and the wine additional energy is required. This energy is needed to power liquid pumps<sup>11</sup>. The required energy for this is determined using Q= P.t, where (Q) is the energy; (P) the power capacity of the pump and (t) the time that the pump is operating. In practice the amounts of energy for these processes are relatively low. The energy for pumping is around 1.32 MJ/kg EtOH (see Annex II for the calculation).

#### 3.5. Total energy requirements of ethanol production

When adding the energy requirements for the ethanol production process this leads to the following figure. Pumping includes displacement of broth, vinasse and ethanol.

<sup>&</sup>lt;sup>10</sup> The current ethanol production unit (2014) designed by Ecoenergy B.G. Ltda., has undergone a number of improvements to increase the energy efficiency.

<sup>&</sup>lt;sup>11</sup> If geography allows, gravity can be used for transport of the wine.



#### Figure 12. Comparison of energy requirement and release of ethanol production process.

It is clearly shown that the distillation process is the main energy consumer of the E90 production process from mucilage. Especially when the broth is producing low levels of ethanol (<5%). It is also shown that the fermentation process generates energy in form of heat which is approximate 2.500 KJ/kg EtOH. As shown in Figure 11, the distillation energy reduces significantly as a function of ethanol level in the broth.

#### 3.6. Hypothesis on current energy use

If purification of low grade ethanol requires high amounts of energy when using conventional distillation technology than alternative separation techniques can be used in order to reduce the energy requirements. Possible solutions could be found in the use of membrane technology. It is expected that these methods can be applied at different steps of the ethanol production process, for example to concentrate sugars or ethanol.

#### 3.7. Membranes as an energy saving alternative

In order to optimize the ethanol production process in terms of energy efficiency, technological alternatives exists. In this section an overview of possible suitable energy saving solutions are presented and evaluated on their energy demand in a later stage. The described technologies will include pervaporation and reverse osmosis. Although other alternatives for energy saving technologies exist that have potential to improve the energy efficiency of small scale ethanol production like insulation, optimizing feeding of the boilers (including the size of the biomass), or using adsorption, liquid-liquid extraction and gas stripping (Vane, 2008), these technologies are out of scope of this thesis research.

#### 3.8. Pervaporation<sup>12</sup>

Pervaporation is the selective evaporation of a component from a liquid mixture with the use of a membrane. In general, a membrane is a selective barrier or interface between two phases.

<sup>&</sup>lt;sup>12</sup> Partly adapted from FACT outlook on membrane technology.

Membranes can be used for various separations, like gas separation, pervaporation and water purification (Mulder, 1996).

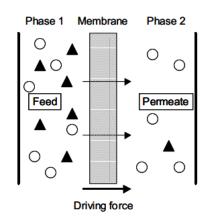


Figure 13. Working principle of pervaporation (source: FACT Outlook Membrane Technology).

Phase 1 (Figure 13) is the feed phase or upstream-side, while phase 2 is referred to as the permeate stream or downstream-side. Separation is achieved because the membrane has the ability to transport one type of species from the mixture more readily than other species. This transport may occur through various transport mechanisms. The driving forces for mass transport are a gradient in the pressure, electrical potential, concentration, temperature or chemical potential. In the case of pervaporation, phase 1 is a liquid phase and phase 2 is a vapor phase. The stream leaving the membrane module at the feed-side is called the retentate. In the field of pervaporation, two main applications have been commercialized. The first one is the dehydration of alcohols and other solvents, and the second one is the removal of small amounts of organic compounds from contaminated waters (Xianshe Feng, 1997). Some other promising applications are aroma recovery and beer dealcoholization in the food industry, and product recovery from fermentation broths for enhanced bioconversions (Fadeev, 2000).

Pervaporation comprises a number of consecutive steps. The membrane selectively adsorbs one or more of the components, which diffuse through the membrane and evaporate at the permeate side. The permeate stream is removed by applying either a vacuum or a sweeping gas.

#### 3.9. Energy requirements of pervaporation

The total energy required for pervaporation is then determined as Q<sub>net</sub>:

$$Q_{net} = \frac{(F3C3)H}{\eta}$$
 (see figure 14)

Where

F3C3 = the mass of permeate (the separated liquid containing high concentrations of ethanol)

- H = heat of evaporation of the permeate
- η = pervaporation efficiency

The mass flows of the liquids can be easily derived using the following picture. Where C1 is the starting concentration of the broth, F1C1 is the mass flow of broth to the membrane and F2C2 is the mass flow of the recirculated feed.

The change in product concentration of the reactor vessel is expressed as:

dVC/dt = -F1C1 + F2C2

As a result the change in total mass is therefore:

VdC/dt = F3C - F3C3 = F3(C-C3) <=> dC/dt = (F3/V)(C-C3)

dV/dt = -F3

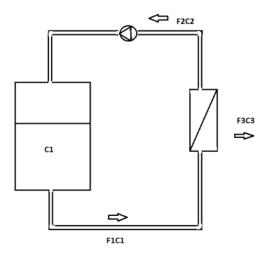


Figure 14. Schematic view of pervaporation system (own elaboration).

The energy requirements for pervaporation are at least the amount of energy needed for the evaporation of the substances in the permeate. For water this is 2.260 KJ/kg while for ethanol 841 KJ/kg is required (at their respective standard boiling points). Assuming a pervaporation efficiency of 90% and knowing the mass flows of the in the pervaporation system, the energy requirement can now easily be determined.

Description (STP)	Symbol	Unit	Amount
Heat of vaporization of EtOH	He	KJ/kg	841
Heat of vaporization of water	Hw	KJ/kg	2.260

η<sub>perv</sub>

Table 8. Data for energy requirement for pervaporation.

**Pervaporation efficiency** 

In practice the energy requirements will be higher since the selectivity of the membrane is currently not high enough to upgrade the broth to a 90% ethanol purity. In order to obtain high ethanol levels the permeate has to pass several times through the membrane. This means that the water, present in the solution, is evaporated and condensed more than once resulting in higher energy demands.

%

90%

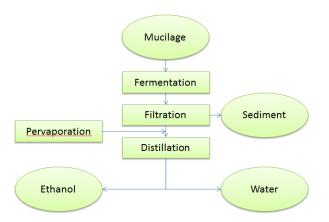
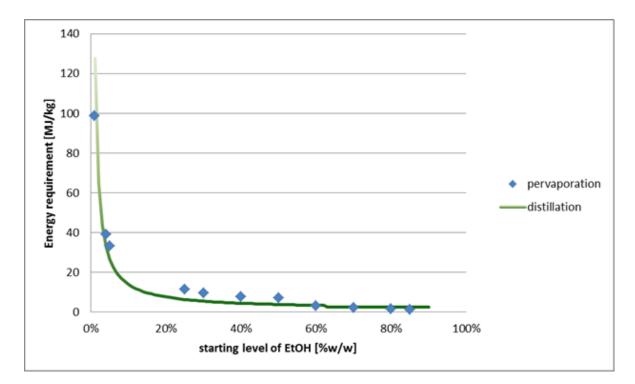


Figure 15. Place of pervaporation in process flow of coffee waste for ethanol (own elaboration).



## Figure 16. Energy requirement for pervaporation using a membrane selectivity of 7 and a pervaporation efficiency of 90%.

Using the mass flows as expressed before, the energy requirement for the purification of ethanol using pervaporation, is similar the energy needed for distillation (see the green line in Figure 16). This is due to the fact that in both cases the ethanol and water has to evaporate. The efficiency of separation highly depends on the selectivity of the membrane. This calculation has been carried out, using a selectivity of seven<sup>13</sup>. This means that the amount of EtOH molecules that pass the membrane is seven times higher than the amount of water molecules. Since the heat of vaporization of water is almost three times higher than that of ethanol, it is the technological challenge to increase the selectivity of the membranes. The energy requirement for pervaporation has also the potential to be improved by using vacuum and using ambient energy for evaporation<sup>14</sup>. Disadvantages for application could be the sensitivity for salts and large organic compounds in the feed.

#### 3.10. Reverse osmosis as an energy saving alternative

The word osmosis comes from the Greek word 'osmos' for 'push'. Osmosis is the passage of a pure solvent into a solution separated from it by a semipermeable membrane. The semipermeable membrane is permeable to the solvent (in this case water) but not to the solute (sugar or ethanol). The membrane might have microscopic holes that are large enough to allow water molecules to pass, but not ions of carbohydrate molecules (Paula, 2009). In the case of **reverse** osmosis (RO), a

<sup>&</sup>lt;sup>13</sup> Membrane module with a selectivity of seven are currently commercially available (personal communication Pervatech).

<sup>&</sup>lt;sup>14</sup> This also applies for distillation.

pressure is applied to the system in order to force the solvent to leave the solution resulting in an increased concentration of the solution.

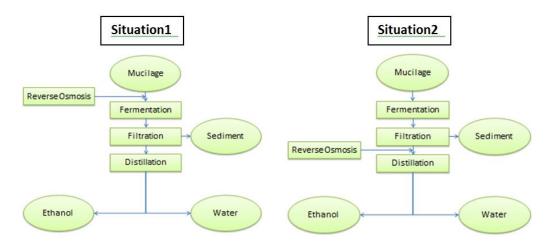


Figure 17. Potential place of reverse osmosis in coffee waste processing for ethanol.

In situation 1 of Figure 17 reverse osmosis will be used to concentrate the sugars in the broth. In the case of situation 2 reverse osmosis is implemented after the fermentation and filtering process and is used to concentrate the ethanol in the wine.

#### 3.11 Energy requirements of reverse osmosis

Reverse osmosis is a broad applied technique for separation of liquids. Here the energy requirements of reverse osmosis in the ethanol production process are analyzed. It would be interesting to see the effects on energy needs if RO is applied for the concentration of sugars i.e. before fermentation, or for the concentration of ethanol during or directly after fermentation (see Figure 17).

The **osmotic pressure** is the pressure that needs to be applied to the solution to stop the inward flow of the solvent (for ideal diluted solutions).

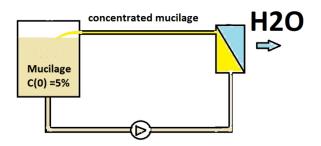


Figure 18 Schematic representation of reverse osmosis in a batch reactor

The osmotic pressure is proportional to the concentration of the solute and is described in the following relation:

 $\Pi V = n_B RT$  $n_B$ 

$$\frac{n_B}{V} = [B]$$

Where

Π	=	Osmotic pressure	[J/m <sup>3</sup> ] = [Pa]
٧	=	Volume	[m <sup>3</sup> ]
$n_B$	=	Number of moles b	[mole]
R	=	Gas constant (8,31447)	[J/K/mole]
Т	=	Temperature	[K]
[B]	=	Molar concentration of solute	[mole/m <sup>3</sup> ]

The osmotic pressure has to be compensated by applying an overpressure to the system. Applied pressures in the range of  $4,0 \times 10^6 - 8,0 \times 10^6$  [Pa] are common using this technology. When the applied pressure is higher than the osmotic pressure, the solvent passes through the membrane and gives a concentrated retentate and a 'pure' solvent (permeate).

The energy required for the process (batch reactor) is calculated based on the applied pressure and related to the amount of retentate. The amount of retentate (concentrated ethanol) is depends on the change in osmotic pressure which in its turn depends on the change in concentration. This results in the fact that the effect of purification is limited at higher permeate concentrations. The applied pressure to the system is constant in this case.

The applied energy (E) for reverse osmosis is derived from the applied pressure and described as:

$$E = \frac{\Delta P J}{\eta}$$
 [J/s] where

η is the pump efficiency of the applied pressure [%]

 $\Delta P$  is the pressure difference applied by the pump [Pa]

J is the flow of permeate and is calculated using:

$$J = \frac{P - \Delta \pi}{R}$$
 [m<sup>3</sup>/sec]  
P = Applied pressure [Pa]  
R = Membrane resistance [Pa.s/m]  
 $\Delta \pi$  = Change in osmotic pressure [Pa]

Simulations on energy requirement for ethanol concentration has been carried out using spreadsheet calculations. The initial sugar concentration was set at 2,5% while different pressures were applied.

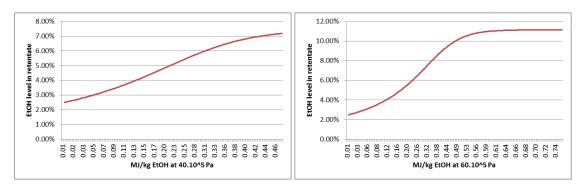


Figure 19. Required energy for ethanol concentration using reverse osmosis at 4x10<sup>6</sup> [Pa] and 6x10<sup>6</sup> [Pa].

It is shown in Figure 19 that the maximum ethanol level that can be reached, when applying  $4 \times 10^{6}$  [Pa] is 7%. At that level the osmotic pressure equals the applied pressure. The cummulative energy needed can be read from the graph and is around 420 [KJ/kg].

Energy requirement for EtOH							
Start %	[%]	2,5	5	2,5	5	2,5	5
End %	[%]	7.18	7.15	11.14	11.09	14.86	14.86
Pressure	x10^5 [Pa]	40	40	60	60	80	80
Energy RO	[MJ/kg]	0.47	0.34	0.75	0.57	1.00	0.77
Energy if distilled	[MJ/kg]	67.8	15.8	82.1	30.1	88.8	36.8

#### Table 9. Data for energy for RO ethanol concentration compared with distillation.

Reverse osmosis can be applied for concentrating the ethanol in the broth and also for concentration of sugars in the mucilage.

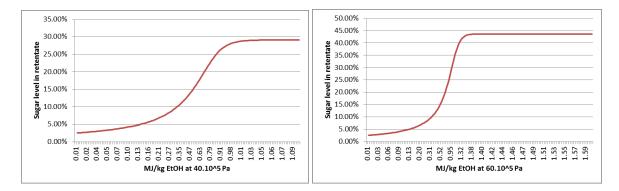


Figure 20. Energy requirement for concentration sugar at 4x10<sup>6</sup> [Pa] and 6x10<sup>6</sup> [Pa].

If the feed contains solutes with relatively high molecular mass (for example sugar), the molar concentration is relatively low compared to the mass concentration of the solution. This makes the required energy for compensation of the osmotic pressure relatively low.

Energy requireme for sugar	ent						
Start %	[%]	2,5	5,0	2,5	5,0	2,5	5,0
End %	[%] Sugar	29,1	28,9	43,6	43,6	58,1	58,1
End EtOH	[%] EtOH	14,8	14,7	22,2	22,2	29,6	29,6
Pressure	x 10^5 [Pa]	40	40	60	60	80	80
Energy RO	[MJ/kg] sugar solution	0,99	0,98	0,98	0,98	0,97	0,95
Energy RO	[MJ/kg] EtoH	1,98	1,96	1,96	1,96	1,95	1,90
If distilled	[MJ/kg] EtOH	89	37	95	43	98	46

#### Table 10. Energy requirement for RO of ethanol at different pressures.

If reverse osmosis is used for the concentrating ethanol, the energy requirements are less favorable than for sugar<sup>15</sup> as shown in Table 10.

From Table 10 we observe that concentrating sugars at higher pressures is the most promising potential implementation of RO. It should be noted that the theoretical conversion rate from sugar concentration is 0,51 and that 43% of sugar in the retentate will potentially yield approximately 22% of ethanol. In practice this may lead to various challenges i.e. batch fermentation will not be possible anymore since maximum ethanol concentration during fermentation is 14% (maximum sugar levels of 28%). Also the technical feasibility for implementation of RO in small scale ethanol units highly depends on the presence of other (non) organic substances in, and the viscosity of the solution that might block the pores of the membrane. In the model the flow rate of the membrane is not a function of the viscosity of the substance. The other question is: what will be the viscosity of such concentrated sugar solution? And what is the effect of high viscosity substances on the fermentation efficiency? In the next section these issues are elaborated.

#### 3.12. Experimental set up for concentrating sugar solutions with RO

#### 3.12.1. Introduction of RO experiment

As shown above, concentrating the sugar content in the feedstock looks like an effective energy saving measure in small scale bioethanol production. Therefore water has to be removed from the mucilage. In this section the practical implementability of reverse osmosis technology will be assessed. This will be carried out on laboratory scale using Labcell from Koch Membrane Systems.

<sup>&</sup>lt;sup>15</sup> In theory a factor 4 since molecular mass of sugar is 180 g/mol while molar mass of ethanol is 46 g/mol.

#### 3.12.2 Objective reverse osmosis experiment

The aim of the experiments is to prove the principles for concentrating sugar solutions using reverse osmosis and compare the outcome with the calculations shown above. There it was shown that an increased pressure has a positive effect on the energy savings for purification. Moreover in the calculations for the RO model, the viscosity of the substance was not taken into account. This experiment will give insight in the possible energy requirements (including viscosity) for reverse osmosis when applied in practice. The objective listed:

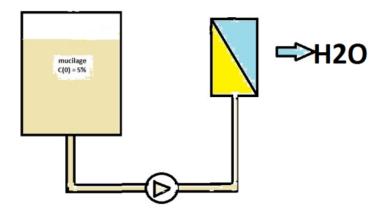
- Practical knowledge on applying RO with regards to required pressure, time, and operation protocols;
- The selectivity of the membrane by measuring sugar in feed and permeate
- Energy requirement for sugar concentration
- Effect of density (dry matter of the solution) on concentration efficiency
- Determine the membrane resistance



Figure 21 labcell Koch CF1

#### 3.12.3 Material and methods

For the RO experiment different feedstock is used, in order to get insight in the RO behaviour of different substrates. The solutions are made using water, crystal sugar, and apple puree. These are prepared at different sugar concentrations and measured using a brix meter before and after concentrating the feed.



#### Figure 22 RO batch system

The apparatus to perform these tests is a Labcell CF-1 from Koch Membrane systems. The membrane used is the SelRO MPF-34 from the same supplier. The approximate retention characteristic is 200 Molecular Weight Cut-off (MWCO).

The membrane is supplied in a soaked solution of 0.7% Benzalkonium Chloride. It was immersed in water using deionized water and filtered water overnight at room temperature, after which the membrane was rinsed with deionized water for 30 minutes and installed in the labcell.

Samples are prepared using demineralized water and crystalline sugar in 500 ml bottle and mixed manually during two minutes. The sample was manually rinsed in the RO vessel, and the lid was closed firmly. Pressure was applied by opening the argon pressure valve and setting the pressure properly. The electrical pump of the Labcell CF-1 was switched on in order to ensure proper mixing and avoid sugar accumulation at the membrane. The permeate flow was measured every five minutes and pressure was adjusted if needed<sup>16</sup>. Every batch was run for approximately one hour. The membrane temperature was 25°C, and total permeate and retentate was measure after each run. The brix values of the sample was determined using an analogue portable refractometer<sup>17</sup>. Later a digital refractometer was used. After each batch the system was flushed two times using 500ml demi water during 15 minutes. It was drained before starting the new batch. A set of samples was made using different substrates, different sugar concentrations and applying different pressures according to table 12. The samples 1 to 12 are sugar solutions while 13 to 19 are puree solutions.

<sup>&</sup>lt;sup>16</sup> Pressure tend to reduce slowly during the separation process since the net volume of the vessel increased due to permeate flux.

<sup>&</sup>lt;sup>17</sup> Brix values were corrected for temperature.

	Suga	ar sol	lutic	ons									Pure	e san	nples				
Sample number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Sugar at t=0 (°brix)	2,5	5		2, 5	· ·	5	10	2,5	5	10	2.5	2.5	2.5	5	10	2,5	5	10	2,5
Applied pressure (x10 <sup>5</sup> Pa)	20	20	2 0	2 0	2 5	2 5	25	30	30	30	20	25	20	20	20	30	30	30	20

# Table 11. Set up of the samples of the RO experiment.

The energy requirement for concentration the sugar solutions is calculated using:

E = PV = nRT	
E= energy	[J]
P= pressure	[Pa]
V= volume	[m <sup>3</sup> ]
<i>n</i> = amount of moles of gas	[mol]
R= gas constant (8,31)	[J/mol.K]
T= temperature	[K]
The energy used for mixing is calculated by:	
E = Pt	[1]
P= power of the engine	[W]
T= time	[s]

### The membrane resistance was calculated using

$R = \frac{P - \Delta \Pi}{J}$	[Pa.s/m]
J is the liquid flux	[m <sup>3</sup> /s]
P is the applied pressure	[Pa]
$\varDelta\Pi$ is the difference in osmotic pressure over time interval t	[Pa]

#### [Pa.s/m]

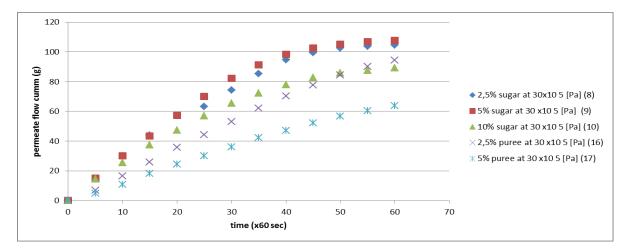
The values are calculated based on the data gathered from the experiment.

#### 3.12.2 Results of RO test

The labcell CF1 was operated first at  $7x10^5$  [Pa] pressure but none of the prepared solutions did pass the membrane. This is not in line with the calculations on reverse osmosis showing an osmosic pressure of  $3,47x10^5$  [Pa] at 2,5% sugar concentrations. Possibly the membrane resistance of the SelRO MPF-34 membrane is higher than modelled.

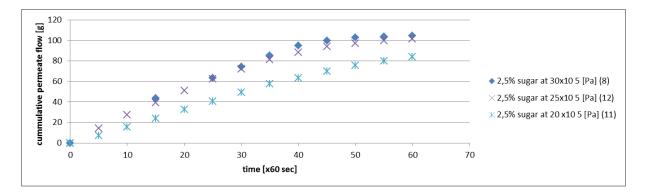
In order to realize higher pressures than  $70 \times 10^5$  [Pa], high pressure tubes were ordered and connected to argon (Ar) which is used as a pressure medium in high pressure experiments.

The experiment continued using 20x10<sup>5</sup>[Pa], 25x10<sup>5</sup>[Pa] and 30x10<sup>5</sup> [Pa] applied pressure and different concentration of sugar solution. At these pressures the following results were achieved:



#### Figure 23. Cumulative permeate flow of RO sugar treatment.

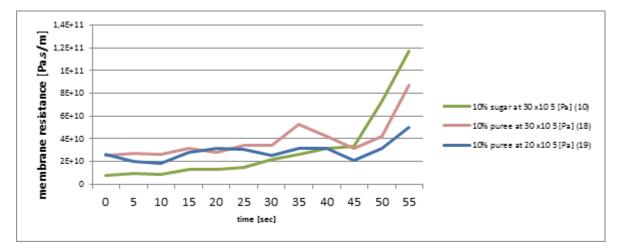
From the figure it can be observed that the cumulative permeate flow reaches its maximum in approximately one hour while applying  $30 \times 10^5$  [Pa] of pressure. The sugar concentrations at t=0 are 2,5%, 5% and 10%. Sugar concentrations of 2,5% and 5% reach a higher cumulative permeate flow than the sample with 10% sugar concentration. The osmotic pressure of higher sugar concentration is higher and therefore reaches it maximum at P= $\Pi$  where P is the applied pressure and  $\Pi$  is the osmotic pressure. The fact that sample (9) reaches a higher permeate flow than sample (8) despite of the fact that the sugar concentration at t=0 is higher, can be explained by the fact that small amounts of water remain in the system after cleaning the system in between every new experiment.



#### Figure 24. cumulative permeate flow of RO sugar treatment at different pressures.

Higher potential ethanol concentrations are reached at higher pressures. We observe clear differences between the sample sets of  $20 \times 10^5$  [Pa],  $25 \times 10^5$  [Pa] and  $30 \times 10^5$  [Pa]. Here the potential ethanol production is calculated based on the sugar concentration using the conversion rate of 0,51 sugar-ethanol. At lower pressures, running time is limiting to reach the maximum concentration. There we observe that the starting concentration is a function of the end concentration. At higher applied pressures the running time is not limiting and the osmotic pressure of the retentate is limiting the concentration process.

The membrane resistance was calculated using the relation between flux, pressure and membrane resistances as shown above. The membrane resistance for different samples as a function of time is expressed in the following figure.



#### Figure 25. Membrane resistance of 10% sugar/puree samples at different pressures.

From the results it is shown that the membrane resistance increases during the purification process. The membrane resistance is higher at higher pressures and at purification of apple puree if compared with sugar/water solutions.

The energy for RO from experimental data show that the high pressure represents only 0,2% of the total energy required for purification (see annex for the detailed calculation). Most of the

energy is used for mixing the feed. This is disproportional to the energy required for the concentration process in practice. The pump is used for mixing while the gas is used to apply pressure in order to create a permeate stream. Mixing can be done alternatively using efficient mechanical mixing or a small air pump. These solutions require little energy and are therefore left out of the calculation.

Description	Unit	Sugar			Puree	
Sample number		1	7	8	16	19
Applied pressure	x 10⁵ [Pa]	20	25	30	30	20
Potential EtOH level (start)	% w/w	1,3	1,3	1,3	1,2	1,4
Potential EtOH level (end)	% w/w	6,3	10,8	12,5	4,7	3,0
Total energy	[1]	1.856	2.347	2.823	2.781	1.798
Total end product	[g]	11,5	3,8	2,2	12,2	31,7
Energy for RO (for this traject)	[MJ/kg EtOH]	0,2	0,6	1,3	0,2	0,1
Energy if distilled (for this traject)	[MJ/kg EtOH]	169	189	192	178	110

#### Table 12. Comparison of Reverse Osmosis and distillation energy requirements.

From the table 12 it can be seen that significant energy saving can be achieved if RO is applied at low concentration sugars or ethanol (starting at 1,2% w/w). Low grade substances show a negative NER if the ethanol concentrations are too low (lower than 4%) and upgraded with distillation only. The energy requirements for extreme low ethanol levels are very high, in the order of magnitude of 200 MJ/kg EtOH. This is by far not feasible and therefore this feedstock is often not be further processed in practice. When RO is applied this NER improves significantly. This is also shown in fruit juice industry e.g. maple production where energy costs for evaporation reduce with 60%<sup>18</sup>

<sup>&</sup>lt;sup>18</sup> Information from Minnesota technical assistance program: <u>http://www.mntap.umn.edu/greenbusiness/water/5FS.membranefiltration.pdf</u>

# 4 Effect of the sugar content of the feedstock on the fermentation efficiency.

### **4.1 Introduction**

Based on the modeled separation alternatives it is shown that significant energy savings can be reached if compared to the current practice (Figure 26). In particular the concentration of sugar levels in the feedstock (before fermentation), will result in lower energy demand for the production of ethanol (see Table 10). Concentration of the sugars in the feedstock could be done by reducing the amount of water **during** the demucilage process or by separating the water from the mucilage substance **after** the demucilage process.

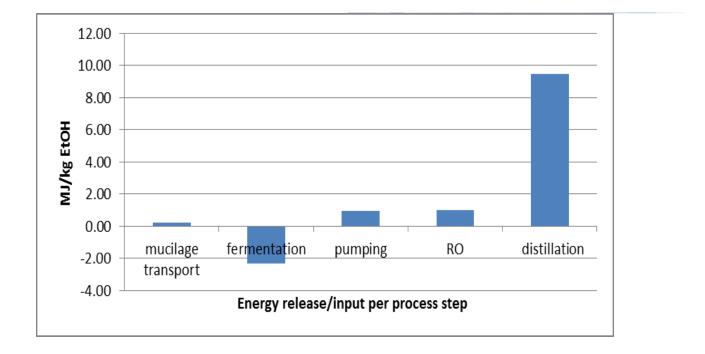
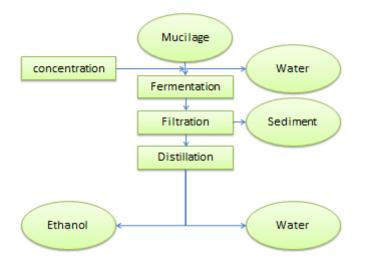


Figure 26 Energy requirements for bioethanol production process when applying RO

Possible drawback of concentrated feedstock (higher viscosity) for the production process may be its difficult displacement (pump ability) and its effect on fermentation efficiency since water is the transport medium for the anaerobic fermenting organisms and may result in reduced feedstock contact and reduced conversion efficiency.





#### 4.2 Effect of concentrating feedstock

The biochemical criteria for a good fermentation include:

- Mixing of yeast
- Mean for temperature control (as a heat buffer)
- Sufficient substrate

So for the optimum maximum ethanol yield, the sugar level should be increased until the level that doesn't cause limitations for the yeast. This is done by reducing the amount of water, but that may have an adverse effect on the fermentation efficiency since water is the transport medium for the yeast. In order to gain insight in the fermentation behavior of different substrates a set of experiments was set up. The practical effect of feedstock concentration (increased viscosity and dry matter content) on fermentation efficiency are tested at laboratory level

### 4.3 Objective

The objective of the test is to determine the effect of sugar level and viscosity of a substrate on the fermentation efficiency.

### 4.4 Experimental procedure

### 4.4.1 Principles

The ethanol production efficiency was tested using apple puree as a feedstock. Mucilage is impossible to obtain in the Netherlands and apple puree shows many similarities with coffee mucilage in terms of texture and sugar content. The apple puree was prepared at different sugar concentrations varying from 5% to 30%. This was done by first concentrating and then diluting the puree into different concentrations. The fermentability of these substrates was compared with its corresponding theoretical maximum fermentability.

The ethanol concentration is determined based on weight measurements. Consequently the amount of fermented sugar is derived from the weight loss of the test units. It is assumed that the produced gas in the test units only consists of carbon dioxide and that the amount of yeast is relatively low<sup>19</sup>.

m sugar ferment	$ted = \frac{\Delta m}{M_{CO2}} c.M_{sugar}$	
<i>m<sub>sugar fermented=</sub></i>	Fermented sugar	[g]
Δ <i>m</i> =	Weight loss test unit (= produced CO <sub>2</sub> weight)	[g]
M <sub>CO2</sub> =	Molecular mass of CO2	[g/mole] (= 44)
C=	factor	[mole sugar/mole CO <sub>2</sub> ] (= 0,5)
<b>M</b> <sub>sugar</sub>	Molecular mass sugar	[g/mole] (= 180)

The mass of ethanol can be both calculated based on the amount of CO2 produced or based on the fermented sugars.

$$m_{EtOH} = \frac{\Delta m}{M_{CO2}} M_{EtOH}$$
  
 $m_{EtOH} = mass of ethanol produced [g]$   
 $M_{EtOH} = Molecular mass of ethanol [g/mole]=46$ 

The potential weight loss of the test units is the total amount of fermentable sugar limited by a maximum amount of 14% (w/w) of ethanol. The fermentation efficiency is expressed by:

$$F_{eff} = \frac{S_{fermented}}{S_{tot}} 100\%$$

$$F_{eff} = Fermentation efficiency [\%]$$

$$S_{fermented} = Fermented sugars [g]$$

$$S_{tot} = Total fermentable sugars [g]$$

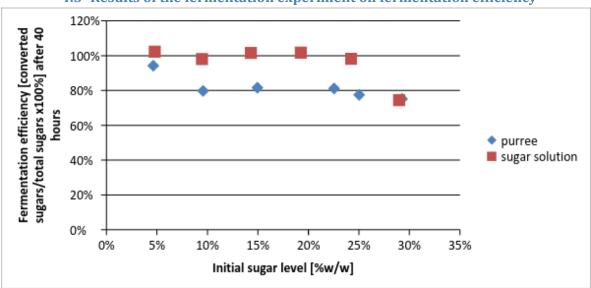
\_\_\_\_\_

#### 4.4.2 Materials Method

In total 12 test bottles of 500 ml were used. Six (nr. 1-6) were filled with concentrated apple puree and six (nr 7-12) were filled with sugar solutions. Both for puree and for crystallized sugar, a concentration range of 5%-30% was set up. See annex VI for the detailed experiment set up.

<sup>&</sup>lt;sup>19</sup> Maximum 2% of total mass and for this indicator experiment therefore neglected.

The feedstock was mixed with yeast (*Saccharomyces cerevisiae* at 100 times the recommended amount in order to speed up the fermentation process) and placed a constant temperature of 28-30 °C during 40 hours. The bottle weight was determined and mixed practically every hour in order to register and facilitate the fermentation process.



4.5 Results of the fermentation experiment on fermentation efficiency

#### Figure 28. Fermentation efficiency of different sugar solutions based on weight measurements.

The fermentation efficiency as derived from the fermentation experiment is shown in Figure 28. It is observed that the fermentation efficiency of apple puree reaches a maximum between 75% and 95%, while the fermentation efficiency of the sugar solutions reach around the 100% except for the bottle 7 (at 30% sugar concentration). The limitations in fermentation efficiency in the apple puree can possibly be explained by the presents of non fermentable sugars or by the higher viscosity of the substrate. The limitation in fermentation efficiency of bottle 7 (and therefore also bottle 1: both at 30% sugar concentration) is explained by reaching the fermentation maximum of 14% ethanol (%w/w).

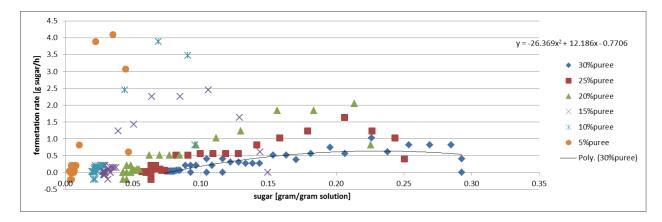
From the fermentation experiment the fermentation rate was measured in hours. For every measured point the substrate concentration was determined by:

Fermer	ntation r	$ate = R_f = \frac{\Delta s_t}{\Delta t}$	[g sugar/h]
<b>s</b> <sub>0</sub>	=	initial sugar level	[g]
S <sub>f</sub>	=	fermented sugar	[g]
s(t)	=	sugar at time=t	[g]
S(t)	=	S <sub>0</sub> - S <sub>f</sub>	[g]

S = substrate concentration[g/g]

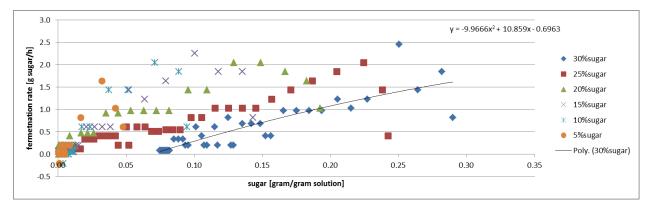
 $S = S(t)/M_0 \qquad [g/g]$ 

M<sub>0</sub> = initial mass [g]



#### Figure 29 Fermentation rate as a function of sugar concentration in puree samples.

It can be observed that the fermentation rate is higher in at low sugar concentrations in particular for the samples with low start concentrations of sugar.



#### Figure 30. Fermentation rate as a function of sugar concentration in sugar solution samples.

Here we observe the same tendency as in the puree bottles. Low starting concentrations of sugar result in high fermentation rates (at these low sugar levels), and high sugar concentrations result in higher fermentation rates (at these high sugar levels). In general it can also be seen that the higher the sugar concentration, the lower the fermentation rate (if we compare between the samples). It was expected to observe a more homogeneous tendency between the sugar and puree samples. In order to model the microbial growth of the yeast and determine the specific growth rate, the Monod equation is used as a base.

 $\mu = \mu max \frac{S}{Ks + S}$ 

Ks is to be determined by Ks is the half saturation coefficient expressed by  $\mu/\mu_{max}=0.5$ 

From the collected data we will first determine  $\mu_{max}$ : the value where the maximum growth rate is reached. We will do this visually by estimation maximum of the Y-as of the trendline (0,64g/h).

In case of higher substrate levels, other factors than substrate levels can limit the microbial growth. That is why  $\mu$  will be derived from the experiment which contained 30% sugar solutions.

Ks can be determined by 0,5 y(y'=0)

Y (Ks) = 0.5\*0.64=0.32; from the graph Ks can be easily determined as well.

Ks = 0,13 [g/g] = 130 [g/kg]

Description	Symbol	Unit	Amount
Maximum growth rate	μmax	[/h]	0,64
Half saturation coef.	Ks	[g/kg]	130
Growth rate	μ	[/h]	1,3

#### 4.6 Laboratory analysis

In order to check the applied method for calculating the rate of sugar conversion and eventually the fermentation efficiency, the samples were analysed in the laboratory of Wageningen University. The raw material (apple puree) was tested on the different sugars while the fermented samples were analysed on ethanol level resulting in the following data for apple puree.

#### Table 13. Composition of tested apple puree.

Composition	Sucrose	Glucose	Fructose	Total
	g/l	g/l	g/l	g/l
Appelmoes HAK	55,6	31,5	74,3	161,4

Sucrose, glucose and fructose are fermentable sugars (C6-sugars) and can potentially yield around 8% of ethanol. In the chromatogram (Figure 31) the samples were tested for the sugar components and ethanol. Propionic acid was used as a marker for the analysis.

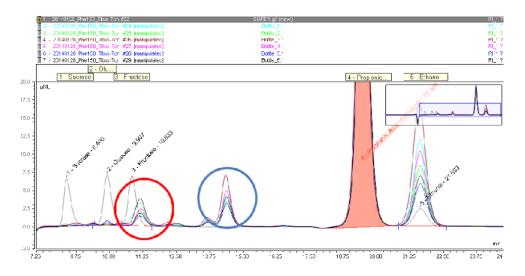
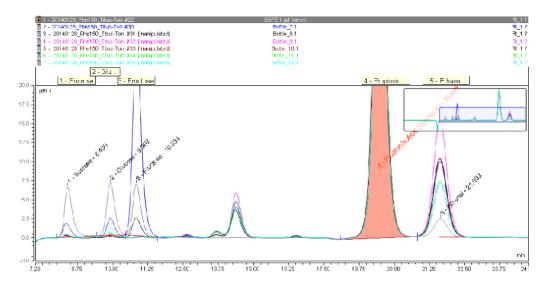


Figure 31. Chromatogram of determination of components in test bottles 1-6 (puree).

In the chromatogram we observe a measured peak very close to fructose. Possibly the composition of fructose slightly changed during the concentration process of the apple puree. This change possibly made it non fermentable and non-identifiable as fructose. The second coloured peak (blue) shows the presents of another component. This is probably an organic acid generated during the fermentation process. The fructose in the sugar solutions (bottle 7-12) was indeed identified see figure 32.





In the table below the quantitative data of the chromatograms are shown. The remaining sugar concentrations, the produced ethanol and the fermentation efficiency were compared. 'Calculated' means the values based on the fermentation experiment and 'measured' indicates the values of the laboratory analysis.

	Remaining sugar		Produced ethanol		Fermentation efficiency	
	Calculated	Measured	Calculated	Measured	Calculated	Calculated from measured EtoH
Bottle nr.	g/l	g/l	g/l	g/l	%	%
1_Puree30%	72,9	1,1	112,4	88,4	75%	59%
2_puree25%	56,3	0,5	99,2	74,5	78%	58%
3_Puree20%	42,5	0,2	93,5	72,4	81%	63%
4_Puree15%	27,5	0,8	62,4	43,9	82%	58%
5_Puree10%	19,4	1,0	39,0	28,2	80%	58%
6_Puree5%	2,7	0,2	22,3	14,9	94%	63%
7_Sugar30%	73,9	97,6	110,4	85,1	75%	58%
8_Sugar25%	4,4	11,5	121,6	96,5	98%	78%
9_Sugar20%	-3,4	1,7	100,1	78,0	102%	80%
10_Sugar15%	-2,3	1,9	74,3	54,8	102%	75%
11_Sugar10%	1,8	2,1	47,5	34,6	98%	72%
12_Sugar5%	-1,1	1,4	25,0	17,3	102%	71%

Table 14. Comparison between laboratory analysis of and measurements from the fermentationexperiment on sugar and ethanol concentrations.

From Table 14 we do observe a difference in the calculated and measured sugar concentration. Especially large differences are shown in the puree samples. In bottles with the puree (1 to 6) we see that the measured sugar values are lower than expected. This can be partly explained by the fact that no fructose was measured in the puree samples (but possibly it was present in a similar form) and partly because sugars were used to produce another substance as we will see later in the gas chromatography. Then we observe both for puree and sugar solutions a difference in ethanol levels if comparing the calculated and measured values. Ethanol levels are in general a factor 0,7-0,8 lower than based on the calculation. This is also explained by the fact that another compound was formed during the process. It is also reflecting in the efficiency. In the green numbers it was assumed that al consumed sugar was converted into ethanol values. It is likely that the total remaining sugar levels in the puree are higher than determined in the lab, but more analyses would be required to check this. Based on this assumption there is the tendency that the fermentation efficiency of puree is lower that the fermentation efficiency of the sugar solutions. This would indicate a possible relation between viscosity and fermentation efficiency.

#### 4.7 Conclusions on fermentation experiment

The **fermentation efficiency** for puree is lower than for the sugar solutions. This is also lower if sugar contents are higher than 28%. Possibly the application of pectinase might increase the fermentation efficiency since sugars will become more freely available for fermentation. The

**fermentation rate** shows a reverse relation with dry matter content of the fermentate. Thus the higher the dry matter content (puree with high sugar content) the lower the fermentation rate. A relation for fermentation rate was found for the first four hours of fermentation, both for the apple puree and for the dissolved sugar. The fermentation generated another product, other than ethanol and carbon dioxide. This could have affected inhibit the ethanol yield.

# **5** Discussion

This thesis aims to optimize the bioethanol production process from coffee waste eventually in order to improve the livelihoods of small coffee farmers. The suitability to implement reverse osmosis in the ethanol production process depends on the local circumstances. There should be sufficient capital, technical knowhow and infrastructure in order introduce and to support this technology. Moreover it should be competitive in terms of economics. It might be hard to compete with cheap fuel wood or waste bagasse that is used for the distillation process in some cases. Then the extra income that the ethanol possibly generates is considered of more value than the unfavorable energy balance of the process. Also the technical feasibility in terms of required prefiltering might cause difficulties for implementation.

It should be noted that low ethanol substances like occur in coffee waste fermentation are currently not processed in reality if the grades are too low. Reverse Osmosis could therefore improve the suitability of the feedstock for further processing. Other possible solutions can be the co-fermentation of mucilage with concentrated starch if this is available.

There are other valuable components in the waste streams of that could be used for higher applications than for the use of energy for example for animal fodder or isolation of organic compounds like pectines. Possibly there exists opportunities on the local market for those organic compounds. Generally in rural settings the demand for energy is more obvious than specific organic compounds. Biogas could also be an interesting alternative for the coffee waste treatment however, the temporary availability of the feedstock and the difficulty to store biogas limits its applicability. Bioethanol can be favorable in **specific situations** where it can substitute indoor wood stove cooking, run agricultural equipment or adapted transport engines. It can also be mixed with ethanol from sugar cane in centralized anhydrous ethanol installations.

### **6** Conclusions

The aim of the thesis is to investigate which role membrane technology can play in small scale production of bioethanol from mucilage in terms of energy efficiency

Ethanol as a fuel is used for transport and indoor cooking. It has potential to generate a positive effect on the environment and human health. The global coffee sector consists of an enormous industry from which the waste streams largely remain unused. The technical feasibility of the production of ethanol from coffee waste has been proven in several small scale pilot projects. In the current production process, the distillation step is the most energy requiring process. Especially low grade broths require relatively high energy input. Membrane technology can be used in order to improve the energy ratio of this process. However a difference in fermentation efficiency was observed between substrates that vary in viscosity. The fermentation rate is lower for higher sugar levels both for puree and sugar solutions. If the energy released during the fermentation could be used e.g. for pumping, it could also have a positive effect on the energy demand of the process. When focusing on pervaporation we observed that this technology as well is a function of the molar concentration since the permeate flux is a direct function of the difference in molar concentration of the filter feed and the permeate. The energy requirement for concentrating ethanol using pervaporation are similar to those of distillation. Pervaporation has potential for energy saving improvements and can be interesting for azeotrope liquid separation as well. Reverse osmosis can be applied for concentration of the broth for the lower range of the purification process. For ethanol purification with reverse osmosis, the energy requirements are lower than those of pervaporation and distillation. When reverse osmosis is applied for the concentration of sugars, significant energy savings can be made as well. Reverse Osmosis can be applied for the lower concentration range of the process preferably prior to the fermentation process. The sugars can then be concentrated up to 28% resulting in 14% ethanol fermentation that is further upgraded by using distillation.

# Annexes

#### **Composition of coffee waste** I.

 Table 15. Calculation of minimum potential ethanol production from coffee mucilage.

Pure mucilage directly from berry		
Wet mucilage	1.000	grams
Dry matter	7,8%	
Of which sugars	80%	
Total sugars	62,2	grams
	6%	
Production of ethanol	28,5	grams
Total mucilage to ethanol	2,9%	
Remaining water	97,1%	
Water use in process		
Water used in de-mucilage	0,06	m <sup>3</sup> /fanega
	0,24	l/kg.berry
	1,5	l/kg.mucilage
	1,3	l/kg.bean
Diluted mucilage		
Wet mucilage	1.000	grams
Water added in process	1.500	grams
Total weight	2.500	grams
Factor for composition of sugars	0,4	
Sugars after dilution	24,9	g/kg
Ethanol after dilution	11,42	g/kg
Ethanol from processed mucilage	1,1%	
Adapted from Cenicafé.		

Adapted from Cenicafé.

# Table 16. Composition of coffee pulp.

Pulpa									
Component	Fresh	Dehydrated	Naturally fermented and dehydrated	Component	Dry Matter	Minerals		Minerals	
Unit	%	%	%		%		%/ppm		ppm
Water	77	12.6	7.9	Tannins	1.80-1.56	Ash	8.3	Zn	4
Dry matter	23,3	87.4	92.1	Pectines	6.5	Са	554	Cu	5
Ether extract	0.48	2.5	2.6	Reducing sugars	12.4	Р	116	Mn	6.25
Fiber	3.4	21.0	20.8	Non reducing sugars	2.0	Fe	15	В	26
Protein (Nx6.25)	2.1	11.2	10.7	Caffeine	1.3	Na	100		
Ash	1.5	8.3	8.8	Chlorogenic acid	2.6	К	1765		
N free extract	15.8	44.4	49.2	Caffeic acid	1.6	Mg	trace		

(Mazzafera, 2002) Composition of Mead (coffee waste water/agua mieles)

Measure/component	Unit	Amount
РН	[-]	3,92
Conductivity	[µs/cm]	232
Total solids	[ppm]	9393
Solved solids	[ppm]	4938
Suspended solids	[ppm]	4455
Ashes	[ppm]	400
Organic matter	[ppm]	8993
COD	[ppm]	9484
NTK	[ppm]	65.6
Dissolved oxygen	[ppm]	3.85
Pectins	[ppm]	3855
Fructose	[ppm]	207
Galactose	[ppm]	64
Glucose	[ppm]	125
Sucrose	[ppm]	511
Total sugars	[ppm] (%)	904 (0,1)
Lactic acid	[ppm]	687
Acetic acid	[ppm]	54
Citric acid	[ppm]	1512
Galacturonic acid	[ppm]	90
Carboxylic acid (sum)	[ppm]	2297
Chlorogenic acid	[ppm]	4,47
Caffeine	[ppm]	26,7
Са	[ppm]	11,6
К	[ppm]	3,5
Na	[ppm]	92,5
Mg	[ppm]	4,5
Fe	[ppm]	1,2
Total metals	[ppm]	113,3
Source: conicate org		

# Table 17. Composition of coffee waste water.

Source: cenicafe.org

# II. Energy for mucilage transport

Mucilage transport		
Engine	0,7	kW
Capacity	250	kg/h
Energy requirement	0,0028	kWh/kg mucilage
Energy requirement	0,01008	MJ/kg mucilage
Amount of mucilage	130,72	kg/liter EtOH
Energy requirement	1,32	MJ/liter EtOH

 Table 18. Energy for mucilage transport.

# III. Energy requirement for pervaporation

	Unit	Amount
Membrane selectivity	rate	7
DIMENSIONS	units	amount
Lenght	mm	250
Diameter in	mm	7
Number of modules		16
Surface per filter	mm2	5497,8
Surface per filter	m2	0,0055
Volume per filter	mm3	9621,128
Volume per filter	m3	9,62113E-06
Total surface of module	m2	0,087964594
Volume of module	mm3	38,5
Total volume of filter	m3	9,62113E-06
Total volume of filter	1	0,009621128
Ethanol in feed [Ya]	%	85%
Water in feed [Yb]	%	15%
Ya/Yb		5,667
Density of ethanol	kg/l	0,780
Density of water	kg/l	1,000
Density of feeded solution	kg/l	0,813
Molecular mass H2O	g/mol	18
Molecular mass of ethanol	g/mol	46
Mass of EtOH solution in membrane	g	7,821976659
Mass of EtOH in membrane volume	g	6,64868016
Amount of molecules EtOH in feed	mol	0,144536525
Concentration of EtOH	[mol/liter]	15,02282609
Volume of water in membrane volume	m3	1,44317E-06
Mass of water in membrane volume	g	1,443169125
Amount of molecules water in feed	mole	0,080176063
Total moles in feed	moles	0,224712588
Parts of water that pass the filter		87,5%

 Table 19. Energy requirement for pervaporation.

Molecules of water removed	mole	0,070154055
Molecules of EtOH removed	mole	0,018067066
Reduced mass of water in feed	g	1,262772985
Reduced mass of EtOH in feed	g	0,83108502
Reduced volume of water in feed	m3	1,26277E-06
Reduced volume of EtOH in feed	m3	1,06549E-06
Remaining total volume	m3	7,29286E-06
Total volume of end product	liter	0,007292861
EtOH in feed	mole	0,12646946
Water in feed	mole	0,010022008
EtOH in feed	g	5,81759514
Water in feed	g	0,180396141
Total mass of feed	g	5,997991281
EtOH in feed	%	0,969923907
Water in feed	%	0,030076093
Energy requirements		
Evaporation EtOH	KJ/kg	841
Evaporation water	KJ/kg	2260
Energy for water	KJ	2,853866945
Energy for ethanol	KJ	0,698942502
Total energy	KJ	3,552809447
Efficiency of pervaporation	%	90%
Energy requirement	KJ	3,947566052
Energy requirement	KJ/I	541,291834
Energy requirement	MJ/I	0,541291834

# IV. Energy requirement for reverse osmosis

GENERAL			
V	reactor volume batch	1000	liter
%Sugar	Sugar concentration in solute	5%	%(m/m)
Mass sugar	mass of sugar in solution	50	[g/l]
M sugar	molar mass of sugar	180	[g/mol]
p sugar	density of sugar	1,58	[g/ml]
V EtOH	volume of sugar	113,92	[ml/mol]
OSMOTIC PRESSURE AT A SI	PECIFIC CONCENTRATION GRADIENT		
[B]	moles of sugar in solution	0,2778	[mol/liter solution]
[B]	moles of sugar in solution	277,8	[mole/m3 solution]
Т	Temperature	298	[K]
R	gas constant	8,31	[J/(mol.K)]
П	Osmotic pressure	687883	[Pa]
П	Osmotic pressure	6,88	[bar]
REQUIRED PRESSURE TO RE	ALIZE A FLOW OF THE SOLVENT		
C.memb	membrane capacity (solute	7,7	[l/m2.hr.bar]
	flow)		
A/membrane	membrane surface	0,5	[m2]
Δt	modeled time interval	ed time interval 360 [secor	
Ρ	applied pressure gradient	50	[bar]
Δ Ρ	effective pressure	43	[bar]
	realized solute flow	16,6016	[l/interval]
REQUIRED ENERGY TO REAL	LIZE A FLOW OF THE SOLVENT		
	effective pressure	4312117	[Pa]
	applied pressure	0,0050	[MJ/I]
	displaced volume during	16,6016	[I]
	time interval		
	required energy	0,0830	[MJ]/time interval
EffPump	efficiency of pressure pump	60%	%
	applied energy	0,1383	[MJ]/time interval

Table 20. Energy requirement for reverse osmosis.

# V. Practical RO Test calculations

Table 21. Comparing	energy for RO and	mixing of Labcell CF 1.
---------------------	-------------------	-------------------------

Work req to reach end concentration	[1]	-82,30	-121,33	-134,28	-47,28	-144,88	-149,13	-124,10	-145,00	-187,85	-196,88	-116,04	-138,92
energy for gas	J	1299	1282	1234	1306	1620	1552	1643	1976	1951	1901	1270	1620
energy for pump incl eff	J	864000	925714	925714	925714	925714	771429	771429	925714	925714	925714	925714	925714

# VI. Set up for fermentation experiment

bottle number	calculated sugar	calculated puree	added water	total mass	applied yeast (x100)
	%	gram	gram	gram	gram
1	30%	50	0	50	1.65
2	25%	50	10	60	1.98
3	20%	50	25	75	2.475
4	15%	50	50	100	3.3
5	10%	50	100	150	4.95
6	5%	50	250	300	9.9
7	30%	30	70	100	3.3
8	25%	25	75	100	3.3
9	20%	20	80	100	3.3
10	15%	15	85	100	3.3
11	10%	10	90	100	3.3
12	5%	5	95	100	3.3

# Table 22. Set up for fermentation experiment.

# Table 23. List of materials for fermentation experiment.

Material	Size	amount
Test bottles	500 ml	12
Concentrated apple puree	300 grams	
Sugar	105 grams	

Yeast	50 grams	
Water	1 litre	
Scale	Accuracy 0.1 grams	1
Insulated box	30x30x30cm	1
Thermocouple		1
Heat source	40W	1
Thermometer		1

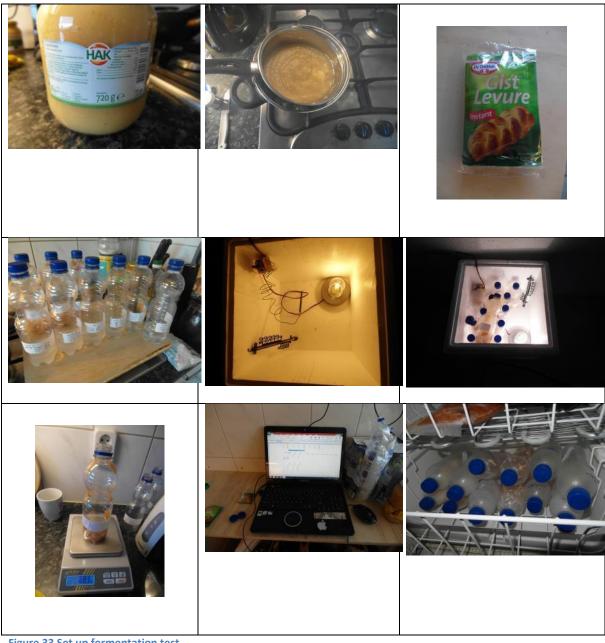


Figure 33 Set up fermentation test

# References

- America, O. (2005). Small Scale Family Coffee Farmers GATHERED in Salvador DECLARE: 'The Coffee Crisis is Not over, AND we must be a part of finding the solution'. from <u>http://www.csrwire.com/press\_releases/21420-Small-Scale-Family-Coffee-Farmers-GATHERED-in-Salvador-DECLARE-The-Coffee-Crisis-is-Not-over-AND-we-must-be-a-part-of-finding-the-solution-</u>
- Bressani, J. E. B. a. R. (1979). Coffee Pulp

Composition, Technology, and Utilization.

- Cenicafe. (2006). Retrieved from <u>http://www.cenicafe.org/</u>
- Chartbin. (2008). Retrieved from http://chartsbin.com/view/581
- Fadeev, M. M. M. (2000). Fouling of poly[-1-(trimethylsilyl)-1-propyne] membranes in pervaporative recovery of butanol from aqueous solutions and ABE fermentation broth.
- FAOSTAT. (2009). Retrieved from http://faostat.fao.org/site/567/default.aspx#ancor
- Goettemoeller, G. (2008). Sustainable bioethanol.
- Graziosi, R. R. a. G. (2005). Potential alternative uses of coffee wastes. *international coffee organisation*.
- Humbert, S., Loerincik, Y., Rossi, V., Margni, M., & Jolliet, O. (2009). Life cycle assessment of spray dried soluble coffee and comparison with alternatives (drip filter and capsule espresso).
   *Journal of Cleaner Production*, *17*(15), 1351-1358. doi: 10.1016/j.jclepro.2009.04.011
- J. Ferrell, K. C. (2012). Closing the production loops with waste to ethanol in Matagalpa, Nicaragua. *Energy for sustainable Development*, 44-50.
- Jorge R. Lara, O. O. a. M. T. H. (2011). Advanced Mechanical Vapor-Compression. intechopen.
- Kaewkannetra, P., Chutinate, N., Moonamart, S., Kamsan, T., & Chiu, T. Y. (2012). Experimental study and cost evaluation for ethanol separation from fermentation broth using pervaporation. *Desalination and Water Treatment*, 41(1-3), 88-94. doi: 10.1080/19443994.2012.664682
- Kazi, F. K., Fortman, J. A., Anex, R. P., Hsu, D. D., Aden, A., Dutta, A., & Kothandaraman, G. (2010).
   Techno-economic comparison of process technologies for biochemical ethanol production from corn stover. *Fuel, 89*, S20-S28. doi: 10.1016/j.fuel.2010.01.001
- Lipnizki, F. (2010). Membrane process opportunities and challenges in the bioethanol industry. *Desalination*, 250(3), 1067-1069. doi: 10.1016/j.desal.2009.09.109
- Madson, P. (2003). *Ethanol distillation: the fundamentals the alcohol textbook* (4th ed.): Nottingham University.
- Mazzafera, P. (2002). DEGRADATION OF CAFFEINE BY MICROORGANISMS AND POTENTIAL USE OF DECAFFEINATED COFFEE HUSK AND PULP IN ANIMAL FEEDING.

Mulder. (1996). Basic Principles of Membrane Technology.

Mutua, J. (2000). Post harvest handling and processing of coffee in African countries FAO, AGSI.

Minnesota Technical Assistance Program

http://www.mntap.umn.edu/greenbusiness/water/5FS.membranefiltration.pdf

- Nijhuis, F. P. C. a. H. H. (1993). Applications of membrane technology to food processing. *Trends in Food Science & Technology September, 4.*
- Paula, P. A. a. J. d. (2009). Elements of physical Chemistry.
- Peter Atkins, J. d. P. (2009). *Elements of Physical Chemistry*.
- Ponte, S. (2002). The 'Latte Revolution'? Regulation, Markets and Consumption in the Global Coffee Chain. *World Development*, 1099–1122.
- Schot, J., & Geels, F. W. (2008). Strategic niche management and sustainable innovation journeys: theory, findings, research agenda, and policy. *Technology Analysis & Strategic Management, 20*(5), 537-554. doi: 10.1080/09537320802292651
- Vane, L. M. (2008). Separation technologies for the recovery and dehydration of alcohols from fermentation broths. *Biofuels, Bioproducts and Biorefining, 2*(6), 553-588. doi: 10.1002/bbb.108

Valencia, N.R., Zambrano Franco, D.A. (2010) Avances Tecnicos Cenicafé: los subproductos del café: fuente de energía renovable

Wei, P., Cheng, L.-H., Zhang, L., Xu, X.-H., Chen, H.-I., & Gao, C.-j. (2014). A review of membrane technology for bioethanol production. *Renewable and Sustainable Energy Reviews, 30*, 388-400. doi: 10.1016/j.rser.2013.10.017

Wesselingh, J. (2013). Distillation.WHO. (2011). FACT sheet.Xianshe Feng, R. Y. M. H. (1997). Liquid Separation by Membrane Pervaporation: A Review.