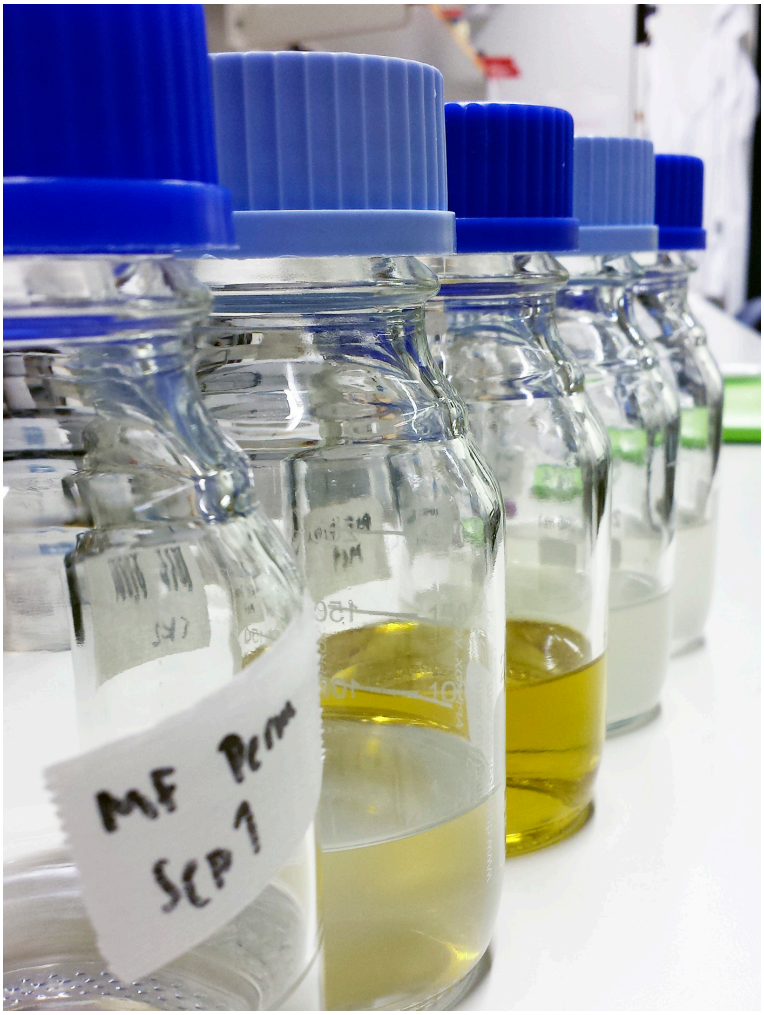
Wastewater from a biodiesel plant

Characterization of streams and suggestions for treatment options



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Water and Environmental Engineering
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by

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Preface

This study was performed at the Department of Chemical Engineering at Lund University between September 2016 and February 2017. I want to send out a thank you to the whole department for welcoming me with warm and open arms. Without the conversation and laughter in the lunchroom this work would not be the same.

I also want to thank my supervisor Ann-Sofi, for your valuable words of feedback. Also, thank you for helping me understand and disentagle this complex process. Thank you Åsa, my examinator, for sharing your expertise within the biogas area.

The wastewater studied was sampled from Ecobränsle with the help of the Lars, Håkan and Charlott. I want to aim a special thanks to Charlott for helping me understand your company's process and answering my questions about the production.

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Finally, a big thank you to my partner Erik. Thank you for your support and understanding. Thank you for making me realise what is important and for making me come home in time for dinner.

Summary

Biodiesel is an important alternative to ordinary diesel when limiting the effects on the climate. However, the production path of biodiesel produces a wastewater with a high chemical oxygen demand (COD) and it needs to be cleaned. The aim of this study was to characterise biodiesel wastewater as well as to suggest treatment options.

The biodiesel wastewater studied came from a biodiesel plant in the south of Sweden. The wastewater is generated when the biodiesel is washed to remove the by-product glycerol, the reactant methanol and a catalyst. Streams from different processing steps were investigated as well as the final mixed stream that today is sent for treatment to at plant in Kristianstad about 56 kilometers away.

The wastewater was characterised by measuring general parameters such as total bound nitrogen, total phosphorus, COD, pH and density. The results varied between the streams but the results of the final mixed stream will be presented here. The mixed water was found to have a high COD of 241 g/L, higher than many compared studies. It also had a high total phosphorus content of 1480 mg/L and a nitrogen content of 57 mg/L. The pH was neutral around 6 and the density was 996 g/L, which is somewhat lower than the density of water.

When the samples were visually examined it was found that the mixed streams were most cloudy whereas some of the non-mixed streams were clear. This was supported by analysing the turbidity of the samples, which also indicated that there were many particles in the water. To find out if the COD was dissolved or particulate the samples were microfiltrated. Prior to the microfiltration the particle size distribution was determined to decide the pore size of the membrane, which was chosen to 0.2 μm. The analyses of the permeate showed that the turbidity decreased but the COD remained virtually unchanged. This meant that the COD was mainly dissolved.

To evaluate the origin of the COD the streams were characterised further with HPLC and gas chromatography (GC). From the HPLC it was found that the final mixed stream had high concentration of glycerol of 41.7 g/L. This is higher than the compared studies. The results from the GC showed that the streams contain residues of biodiesel and some other unidentified components.

Anaerobic digestion was evaluated as a treatment method by testing the biochemical methane potential (BMP) for the wastewater. The BMP of the mixed stream was 185.5 NmL CH_4/g COD. It was found that codigestion of the wastewater with the glycerol by-product would have a higher BMP of 263.8 NmL CH_4/g COD. This means that not only would the addition of glycerol to the stream generate a larger volume for anaerobic digestion but the potential of that stream would be higher.

The results from the BMP tests were used to estimate the biogas production. The biogas production was then compared to the mean yearly energy consumption of a Swedish house. Using only the mixed stream the yearly production could cover the consumption of 8 houses per year. With the codigestion of the streams the yearly production could cover the yearly consumption of 67 houses.

Sammanfattning

Biodiesel är ett viktigt alternativ till vanlig diesel för att begränsa effekterna på klimatet. Produktionen av biodiesel ger ett rejektvatten med hög kemisk syreförbrukning (COD) och det behöver därför behandlas. Syftet med denna studie var att karakterisera avloppsvatten från en biodieselanläggning samt att föreslå behandlingsalternativ.

Den studerade biodieseln kom från en biodieselanläggning i södra Sverige. Rejektvattnet genereras när biodieseln tvättas för att avlägsna biprodukten glycerol, reaktanten metanol och en katalysator. Strömmar från olika processteg undersöktes liksom den slutliga blandade strömmen som idag skickas för rening till Kristianstad som ligger 5,6 mil bort.

Rejektvattnet karakteriserades genom att mäta generella parametrar som totalt bundet kväve, total fosfor, COD, pH och densitet. Resultaten varierade mellan strömmarna och resultaten av den slutliga blandade strömmen kommer att presenteras här. De blandade strömmen hade ett högt COD på 241 g/L, högre än många jämförda studier. Den hade också en hög total fosforhalt på 1480 mg/L samt en kvävehalt på 57 mg/L. pH-värdet var neutralt omkring 6 och densiteten var 996 g/L, vilket är något lägre än densiteten hos vatten.

När proverna undersöktes visuellt visade det sig att de blandade strömmarna var mest grumliga medan några av de icke-blandade strömmarna var klara. Detta stöddes genom att analysera turbiditeten hos proverna analysen visade även att det fanns många partiklar i vattnet. Att ta reda på om COD var löst eller partikulärt mikrofiltrerades proverna. Före mikrofiltrering bestämdes partikelstorleksfördelningen för proven för att bestämma porstorleken hos membranet, som valdes till 0,2 µm. Analyserna av permeatet visade att grumlighet minskade men att COD i stort sett var oförändrad. Detta innebär att det höga CODt är främst i löst form.

För att utvärdera ursprunget av COD karakteriserades strömmarna ytterligare med HPLC och gaskromatografi (GC). Från resultaten av HPLC konstaterades det att den slutliga blandade strömmen hade en hög koncentration av glycerol på 41,7 g/L. Detta är högre än de jämförda studierna. Resultaten från GC visade att strömmarna innehåller rester av biodiesel och vissa andra oidentifierade komponenter.

Rötning utvärderades som en behandlingsmetod genom att testa den biokemiska metanpotentialen (BMP) för avloppsvattnet. BMP av den blandade strömmen var 185,5 NmL CH_4/g COD. Man fann att samrötning av avloppsvattnet med glycerol biprodukten skulle ha en högre BMP på 263,8 NmL CH_4/g COD. Detta innebär att tillsatsen av glycerol till strömmen inte bara kommer generera en större volym för rötning men potentialen av denna ström är också högre.

Resultaten från BMP-testen användes för att uppskatta biogasproduktionen. Biogasproduktion jämfördes sedan med den genomsnittliga årliga energiförbrukningen för ett svenskt hus. Genom att bara använda den blandade strömmen skulle den årliga produktionen kunna täcka konsumtionen för 8 hus per år. Med samrötning av strömmarna skulle den årliga produktionen kunna täcka den årliga förbrukningen för 67 hus.

Populärvetenskaplig sammanfattning

AVLOPPSVATTEN FRÅN EN BIODIESELANLÄGGNING: VAD INNEHÅLLER DET OCH HUR BEHANDLAR MAN DET?

Avloppsvatten från biodieselproduktion innehåller b.la. höga halter av organiskt material. Det betyder att vattnet måste behandlas för att få släppas ut. Innehållet i avloppsvattnet från en biodieselanläggning i Blekinge och förslag till behandling diskuteras i detta arbete.

Biodiesel är ett viktigt alternativ till vanlig diesel eftersom användandet av biodiesel kan bidra till att minska klimatpåverkan från fordonstrafik. Biodiesel kan tillverkas av olika råmaterial så som tallolja, animaliskt fett och rapsolja. I det undersökta fallet är råvaran rapsolja och ger s.k. rapsmetylester (RME).

Vid tillverkningen av biodiesel bildas glycerol som en biprodukt. En annan biprodukt från den vanligaste tillverkningsprocessen är förorenat vatten. Detta vatten innehåller vanligtvis höga halter av organiskt material som kan leda till övergödning och syrebrist, om det når vattendrag och sjöar obehandlat. Alltså behöver vattnet behandlas innan det kan släppas ut igen.

Idag skickar företaget som tillverkar RMEn sitt vatten för behandling i Kristianstad. Problemet är att det är ganska långt att transportera avloppsvatten på en lastbil 5,6 mil och det är inte heller särskilt miljövänligt. Därför har möjligheten till att behandla vattnet på plats undersökts i detta arbete. En stor del av arbetet har även handlat om att undersöka vad som finns i vattnet för att komma fram till den bäst lämpade behandlingen.

Genom analyser av vattnet har det konstaterats att det innehåller höga halter av organiskt material. Detta var förväntat men det är intressant att värdena var högre än i de studier som jämförts (Phukingngam et al., 2011, Srirangsan et al., 2009). Biprodukten glycerol identifierades som en del av det organiska materialet. Genom ytterligare analyser har det konstaterats att vattnet innehåller höga halter av fosfor. Fosfor är viktigt att ta hänsyn till då det också bidrar till övergödning.

Ett sätt att behandla vattnet är att röta det för att få fram biogas. För att analysera hur mycket biogas som kan produceras så gjordes försök där mikroorganismer från en fungerande rötkammare användes. Mikroorganismerna matades med det förorenade vattnet och det mättes hur mycket biogas som producerades. Resultaten visade att med dagens produktion skulle företaget kunna producera 66 950 normaliserade kubikmeter metan per år (Nm^3_{metan}/år). Det, lågt räknat, skulle kunna täcka energibehovet för 8 villor per år (Eon, 2017a, Myfuelcell, 2017, Petersson, 2011). Försök gjordes även på en blandning av den tillverkade glycerolen och det förorenade vattnet. Genom att blanda dessa skulle produktionen kunna bli 563 900 Nm^3_{metan}/år och kunna täcka behovet för 67 villor.

Att röta vattnet är ett miljövänligt alternativ för behandling, eftersom processen ger ett mervärde genom biogasen som ett extra energitillskott. En del av fosforn i vattnet kan dessutom tas upp av mikroorganismerna och gör det då möjligt att potentiellt använda överskottet av slam som gödsel (Jarvis, 2012, Jonstrup et al., 2011). Dock är rening genom rötning inte det enda alternativet och det behövs mer studier för att fastställa vilket reningsalternativ som passar bäst.

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Table of abbreviations

BMP – Biochemical methane potential

COD – Chemical oxygen demand

FAME - Fatty acid methyl ester

MF – microfiltration

RI – Refractory index

RME – Rapeseed oil methyl ester

VSS- Volatile suspended solids

1 Background

1.1 Introduction

Biodiesel can be a conceivable alternative in limiting the effects on climate change from diesel combustion. Biodiesel can be made from numerous vegetable fat sources or from fat residues from the meat industry. This thesis focuses on the treatment of the wastewater derived in the manufacturing process of biodiesel from rapeseed.

The biodiesel wastewater studied in this thesis comes from a biodiesel plant in Karlshamn, located at the south-coast of Sweden. The plant is run by the company *Ecobränsle* who produce their biodiesel from Swedish-grown rapeseeds. The biodiesel is produced in a way that generates wastewater that needs to be treated due to its high content of COD (Chemical oxygen demand). The company wants to find a solution for treating the wastewater, instead of sending it to a treatment plant.

1.2 Ecobränsle's production

Ecobränsle produces biodiesel from 99% Swedish rapeseed. They use methanol as reactant and potassium methylate ($KOCH_3$) as catalyst. The crude biodiesel is cleaned with water which needs to be treated. Ecobränsle produces approximately 6.2-6.5 m^3 rapeseed oil methyl ester (RME) per hour in shifts of 8-16 hours per day. For every 100 L biodiesel produced they produce approximately 10 L of wastewater. In October 2016 they were running the factory for 2-3 days a week. (Lorentzen, 2016) With that capacity they produce maximum 312 m^3 RME per week. This gives a small production of approximately 31.2 m^3 of wastewater per week.

Apart from the wastewater glycerol is also a by-product from the production. At the moment Ecobränsle is selling their glycerol at 130-180 € per tonne as an additive in a biogas reactor. The theoretical weekly production of glycerol can be calculated based on the molar relationship between RME and glycerol, and the weekly production of RME. Rapeseed oil consists mainly of oleic acid (Bart et al., 2010a) which is why the molar mass of oleic acid is used to calculate the volume of glycerol produced. The calculated production of glycerol is 24 m^3 per week or expressed in mass: 30 tons per week. For calculations see Appendix 1.

Ecobränsle's production will be further explained below in the context of other possible production methods.

1.3 Aim

The aim of this work was to characterise the wastewater produced in Ecobränsle's plant and to evaluate different treatment solutions for the wastewater. In order to simplify the investigation some questions were formulated which are presented below.

- What characterises the wastewater produced by Ecobränsle?
- What kind of wastewater treatment solutions are possible for biodiesel wastewater?
- What kind of wastewater treatment is suitable for Ecobränsle's plant, when aiming to find an environmentally friendly solution?

2 Production of Biodiesel

In order to treat the biodiesel wastewater it is important to know what it consists of and what kind of problems that are related to the treatment. Thus a literature study was performed to learn more about the production of biodiesel as well as the production of its wastewater. The treatment of the wastewater was also considered by presenting different treatment methods.

2.1 Biodiesel - How is it made?

Biodiesel is made from fats (Ma and Hanna, 1999). The fats can be of either vegetable or animal origin. The fat is then processed through pyrolysis or transesterification or used in its original form as a microemulsion or directly blended. By definition the transesterification process gives biodiesel as specified in Europe and USA (Ma and Hanna, 1999). Transesterification is also the most commonly used processing method (Daud et al., 2015), and therefore it will be considered from here on.

Transesterification is the reaction between fat and alcohol to create esters and glycerol, as shown in Figure 1 (Ma and Hanna, 1999). The reaction is catalysed by alkalis, acids or enzymes (Daud et al., 2015). The mixture is then treated to remove alcohol, glycerol, fat and by-products from the crude biodiesel (Bart et al., 2010b). The definition of biodiesel depends on composition specifications thus the mixture of esters needs to be treated before it is defined as biodiesel. The mixture of esters is often called crude biodiesel and that is what it will be referred to as from here on.

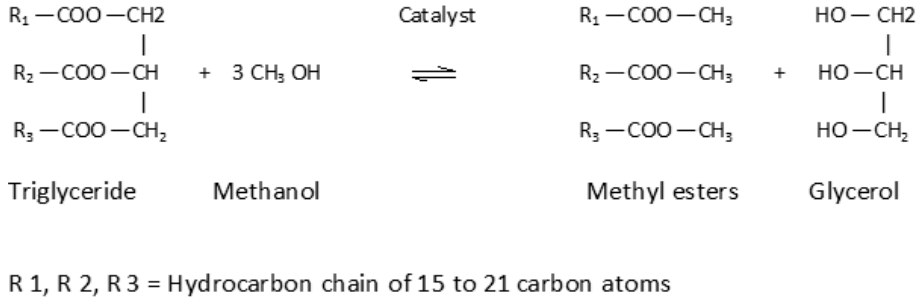


Figure 1. Overall reaction of transesterification triglyceride with methanol. Published with permission. (Rishabh186, 2016)

2.1.1 Alcohol

Methanol is the most widely used alcohol in the transesterification (Bart et al., 2010b). Methanol is cheap, reacts quickly and reduce formation of soap. However, ethanol and other alcohols can also be used. Methanol can be disadvantageous in cold climates because the flow characteristics of methyl esters (biodiesel from methanol) are deteriorated at colder temperatures. Another problem with methanol is related to its ability to hold water. If water is present in the air it can be absorbed by the methanol. (Bart et al., 2010b) Contamination by water enables soap formation during the transesterification, which is negative for the conversion and obstruct the removal of glycerol in the succeeding cleaning steps (Ma and Hanna, 1999).

2.1.2 Catalyst

As mentioned before the catalyst used can be either alkali, acid or enzymatic (Ma and Hanna, 1999). The alkaline catalysts are the most efficient ones and thus they are most widely used,

examples are NaOH and KOH (Ma and Hanna, 1999). The acid catalysts can be advantageous when the content of free fatty acids (FFA) is high since the acid converts the FFAs into biodiesel (Leung et al., 2010). The enzymatic catalysts are useful because they are easily recovered and minimize the production of by-products (Bart et al., 2010d). The main disadvantage of enzymes is their long reaction time. (Bart et al., 2010d)

Apart from their chemical properties catalysts can be classified as heterogeneous or homogeneous, depending on their physical properties (Taylor et al., 2016). NaOH and KOH are examples of homogeneous catalysts. A heterogeneous catalyst is not present in the same state or phase as the reactants (Taylor et al., 2016). An advantage with heterogeneous catalysts is that these catalysts are easier to separate when the conversion is stopped (Bart et al., 2010c). An example of a heterogeneous catalyst is metal surface or fine metal particles that are dispersed in the liquid. A disadvantage with heterogeneous catalysts is that they are more expensive and need to operate at higher temperatures. They might also require pressurization to keep the methanol in liquid phase at a high temperature. (Bart et al., 2010c)

2.1.3 Purification of biodiesel

After the reaction the biodiesel needs to be purified to get a product that can be classified as biodiesel (Leung et al., 2010). The first step is to remove the main by-product, glycerol, which is present in large amounts. This is usually achieved by phase separation simply based on differences in density, or with the help of a centrifuge. When the glycerol has been removed the crude biodiesel needs further cleaning to become biodiesel. (Leung et al., 2010) A schematic illustration of the process stages in the biodiesel process is shown in Figure 2.

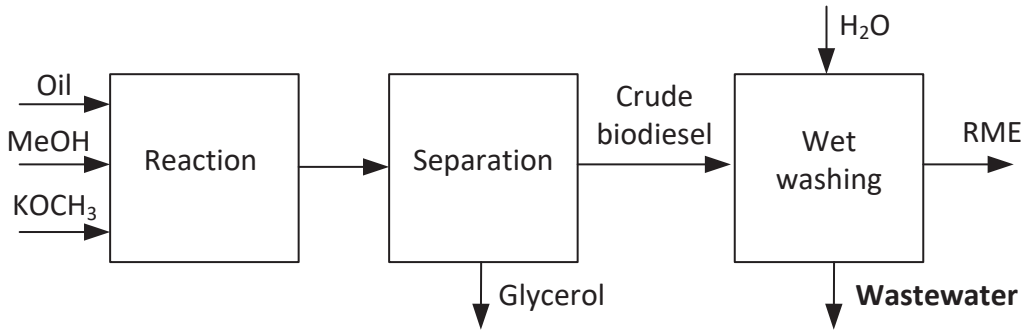


Figure 2. A schematic illustration of the biodiesel process used at Ecobränsle.

The cleaning can basically be divided into the three most common methods: wet washing, dry washing and membrane extraction (Stojković et al., 2014). The most common method is wet washing followed by dry washing (Leung et al., 2010). Wet washing includes washing the crude biodiesel with water to remove the residual water soluble contaminants such as glycerol, alcohol, catalyst, etc. The washing is mainly done with warm deionized water and gives a clean biodiesel product but also a wastewater with a high COD content. This means that the water needs treatment before it can be discharged. (Leung et al., 2010)

The dry washing process was explained by Atadashi (2015) and utilizes adsorption with different types of ion exchange adsorbents e.g. ion exchange resins. The dry washing does not generate wastewater which is positive, but the standards for biodiesel cannot be reached only by dry washing. This makes it less attractive as a cleaning method. (Atadashi, 2015) Membrane

separation is positive because it uses less water and avoids the formation of emulsions. However, the problem is that it is more expensive (Daud et al., 2015).

2.2 Wastewater handling

2.2.1 Wastewater content and treatment options

Biodiesel wastewater contains residues from the production process such as: oil, soap, methanol, glycerol etc. (Daud et al., 2015). This means that the content of COD is quite high and the wastewater needs to be treated. The COD content varies a lot between different processes (Daud et al., 2015). COD is a measurement of the organic content in water. It is measured by using an oxidative that primarily oxidise the organic matter in the water (Nationalencyklopedin, 2017).

The pH is another factor that also varies between studies. The pH is important because it can affect the coagulation process, which is used as a pre-treatment in some cases (Rattanapan et al., 2011). A low pH may result in need of more coagulant to remove COD at the same rate as for a pH around 6 or 7 (Rattanapan et al., 2011). The pH is also important when biological treatment is applied. The organisms used have different preferred pH's but e.g. bacteria prefer a neutral pH (Jonstrup et al., 2011).

Biodiesel wastewater usually has low levels of nitrogen and phosphorus, which is a problem when using biological treatment. This can be regulated by addition of N and P or other nutrients. (Phukingngam et al., 2011, Queiroz et al., 2016) The nutrients need to be balanced to achieve complete degradation (Jonstrup et al., 2011). The preferred balance of COD, nitrogen and phosphorus does however vary between biological treatment systems. (Jonstrup et al., 2011)

Current literature suggests many ways of treating biodiesel wastewater. In order to treat the water efficiently a combination of treatments is necessary (Daud et al., 2015). With the high amount of oil and COD a grease trap tank could be a solution but the water is a highly stable emulsion which makes a grease trap tank useless (Veljkovic et al., 2014). Veljkovic et al. (2014) concludes in their review that a combination of acidification, coagulation with flocculation by chemical or electrical means and finally a biological process is probably the right choice for treating alkali catalysed biodiesel wastewater. These treatment methods will be explained further below. However, they emphasize that it is hard to compare the different results of the different treatments since the wastewater streams differ a lot in composition. (Veljkovic et al., 2014)

2.2.2 Acidification

Acidification is common in alkali catalysed biodiesel production. The acidification adjusts the pH and demulsifies the liquid. This allows for further separation of oil and biodiesel from the wastewater. (Siles et al., 2010, Veljkovic et al., 2014) This step is already implemented in Ecobränsle's treatment in order to extract more biodiesel.

2.2.3 Coagulation and flocculation

Coagulation followed by flocculation is one way of treating the wastewater (Veljkovic et al., 2014). It can be achieved by using chemicals or electricity. The chemical coagulation process requires rapid mixing for the coagulant to disperse thoroughly (Veljkovic et al., 2014). The coagulant then neutralizes the charge of the particles that are to be removed (Russell, 2006). The coagulation is then followed by flocculation and then the mixing is slower to enhance the formation of flocs (Veljkovic et al., 2014). The flocs are then removed when they are allowed to sediment in sedimentation tanks (Britannica, 2017). In chemical coagulation and flocculation

the chemical additive used to coagulate the particles consist of either charged inorganic salts or inorganic polymers (Veljkovic et al., 2014).

In electrocoagulation the wastewater is treated by an electric current in an electrochemical cell. The anode is usually of aluminium and the cathode can be of carbon. (Daud et al., 2015, Veljkovic et al., 2014) The anode reaction converts e.g. the aluminium to aluminium ions and electrons and the cathode reaction converts water and electrons to hydrogen gas and hydroxyl ions. The metal ions and the hydroxyl ions react and form flocs of metal hydroxide. The flocs then adsorb organic compounds. The flocs in both chemical and electrical flocculation are then removed by sedimentation or flotation. In electrocoagulation the flocs can be floated by using the hydrogen gas that is produced.(Veljkovic et al., 2014) It should be noted that electrocoagulation has only been reported in lab scale experiments (Veljkovic et al., 2014), whereas chemical coagulation is a common treatment method in drinking water treatment (Britannica, 2017).

For biodiesel wastewater, electrocoagulation has been suggested by Srirangsan et al. (2009) as a good pre-treatment. Using an aluminium anode and a graphite cathode the removal of oil and grease and suspended solids is around 97 % but the removal of COD is only 57 %. The removal efficiencies of methanol and glycerol were however limited to 3.5 % for glycerol and 16.9 % for methanol.

2.2.4 Biological treatment

When considering biological treatment it can be divided into two main areas: aerobic treatment and anaerobic treatment. Aerobic treatment alone is not cost-effective for wastewaters with high strength as is the case for biodiesel wastewater (Hamza et al., 2016). However, it can be interesting in a combined anaerobic-aerobic system (Hamza et al., 2016). Combined wastewater systems will be discussed after the anaerobic treatment has been presented.

Anaerobic digestion is a way of treating wastewater using anaerobic bacteria (Jonstrup et al., 2011). In short the bacteria degrade the organic matter to create methane and carbon dioxide. The anaerobic digestion can be performed under different temperature conditions, usually mesophilic or thermophilic. The mesophilic temperature interval is defined as between 25°C and 40°C whereas thermophilic conditions are defined as temperatures over 45°C. (Jonstrup et al., 2011)

The amount of methane that can be produced vary for different substrates depending on composition. A way of assessing the anaerobic biodegradability of the substrate, in this case biodiesel, is to perform a biochemical methane potential test (BMP) (Carlsson and Schnürer, 2011). Hansen et al. (2004) have developed a method for BMP evaluation. An interesting aspect is that they also found that samples high in fat and oil have a lag phase of several days.

There are different types of anaerobic reactors and according to Speece (1983) they can mainly be divided into two categories: suspended mobilised and immobilised. The difference lies in how the majority of microorganisms are situated in the reactor. In the suspended mobilised reactors the microorganisms are free floating as in the contact process. However, the treated water needs to be separated from the solids or microorganisms. A settler is usually used and the bottom phase is recycled. A settler is usually not needed in an immobilised reactor type. There the organisms are attached to different types of materials as in the packed bed or the fluidised bed. The organisms can also be immobilised as a granular sludge as in the upflow anaerobic sludge blanket (UASB)-reactor. (Speece, 1983)

2.2.5 Combined biological treatment ways

Anaerobic treatment is often not alone sufficient to reduce the COD enough (Hamza et al., 2016). The anaerobic treatment then needs to be combined with other methods, some of which are presented here.

Combined biological treatment methods as suggested by Hamza et al. (2016) will be discussed below. Membrane bioreactors are one way of combining treatment techniques: biological treatment and membranes. The microorganisms and solids are held back by the membranes while the treated water can pass through. Some advantages of this system are a cleaner outflow, less sludge production, there is no need for a clarifier, making the system compact etc. The main drawback is membrane fouling and the maintenance of the membranes lead to increased costs. The fouling can be prevented by e.g. changing the membranes for more hydrophilic ones as well as avoiding high salinity feeds and operating at constant flux rather than constant pressure.

Another way of combining treatments is an anaerobic-aerobic system. The combination provides advantages such as increased nutrient removal and biogas production compared to applying the systems alone. It also reduces energy requirement and minimize the amount of volatile compounds, both which are arguments against aerobic treatment alone. The surplus of biomass from the aerobic reactor is easily handled by digesting it in the anaerobic reactor, which leads to less production of sludge compared to aerobic treatment alone. However, implementing two systems rather than only one gives a higher capital cost as well as larger space requirements. (Hamza et al., 2016)

2.2.6 Treatment of by-products

Glycerol is the major by-product of biodiesel manufacturing. The market for selling glycerol as a chemical has declined because the increased amount of biorefineries producing glycerol (Yazdani and Gonzalez, 2007). This makes it interesting to use glycerol in an alternative way to make it more valuable. (Yazdani and Gonzalez, 2007) One possible way is to anaerobically digest glycerol as it is easily degradable (Kolesárová et al., 2011). Another way is to co-digest it with wastewater. This was studied by Siles et al. (2010). They managed to get a methane yield of 310 mL CH_4/g COD removed at 1 atm, 25°C. This can be converted in to normalised mL and the value is 284 NmL CH_4/g COD. When the initial amount of substrate was compared to the removed amount the biodegradability was found to be around 100 %. However, the wastewater was pre-treated before anaerobic digestion. This was done to reduce a lag phase in methane production that is observed with samples containing long-chain fatty acids. The pre-treatment applied was electrocoagulation.

3 Materials and methods

The methods used for characterisation and the method for evaluating the biochemical methane potential of the samples will be described in this section. Other aspects as the identification of streams and storage conditions will also be dealt with.

3.1 The biodiesel plant at Ecobränsle

Initially a flowchart of the process at Ecobränsle was created. This flowchart was based on the flowchart in the control system at Ecobränsle and through communication with the production manager. From this chart five wastewater streams and one glycerol stream were identified and investigated in this work. The streams were named: SEP1, CK2, Met, Harp, Saml and Glycerol respectively.

Samples of the streams were delivered at two different occasions but were sampled on the 11th, 17th and 19th of October. Not all streams were sampled on the first occasion thus two new samplings were made on the 17th and the 19th. However, on the 17th only a mixed stream which is sent to the treatment plant was sampled and thus this sample was sent with the samples from the 19th. The transfer took approximately 2 days and the temperature was ambient. Upon arrival the samples were placed in the fridge. All analyses were performed at the Department of Chemical Engineering at Lund University between October 2016 and January 2017. The samples were delivered and stored in steel containers in the fridge. The storage in steel containers might have led to rust particles being formed during the storage.

The samples were analysed to characterise the streams. The different analyses are described below.

3.2 General analyses

Initially general analyses were performed. These were pH, density, COD, total bound nitrogen and total phosphorus. The pH was measured with a *WTW pH 320* pH-meter. The density was measured using hydrometers of different ranges designed for liquids at 20°C. The temperature of the liquids was about 10°C upon measurement since they were not allowed to reach room temperature before measurement.

The COD, total bound nitrogen and total phosphorus were measured using *Hach Lange cuvette tests LCK114, LCK138 and LCK350.* Some of the samples needed to be diluted to reach to the range of measurement. The dilution was done volumetrically with distilled water. For the COD measurements the dilutions were at least 100 times, and often more.

3.3 Microfiltration

To investigate the amount of dissolved COD microfiltration (MF) was used to separate particulate and dissolved COD. The dissolved COD could then be measured in the permeate. Before the MF the samples were centrifuged at 4500 rpm. If there was an oily top phase and/or a pellet after the centrifugation it was removed.

The turbidity of the samples was also measured to evaluate the amount of particles in the samples. The turbidity was measured using a Hach 2100P ISO turbidimeter.

The particle size distribution was measured prior to the membranefiltration to determine the suitable pore size of the membrane. However, prior to the particle size distribution the samples were filtered with a *Munktell all purpose paper filter*. The particle size distribution was measured with a Malvern *Zetasizer nano series*. One sample was run 3 times in a row with 20 measurements for each sample during 10 seconds. Polystyrene latex was used as standard as the properties of the components in the samples from Ecobränsle was not known. The preset parameters of Polystyrene latex were the refractory index (RI) of 1.590 and the absorption of 0.010. The RI is used when converting the intensity based distribution to volume based distribution. The dispersant was set to water. The Zetasizer is more sensitive to larger particles than smaller. This means that in order to present a correct distribution the sizes have to be weighted. This is done by defining that Polystyrene latex is used as standard before measuring. The real RI of the material was not known which makes the results from the particle size distribution measurements subject to some uncertainty.

MF was performed with an *Alfa Laval MFP2 membrane*. This membrane has a pore size of 0.2 µm. The membrane was inserted in a small filtration module with stirrer and pressurised air of 1 bar was applied. For all streams except CK2, 80 % of the feed passed through the membrane and was collected as permeate. For CK2 the whole sample passed through the membrane. For sample Harp the stirring was not on until 50 % of the permeate had been collected. After MF, the COD and the particle size distribution of the permeates were measured. The membranes were dried directly after filtration, without washing, and then photographed.

3.4 HPLC

HPLC was used to identify the components in the wastewater. The samples were prepared by weighing the samples and diluting ten times by weight with distilled water. The samples were then filtered through a 0.2 µm filter into an Eppendorf tube. The grading of the tube was used and approximately 1 mL was filtered. Then 1 mL of distilled water was added with a micropipette. Uncertainties reading the 1 mL mark on the Eppendorf tube might have introduced dilution errors. The standard used was glycerol with a maximum concentration of 5 g/L. However, other standards e.g. methanol, acetic acid and citric acid had been injected on the column previously with the same eluent.

The eluent used for the HPLC was 5mM H_2SO_4 in water and the column was a *Aminex HPX-87H*. The HPLC run was performed on the 21th of October. However, two samples were forgotten and analysed on the 29th of November instead. However since only the concentration of glycerol was measured and glycerol is stable the results should not have been affected.

3.5 Gas Chromatography

Gas chromatography was used to identify more of the components e.g. components that might not have been identified by the HPLC. Before the chromatography the samples were extracted in hexane. For the extraction 5 mL of hexane was used for 45 mL of sample. One extraction per sample was performed for all the wastewater samples except for the Saml sample. For Saml three extractions were performed and the solvents containing extract were then mixed.

The hexane phase was analysed on a *Zebron capillary column ZB-5HT Inferno* with length 15 m intended for biodiesel. The detector was a flame ionization detector (FID) and the carrier gas was nitrogen. The standards used were one F.A.M.E. GLC-10 ampule diluted in ethanol, glycerol diluted in hexane, methanol and hexane. The method used for the samples was a quick

ramping method which started at 50°C and holding it there for 1 minute. It was then ramped to 300°C by 20°C/min. The FID heater was set to 350°C and the injector to 360°C. The air, hydrogen and makeup flows were 400, 30 and 25 mL/min respectively. The injection volume was 0.3 µL and a split ratio of 100:1 was applied.

The methods used to evaluate the FAME (Fatty acid methyl ester) standard (biodiesel standard) were in addition to the method described above a bit slower. One method started at 40°C and after holding the temperature constant for a minute ramped up to 65°C with a rate of 25°C/min. Then the temperature was increased to 160°C with a rate of 100°C/min. Finally, a slow ramping rate of 3°C/min was applied until the temperature had reached 210°C. The gas flows were the same as the previous method. The FID heater was set to 380°C and the injector was set to 350°C. The injection volume was 1µL and a split of 50:1 was applied.

The FAME biodiesel standard contained five components of biodiesel: methyl linoleate (C18:2), methyl linolenate (C18:3), methyl oleate (C18:1), metyl palimitate (C16:0) and methyl sterate (C18:0). The components were divided in equal amounts. Thus peaks with equal areas were expected to appear.

Another method applied for the standard was an application method available for the column. This method was used to evaluate free and total glycerol in biodiesel. The starting temperature of the oven was 50°C for 1 minute. The temperature was then increased to 180°C with a rate of 15°C/min and then increased to 230°C with a rate of 7°C/min. Finally, the temperature was increased to 380°C/min with a rate of 30°C/min, and held there for 10 minutes. The carrier gas used was helium and the injection volume was 1 µL. The injector had a temperature of 53°C and the FID heater was 380°C. No split was applied.

The chromatograms with the quick ramping method were run in series, i.e. when one sample was finished the oven was cooled to the initial temperature and then the next sample was injected. The series order was: SEP1, methanol, Glycerol, CK2, Met, Harp and Saml. The standard had been run prior to the series but some other methods were used in between. This might affect the chromatography because if there are components left in the column due to a bad method they might interfere with the next sample.

3.6 Anaerobic digestion

To evaluate the biochemical methane potential (BMP) the test method that Hansen et al. (2004) developed was used. The adaption of the method will be described in short below. Sludge from a mesophile anaerobic digestor at a municipal wastewater treatment plant was used as inoculum. The sludge was degassed for 3 days at 37°C. After 3 days the COD of the sludge was measured by weighing the sludge and diluting it 100 times. The COD was measured to 304 g/L.

A series of inoculum, standard, SEP1, CK2, Met, Harp, Saml and a mixed stream of glycerol and Saml called RGlyc was created. The inoculum contained only the sludge in equal amounts as the sludge dosed in the other reactors. The standard contained a 1:1 mixture of Avicel® and microcrystalline cellulose. One stream was dosed in three bottles giving triplicates for each sample and in total 24 BMP reactors.

After the degassing the sludge was then dosed into glass bottles of approximately 2.1 L. A ratio of 2:1 between the COD of the inoculum and the sample was used and the volume of the inoculum and the sample was allowed to be maximum 0.5 L. With these premises the amount of COD to be dosed was calculated. The COD of the sample with the lowest concentration, SEP1, was used to calculate the amount of COD that should be added. The amount of added COD was 9.4 g_{COD} ±0.3 for all the samples. If the amount of added sample was below 20 g, water was added to reach a volume of 0.5 L. If the amount of added sample was above 20 g no water was added. When the inoculum and the samples had been dosed the bottles were flushed with nitrogen, closed with a rubber cork and a metal lid and placed in an incubator at 37°C.

The bottles were sampled with a Pressure lok® precision analytical syringe from *Vici.* The syringe was flushed with the gas in the bottle two times before the sample was taken. The sampled amount was 0.2 mL which was injected manually into a GC. The column used was a 30 m HP-1 capillary column by Agilent. The gases used were nitrogen and hydrogen. Methane was used as reference gas. The peak area was noted and later used with a calibration curve to calculate the concentration of methane. Three samples from each bottle were injected.

If the rubber cork of the bottle bulged the bottle was emptied and then a new sample was taken and injected. If one of the bottles needed emptying all of the bottles were emptied. However, the injection before emptying was performed for all of the bottles before they were emptied and then the emptied bottles were sampled. With this method some hours passed before the bottles were emptied and sampled for the second time.

When 35 days had passed and the BMP curve had reached a plateau the experiment was ended. The gas in the bottles were analysed and the bottles were emptied. The pH in the bottles was measured, the weights were recorded and COD samples were taken from one of the triplicates.

4 Results and Discussion

Ecobränsle uses the alkali catalysed transesterification process. The base used is $KOCH_3$. The crude biodiesel is cleaned using wet washing with a slightly acidic water to neutralize the catalyst. (Lorentzen, 2016) This means that they end up with a wastewater that needs to be treated. Approximately 10 L of wastewater is generated per 100 L biodiesel (Lorentzen, 2016). Which is less than Daud et al. (2015) summarized in their review, where the smallest amount reported was 20 L waste water per 100 L biodiesel. However, the studies in the review were conducted during the last decade.

In order to investigate the treatment options for the wastewater from Ecobränsle, the characteristics of the different streams were evaluated. The results of the analyses are presented below. The anaerobic digestion was evaluated as a possible treatment option by conducting BMP tests.

4.1 Flowchart

In order to be able to characterise the wastewater streams of the process they had to be identified. Therefore, a flowchart of the whole process was made. This was done with the help of the flowchart used in the control system at Ecobränsle and through communication with the production manager. It was found that the cleaning process of Ecobränsle's biodiesel generates three wastewater streams from a centrifuge, an evaporator and a distillation column. These streams are mixed, the mixture is evaporated and the concentrate is sent to a wastewater treatment facility. A schematic overview of this process is shown in Figure 3.

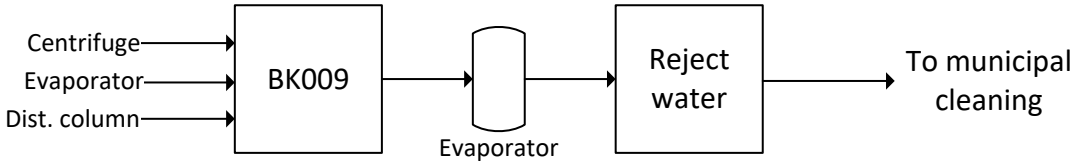


Figure 3. Schematic overview of the wastewater streams of Ecobränsle.

The whole flowchart is shown in Figure A1 in Appendix 2. A simplified flow chart showing mainly the waste streams is shown in Figure 4.

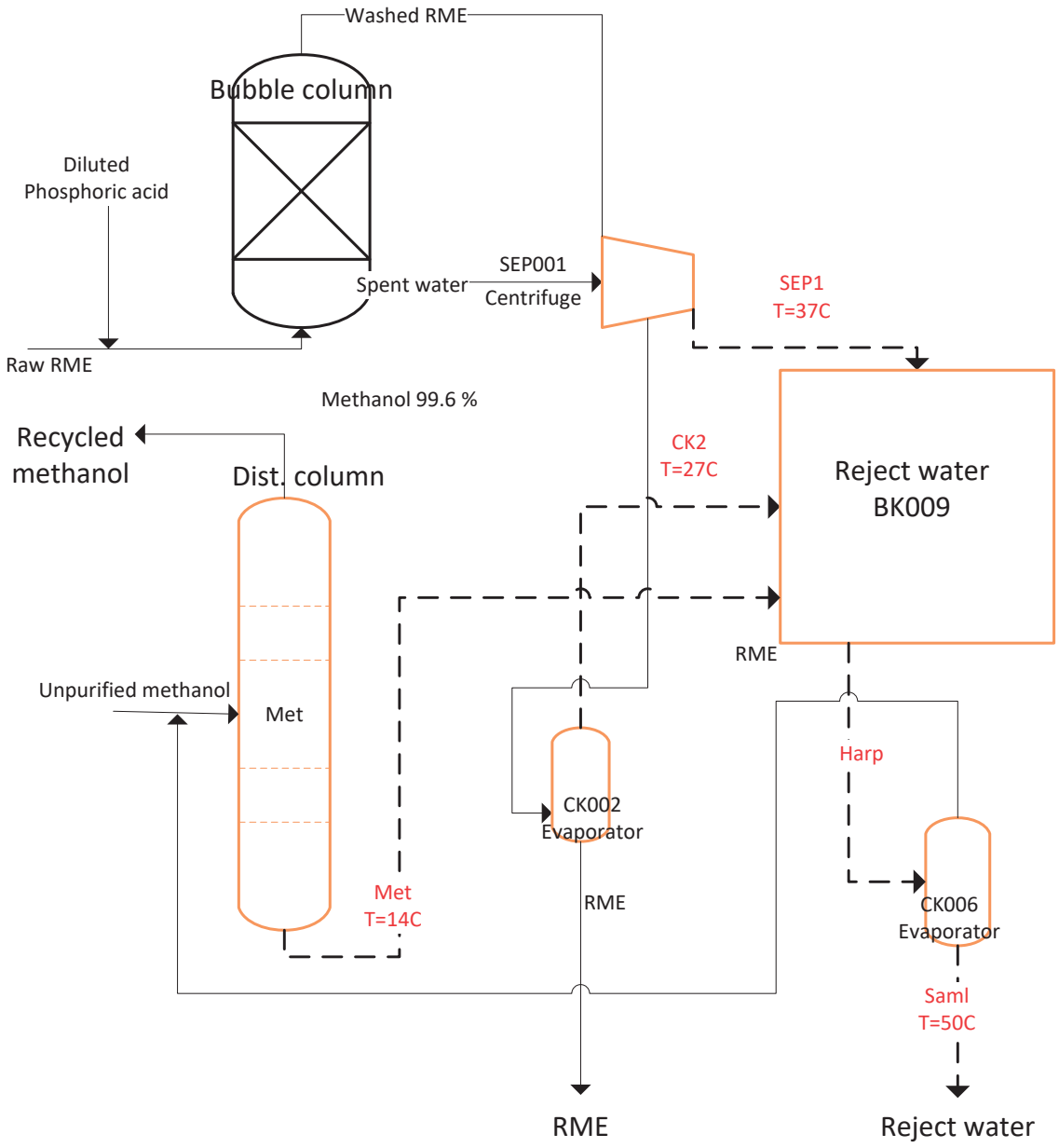


Figure 4. Flowchart of the process streams at Ecobränsle.

Considering Figure 4, the streams in dashed lines are the streams that are analysed in this work. The samples taken from these streams are named according to the figure and those names will be used from here on. To further emphasize the origin of the wastewater streams they will now be explained. In order to simplify identification of the sample names they are written in italics.

SEP1 originates from centrifuge SEP001, separating the RME from the washing water. The stream containing water, *SEP1*, is lead to BK009. The evaporator CK002 takes the RME stream from SEP001 and evaporates it to remove more water. The RME is withdrawn and the water stream is labelled *CK2* and joined in BK009.

The stream *Met* originates from the bottom of the distillation column that separates methanol to recycle it to the transesterification. The stream *Harp* is the stream that exits the collection

unit BK009. The stream *Harp* enters the final evaporation unit CK006 to evaporate more methanol. The final wastewater stream is *Saml* which is collected in a collection vessel. This water is then sent to the treatment plant. In short the streams *SEP1*, *CK2* and *Met* constitute the streams *Harp* and *Saml*.

4.2 General Analyses

The identification of the wastewater streams was followed by sampling and characterisation of them. The first characterisation analysis was an ocular examination of the samples, shown in Figure 5. The streams differ quite a lot and samples CK2, Harp and Saml are cloudy indicating particles and /or colloidal material in the liquid. Met has a yellow colour which is similar to the substrate, rapeseed oil.

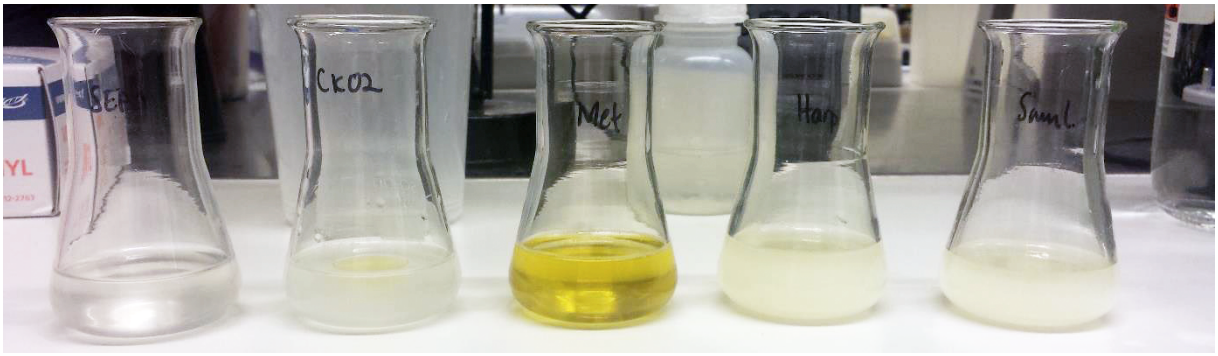


Figure 5. A visual overview of the samples in the order: SEP1, CK2, Met, Harp and Saml.

Following the ocular examination some general analyses were performed. In Table 1 the general parameters analysed are presented. The sampling was performed by the operators at Ecobränsle and the streams were sampled at three different occasions since not all streams were sampled at the first occasion. Stream Saml was sampled on the 17th of October when the reject water tank was emptied and the wastewater was sent for treatment.

Table 1. Results from analyses of different streams from the biodiesel plant.

	SEP1		CK2		Met		Harp	Saml
Batch	11-Oct	19-Oct	11-Oct	19-Oct	11-Oct	19-Oct	19-Oct	17-Oct
Density (g/L)	902.5	996	991	906	950.5	991	992	996
COD (g/L)	211	229	672	809	493	452	296	241
pH		4.19		5.4		12.4	6.26	6
Total Phosphorus (mg PO_4^{3-}-P/L)		1700		0.5*		11.8	1390	1480
Total Nitrogen (bound) (mg/L)		37.6		88.5		483.5	57	57

**Below detection interval.*

As can seen in Table 1 the density of all streams is below 1000 which indicates the presence of oily compounds since the density of oil is lower than that for water. However, the density was measured in cold water with a temperature around 10°C using hydrometers designed for 20°C liquids. The density of water increase with decreasing temperature, above 4°C, thus this might have an effect on the measurement.

The COD values are another indicator since oily compounds are included in the COD concept. However, the COD concept also include glycerol which contradicts this. Still, glycerol has a higher density which should give a higher density of the liquids.

The low density can also be compared with the ocular examination of the samples. The opaque samples indicate that there are particles in the samples. These are probably micellar particles which allows for the oily compounds to stay in the water. This indicates that unwanted surfactants or soap compounds are produced in the process.

The pH varies a lot between the different streams. The pH is low in streams SEP1 and CK2, while the stream Met has a very high pH. The low pH in streams SEP1 and CK2 might be an effect of the phosphoric acid added in the bubble column. The stream Met is not exposed to the phosphoric acid but might instead have leftovers of the alkaline catalyst. In the mixed streams Harp and Saml the pH is almost neutral. This indicates that the streams SEP1 and CK2 have a larger contribution than Met.

The difference in COD between batches is 8% for SEP1 and CK2 but 20 % for CK2. CK2 has the highest COD, which also generates a larger source of error due to more dilution of this sample. The COD of the mixed streams is close to the value of SEP1 which indicates that the largest stream contribution is from SEP1. In general the COD values are high compared to the majority of the wastewaters analysed in the studies by Daud et al. (2015) and Veljkovic et al. (2014).

The phosphorus values also differ for the different streams. The interval is big since the lowest value is 0.5 mg PO_4^{3-}-P /L and the highest is 1700 mg PO_4^{3-}-P /L. In the mixed streams the concentrations are in the higher range which strengthens the hypothesis of SEP1 having the biggest contribution. This is also confirmed when considering the bonded nitrogen concentrations. The high concentration of the stream Met is not reflected in the mixed streams, rather the mixed streams have a value between the concentrations of SEP1 and CK2. Although it is not clear how the nitrogen is bound or to which molecules the only probable source of bound nitrogen is from the rapeseed oil.

4.3 Microfiltration

MF was used to determine the amount of dissolved COD in the samples. Before and after the filtration the COD, the turbidity and the particle size distribution were measured. The measurements after MF was performed on the permeate. The particle size distribution was measured to determine what kind of membrane pore size would be suitable. The turbidity was measured to see if there was a difference in the quantitative number of particles.

4.3.1 Turbidity

The turbidity of the samples before and after micro filtration were measured and is shown in Table 2. The turbidity of the mixed streams Harp and Saml is much higher than the turbidity of

SEP1, CK2 and Met. This is hard to explain but the mixing of the streams might cause more formation of micelles resulting in more particles and a higher turbidity.

Table 2. Turbidity of different streams before and after MF in NTU (Nephelometric turbidity unit).

Sample	SEP1	CK2	Met	Harp	Saml
Feed	11	113	5	1058*	1012*
Permeate	1	11	1	398	224

**Diluted 2 times to get the values displayed*

4.3.2 COD

As shown in Table 2, the turbidity is lower in the permeate than in the feed in all samples. The largest difference in percentage is seen for Harp with a 62 % decrease in turbidity. The relatively large decrease in turbidity of the streams can be compared to the change in COD. The COD results shown in Table 3 all show a decrease in COD concentration after MF. However, the decrease is small and might also be a part of the uncertainty of the measurement method.

Table 3. COD of different streams before and after MF in g/L.

Sample	SEP1	CK2	Met	Harp	Saml
Feed	228.5	809.0	452.0	296.0	241.0
Permeate	220.8	751.0	441.0	285.0	224.5

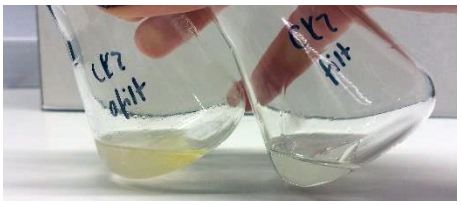
Compared to the decrease in turbidity the difference in COD is very small. This might indicate that the COD is independent of the particle size since the particles are removed but the COD is virtually unchanged. Larger particles disperse more light and give higher turbidity values. The decrease in turbidity either indicates that the particles are destroyed or held back by the membrane. The COD values might indicate the former, but there might also be problems with the measurement method for COD. It is not known if it is problematic to measure COD in micellar form. However, if it is, there might be a problem. In order to try to clarify this particle size distribution in the permeates was measured.

4.3.3 Particle size distribution and visual changes

The size distribution of the samples was measured before MF. Prior to the particle size measurement the samples were pre filtered through a general purpose filter paper. The purpose of this filtration was to remove larger particles such as rust which might otherwise have a big influence on the results. Figure 6 shows the difference of the samples before and after the paper filtration.

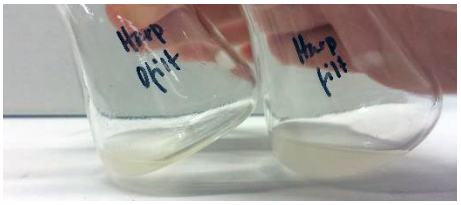
SEP1

CK2



Met

Harp



Saml

Figure 6 Wastewater streams from Ecobränsle before (bottle to the left) and after (bottle to the right) filtration with an all purpose paper filter.

There is a difference between the filtered and the unfiltered samples. The filtered samples are less opaque, shown in Figure 6. This is more visible in the samples SEP1 and CK2. The difference is not as big in the other streams. The sample that stands out is the Met sample which has a yellow colour. The difference in the samples indicates that the paper filtration not only removed larger particles such as rust particles, but also some other particles. The paper filtration of the samples was only performed for the samples before MF i.e. in the samples after MF paper filtration was not performed. This was motivated by the pore size of the filters.

The MF permeates are shown in Figure 7. The permeates do not differ significantly from the paper filter filtrates. The MF membranes were dried in room temperature and saved to see if there was any visual difference on the membrane surfaces, these are shown in Figure 8.

Figure 7. Permeate from MF. The order of the samples are, from left to right: SEP, CK2, Met, Harp, Saml.

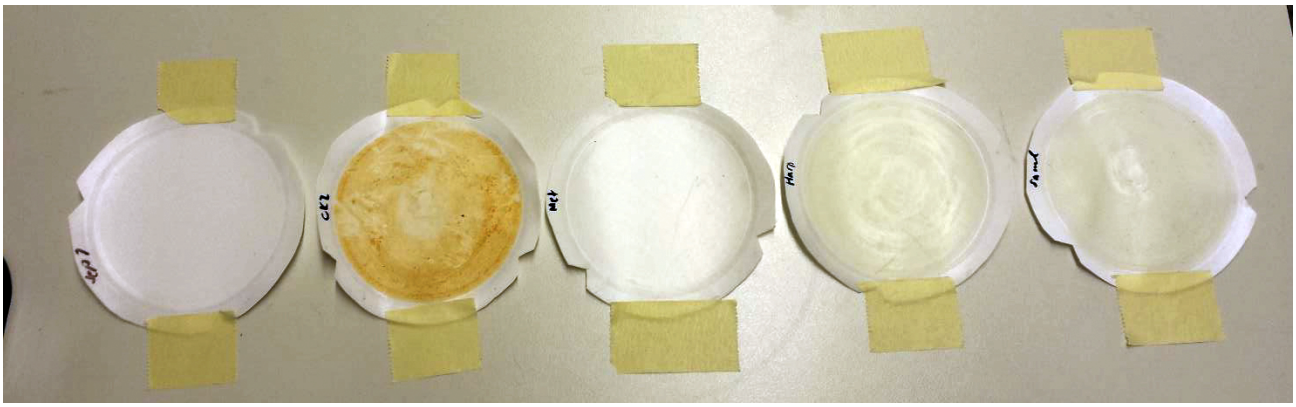


Figure 8. Display of membranes after MF. The order of the samples are from left to right: SEP, CK2, Met, Harp, Saml.

The membrane used to treat the CK2 sample shows the largest change in colour. There is also a slight change of colour towards yellow for the two membranes used when treating Harp and Saml. The other membranes have no apparent colour change. The colour change in CK2 might be because of rust. The change is clearly visible when looking at pictures of the sample, shown in Figure 9. The colour has gone from light yellow to orange in three months. Even though the batches are different the colour of the batch from 19/10 is shown in Figure 5, the photo was taken eight days after sampling. Figure 6 shows sample CK2 before paper filtration. This picture was taken 2 months after sampling and even though there is a tendency for the colour

towards orange it is not as clearly orange as shown in Figure 9. The fact that the samples were stored in steel containers support this theory.

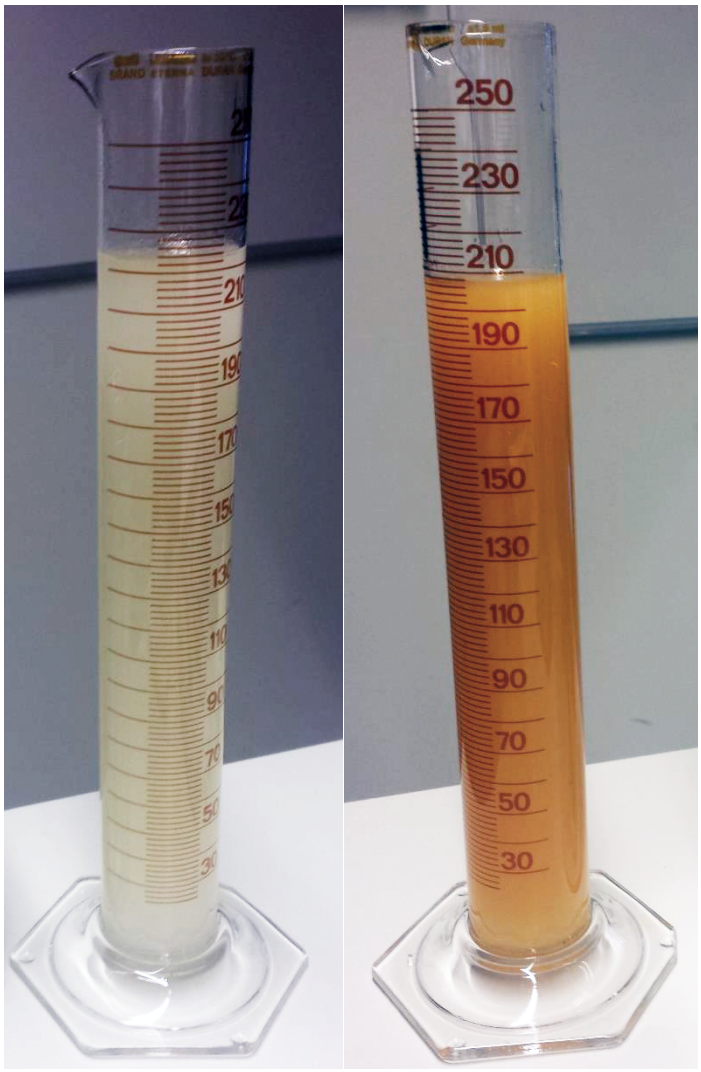


Figure 9. Colour change in sample CK2. The picture to the left is from the batch of 11/10 and taken eight days after sampling at the plant. The picture to the right is from the batch of 19/10 and taken three months after sampling.

In Figure 10 the particle size distribution by % volume of the particle size is presented. The particle size distribution of the feed solution was measured to get an idea of the suitable membrane pore size of the MF membrane. The particle size distribution of the MF permeates was also measured. However, the latter particle size distribution measurements were measured about a month after the MF.

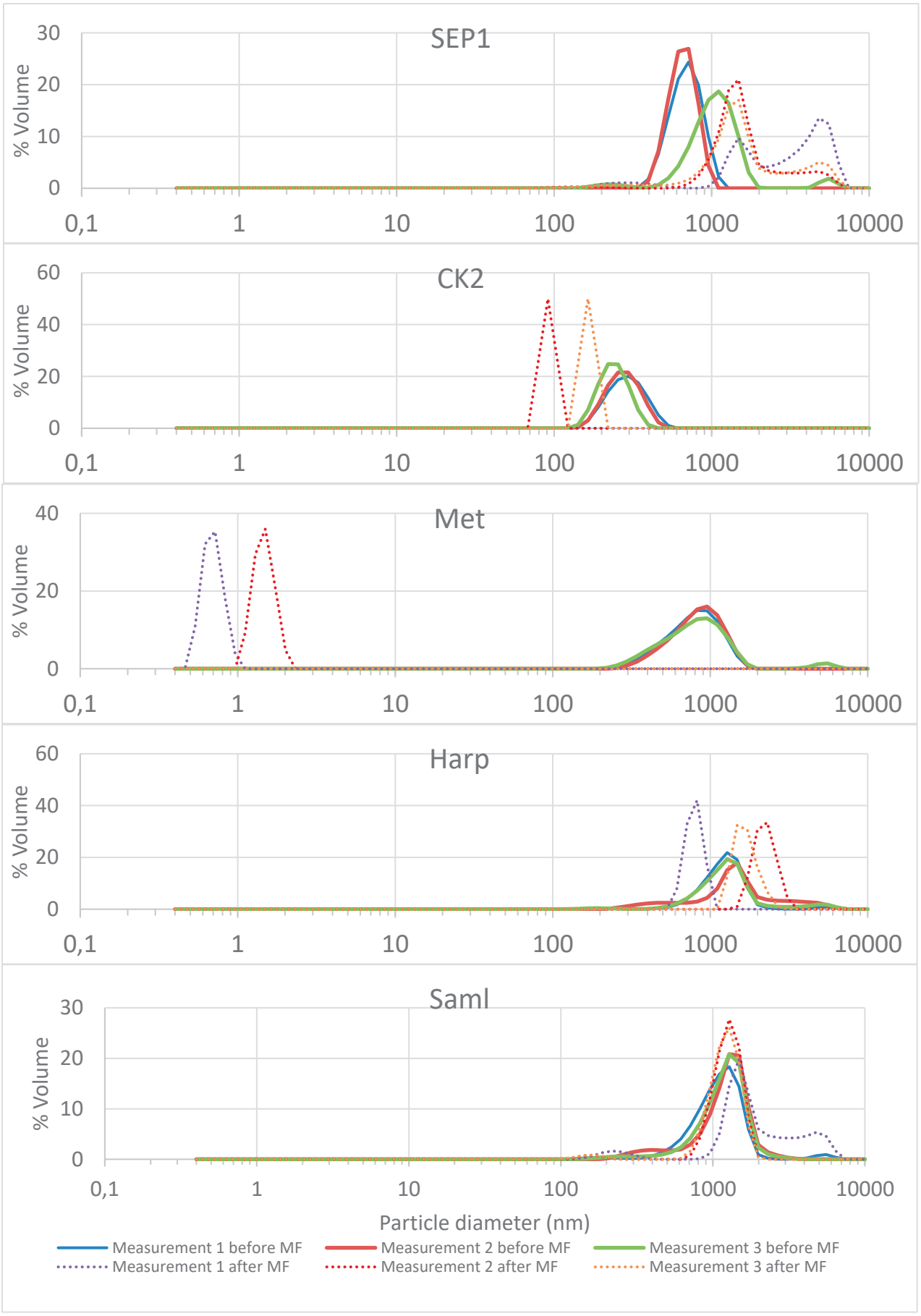


Figure 10. Size distribution by % volume of particle size in nanometer for the process streams from Ecobränsle. Three succeeding measurements on each sample was performed. Full lines shows the size distribution of the feed and the dashed lines show the size distribution of the permeate.

In all of the samples before MF the majority of the particles were located above 200 nm. This means that a membrane with that pore size is a good choice. However, the particle size distribution in the permeates was also measured and some of the results are puzzling. For SEP1 and Harp the particle sizes have increased and for Saml no difference is observed. It is only for CK2 and Met that a decrease in particle size distribution is observed. However, in these samples only two of the triplicate measurements give a result i.e. one of the triplicates does not show any particles. The first measurement of Harp stands out and indicates that the distribution is located below 1 μm in contrast to the two latter measurements in which the peaks are located above 1 μm.

One reason for the increase in amount of bigger particles after the MF might be due to the fact that the particles size distribution was not measured directly afterwards but after a month which provides time for the different compounds to aggregate. The COD of the samples before and after also give a hint that the COD is not removed by the filtration.

In a study by Jönsson and Jönsson (1991) the size of surfactants was presented. The ionic surfactant potassium oleate has the size of 22 Å i.e. 2.2 nm. The study found that the ionic surfactants were better held back than non-ionic surfactants using ultrafiltration membranes. (Jönsson and Jönsson, 1991) The surfactants thus have a possibility to pass the membranes. Since the samples were left for one month before the permeates were measured new micelles were probably formed. However, some of the samples were already opaque. This is showed in Figure 7, which was taken on the 19th of December, which is the same day as Met and Harp were filtered and 3 days after the filtration of SEP1, CK2 and Saml.

4.4 Measurement of glycerol using HPLC

HPLC was used to characterise the individual components of the samples. The main focus was to quantify how much glycerol was present in the samples. The results from the HPLC tests are shown in Table 4. The standard that was used only contained glycerol which is why it is not possible to quantify the amount of other components. Therefore, the other components only have areas of the peaks from the chromatograms given. Other standards have however been injected before on the same column which can indicate the elution time for e.g. methanol. From here on the component exiting close to methanol will be called methanol since it is the most probable component because of its presence in the system. The component sold by the company as non-purified glycerol was also analysed in order to try to determine the impurities.

Table 4. Results of HPLC analyses.

Sample	SEP1	CK2	Met	Harp	Saml	Glycerol from plant
Glycerol concentration (g/L)	40.9	0.47	79.1	40.3	41.7	774.2
Glycerol (area units)	$2.1 \cdot 10^6$	$0.025 \cdot 10^6$	$4.1 \cdot 10^6$	$2.1 \cdot 10^6$	$2.2 \cdot 10^6$	$8.1 \cdot 10^6$
Methanol (area units)	$0.96 \cdot 10^6$	$4.5 \cdot 10^6$	$1.5 \cdot 10^6$	$1.3 \cdot 10^6$	$0.95 \cdot 10^6$	$0.024 \cdot 10^6$
Other components (area units)	-	$0.22 \cdot 10^6$	$0.19 \cdot 10^6$	$0.029 \cdot 10^6$	$0.018 \cdot 10^6$	-

The concentration of glycerol, shown in Table 4 are not very accurate because of the dilution method. Nevertheless, the relative sizes are useful for comparison of the streams.

The concentrations of glycerol vary for the different samples. The sample Glycerol have for obvious reasons the highest glycerol concentration. Out of the wastewater streams the sample Met has the highest glycerol concentration while the concentration in CK2 is very low. The stream Harp has a similar concentration to SEP1. The concentration in Saml is higher than in the step before; Harp. The concentrations of glycerol in Harp and Saml is close to the concentration in SEP1 which further strengthens the reasoning that SEP1 is the biggest of the three streams mixed in BK009.

Met has a very high concentration of glycerol. Met originates from a distillation column with four input streams, shown in Figure A1. Two of the streams originate from the upper oily phase in the transesterification. The other two streams originate from the heavy bottom phase. It is more likely that the glycerol comes from the two latter streams. These two streams both originate from two evaporators in series. The condensate is lead to the distillation column. One reason for the high concentration in Met might be because the first evaporator CK003, separating methanol and glycerol, is working poorly. The following evaporator, CK004, might also be underperforming. However, entering CK004 is not only the stream with a higher boiling point from CK003 but also a stream from a centrifuge that separates added glycerol. The glycerol is added to the crude biodiesel to remove small glycerol particles. Meaning that CK004 has even more glycerol to deal with than just the addition from CK003. It is hard to say which of them that has the biggest contribution without knowing the size of the streams.

It was previously concluded that the streams from the bottom phase of the transesterification would probably have the largest concentration of glycerol. Thus the streams from the upper phase was neglected as a large source of glycerol. However, stream SEP1 contains a lot of glycerol and originate from the upper phase. This is explained by the fact that glycerol is added to the upper phase streams after the removal of them. The efficiency of the centrifuge removing the glycerol can be questioned. Although the problem might also lie in poor removal of glycerol

from the crude biodiesel. If this process is not efficient enough the glycerol might not be removed until the biodiesel is washed with acidified water. This water is then the main part of SEP1, meaning that the glycerol end up here.

According to Lorentzen (2016) methanol is added in excess to get a high yield of the rapeseed oil. Approximately ¼ of the methanol added to the transesterification is new and the rest is methanol that is recycled (Lorentzen, 2016). Part of the added methanol compensates for the loss of methanol in Saml. However, without the knowledge of the concentration or the size of the streams it is hard to say how much methanol that is lost with the wastewater. Moreover, the purity of the RME is above 99 w/w % (Lorentzen, 2016), which indicates that only a minor part of the methanol is in the biodiesel. Furthermore, the area of the methanol detected in the glycerol sample was the smallest. Thus the main part of the methanol is found in the wastewater.

In sample CK2 the peak area of methanol was the biggest compared to the other samples. This methanol is probably recovered in the evaporator between Harp and Saml, from which the condensate is lead to the distillation column. The same goes for sample Met which also has the next largest methanol area. Another aspect of Met's big methanol area is the efficiency of the distillation column. The methanol exiting at the top has a purity of 99.6 % (Lorentzen, 2016). This indicates that the distillation column is optimised on purity of product rather than yield. Had the distillation been optimised on yield instead the loss in methanol would be lower since more would be recycled. However, this would probably mean that some other components present in the bottom phase would also be recycled into the system. The harm of this has to be evaluated before it is done.

In samples CK2, Met, Harp and Saml there was a peak exiting close to the peak of the previously injected standard of citric acid. Samples CK2 and Met have similar peak areas for this component. The same goes for samples Harp and Saml although their peak areas are essentially lower. The component was not detected in samples SEP1, and Glycerol. This peak might be a response on the phosphoric acid in the system. Although this is hard to prove without running another analysis with a phosphoric acid reference sample phosphoric acid is the most probable component. However, SEP1 should contain some phosphoric acid since it is a stream downstream of the addition of phosphoric acid but also because it has a rather low pH, but no peak is present. This makes the assumption that the peak is phosphoric acid less valid and this will not be discussed further.

4.5 Analysis of compounds soluble in hexane using gas chromatography

Gas chromatography (GC) analyses were performed on the samples to try and further quantify the components of the samples. Some of the components in the samples were possibly not identified in the HPLC analysis due to the dilution with water and filtration through a 0.2 µm filter. It was hoped that a GC analysis would cover those components.

As a first step the samples were extracted with hexane to remove the water. The results of the extraction will be presented below as well as the results from the chromatography.

4.5.1 Extraction with Hexane

The extraction of the different samples showed different results. In some of the samples, SEP1 and CK2, there were initially a clear phase separation into two phases. However, when the bottom phase (the water) had been removed there seemed to be a third phase precipitating from the supposed hexane phase. This was observed as droplets falling out and creating a phase at

the bottom of the separation funnel. These droplets were removed after a time and considered as a water phase. The remaining phase was considered as the hexane phase. For the samples Harp and Saml three phases were observed shortly after shaking the separation funnel. In Figure 11 the three phases of sample Harp are shown. The wanted hexane phase was assumed to be at the top so the other bottom phases were discarded.

The sample Met had some foam formation before it was poured into the funnel and mixed with the hexane. When the funnel was shaken even more foam was formed. The foam was left to rest and the water phase was then removed. When the hexane phase was to be removed the liquid turned out to be very viscous. The viscous phase was anyway sampled. After leaving it for a while the viscous sample had separated, shown in Figure 12. The hexane phase was now assumed to be at the bottom since that liquid was less viscous.

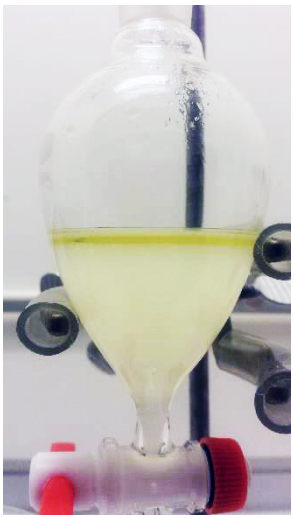


Figure 11. Hexane extraction of sample Harp showing 3 phases.

Figure 12. Hexane phase of Met. The phase has separated into two phases after being left for a while.

4.5.2 Chromatograms

The chromatograms are shown in Figure 13 - Figure 19. The samples analysed were apart from the five sample streams, glycerol dissolved in hexane, pure methanol and a biodiesel standard diluted in ethanol. The solvents are eluted first after around one and a half minute and are not included in the chromatograms. If not stated otherwise the GC measurements have been performed with the quick ramping method described in material and methods.

Biodiesel Standard

The biodiesel standard used in this work was F.A.M.E Mix GLC-10 from Sigma Aldrich. The ampule with the standard had been opened 10 months before and the standard had been diluted in ethanol and stored in the freezer. The chromatograms from the standard is shown in Figure 13.

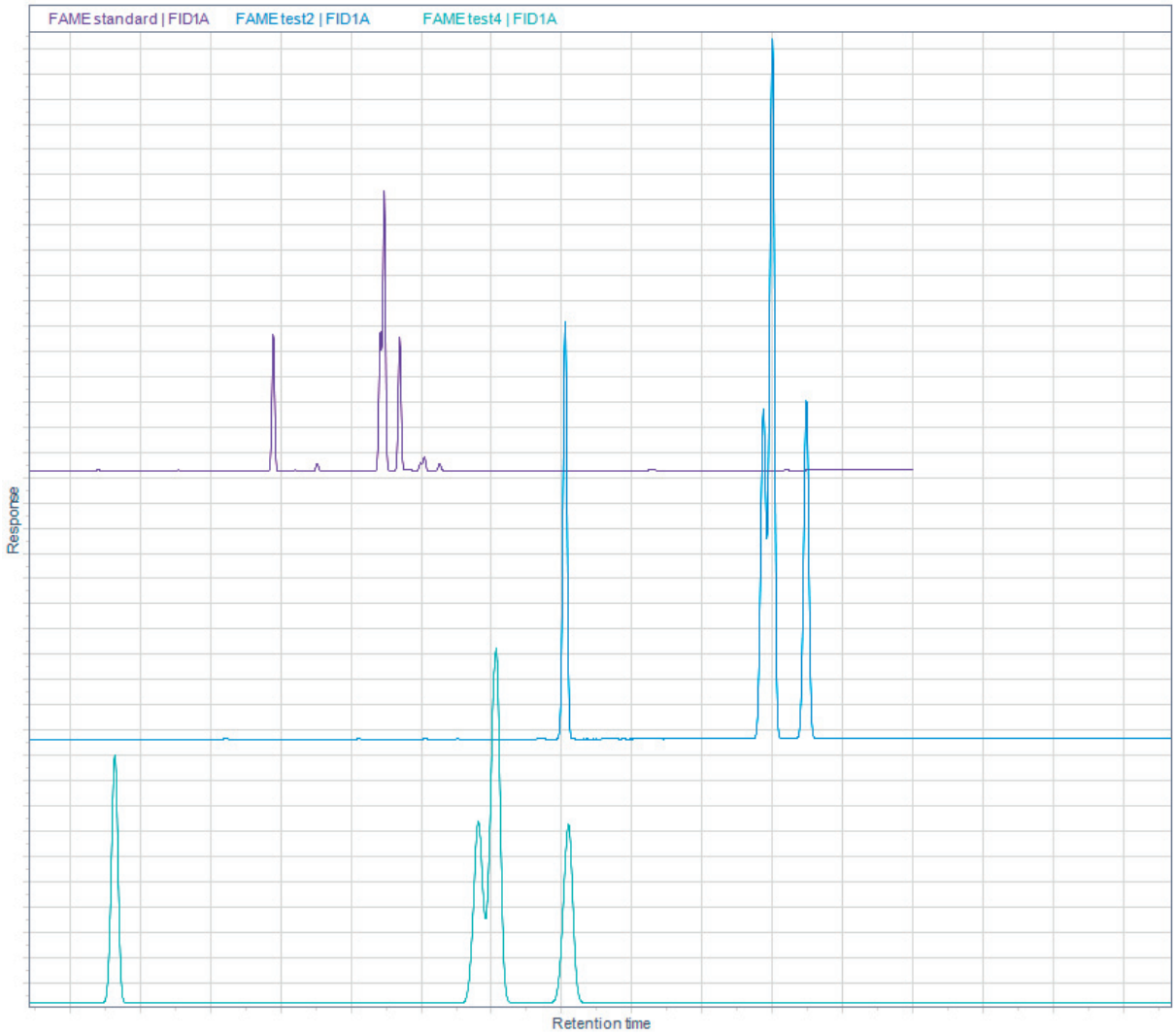


Figure 13. Chromatograms of biodiesel standard with different methods. The methods applied from top to bottom are: the fast ramping method, the application method from the column manufacturer and the slow ramping method with a slow temperature increase over the elution temperatures of the components.

The biodiesel standard contains five components: methyl linoleate (C18:2), methyl linolenate (C18:3), methyl oleate (C18:1), metyl palimitate (C16:0) and methyl sterate (C18:0), of equal concentrations. However, six peaks are shown in the top chromatogram. The highest peak is twice as high as the others and is not separated from the close by peak which indicates that it contains two components. The small peaks are probably not the standard components since they

have a smaller area, than the other peaks. They might however be degradation products of the standard since it had passed the expiration date.

The top chromatogram shown in Figure 13 is the result from running the standard with a quick ramping method. The temperature increment might have been too high to allow the separation of the peaks properly. In order to improve the separation, the temperature increment over the interval where the standard peaks elute was lowered. The result of this is shown in the middle and the bottom chromatograms.

The method that was used in the middle is an application method for biodiesel provided by the manufacturer of the column. The peaks are still not separated and instead of five separate peaks, only three are shown in the chromatogram. The same applies to the chromatogram shown in the bottom that shows an additional method with a slow temperature increase.

Glycerol standard

A standard of glycerol was also evaluated and the chromatogram is shown in Figure 14. Glycerol has a high boiling temperature of 290 °C which means that it should elute at the end of the measurement. No significant glycerol peaks were eluted even though the glycerol concentration was ten times higher than any of the components in the RME standard. Calculations of glycerol concentrations are found in Appendix 1. With this in mind the comparison using overlapping chromatograms was found unnecessary.

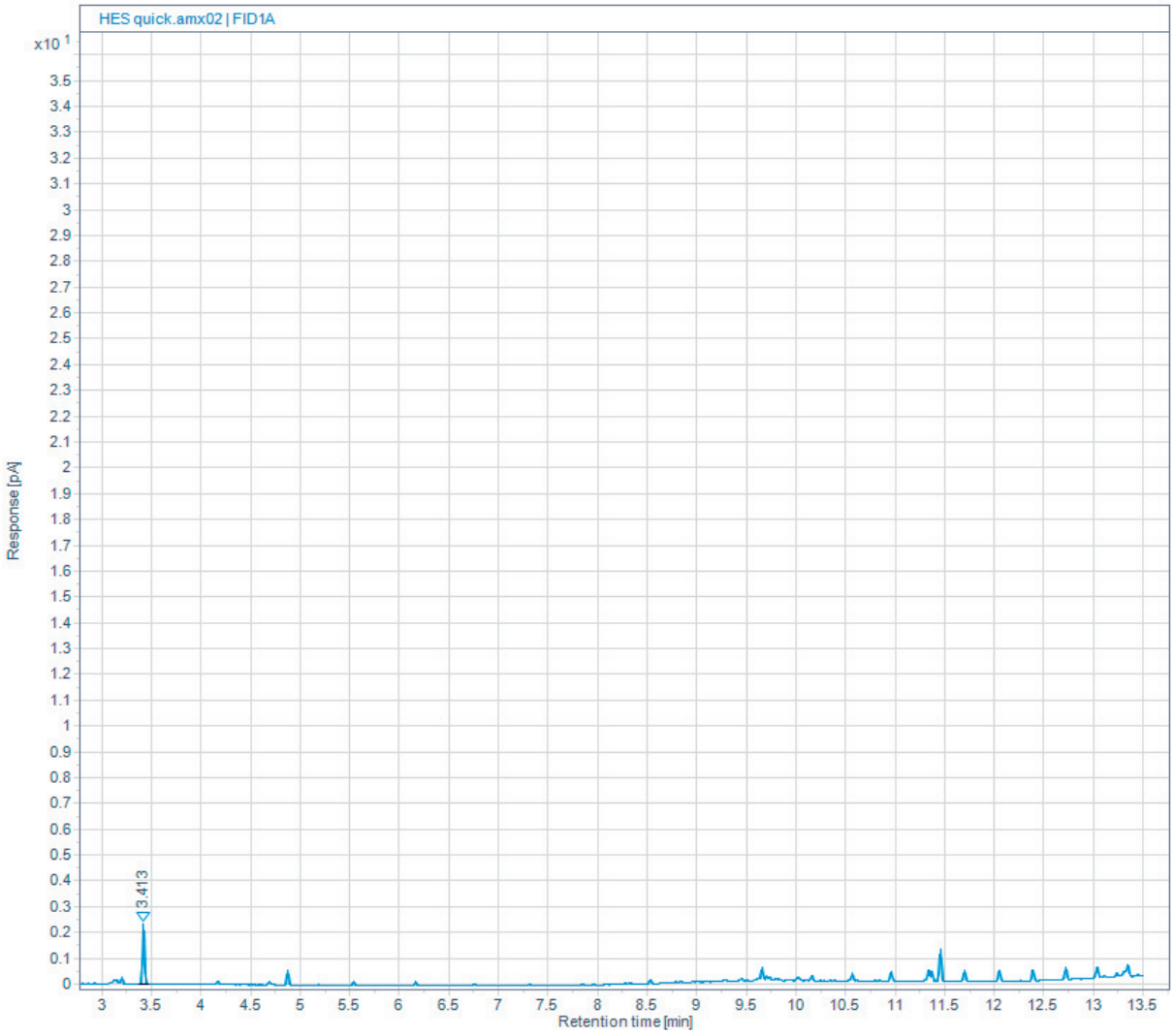


Figure 14. Chromatogram of the glycerol standard extracted with hexane

Even though no suspected glycerol peaks were found in the chromatogram of the glycerol standard, one peak was found at 3.4 minutes, but as the temperature at this point is only 100 °C it is probably a decomposition product of hexane.

When comparing the results of the GC with the results of the HPLC, the glycerol is not visible in the GC chromatograms. Why is the glycerol is not visible? The chromatogram of the glycerol standard indicates that the method is not correct, since it does not show any glycerol. This might be related to the fact that the boiling point of glycerol is 290 °C and the run ends at 300 °C. In

that case it might be that the glycerol elutes continuously during the series of runs for the different samples. However, the concentration of glycerol was rather high in some of the samples this should give a response of one peak in the chromatograms, which is not visible. A way to evaluate the existence of glycerol is to run the samples, including the standard, with another method with a higher maximum temperature. If there is a response there is a fault in the method. Without a response in the samples, the glycerol does not end up in the hexane phase.

A more likely reason for the lack of a glycerol peak is that the glycerol is not sufficiently dissolved in the hexane during extraction. This hypothesis is strengthened by the statement from The Soap and Detergent Association (association, 1990) that glycerol is virtually insoluble in hexane.

Samples compared to standard

The standard for biodiesel had indeed expired but still gave an indication if there were any biodiesel components in the samples. Therefore, the standard was used and the comparison of the samples with the standard will be presented below.

In Figure 15 the chromatogram of SEP1 versus the standard is displayed. There is a large peak in SEP1 at around 9.7 minutes which also has a corresponding peak in the standard. As well as some other corresponding peaks. This shows that SEP1 contains biodiesel. The peaks of the solvents come early, are high and have different elution times. This is expected since the different solvents are hexane and ethanol. There are also some small peaks that elute after 10.5 minutes which are hard to identify.

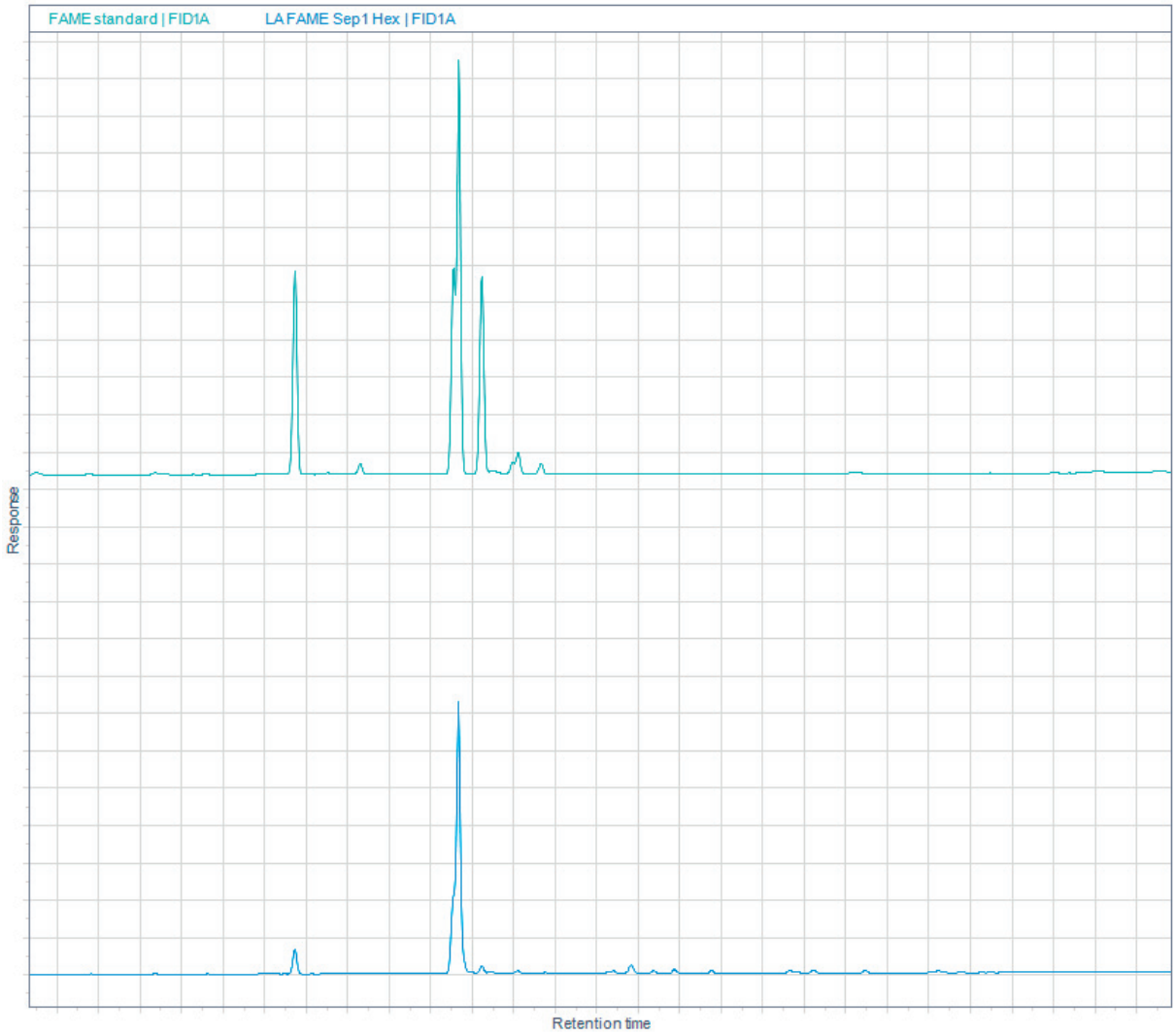


Figure 15. Chromatograms of SEP1 at the top in blue and Standard in the bottom in green.

Figure 16 show the comparison of CK2 and the biodiesel standard. The sample CK2 show a lot of peaks which have not been identified with the standard used. Some of the peaks from the standard elute close to peaks in the CK2 sample however the peaks are not as nicely covered as for e.g. SEP1.

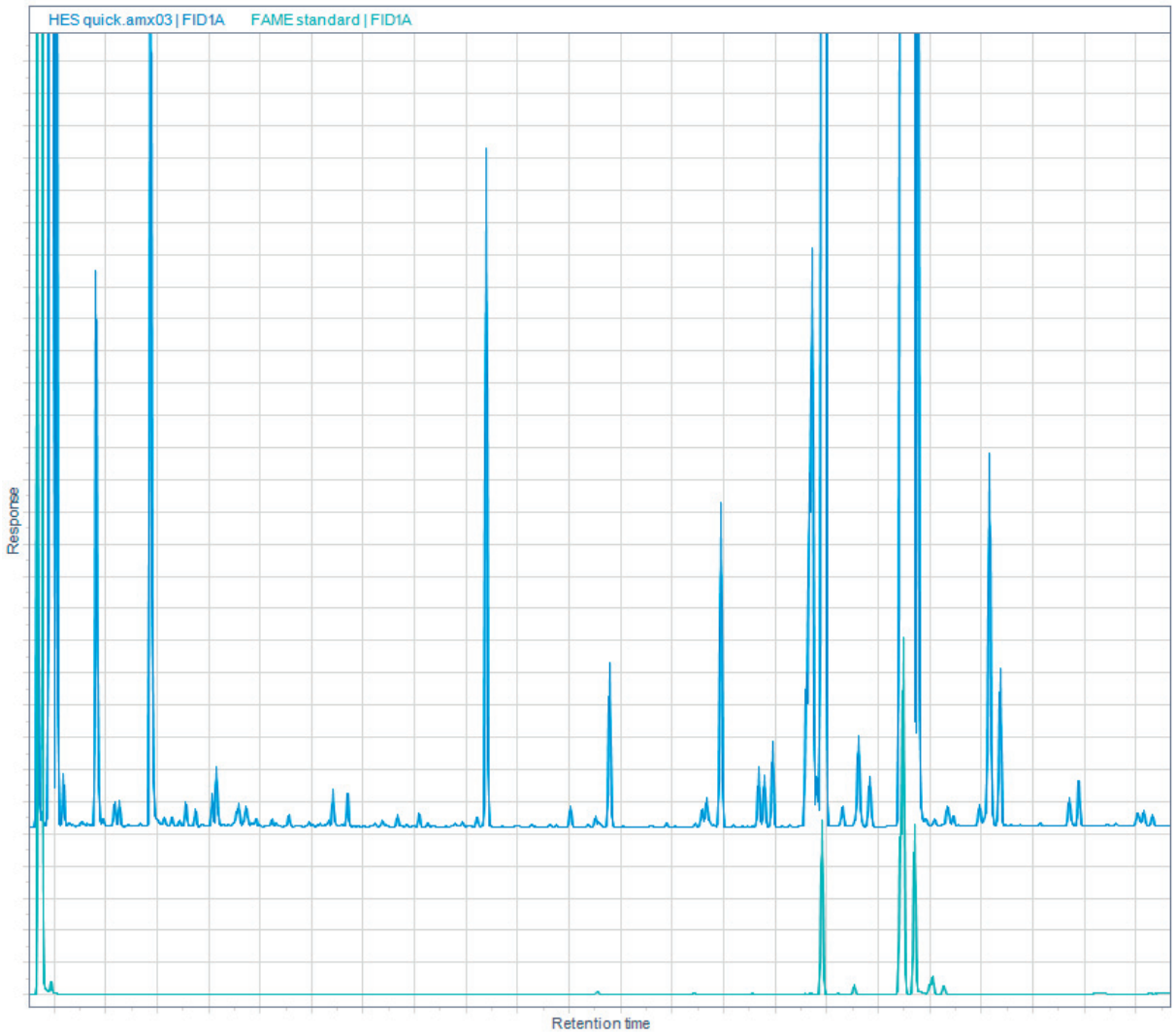


Figure 16. Chromatograms for CK2 at the top in blue and standard in the bottom in green.

In Figure 17 the chromatogram of Met is presented. Some of the peaks overlap with the standard. However, there is a puzzling, wide peak between 3.2 and 4.5 minutes, which is not possible to identify, neither are the two peaks at around 2 and 2.5 minutes. The strange peak between 3.2 and 4.5 minutes was not found in any of the other samples but was found again when a second run of Met with the same method was done.

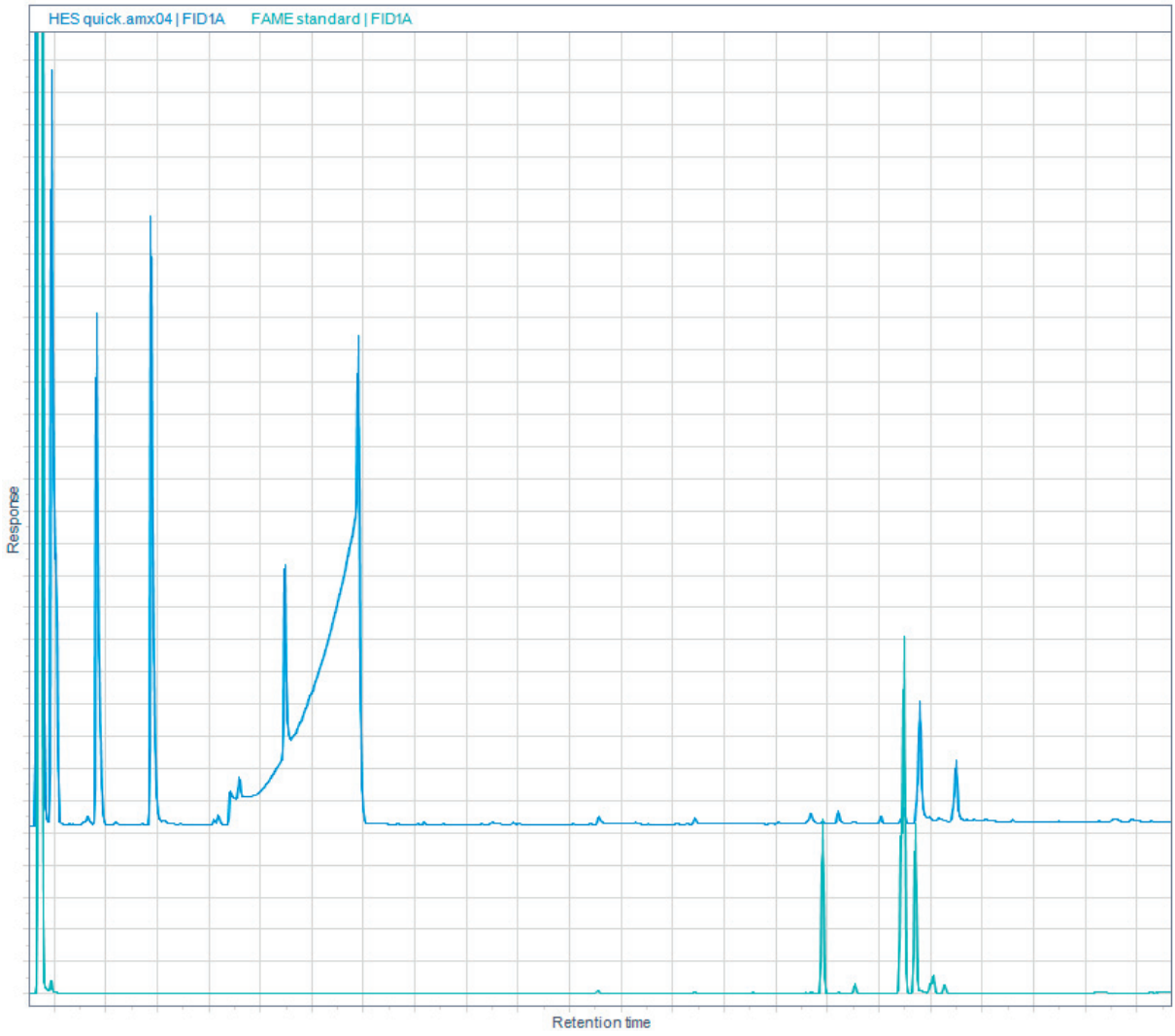


Figure 17. Chromatogram of Met at the top in blue and Standard in the bottom in green.

Figure 18 shows the chromatogram of Harp. There are some peaks that overlap with the standard. However, there are also a lot of peaks that are unidentified.

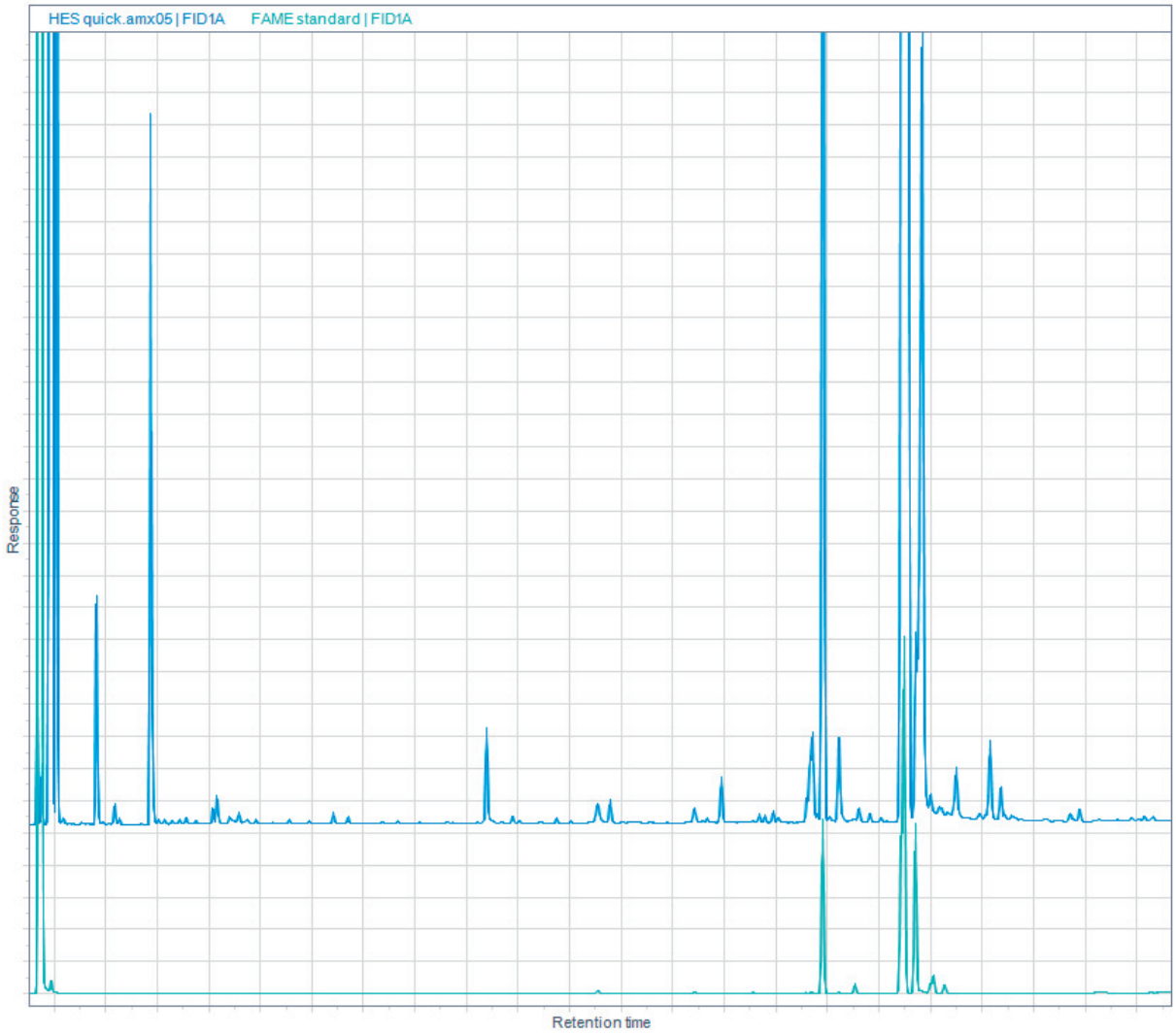


Figure 18. Chromatogram of Harp at the top in blue and standard in the bottom in green.

Figure 19 shows the chromatogram of Saml. Some of the peaks overlap with the standard. There are some peaks that are not possible to identify but they are fewer than in the Harp sample.

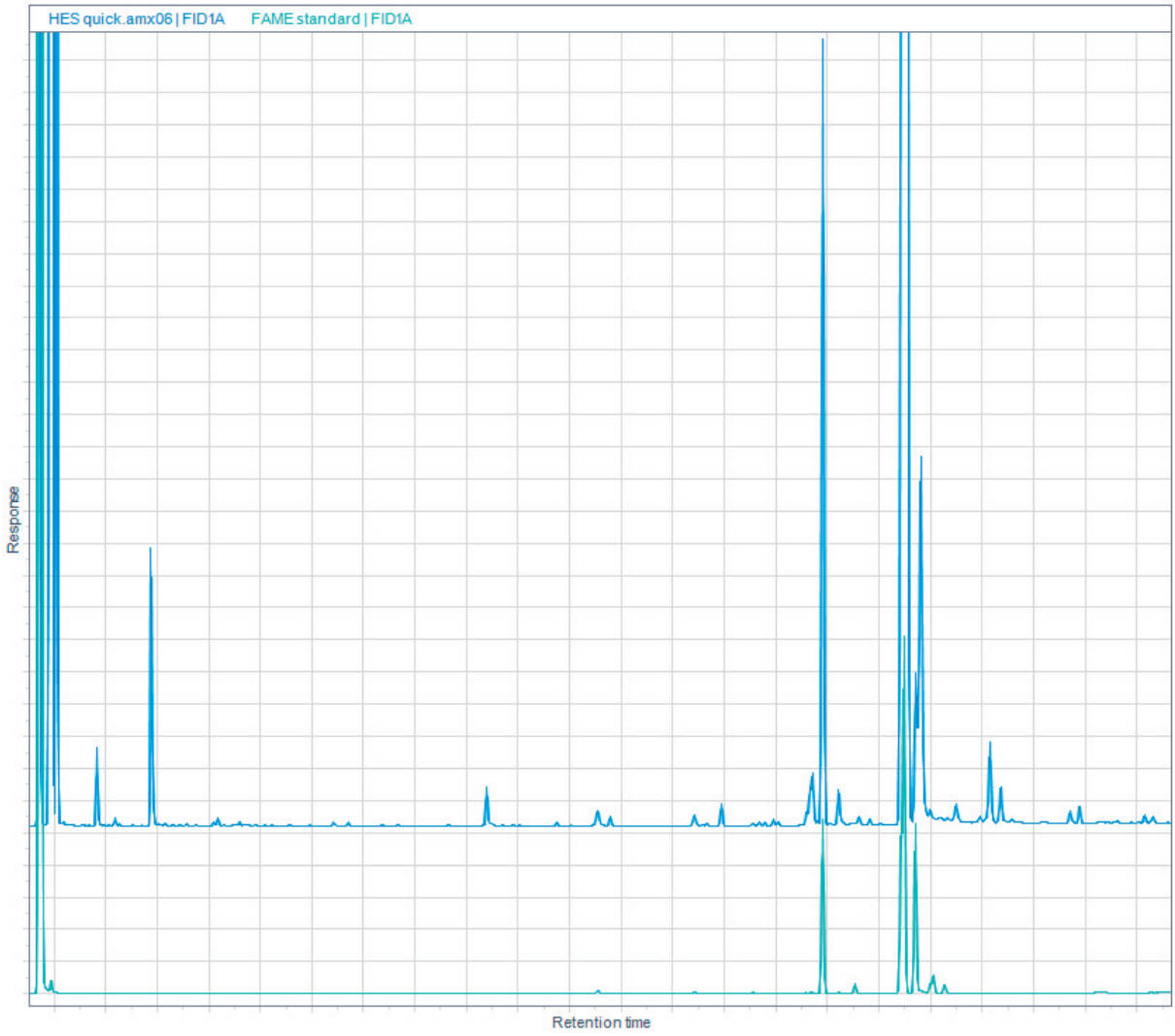


Figure 19. Chromatogram of Saml at the top in blue and standard in the bottom in green.

As mentioned previously glycerol is not dissolved in hexane this might also be the case for other components. The volume of hexane used for extraction was rather small compared to the amount of wastewater. This could mean that not all of the components soluble in hexane end up there. A way to evaluate this would be to extract the samples multiple times with small volumes of hexane which are joined and then run the extract with the same method. The small amount of hexane used could also mean that other components present are not dissolved, and those who are dissolved are hopefully dissolved proportionally.

The content of the observed viscous phase of Met is still not known. It is also unclear why the phase became viscous. One possibility is to try and dissolve the phase in another solvent and then analyse it. The viscous phase could also contain surfactants. Which would create an emulsion when shaking with hexane. This could be evaluated using an acid to lower the pH and see if the surfactants are protonated which would result in a phase separation since the emulsifiers would be destroyed.

In some of the chromatograms it is observed that the baselines do not really overlap for some of the comparisons, but this is of no importance here as the concentration was not determined. Since the samples from Ecobränsle have the same x-axes and y-axes it is possible to compare

the peaks between the chromatograms. When comparing them, it can be seen that CK2, Harp and Saml have higher peaks of biodiesel. If the area of these peaks is larger as well the concentrations of these components are higher.

4.6 Biochemical methane potential

One of the previously presented treatment options suggested for biodiesel was anaerobic digestion. A first step in evaluating the biogas potential is to evaluate the BMP. Therefore, a BMP study was performed. The samples analysed were: all five streams from Ecobränsle, one reference, one inoculum and one sample with glycerol mixed with Saml called RGlyc. The reference contained a control of cellulose standard at a weight based ratio of 1:1 of Avicel and microcrystalline cellulose. The results from the BMP experiments are presented as a mean of the triplicate samples and shown in Figure 20. The methane potential from the inoculum has been subtracted from all samples.

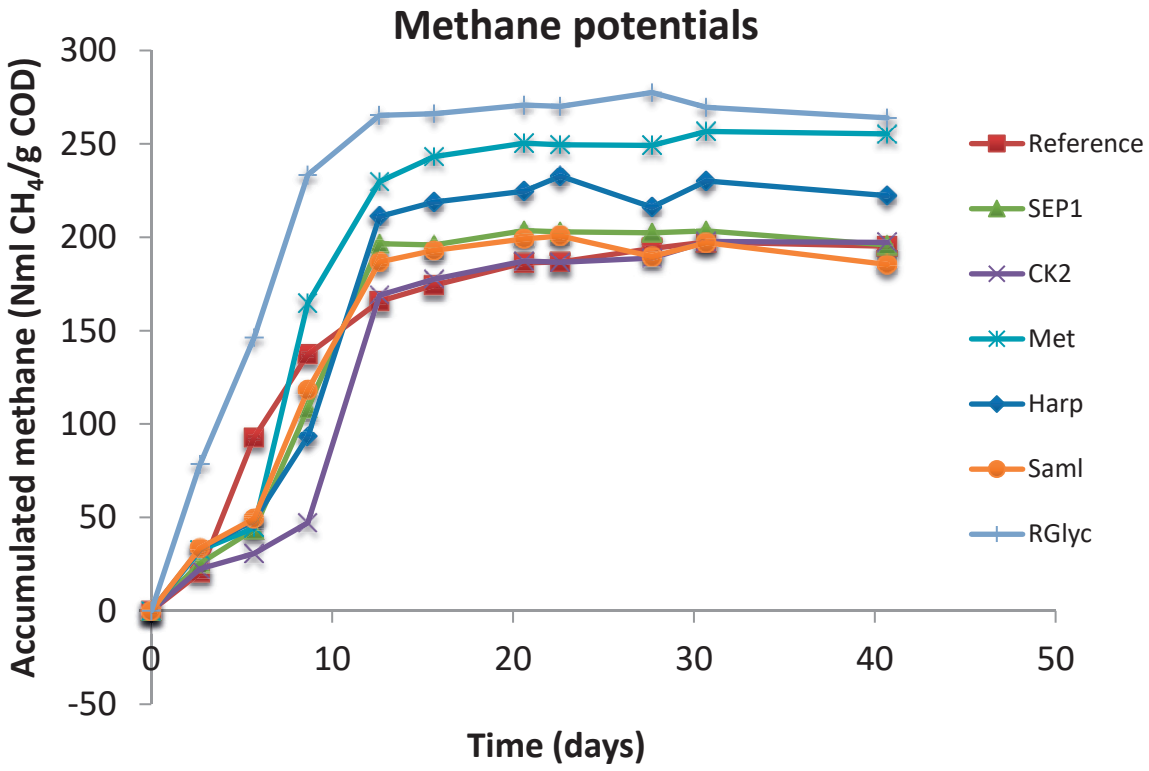


Figure 20. Biochemical methane potential of different streams at the Ecobränsle biodiesel plant. The methane potentials are presented as Normal mL CH_4 per g COD per day.

Figure 20 shows that the sample RGlyc has the highest BMP. This means that the glycerol mixed with Saml has a high biogas potential. The stream Met has the next highest BMP. The potential decreases in the order: Harp, SEP1, Saml and CK2. Met has a high glycerol concentration which is important for a good potential. Harp also stands out with a potential a bit higher than the other samples. Harp has similar glycerol concentrations compared to Saml and SEP1 but has a higher methanol content. The highest methanol content can be found in CK2 but it has a very low glycerol concentration and a potential in the lower range of the samples. This confirms the importance of glycerol and possibly that it is a more high-quality energy source than methanol.

The production of methane in all samples except RGlyc, seems to be a bit lower in the beginning. This is maintained until day 5 or even day 8 for CK2. Then there is a steep increase in the production of methane until day 13 from which the production seems to stagnate. The slow production in the beginning indicates a lag phase which was also observed for fats and oils by Hansen et al. (2004).

However, some of the streams had large standard deviations between the triplicates. This could be related to that the samples reached a plateau relatively fast. Hansen et al. (2004) have examples of waste that reach the plateau after more than 20 days. Due to the relatively fast increase in gas production the bottles might have been overfilled causing leakage of gas before they were emptied. This makes it hard to compare the biogas production between the samples. Also another issue is related to the sample preparation. Inhomogeneity in the samples might have resulted in differences in dosage of COD.

The potential of the reference is a bit lower than expected. Hansen et al. (2004) found a potential of 379 N mL_{CH4}/g VS for the cellulose, assuming that 1 g cellulose equals 1 g VS. However, the potential was given in per grams VS. In order to correlate this to COD, the COD of the cellulose was measured using the same method as for the wastewater. The results are shown in Figure 21.

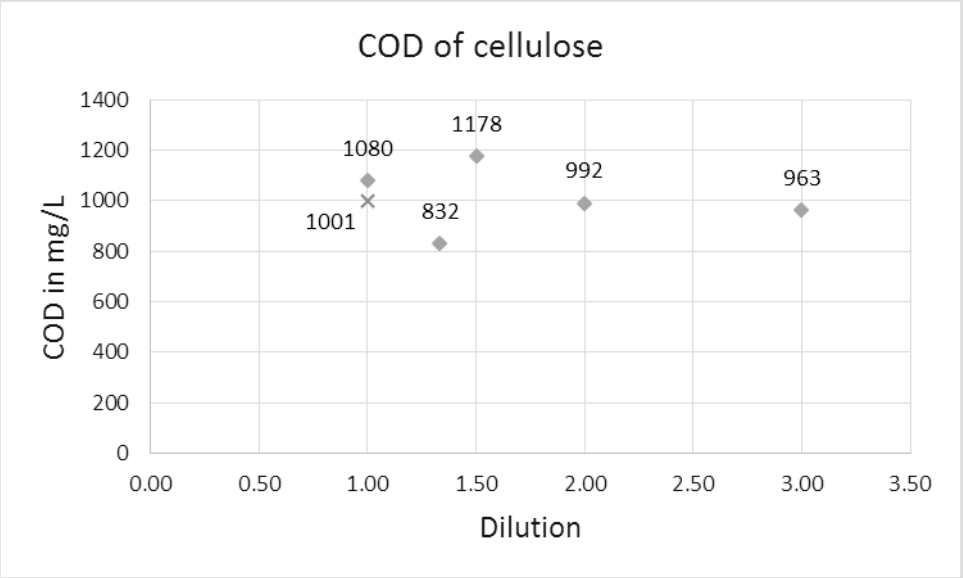


Figure 21. COD of cellulose with different dilutions measured using Hach Lange cuvettes. Dilution 1 means no dilution. The cross indicates concentration assuming 1 $g_{cellulose}$= 1 g_{COD}.

The results of the COD measurements, shown in Figure 21, show that the assumption that 1 $g_{cellulose}$= 1 g_{COD} is valid. The measured COD values vary but it is probably an error related to the uncertainty of the method.

4.6.1 COD before and after anaerobic digestion

The change in COD was measured as a way to evaluate the efficiency of the anaerobic digestion. The BMP shows the biogas produced and the COD is important since it is related to the goal of the treatment. The change in COD after the anaerobic digestion is shown in Table 5. The table also includes the change in weight after the anaerobic digestion. The starting values for the COD was 28.1 g_{COD} ±0.3 for the samples and 18.7 g_{COD} ±0 for the inoculum.

Table 5. Change in COD and weight after anaerobic digestion.

Sample	Inoculum	Reference	SEP1	CK2	Met	Harp	Saml	RGlyc
Alteration of COD during BMP (g) *	0.2	-6.5	-9.6	-7.3	-6.9	-8.7	-5.4	-3.2
COD consumed (%)	-1.3	23.1	34.2	25.7	24.7	30.8	19.2	11.8
Mean weight alteration (g)	-2.1	-12.3	-7.1	-8.2	-7.6	-7.2	-6.7	-7
Mean weight alteration (%)	-0.4	-2.4	-1.4	-1.6	-1.5	-1.5	-1.3	-1.4

* *Change calculated from final value from 1 of the triplicates*

Table 5 shows that the weight and COD decreased in all samples except for one; the COD in the inoculum increased. The increase in COD is not reasonable and probably a cause of the measurement error when diluting the samples for the measurements. The largest weight drop occurred in the reference and the largest COD drop occurred in sample SEP1. This does not correspond to the BMP results. The changes are however hard to relate to the BMP results because of the uncertainty of the measurements. Especially the COD is hard to relate because of the method used for measurement but also the fact that a measurement from one of the triplicates represents all three samples.

4.6.2 Alteration in pH

In order to evaluate the effect of the differences in pH, the values at the end of the experiment were measured. The mean pH values are shown in Figure 22.

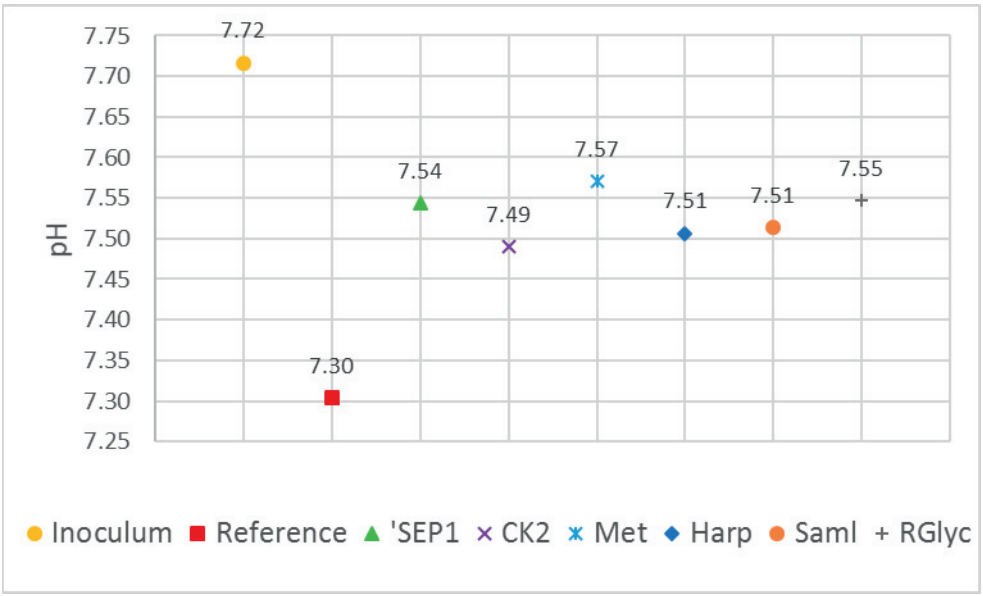


Figure 22. pH of samples at the end of the BMP experiment.

The pH values of the different streams can be compared to the values of the inoculum at the start of the experiment which was 8.1. The pH of all samples decreases more than the pH of the inoculum. The pH is similar in all samples, indicating that the inoculum had a good buffering capacity to handle the different pH's of the samples. All pH values are around 7 indicating that the degradation process was stable.

SEP1 is the biggest wastewater stream but it has not the highest BMP. This makes it unnecessary to digest it alone to achieve a good biogas production. Harp has the highest potential of the bigger streams but some methanol is recycled to Met which is useful for the process. Also SEP1, CK2 and Met have more extreme pH's making them less suitable. Thus the two streams left for anaerobic digestion is Saml and RGlyc.

The temperature for anaerobic digestion was set to 37°C and a mesophilic inoculum was used. The temperature of the stream Saml was 50°C which allows for thermophilic microorganisms to be used instead. However, the production is not continuous which means that a buffering tank would be needed before feeding the wastewater to the anaerobic digester. This would mean that the temperature of the wastewater would decrease before it enters the reactor. Then the reactor would need more heating. A heat exchanger could be used to partially heat the digester with the heat of the wastewater stream. To be able to compare the pros and cons of the process temperatures further a heat balance needs to be made. An evaluation of the samples BMP of a thermophilic process could also be useful to be able to compare the digestion temperatures further.

To maintain healthy organisms in the biogas reactor the balance between the COD and the nutrients is important. A rule of thumb is that the relationship should be 250:5:1 for COD:N:P (Jonstrup et al., 2011). In the case of Saml the relationship is 163:0.04:1 and for RGlyc the relationship is 977:0.04:1. This means that nutrients needs to be added to get a correct balance.

If only Saml is used only addition of N is needed and but the remaining sludge will have a high content of P. However the P is attractive as a fertiliser and the sludge might be spread on agricultural land. If RGlyc is used addition of both P and N is needed. This also means that the sludge will not have a high content of P. The addition of nutrients adds and extra cost making anaerobic digestion less attractive.

4.7 Estimated biogas production

Considering Saml the yearly production of methane, with today's production volumes, is estimated to 66 950 $Nm^3_{CH4,}$ for calculation see Appendix 1. Using values of energy content from *biogasportalen* the energy content of 1 Nm^3 biogas with 97 % methane is 9.67 kWh (Petersson, 2011). Thus 1 Nm^3 100 % pure methane would generate 9.96 kWh. The yearly energy production can then be estimated to 667 MWh. This can be related to a yearly consumption of energy in an average Swedish house which is 25 000 kWh per year (Eon, 2017a). Thus the energy produced could supply around 26 households. However, this would mean that the efficiency of the conversion is 100 % which is not very likely. Still with an efficiency of only 30 % as suggested by the company Myfuelcell (2017) the electricity produced would supply 8 households and the yearly production would be around 200 MWh. This can be related to the biogas plant in Kristianstad which produces 41 000 MWh per year (Jarvis, 2012). The production would be rather small if only the wastewater was used.

Considering the stream RGlyc it consists of 56 % Saml and of 44 % glycerol. This corresponds to the volumetric relationship of the produced amount of waste from both streams, for calculations see Appendix 1. The methane production of this stream is higher because of the higher BMP but also because of the addition of more substrate. Using these streams the yearly methane production can be estimated to 563 900 Nm^3_{CH4}. Resulting in a yearly production of 5616 MWh. With the efficiency of conversion of 30 % the production would be 1685 MWh. This is enough to supply 67 households. If the glycerol was used for biogas production the amount of biogas would increase but the production is still quite small. The small production means that the investment cost would be higher per produced amount.

A way of using the biogas would be to combust it in a steam-boiler to create steam. This is done by the company Norrmejerier in their plant in Umeå (Jarvis, 2012). Another alternative is to use it as biogas fuel. However, as car fuel the carbon dioxide present needs to be removed (Jarvis, 2012). This upgrading of the biogas would add an extra cost.

The calculations above are calculated for today's production when the plant is run for maximum 3 days a week. If the production was increased the methane production could also be increased. For example, running the plant for 5 days a week would result in a 40 % increase in methane production. A larger production also means that the biogas reactor and potential upgrading or steam boiler equipment would need to be dimensioned for small production and a larger production. The addition of more equipment also requires extra personel to handle the reactor etc. This would add an extra cost.

It was mentioned in the beginning that the company sell their glycerol to a biogas reactor. They get paid 130-180 € per ton. For the company to invest in a biogas reactor the price of the biogas would have to exceed the prize of the glycerol. For a comparison the prize of the biogas sold as car fuel was used as well as the approximate density of the fuel biogas of 0.8 kg/Nm^3 (Gasbilen, 2016). The price for the biogas would need to be 0.60 €/kg to cover the loss of the income from

the glycerol. Using the exchange rate from the 3rd of March 2017 this is 5.7 SEK/kg. The average price of biogas fuel in Sweden was 17.65 SEK/kg in March 2017 (Eon, 2017b). Thus the biogas price is triple the glycerol price. However, the investment costs dealt with above have not been covered and the difference in price would need to cover for at least that. The costs for transportation of the gas have not been covered for either, not have the fluctuations in the biogas price been considered. For calculations see Appendix 1.

5 Conclusions

The conclusions of this report will be related to the scientific questions asked in the introduction. *What characterises the wastewater produced by Ecobränsle?* The wastewater of Ecobränsle is characterised by high COD values compared to other studies compared in a review article by Veljkovic et al. (2014). Out of the components measured as COD the content of glycerol is high compared to two other studies (Phukingngam et al., 2011, Srirangsan et al., 2009). Another factor important for wastewater treatment is the phosphorus and nitrogen content. The phosphorus content was high and higher than the nitrogen content. This is interesting when considering anaerobic digestion since the microorganisms require a nutrient content that is balanced with the COD content.

What kind of wastewater treatment solutions are possible for biodiesel wastewater? One possible treatment solution is anaerobic digestion, but more work is needed to evaluate other treatment solutions.

What kind of wastewater treatment is suitable for Ecobränsle's plant, when aiming to find an environmentally friendly solution? Anaerobic digestion allows for the wastewater to give the company additional value from their waste. The wastewater can also be mixed with the glycerol produced at the plant and co-digested anaerobically. Co-digestion would result in a higher gas production due to the bigger volume but also because of the higher biochemical methane potential for the mixed streams. However, the possible production of biogas is not that high compared to other biogas plants. Nevertheless, the biogas produced can be combusted in a steam boiler, which would generate steam which can be used at the plant.

6 Future Work

When considering anaerobic digestion as an option there are some issues that needs to be considered. Which type of anaerobic digester would be suitable? Where should it be placed? Which permits are needed when running an anaerobic digester? Another factor is the investment cost. No cost-estimate has been done for investing in an anaerobic digester, a heat exchanger for recovering the heat of Saml or a steam-boiler for steam production. This is also important to consider as the yearly production of biogas is quite small. The sludge production also needs to be considered. It needs to be discarded as a waste. The high phosphorus content of Saml will probably be reflected in the sludge. Efforts could be spent on extracting the phosphorus which might be a valuable source for fertilisation.

7 Reference list

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8 Appendices

Appendix 1.

8.1.1 Calculations for glycerol production

The amount of RME produced a week is 312 m^3. It is expressed as V_{RME}. The molar ratio of RME to glycerol is 3 to 1. The other parameters, molar weight (M_w) and density (ρ) are presented below. The molar weight used is the one for oleic acid since this is the dominating component of RME. The density for the RME was measured in 2015 when the company did an analysis of their RME.

$M_{w,RME} = 282.46\ kg/kmol,\ \rho_{RME} = 883.6\ kg/m^3$

$M_{w,glycerol} = 92.1\ kg/kmol, \rho_{glycerol} = 1260\ kg/m^3$

The molar production is calculated using the equation below.

$$n_{RME} = \frac{V_{RME} \cdot \rho_{RME}}{M_{w,RME}} = 976\ kmol/week$$

Using the molar production of 976 kmol/week the weekly production of glycerol expressed in volume was calculated.

$$V_{glycerol} = \frac{n_{RME} \cdot M_{w,glycerol}}{\rho_{glycerol} \cdot 3} = 23.8\ m^3/week$$

The production can also be expressed as mass:

$$m_{glycerol} = V_{glycerol} \cdot \rho_{glycerol} = 30\ tons/week$$

8.1.2 Calculations for glycerol standard concentration versus RME standard

The content of glycerol in hexane was calculated using the equations below.

$$m_{glycerol} = 55.9\ mg$$

$$V_{Hexane} = 5\ mL$$

$$\rho_{glycerol} = \frac{1260\ mg}{mL}$$

$$V_{glycerol} = \frac{m_{glycerol}}{\rho_{glycerol}} = 0.044\ mL\ /mL$$

The content of glycerol in hexane was calculated to:

$$\frac{V_{glycerol}}{V_{Hexane}} = 0.0089\ mL_{glycerol}/mL_{Hexane}$$

The content of RME or specifically oleate in ethanol was calculated using the equations below.

$$m_{RME} = 100\ mg = m_{oleate} = 20\ mg$$

$$V_{ethanol} = 25\ mL$$

$$\rho_{oleate} = 895\ mg/mL$$

$$V_{oleate} = m_{oleate}\ /\rho_{oleate}\ = 0.022\ mL\ /mL$$

The content was calculated to:

$$\frac{V_{oleate}}{V_{ethanol}} = 0.00089\ mL_{oleate}/mL_{ethanol}$$

If the two solutions are compared the amount of glycerol in hexane is ten times higher than the amount of oleate in ethanol.

8.1.3 Calculations for glycerol dosage

The amount of glycerol produced was related to the amount of total wastewaster produced (Saml). This was used when calculating the amount of glycerol that could be used in codigestion with Saml.

The molar relationship between Glycerol and RME is 1:3. Assuming that the molarmass for oleic acid is the same as the molar mass for RME this can be converted to mass. The same goes for glycerol.

$m_{RME} = M_{RME} \cdot n = 282 \cdot 3 = 846\ g$

$$m_{Glyc} = M_{Glyc} \cdot n = 92 \cdot 1 = 92\ g$$

Using the density for oleic acid the volume of RME can be calculated

$$V_{RME} = \frac{m}{\rho} = \frac{846}{895} = 0.945\ L$$

And the volume for glycerol:

$$V_{Glyc} = \frac{m}{\rho} = \frac{92}{1261} = 0.073\ L$$

Then the volumetric production can be calculated to:

$$Production = \frac{V_{Glyc}}{V_{RME}} = \frac{0.073}{0.945} = 7.7\ vol\%$$

Given that 10 L of wastewater is produced for every 100 L RME, the amount of glycerol produced per 100L RME is about 8 L. Given a 100mL sample the amount of glycerol is:

$$V_{Glyc,RGlyc} = \frac{8}{(8+10)} \cdot 100\ mL = 44\ mL$$

$$V_{Saml,RGlyc} = \frac{10}{(8+10)} \cdot 100\ mL = 56\ mL$$

Using the COD value for Saml and the theoretical COD values for glycerol the COD of the sample can be estimated to:

$$COD_{RGlyc} = 0.44 \cdot 1533500 + 0.56 \cdot 241000 = 809700\ mg/L$$

However,using the actual weights (substracting the average mass of glycerol left in the beaker after the glycerol had been added to the sample). The COD is more likely to be approximately:

$$m_{Saml,added} = 7.1\ g$$

$$m_{Glyc,added} = m_{weighed} - m_{left,average} = 6.1 - 1.57 = 4.53\ g$$

$$COD_{RGlyc,actual} = \frac{4.53}{4.53+7.1} \cdot 1533500 + \frac{7.1}{4.53+7.1} \cdot 241000 \sim 731300\ mg/L$$

8.1.4 Calculations for methane production

Production of methane for Saml:

$$V_{Saml} = 0.65\ m^3/hour$$

Shifts are: 16 hours per day, 3 days a week, giving:

$$Production_{Saml} = 31.2 \frac{m^3_{ww}}{week}$$

Estimate number of running weeks to 48 weeks per year, giving a yearly production of:

$$Production_{Saml} = 1498 \frac{m^3_{ww}}{year}$$

$$COD_{Saml} = 241000\ g/m^3$$

Which gives a yearly production of COD of:

$$Production_{Saml,COD} = Production_{Saml} \cdot COD_{Saml} = 3.6 \cdot 10^8 g_{COD}/year$$

With a BMP for Saml of:

$$BMP_{Saml} = 185.5\ NmL_{CH4}/g_{COD}$$

This gives an approximate methane production of:

$$V_{CH4,Saml} = BMP_{Saml} \cdot Production_{Saml,COD} = 66950\ Nm^3_{CH4}/year$$

Production of methane for RGlyc:

Using the volumetric production rates of the different streams, the total yearly production can be calculated to:

$$V_{Saml} = 31.2\ m^3/week$$

$$V_{Glyc} = 23.8\ m^3/week$$

$$Production_{RGlyc} = (V_{Saml} + V_{Glyc}) \cdot 48 = 2640\ m^3/year$$

Using the COD calculated above the yearly production expressed in COD can be calculated.

$$Production_{RGlyc,COD} = COD_{RGlyc} \cdot Production_{RGlyc} = 2.1 \cdot 10^9\ g_{COD}/year$$

The BMP for RGlyc was found to be 263.8 NmL_{CH4}/g_{COD}. Using this the yearly methane production of RGlyc can be estimated to:

$$V_{CH4,RGlyc} = BMP_{RGlyc} \cdot Production_{RGlyc,COD} = 563900\ Nm^3/year$$

Production of methane Saml with 5 days operation of plant

$$V_{Saml} = 0.65\ m^3/hour$$

Shifts are: 8 hours per day, 5 days a week, giving:

$$Production_{Saml} = 52 \frac{m^3_{ww}}{week}$$

Estimate number of running weeks to 48 weeks per year, giving a yearly production of:

$$Production_{Saml} = 2496 \frac{m^3_{ww}}{year}$$

$$COD_{Saml} = 241000\ g/m^3$$

Which gives a yearly production of COD of:

$$Production_{Saml,COD} = Production_{Saml} \cdot COD_{Saml} = 602 \cdot 10^6 g_{COD}/year$$

With a BMP for Saml of:

$$BMP_{Saml} = 185.5\ NmL_{CH4}/g_{COD}$$

This gives an approximate methane production of:

$$V_{CH4,Saml,5days} = BMP_{Saml} \cdot Production_{Saml,COD} = 111584\ Nm^3_{CH4}/year$$

8.1.5 Calculations for biogas price

The income from the glycerol is 130-180 €/ton. Ecobränsle produce 8 L glycerol per 10 L wastewater. With a yearly production of Saml of 1498 m^3/ year. The production volume of glycerol is:

$$Production_{Glyc} = Production_{Saml} * \frac{8}{10} = 1198.4\ m^3/yr$$

This can be converted into weight units using the density of glycerol of 1260g/ m^3.

$$Production_{mass,Glyc} = 1198.4 * 1260 = 1510\ ton/yr$$

With a price of 180 €/ton the yearly income is:

$$Income_{Glyc} = 1510 * 180 = 271\ 797\ €/ton$$

The volumetric production of methane is 563900 Nm^3/ year. Using the income of the glycerol the price per Nm^3 is:

$$Price_{RGlyc,CH4,Volumetric} = \frac{271797}{563900} = 0.48\ €/Nm^3$$

With a mean density for the biogas fuel of 0.8 kg/ m^3 the price per kg can be calculated.

$$Price_{RGlyc,CH4,Weight\ based} = \frac{0.48}{0.8} = 0.60\ €/kg$$

This can be converted to Swedish kronor using the exchange rate from 3rd of March of 9.54 SEK/€.

$$Price_{RGlyc,CH4,Weight\ based} = 0.6 * 9.54 = 5.7\ SEK/kg$$

Appendix 2. Flowchart

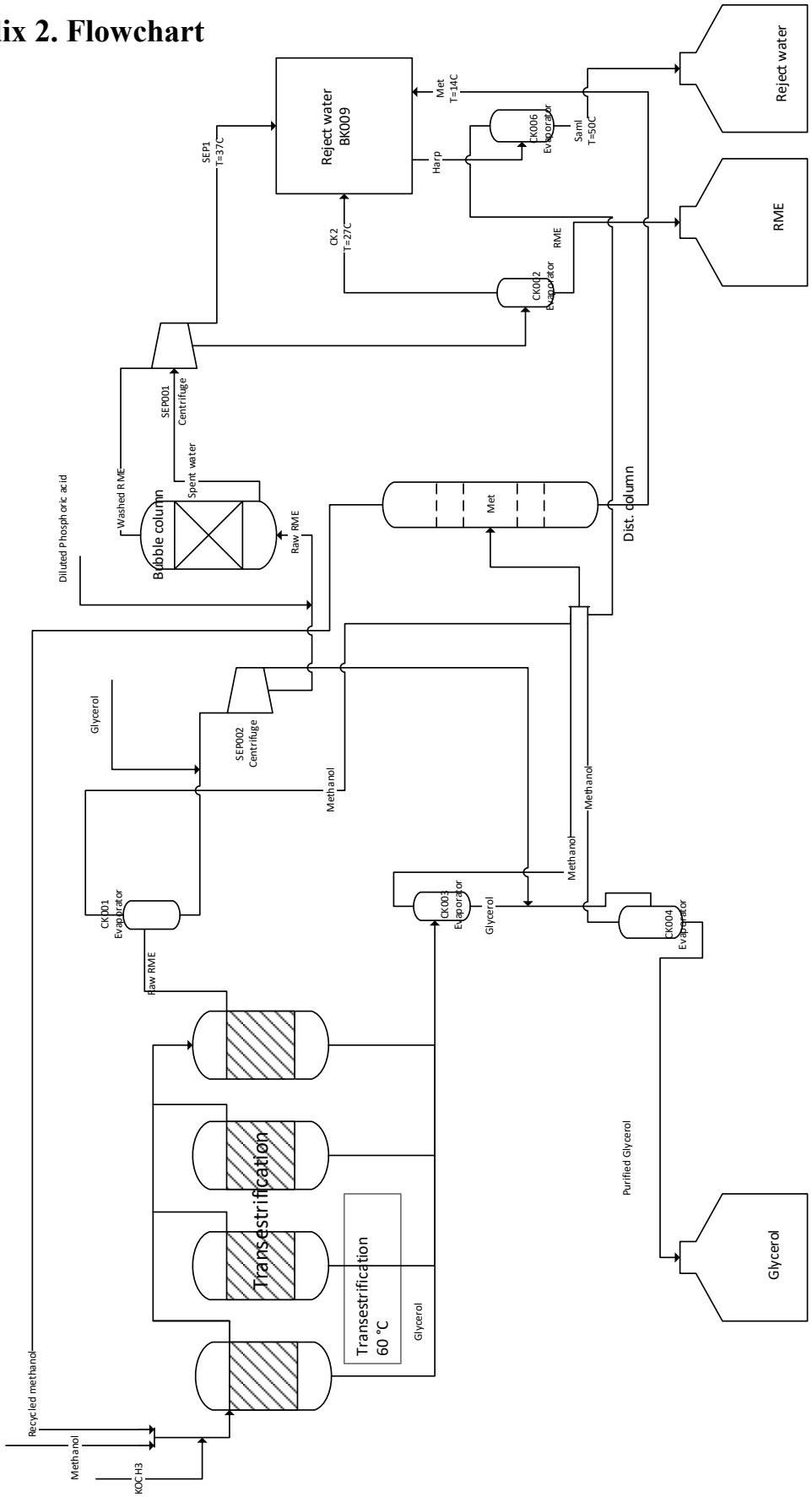

Figure A 1. Flow chart for the biodiesel plant.