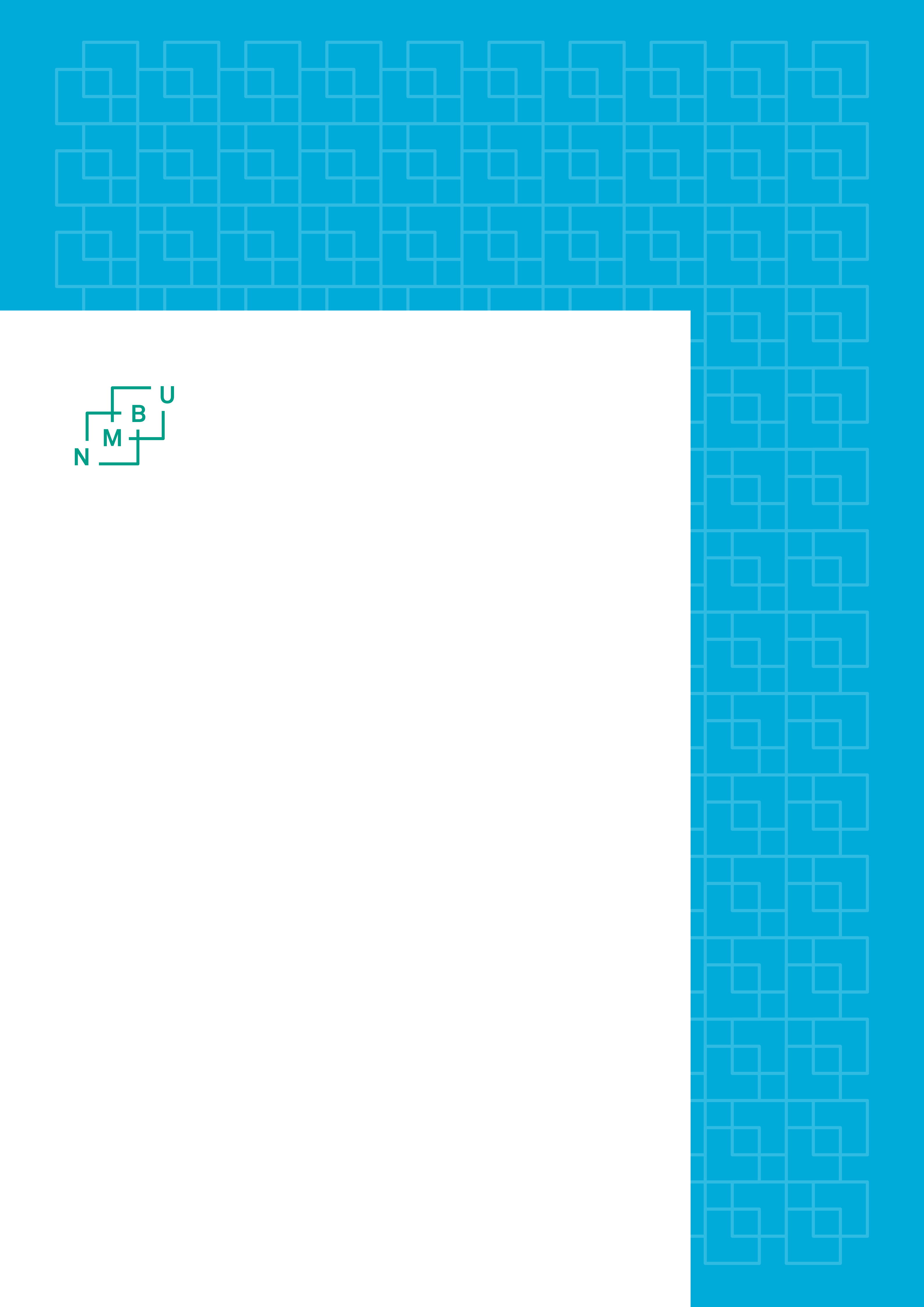
NMBU

Preface

This thesis is the result of a master project in biodiesel production at the Norwegian University of Life Sciences (NMBU) Department of Mathematical Sciences and Technology and marks the end of a five-year Master of Science in Environmental Physics and Renewable Energy. During the years at NMBU, my interest and knowledge for renewable energy has increased exponentially and it was therefore a great privilege to be able to write a thesis within the topic process and bioenergy, more specific biodiesel production.

Since my background is energy physics and process, I did not have that much experience with more practical simulation tools like “Aspen Plus” and “SuperPro”, but I feel that I have learned a lot during this masterperiod and I am very proud of the result.

Ås, May 15th, 2015

Kristian Sørby Omberg

Acknowledgements:

First of all I would like to thank my supervisor Dr. Jorge Mario Marchetti for excellent supervising and motivation during the time of this thesis. Dr. Marchetti introduced me to the exciting world of biodiesel and the field of chemical engineering which lead to a wider understanding of bioenergy which I am forever grateful for.

Thanks to the student organization TEKNA for providing financial support and extra motivation. In addition I am also very grateful for the assistance received from the students Rene Boogaard, Kristian Roderburg and Aleksander Hykkerud. They helped with interpreting the Aspen model into a solidworks design and contributed to interesting conversations during the course of the thesis. Thanks to the companies “OEM Automatic”, “Selko Motor” and “Noreko” for their contribution to this thesis. In addition I would like to thank Håkon Sverdvik for creating a masterpiece of an animation film related to the thesis. A final thanks goes to my family and especially my brother Ola Sørby Omberg who was a significant driveforce behind this project.

Kristian Sørby Omberg

Abstract

In a world where the growing concern for global warming and the problems concerning planet earth is confirmed by the Intergovernmental Panel on Climate Change (IPCC) [1]. The search for alternatives to replace the use of finite fossil fuels and cut green house gas (GHG) emission has commenced.

Biodiesel, a biofuel derived from fat and vegetable oil based feedstock is one such alternative. However, a large enough biodiesel production to supply the demand for fuel is being limited by cost in terms of raw materials and a sustainable production.

The feedstock limitations and failing biodiesel production strategy in Norway necessitates the development of more efficient production technology more suited for the Norwegian marked. This thesis examines an alternative viable biodiesel system based on heterogenous production technology in a small-scale plant were the feedstock is mainly waste vegetable oil. In order to identify the most suitable technology, the following three objetive were set:

- *Identify a suitable heterogenous technology for a small-scale biodiesel plant.*
- *Present a model for the suggested production method.*
- *Determine the economical sustainability of the model.*

In order to achive these goals a detailed litterature review of conventional biodiesel production technology and a comparison of it to heterogenous technology will be performed. From this review, heterogenous catalysed technology was identified as a suitable method for small-scale biodiesel production from waste vegetable oil. As a continuation, a review of some existing heterogenous acid and alkaline catalysts was preformed. From the review, it was purposed that combining a heterogenous acid catalyst such as “Amberlyst BD20” and an alkaline catalyst like “Calcium oxide” (CaO) in a two-step heterogenous process. This process could result in a more efficiant conversion of waste feedstock and create a viable biodiesel production model.

The two-step production model, based upon small-scale operations, was presented and simulated in the software “Aspen Plus”. The Aspen simulation provided a flowsheet of a potential plant, data for the operation parameters and the mass flow over the plant. The flowsheet gained from Aspen made it possible to create a conceptual design of small-scale plant in “Solidworks” and a review of proposed equipment for use in a potential plant.

As a practical supplement to the thesis some critical modules were constructed that later could be implementet in a larger plant, but also work as a standalone. An example of this was the centrifuge modul created during the run of this thesis. In addition, a conceptual design of the small-scale plant was made using the solid modelling program “Solidworks”.

To create an economic analysis of the plant, the data gained from Aspen was transferred to the economical evaluation tool “SuperPro” and a new simulation was preformed focusing on the economical aspect.

Two scenearios was simulated: one for a commercial use small-scale plant in a Renovation company and one simulation for a single producer, in this case a Norwegian farmer. The aim was to determine the payback time of the investment in a biodiesel plant by varying the selling price of the final product in the two scenerios between $ 1, 75 down to $ 0, 83 pr liter biodiesel and changing the production intervall. The most realistic results showed that a resonable payback time of 1.9 years (singel producer) and 4.2 years (commerical scenario) could be achived even if the retail price was much lower than the ordinary retail price.

Based on the data collected and the results from the simulations, the combination of a heterogenous technology and a small-scale production model, seems to be a very interesting option for the future biodiesel production in Norway.

Sammendrag

I en verden der bekymringen for oppvarming planeten vår setter større preg på hverdagen, en bekymring som blir bekreftet av FNs klimapanel (IPCC) [1]. Har letingen etter alternativer for å erstatte bruk av fossile brensler for å kutte drivhusgasser (GHG) utslipp blitt påbegynt. Biodiesel, et biobrensel produsert fra vegetabilsk olje basert råstoff er et slikt alternativ. Det produserers imidlertid ikke nok biodiesel til å forsyne etterspørselen etter drivstoff som blir begrenset av kostnadene i råvarer og en lite bærekraftig produksjon.

Som et resultat av begrenset råstofftilgang og en sviktende biodiesel produksjonsstrategi i Norge, undersøker denne avhandlingen en alternativ levedyktig biodiesel system basert på heterogene produksjonsteknologi i et småskala anlegg som bruker avfall som råstoff.

I jakten på en levedyktig biodiesel produksjon, er følgende tre mål satt:

- *Identifisere en passende heterogen teknologi for en småskala biodieselanlegg.*
- *Presentere en produksjonsmodell for den foreslåtte teknologien.*
- *Bestemme om modellen er økonomisk levedyktig.*

Målene som er satt fører til et behov for en detaljert gjennomgang av konvensjonell biodiesel produksjonsteknologi og sammenligne det med heterogen teknologi. Fra denne gjennomgangen, ble heterogen katalysert teknologi identifisert som en egnet metode for småskala produksjon av biodiesel fra avfall. Som en fortsettelse, ble en gjennomgang av noen spennende heterogene syre og alkaliske katalysatorer gjennomført. Fra denne sammenligningen, ble det teoretisert at ved å kombinere en heterogen syrekatalysator som f.eks Amberlyst BD20 og en alkalisk katalysator som "Kalsiumoksyd (CaO) i en to-trinns prosess kan resultere i en effektiv omdannelse av avfallsråstoff og skape en levedyktig biodiesel produksjonsmodell.

Denne to-trinns produksjonsmodell, basert på småskala operasjoner, ble presentert og simulert i programvaren "Aspen Plus". Aspen simulering produserte en flytskjema av et mulig anlegg, data for operasjonsparametere og massestrømmen over anlegget. Flytskjemaet fra Aspen gjorde det mulig å lage et konseptdesign av småskala anlegg i "Solidworks" og en gjennomgang av foreslått utstyr for bruk i en potensiell anlegg.

Som et praktisk supplement til avhandlingen ble noen kritiske modulene bygget som senere kan bli brukt i et større anlegg, men også fungere som en frittstående modul. Et eksempel på dette var sentrifugemodulen bygd under denne masterperioden. I tilegg ble et konseptuelt design av biodieselanlegget tegnet i «Solidworks».

For å utføre en økonomisk analyse av anlegget, ble data fra «Aspen» overført til det økonomiske evalueringsverktøy "SuperPro" og en ny simulering ble gjennomført med fokus på det økonomiske aspektet. To senarioer ble simulert: en for kommersiell bruk av småskala anlegg i et Renovasjonsselskap og en simulering for enkelt produsent, i dette tilfellet en norsk bonde. Målet var å bestemme tilbakebetalingstid på investeringen i et biodieselanlegg ved å variere salgspris på sluttproduktet i de to senarioene mellom $ 1.75 ned til $ 0.83 pr. kg biodiesel produsert og endre produksjonenintervallet. Resultatene viste at en rimelig tilbakebetalingstid kunne oppnås på 1.9 (enkelprodusent) og 4.2 år (renovasjonselskap), selv om salgspris var mye lavere enn den ordinære utsalgspris. Basert på innhentet data og oppnådde resultater, kan det bety at kombinasjonen av en heterogene teknologi og et småskala anlegg er en meget interessant alternativ for fremtidens biodieselproduksjon i Norge.

Table of contents:

Abbreviations and Glossary:

BtL	Biomass to Liquid
CSS	Calcined Sodium Silicate
DG	Diglycerids
DIY	Do It Yourself
EU	European Union
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GHG	Greenhouse gases
HDPE	High Density Polyethylene
IPCC	Intergovernmental Panel on Climate Change
KOH	Potassium Hydroxide
MeOH	Methanol
MG	Monoglycerids
NaOH	Sodium Hydroxide
NMBU	Norwegian University of Life Sciences
OECD	Organisation for European Economic Co-operation
LDPE	Low Density Polyethylene
PAH	Polycyclic Aromatic Hydrocarbons
TG	Triglycerids
USD	The currency used in this thesis will be in dollars ($)
WCO	Waste Cooking Oil

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1. Aim and background

One of the key factors in my choice of topic for the thesis was my involvement the studentproject “UMBio”. The purpose of the UMBio project was to develop a method for producing biodiesel from waste whit the main focus on developing a pretreatment process of the waste to make it suitable for biodiesel production. The project group consisted of *Kristian Omberg, Marius Trebostad, Gubrand Askvig, Ola Omberg and their supervisor Dr. Jorge M. Marchetti*. Through experiments, the UMBio group gathered data to make a comparison of available feedstock in Norway. The collect samples was analyzed for free fatty acid (FFA) and water content. In addition, the UMBio project also tested new method and existing methods of converting the waste into biodiesel. Emphasis was on testing different heterogeneous (solid) catalyst for finding the optimal waste pretreatment. As a result, the group saw a need for an efficient and reliable small-scale processing technology, which is the focus of this thesis [2].

The goal of this thesis is to examine a suitable production technology and alternative ways to make the production of biodiesel more efficient and economical viable. This is done by developing a production model, based upon small-scale (less than one million L/yr) biodiesel production which could be more suitable for the norwegian marked as a result of limitations in terms of avalible feedstock in Norway.

The objective of this thesis is to:

- Identify a suitable heterogenous technology for a small-scale biodiesel plant.
- Present a model for the suggested production method.
- Determine the economical sustainability of the model.

2. Introduction and litterature review:

The IPCC report released in 2013-2014 states that an in increase in the global temperature due to an increase in atmospheric GHG emssions could lead to drastic climate changes, affecting billions of lives in the process. In order to limit the effects, effort is directed toward reducing emissions from dominant global emitters of GHG – the power-generation industry and the transportation sector [3].

Proposed alternatives are electrochemical (battery powered electrical vehicles), hydrogen fuel cells, bio-ethanol and biodiesel [4]. These alternatives are considered a less economical viable option, due to lower range or higher production and investment costs [5]. As there are challenges associated with all of these technologies, none arises as a clear future substitute to fossil fuel. The more likely scenario is for the technologies to coexist and in near future serve as a diverse range of fuel alternatives. Thus bearing resemblance to the renewable power-generation-mix. Although feedstock constraints limit the large-scale development of biodiesel, to put it in perspective if every non-fossil oil and fat known to humankind were converted to biodiesel, it would provide at most 10% of our current diesel consumption [6]. However, a strong argument for using biodiesel lies in the potential in the utilization of waste, which is necessary in order to create a more sustainable fuel production. The report "*Biofuels Markets and Technology*" predicts the global biofuel marked will double over the next decade. This is due to that biodiesel has potential to smooth the transition from a fossil fuel to a new sustainable energy system such as a renewable power-generation-mix because of its ability to easy be implemented in diesel engines [7].

This thesis will discuss some aspects in biodiesel technology, with a focus on the application of heterogenous technology to a small-scale biodiesel plant. The scope of this thesis is to present a technical review of different productions models, create a preliminary design and a set-up of a small-scale-plant.

2.1 What is biodiesel?

Biodiesel is considered a renewable, clean burning and nontoxic fuel alternative for diesel engines [8]. Figure 2.1illustrates the cycle: how biodiesel is produced from vegetable oils from oil crops (such as soy or sunseed). The main reaction behind the biodiesel production is the transesterification reaction. The vegetable oils (consisting mainly of mono, di and triglycerides) is converted into Fatty Acid Methyl Esters (FAME) and the byproduct glycerol if using methanol. Other sources for raw material can be waste vegetable oil, but when cooking with vegetable oil the carbon chains of the glycerides could be broken and forming free fatty acids (FFA). FFA can be converted into biodiesel through a process, called esterification.

The biodiesel can be used as a direct substitute for fossile diesel f.ex in public transportation. The emission (mostly CO_2) does not contain sulphur and represents a closed carbon cycle, is therefore called carbon neutral fuel, and is easily absorbed by the crops, producing oxygen, and more crops by photosynthesis [9].

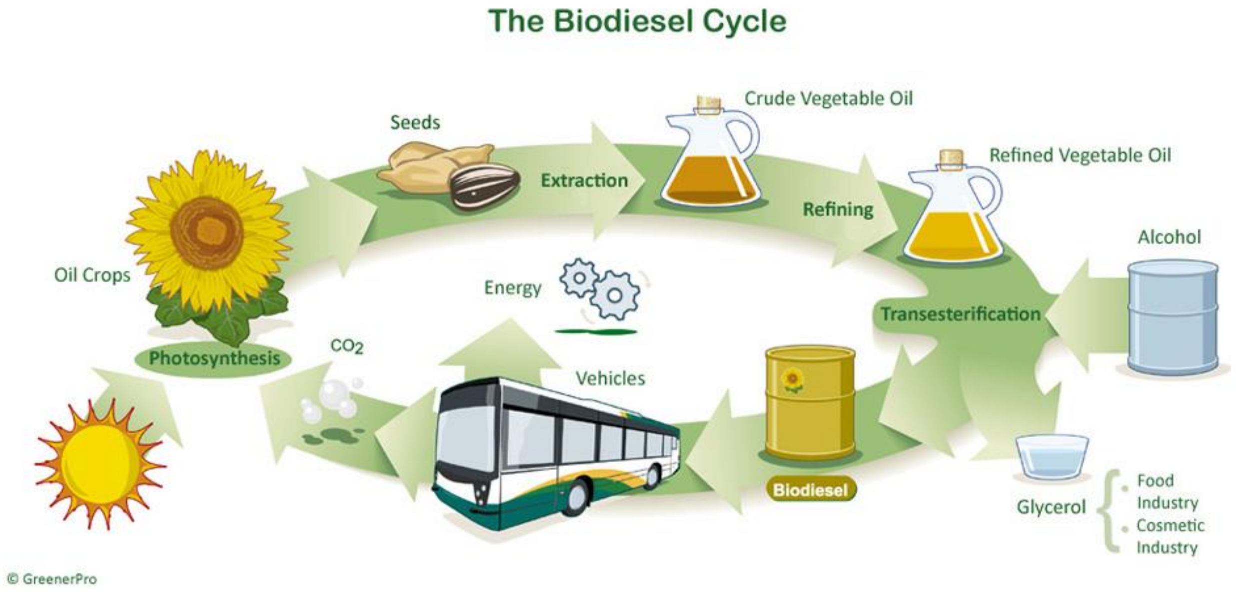


Figure 2.2: Illustrates the prosess from growing the crops to production and the use of biodiesel [10].

Esters are organic compounds composed of an alcohol and an organic acid. Glycerol makes up ten percent of the total product and cannot be used as fuel, but it is used in many common products like cosmetics (moisturizing cream). Currently, methanol a petroleum based product, is the most commonly used alcohol due to low cost and high availability.

2.2 Biodiesel compared to fossil diesel:

When comparing biodiesel to fossil diesel, the main advantages of the use of biodiesel: less pollution from the combustion of biodiesel than fossile diesel. However, there is still some disadvantages. Biodiesel is one the other hand more expensive than diesel, has an increase of NOx emission when combusted and is limited by the storage time. Table 2.1 presents the average exhaust emission from biodiesel compared to regular diesel.

Table 2.1: Average Exhaust Emissions for Biodiesel Compared to fossile Diesel [9]**.**

Emission type	Reduction
Carbon dioxide	-78%
Total Unburned Hydrocarbons	-68%
Carbon Monoxide	-47%
Particulate Matter	-48%
Nitrogen Oxides (NOx)	increase
Sulfates	-100%
Nitrated Polycyclic Aromatic Hydrocarbons (nPAH)	-90%
Polycyclic Aromatic Hydrocarbons (PAH)	-80%
Speciated Hydrocarbons Ozone Forming Potential	-50%

Polycyclic Aromatic Hydrocarbons (PAH and nPAH): These compounds are identified as carcinogenic (causing cancer) compounds. Biodiesel reduces emissions of these compounds by up to 85% for PAH compounds and 90% for nPAH compounds [9].

Speciated Hydrocarbons: The ozone forming potential of biodiesel combustion is approximately 50% less than that of fossil diesel. In cities where smog is a growing problem, this characteristic is directly beneficial [9].

2.3 Basics of the transesterification reaction:

The transesterification reaction is a reversible equilibrium reaction and only occurs at an acceptable rate in the presence of a catalyst. Figure 2.2 depicts a simplified form of the reaction, where one mole of triglycerides (TG) reacts with three moles of an alcohol. In vegetable oil, there is also mono and di glycerides that reacts with alcohol.

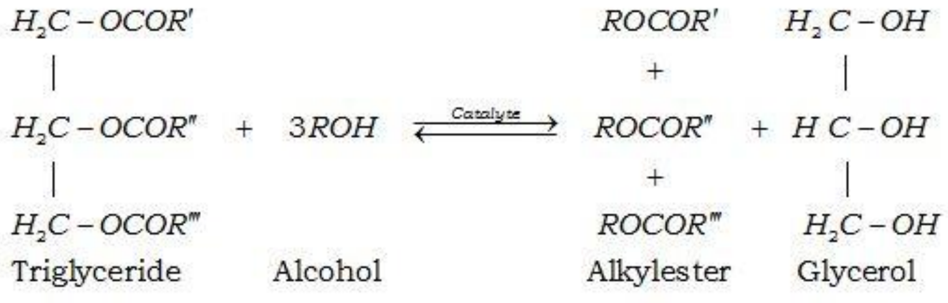


Figure 2.3: The transesterification of triglycerides [11].

Most biodiesel production processes uses a strong alkaline liquid (sodium hydroxide (NaOH) or potassium hydroxide (KOH)) as a catalyst to initiate the transesterification reaction [12]. A byproduct of the transesterification reaction is the glycerol that have has several fields of uses depending on the grade of purity. The more traditional uses of high-grade (pharmaceutical quality) glycerol are in cosmetics and pharmaceutic applications. Because of a saturated glycerolmarket, research for new uses of glycerol has increased worldwide. Recently a new biofuel concept as been developed by researchers at Michigan State University allows biodiesel production-plants to eliminate the waste glycerol and create a high-value product. The process uses microbes named “*Geobacter sulfurreducens’’* that generates ethanol from glycerol and has the added benefit of cleaning up the wastewater and could open the possibility of onsite production of ethanol [13].

2.4 Basics of the esterification reaction

As mention before, high FFA feedstock can also be converted into biodiesel, but through a process called esterification. Figure 2.3 illustrates the reaction model, where one mole of FFA reacts with an alcohol forming FAME:

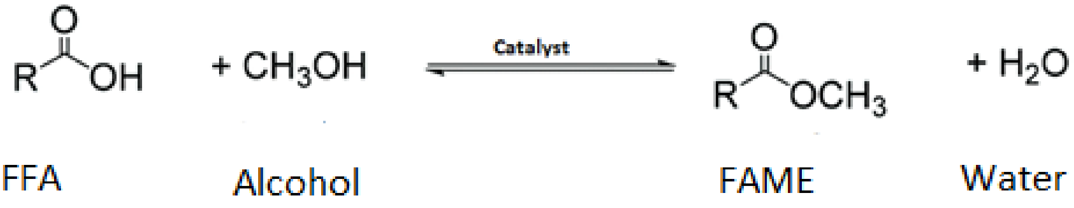


Figure 2.4: The esterification of FFA and alcohol, forming biodiesel and water.

The byproduct in this reaction is water instead of glycerol. To catalyze the reaction a strong homogeneous acid catalyst, such as sulfuric acid (H_2SO_4), is commonly used. This is due to the fact that a reaction occurs between the homogenous base catalysts and FFA. The result of this reaction is the formation of soap and water. The esterification process is illustrated by Figure 2.4, where the feedstock (cooking oil) reacts with the homogenous acid catalyst that catalyzes both the esterification and transesterfication reaction. The result of the reactions is the formation of FAME, water and glycerol (middle glass dark color).

Figure 2.5: Esterification of used cooking oil with sulfuric acid illustrated [14].

2.5 Catalyst:

2.5.1 What is a catalyst?

The transesterification and esterification reaction are both endothermic and reversible. A catalyst is necessary to promote the forward reaction towards biodiesel and to reduce the reaction time and energy input required to reach sufficient conversion. In other words, a catalyst is the component in a chemical reaction that makes the reaction occur. The catalyst component in the biodiesel production can be considered a “bottleneck” for further development to the process and there is extensive research done in this field. With this in mind, a brief review of literature demonstrates how biodiesel production technologies is categorized according to the catalyst used in the process:

2.5.2 Types of catalyst:

- Homogeneous catalyst
  - Alkaline
  - Acidic
- Heterogeneous (solid) catalyst
  - Alkaline
  - Acidic
- Enzymatic catalyst

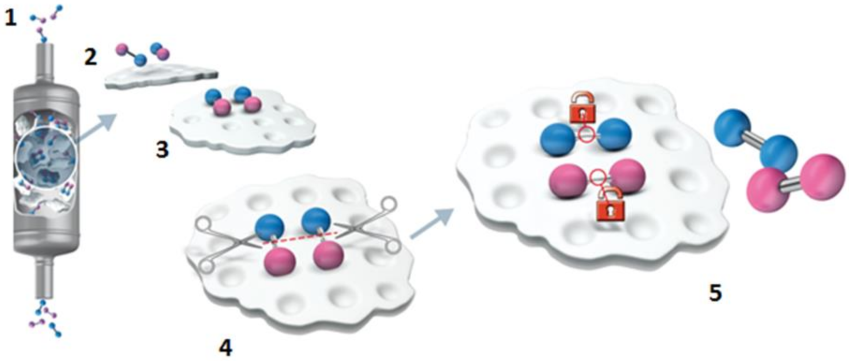
In a commercial setting the application of homogenous catalyst is a more mature technology, while the last two contain new methods that are currently under development. In this thesis, the focus will be on the heterogenous catalyst.

2.5.2.1 Homogenous catalyst:

By definition, homogeneous catalysts are in the same phase as the reactants and products. In the case of biodiesel production, these catalysts dissolves in the liquid alcohol present in the reaction. There are two forms of homogeneous catalysts: Alkaline and acid, however, acid catalysts are very rarely used as the reaction rates are 4000 times slower than their alkaline counterparts. Therefore when reviewing the homogenous technology, the focus will be on alkaline catalysts [15, 16].

2.5.2.2 Heterogeneous catalyst:

This involves the use of a catalyst in a different phase from the reactants. Typical examples involve a ***solid*** catalyst with the reactants as either ***liquids or gases***. Most examples of heterogeneous catalysis go through the same stages as illustrate in Figure 2.5:



1. *Inlet of reactants*
2. *Active site*
3. *Adsorption*
4. *Surface reaction on active sites:*
5. *Desorption*

Figure 2.6: Different stages during heterogeneous catalysis [17].

One or more of the reactants are adsorbed on to the surface of the catalyst at ***active sites***. The active site can be seen as places on the catalyst surface where highly reactive intermediates are stabilized long enough to react. Adsorption occurs, when reactants are attracted to the catalyst surface and must not be confused with the similar term absorption, where one substance is added within the structure of another substance. During the adsorption an interaction between the surface of the catalyst and the reactant molecules occurs which makes them more reactive. After the adsorption the surface reaction ensues. At this stage, the reactant molecules might be attached to the surface. After the reaction, the newly formed product molecules are desorbed. Desorption implies that the product molecules break away and the active site is available for a new set of molecules to attach to and react.

Criteria for a catalyst is mainly to have excellent adsorption abilities, meaning that the reactant molecules is adsorbed long enough for them to react and hinder the product molecules stick permanently to the surface. Some of the best catalyst materials is f.ex platinum and nickel and is applied to the active sites on the surface of the catalyst [18].

2.6 Feedstock:

This part of the theory examines biodiesel feedstocks. Biodiesel technology can divide into three main categories or generations based on the different feedstocks [19]:

- **First Generation biodiesel:** Produced directly from food crops by extracting the oils for use in biodiesel instead of food production, but also organic waste.
- **Second Generation biodiesel:** Developed to overcome the limitations of first generation biofuels. Produced from non-food crops such as wood, waste from food crop and specific biomass crops.
- **Third Generation of biodiesel:** Based on improvements in the production of biomass. It takes advantage of specially engineered energy crops such as algae as its energy source.

In this thesis, the focus will be on the biodiesel produced from waste vegetable oil.

2.6.1 Current Feedstocks:

Traditionally, feedstocks for biodiesel production are the refined plant oils. Such as refined soybean, palm, sunflower as seen in Figure 2.6 and canola oils, oils that contains over 99 wt% of triglycerides, are considered as refined oils. As a rule of thumb, the higher the quality of the feedstock, the more expensive it will be. Waste vegetable oils and animal fats are the cheapest feedstock, but the cost of production of biodiesel may be highest due to the high content of FFA and contaminants (water, particles, phospholipids, etc.). The use of high FFA feedstock tends to lead to increase in cost because of implementation of more process steps to handle the waste. As the biodiesel industry continues to expand, the exploration of alternative feedstock options is constant. These feedstock's can be broadly summarized into two groups; firstly feedstock's that are traditionally available at low cost (e.g.: tallow and used vegetable oil) and secondly, non-traditional feedstock is including non-edible oils and algae.

Figure 2.6: Oil derived from sunflower seeds [20].

Low cost feedstocks include animal fat, used cooking oils and by-products from agricultural refining. The issue with this type of feedstock is that it exhibits increased FFA content and thus higher viscosity and cloud point when compared to the virgin oil. FFAs are a crucial compound in the feedstock and determine the quality of the raw material. F.ex refined oil contains a FFA amount less than 0.1 wt%, crude vegetable oil has FFA level higher than 0.1 wt% and waste vegetable oil has a FFA level beyond 5 wt%. Table 2.2 provides the approximate concentration of FFA in refined vegetable oils, crude vegetable oil and waste vegetable oil.

Table 2.2: Quality of different oils related to the FFA-content (wt%) [21].

Type	Wt%	grade
Canola	0.34	refine
Sunflower	0.04	refine
Jatropha	1.17	crude
Used cooking oil	5.72	waste

To overcome the problems involved in processing low cost feedstock’s extensive research into new processing methods has taken place. The background for this research is the low cost of this feedstock compared to traditional refined vegetable oils. Low cost feedstock’s are typically by-products from existing processes and thus exposed to significant short-term prices swings. As demand for them rapidly increases, so does their price. This is due to supply inelasticity as almost all low cost feedstocks are by-products of other markets. Consequently, the scope for increasing the supply is extremely limited. On top of this, there is competition for low cost feedstocks from other established industries as they are used as a dietary energy source in the animal feed industry and in the manufacture of soaps and detergents. As a result, low-cost feedstock’s should not be the basis for the development of the biodiesel industry, but rather a supplement until future feedstock like algae is more viable. During the UMBio project, the group estimated the amount of waste vegetable oil available in some local areas and identified some large sources of waste cooking oil (WCO). The group also analyzed FFA present in the different feedstock samples gathered. The total amount of WCO was estimated to 270 000 liters per year. In addition to the major sources of feedstock, info and samples obtained from Vestby in Akershus and Kongsberg in Buskerud. Feedstock sources like McDonalds where each restaurant produces roughly 200 – 300 L of WCO per month. In addition, a small sample of fish oil was gathered from NMBU [2].

The samples were then tested and analyzed. The amount of FFA in the samples was determined by titration. The data collected from the analysis showed that the level of FFA in the different samples ranged from 1% -32%. The experience and knowledge gained during this experiment resulted in a focus from the group on small-scale production (less than 1 million L/year) as a viable and sustainable model [2].

In response to the insatiable demand for vegetable oils and the limited potential of low cost feedstocks, a range of new feedstocks is investigated as a future supplement to traditional biodiesel production.

2.6.2 Future Feedstocks:

Among the most interesting is algae cultivation as a potential replacement to land crops and biodiesel from wood in the BtL process (Biomass to Liquid).

The technolgy that is closest to commerilazation is the BtL technology. In this process, wood chips converts into “syngas” (carbonmonoxide and hydrogen) in a gasification process. This can especially be of interest to Finland, Norway and Sweden since they have significant biomass resources located in the forrest. In a recent report on the potential of biofuel in aviation from the consulting company “Rambøll”. The report concludes that it would be technically and economically feasible to produce jet fuel from Norwegian forests within 2020-25 using the Fischer Tropsch process [22].

Algae may be an alternative, sustainable and promising source of feedstock in the future. Algae are attractive because of their extremely fast growth rate, possibly high lipid content (80 times more vegetable oil per unit area as f.ex canola). In addition, it has a limited requirement of farmland; it can be cultivated in areas unsuitable for food production. Furthermore, they have a reduced requirement for fresh water and perhaps an important thing the uses carbon dioxide for nutrition contributing to the photosynthesis. This could be considered both as a way of carbon capture and as a viable method of cultivating algae on land. Despite these advantages, there are still many issues to be solvedalgae. Algae still holds great promise for future biodiesel and biomass production. However, the economic aspects of algal production require further development and it will requires several years of further research and development before they can build plants for the production of algal fuel on a commercial scale [23].

2.7 Production methods for biodiesel:

The objective behind this part of the thesis is to provide a walkthrough of the methods of producing biodiesel (industrial and heterogenous) and their respective process steps with a focus on the industrial approach using homogenous technology. For the industrial process, a detailed description of the process is presented. Regarding the heterogeneous approach, a description of the two process developed by companies using heterogenous technology.

2.7.1 The conventional biodiesel process:

Currently, the majority of biodiesel production plants use refined vegetable oil, methanol (MeOH) and NaOH (Sodium hydroxide) or KOH (Potassium hydroxide) as the three primary raw materials. Due to the lower cost, alkaline/basic (KOH, NaOH) homogenous catalyst for the transesterification reaction is most widely used. This is because it has the advantage of being many times faster than other commercially available catalyst such as sulfuric acid. However, the sulfuric acid has a high tolerance to FFA and does not form soap when used in waste vegetable oil. The disadvantage of alkaline catalyst is that the catalyst is intolerant to FFA in the feedstock. In order to overcome this issue, a different catalyst, or pre-treatment may be required to reduce the FFA content to an acceptable level.

Figure 2.7 illustrates a typical biodiesel plant from Alfa Ageratecs. Alfa Laval Ageratec systems are intended for industrial-scale production of biodiesel with a throughput corresponding to 330 days of full-rate operation per year.

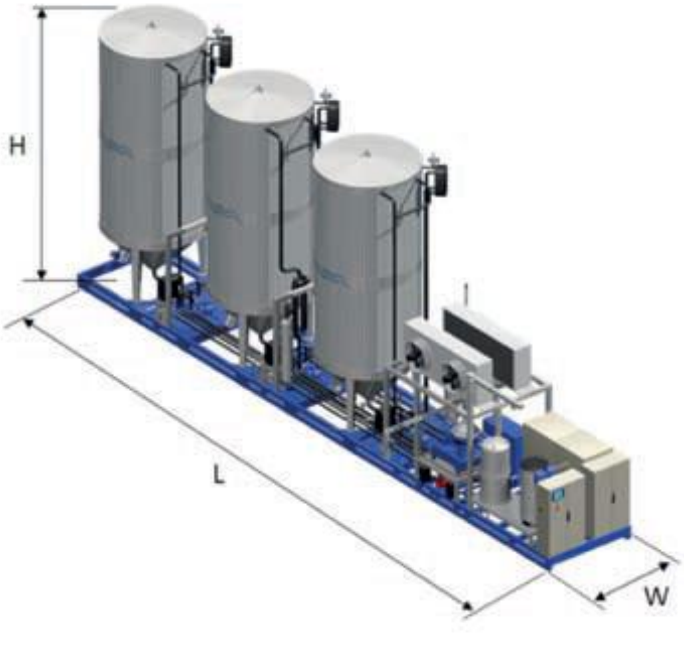
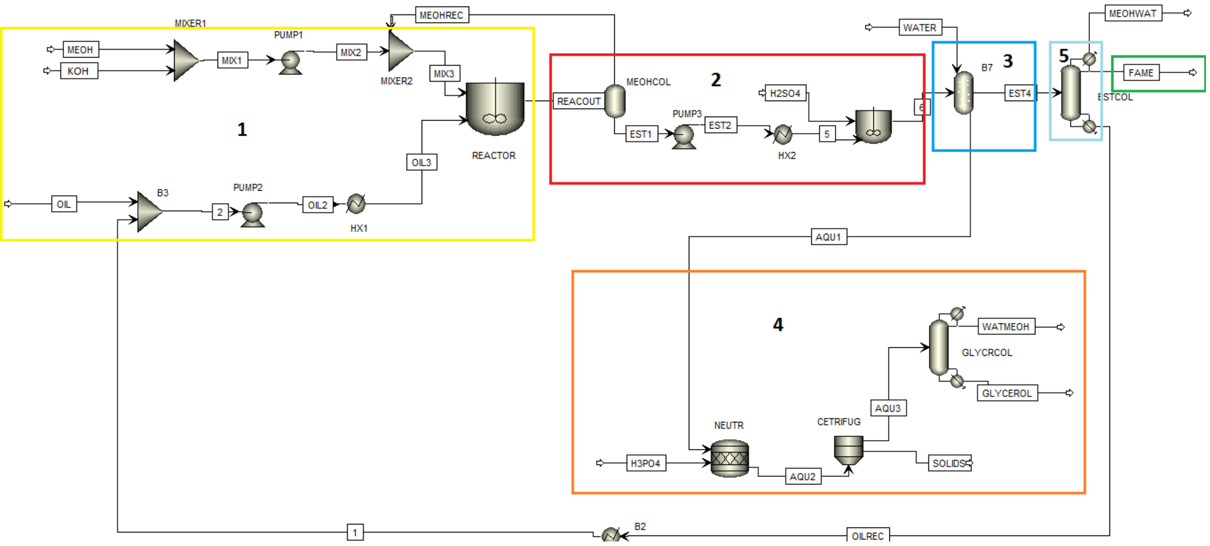


Figure 2.7: Ageratecs biodiesel process plant based on homogenous technology [24].

Process steps in a conventional biodiesel plant:

The process divides into three production phases: **reaction, separation**, and **purification.** In adittion to the treatment of glycerol and methanol recovery. In Figure 2.8, a flowchart (made in Aspen) can be seen that explains the biodiesel process with its respective process steps.



Figur 2.8: Flowchart for the production of biodiesel based on homogenous technology.

1. *Reaction (reactor):*

Analyzing the process described in Figure 2.8, in the yellow area the methanol, the alkaline homogenous catalyst and the feedstock are mixed in a reactor for one hour at approx. 60 °C. Here the transesterification takes place at their respective conditions and biodiesel along with it respective byproducts is formed. Todays industrial plants (more than 4 million lt/year) uses a continuous stirring reactor (CSTR). While smaller plants employs a batch reactor with a fixed volum.

The reaction generally includes two steps:

- 80% of the total amount of methanol and the homogenous catalyst are mixed into the feedstock.
- The reactor output stream leads to the removal of glycerol, before mixing in the remaining 20% of methanol.

Often, after the completion of the transesterification, water is added to the reaction mixture to improve the glycerol separation [25].

2. Separation:

FFA-separation and *removal of glycerol*: After the reaction, the next phase is the separation of biodiesel and glycerin in the red area of Figure 2.8. Biodiesel is non-polar and less dense than water; glycerol is polar and denser than water meaning a separation can be preformed. Much of the glycerol produced from the reaction can be mechanically removed (centrifuge) or via a two phase, liquid-liquid separator (settling tank) due to substantial differences in density compared to FAME.

The separation of FFA is a step where an acid (f.ex sulfuric acid) to remove the remaining FFA in the biodiesel by neutralization of the residues from the basic catalyst and separates soap residue that could have been formed during the reaction. The soap reacts with the acid forming salts and FFA given by the following reaction.

$$Soap + FFA + Acid \Rightarrow \text{salt} \qquad (2.1)$$

Settling Tank:

A settling tank uses gravity to separate substances based on density as seen in Figure 2.9. This is a low-cost, passive system requiring little to no added energy other than that already possessed by the effluent. It may be possible to perform glycerol separation co-currently with methanol recovery. Feasibility will likely depend on the reactor flow rate and rate of separation, which dictate the size of the settling tank needed for the glycerol to sufficiently separate from the FAME before leaving the settler [25].

Figure 2.9: Separation of glycerol (bottom) and biodiesel (upper) in a settling tank [26].

Centrifuge:

A centrifuge uses energy to separate substances based on differences in density, with the more-dense liquid (in this case glycerol) pushed toward the outside of a cylinder via centrifugal force imparted by a spinning rotor or by the cylinder itself rotating. Centrifuges have moving parts and thus will likely both cost more and require maintenance more often than settling tanks; however, centrifuges offer very effective separation.

After the separation, the excess alcohol is recovered and recycled, but further purification is needed to reach the high level of purity necessary to meet the standards, which is accomplished by the final biodiesel purification system. One-step is the neutralization and removal of methanol from the FAME stream. The first step to introduce acid (sulfuric) to the stream [25].

This will neutralize the stream meaning reduce the Ph-level and produce salts. Then methanol impurities are via an extraction process through an evaporator.

3.Purification:

In the purifying phase depicted in the blue area of Figure 2.8, the purpose is to remove any remaining impurities in the biodiesel, such as residual methanol, glycerol, salt, and catalyst. The biodiesel purification system must be capable of removing these contaminants to levels low enough to meet all standard set.

Washing:

The most widely used purification method of FAME is a wash cycle and involves the rigorous mixing of water with the biodiesel product and a following separation. The water wash helps to remove any remaining contaminants like salts from the FAME. The removal of the salts occurs during the wash cycle, while the FFA remain in the biodiesel. Neutralization of the mix before washing reduces the amount of water needed and minimizes the emulsions produced. The main advantage of this method over the others is the low material costs of distilled water and separation vessel [25].

Disadvantages include the difficulty of converting the process into a continuous method. This is caused by slow cycle times due to the need for multiple wash cycles, non-polar contaminants can be left behind in the biodiesel, high operating costs associated with removal of all traces of water in order to meet the required specifications, and the cost associated with treatment of the wastewater [27].

After washing, the water left in the biodiesel is distilled off under vacuum.

Ion exchange:

An ion-exchange resin column is an alternative to washing. Its main application is to remove the glycerol and other contaminants from the FAME. Ilustrated in Figure 2.10, the resin (purple spheres) is prepared in a purification column and the unpurified biodiesel passes through it. The polymer resin absorbs all of the glycerol and impurities while allowing the biodiesel to pass though until the resin becomes saturated. One kilo of resin is able to purify 900 to 1600 times its own weight of biodiesel depending on the amount of impurities [58].

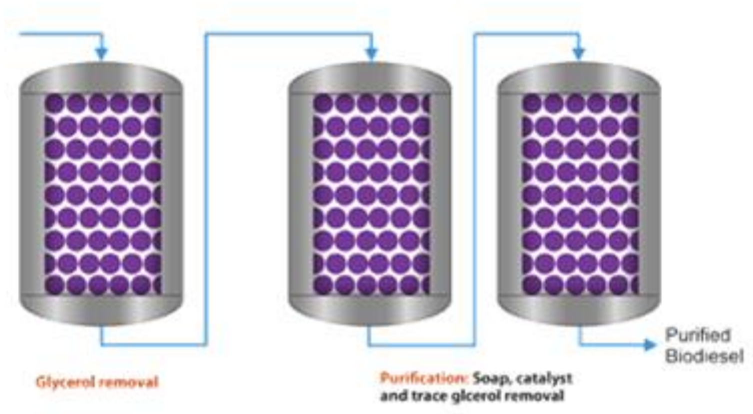


Figure 2.10: Closer look at a set-up of ion - exchanger columns using Amberlite resin [28].

An added benefit is that this resin can be regenerated by a methanol wash cycle that removes the glycerol from the column and returns the resin to its original state. Downsides to this method of purification are the costs of the Amberlite resin at 13 $ pr kg.

4.*Treatment of Glycerol:*

In the orange area in Figure 2.8: the diverted stream from the separator contains 50% glycerol or more. In addition the stream contains some excess alcohol (methanol) and the catalyst and soap formed during the reaction. This crude glycerol has little value and its commercial application is limited. Therefore, there is a need to obtain a higher purity of glycerol. The first step is to introduce acid to the waste glycerol stream. This will convert the soap into FFA and salts by neutralization [25].

FFA are not soluble in glycerol and is therefore separated to the upper layer of the mixture. Where the FFA is removed and then recycled. Still, the salts are in glycerol.

After acidification and removal of FFA, in addition an evaporator extracts alcohol impurities. The product will be glycerol with an approximate 85% purity, which allows it to be transported to a glycerol refining plant. In such a plant, further distillation and removal of salt can lead to a glycerol purity increase between 99.5 to 99.7% purity [25].

5. Methanol recovery:

The amount of unreacted methanol functions as a solvent causing a delayed separation of the products. However, excess methanol is usually not removed from the mixture until a fully separation of FAME and glycerol is achieved. To help tilt the FFA and triglyceride reaction equilibria toward the desired FAME product, the reactor feed contains significantly more methanol than the required stoichiometric amount. The excess of methanol is added in order to shift the equilibrium in the direction of the product (Le Chateliers). The reaction also be shifted by increasing the temperature, but degradation (breaking of molecules into it's elements) of glycerol will hinder the operating range of the temperature.

As a result, it is beneficial that the unreacted methanol is diverted and recovered. The reason alcohol recovery is applied; the first of which is the produced fuel's quality. If unused alcohol remains in the reactor effluent, the product will contain excessive low-boiling alcohol, which would adversely affect the diesel combustion characteristics. The second reason for this recovery is cost; amounts of unreacted methanol would be unnecessarily wasted [25].

Types: *Vacuum-Assisted Evaporative Distillation*

Methanol, removed from the product stream of FAME and glycerol will bound together with the water produced during the process, since it miscible with water. This methanol-water mixture pass into to a distillation column. In the column, the methanol becomes separated from the stream as seen in the bright blue area in Figure 2.8 and reused in the reaction.

Other alcohols like ethanol or isopropanol could be employed in this stage, but is more difficult to separate due to the azeotropic mixture which is created with water it is considered to contribute to making the process more complex [25]. By utilizing a vacuum distillation, one uses the fact that the flash point decreases with a decreasing pressure. By using vacuum, the system requires less energy. As the reactor stream out is generally is warm, resulting in a fairly, energy-efficient separation that requires only some vacuum. As a sealed system, there is little risk of methanol escaping into the atmosphere.

The final biodiesel product is then dried in the green section of figure 2.8 and tested to check if the EU standard (see appendix A) is achieved before being shipped.

2.7.2 Heterogeneous biodiesel production:

Around 90% of the current biodiesel production is using a homogeneous catalyst. Of the remaining 10%, the majority is empolying heterogeneous catalysts. The larger the capacity of the plant the more likely the plant will use the homogenous technology. The main difference between heterogeneous and homogenous approach is that the heterogenous catalyst has the ability to be regenerated and used several times.

Axens, a french company has shown that heterogenous catalysts work on a commercial scale in 2005 in the technology called “Esterfip-H”. The layout illustrated in Figure 2.11 of an Esterfip-H plant consist of two packed bed reactors (R1 and R2) each containing an equal amount of heterogenous catalyst (zinc aluminate oxide). The operating temperature is at 210℃ and 62 bar. The partially processed stream is transported to a settling tank after passing through the first reactor and some glycerol is removed in order for shifting the equilibrium of the transesterification reaction. This will result in a more complete transesterification with a higher yield [29].

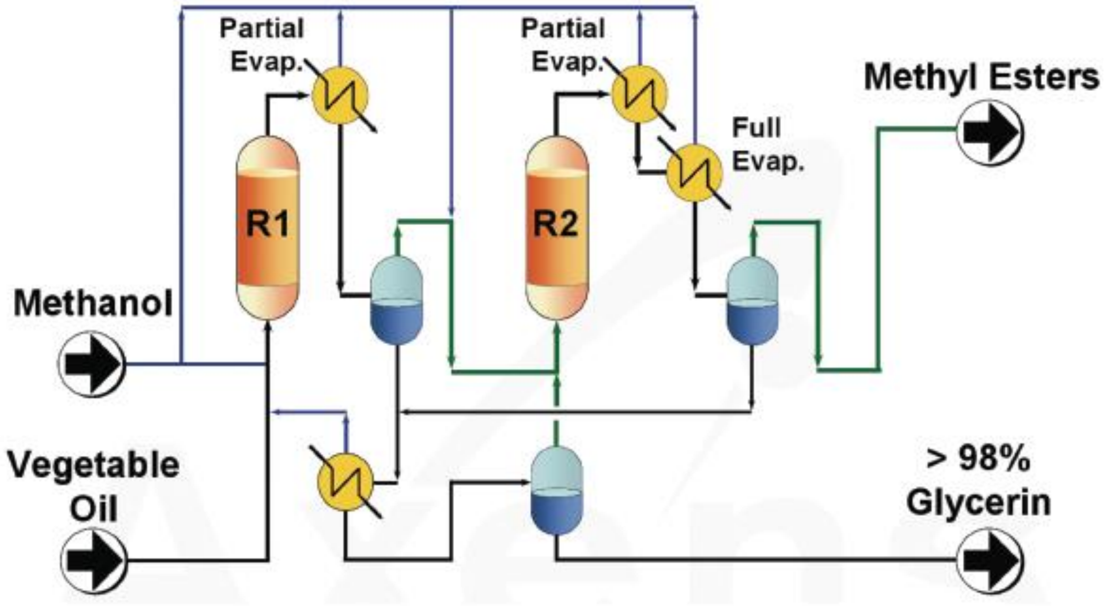


Figure 2.11: The layout of an Esterfip-H plant [29].

During the second step, the transesterification occurs at a slightly higher temperature (compared to the conventional homogenous technology), in the presence of an excess of methanol, which is in later process step removed by vaporization and recycled back to the reactors. The reactors are identical and utilizes the same catalyst. Because of no soap formation in the process, washing the fuel is not necessary. The glycerol needs no further processing to reach technical grade, so several process steps used in a conventional plant are eliminated. The four main advantages of the Esterfip-H technology are [27]:

- Purity of the glycerol is above 98%.
- The yield is higher than with homogeneous catalysts.
- There are no side reactions producing soap.
- Long lifetime for catalyst, keeping the catalyst cost below €4 per tons of fuel produced.'

However, there is a major issue; like the conventional process Esterfip-H technology can only use refine oils.

Another biodiesel company "Benefuel" has developed a catalytic process "ENSEL" in 2006 based on the heterogeneous approach. Benefuel's ENSEL process combines esterification of FFA and transesterification of triglycerides into a single process step.

The process involves three main components [30]:

- Packed bed reactors (PBR)
- Oil–glycerin separation stage
- Pair of distillation columns.

The schematic of the Ensel process is shown in Figure 2.12, begins with introducing a feedstock in to a PBR, The catalysts used are based on metal oxides This occurs at operating conditions of temperature (190 to 210 ℃)pressure (40 to 50 bar) and flow rate (weight hourly space velocity = 0.4–0.6/ hr). As the the reactants is exposed to the active sites on the catalyst's surface that accelerates the conversion of feedstock into FAME.

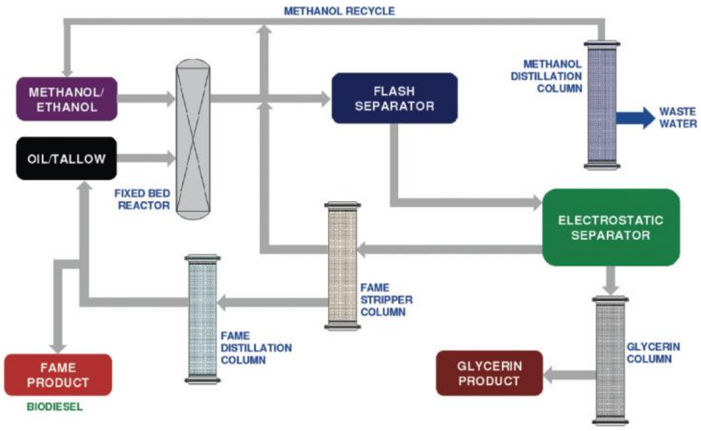


Figure 2.12: Flowchart of Benefuels Ensel process [31].

As the liquid stream exits the reactor, the pressure is reduced, and the methanol (and water if the feedstock contains FFA) quickly flash to vapor and are carried directly to the methanol refining distillation unit.

The separation stage is identical to the conventional process as previous mentioned in chapter 2.7. The recovered glycerol can be pumped to a small vacuum distillation column while the volatiles, consisting mostly of water and methanol, is transferred to a methanol recovery system.

Distillation or refining of the recovered oil phase is the last stage of the process. Refining the FAME and removing any higher boiling impurities (f.ex unreacted glycerol) requires higher temperature. Because of the higher temperature and pressure in the process the fixed equipment costs are higher, but according to Benefuel the benefits of this process is due to its simplicity, no need for further processing in order to upgrade the biodiesel, no need for pre-treatment of the feedstock and no need for a glycerol-treatment unit. The total investment cost for a bio-refinery using Benefuel technology is estimated to be less than the fixed cost for a typical biodiesel production plant using conventional technologies in order to process a feedstock with a high FFA content [29].

Advantages of the Ensel process:

- **Expands feedstock choice** - process a much broader variety of feedstocks, like waste vegetable oils.
- **Increases process efficiency** - no by-products are created, no water is used and it is a continuous flow process with a nearly complete recovery of FAME and glycerol.
- **Provides the lower cost of production**

What the esterfip-H and Ensel process shows is that there is an alternative to the conventional technology in industrial scale plants. However, these processes operates at relativly high temperature and pressure, making it quite energy demanding. Therfore a lot of attention is on developing new catalysts that operates at lower temperature and pressure.

2.7.2 Small Scale Production:

The basis of this approach is to use highly efficient small-scale technology at the feedstock production point. This approach capitalizes on the numerous benefits offered by biodiesel that are often lost in large-scale production, but is more labour intensive [32].

- Regional development
- Reduction of transportation costs
- On-site energy (electricity and heat) production
- Use of by-products
- Low cost integration into existing operations

The small-scale approach is not something new. The USA has in the recent years seen a blooming of small-scale biodiesel communities all around the country. The plant like the BioPro 150 from "Springboard biodiesel" as seen in Figure 2.13 is one of the most popular plants on the marked. The technology behind the BioPro is the homogenous approached discussed earlier [33].

Specification:

- **48 Hours From Start To Finish**
- **Processes, Washes, & Dries Biodiesel**
- **Up To 150 L Batches**

Figure 2.13: BioPro 150 [33].

The specification of this biodiesel processor will act as a comparison when creating a new production system. As this model seems to have found the set of conditions that appeales to the Do it Yourself «DIY» biodiesel marked. In the next part of the thesis, a catalyst review is preformed where the aim is to locate a catalyst that is more suitable for a small-scale plant.

3. Heterogenous catalyst review and concepts:

As an introduction to the review, some understanding of crucial concepts requires more exploration. The concepts are conversion, yield, kinetics and activity (Arrhenius). Understanding these concepts will contribute to a wider understanding of the following catalyst review. By applying, these terms to a catalyst and by studying these related it to time; one can determine a suitable catalyst for biodiesel production.

3.1 Conversion and yield:

Conversion can be viewed as a mean to measure the amount of the reactant that has been converted into a product. Yield is illustrated by equation 3.1 [34].

$$Conversion = \frac{Amount\ of\ reactants\ consumed}{Amount\ of\ inital\ reactants} \qquad (3.1)$$

In most cases when studying a reversible reaction, the equilibrium conversion is the optimal conversion or maximum. Conversion of vegetable oil in transesterification reaction can be displayed by the three reversible reactions R1, R2 and R3 seen in the following page.

If the reactants do not react completely and results in a smaller amount of product formed than anticipated. The amount of product achived during the reaction is the actual yield. As a example the yield in the biodiesel process is illustrated by equation 3.2:

$$Yield = \frac{Moles\ of\ metylester\ formed}{Moles\ of\ oil\ supplied} \qquad (3.2)$$

Yield can be seen as measurement of the performance of a plant.

3.2 Biodiesel kinetics:

Kinetics refers to the reaction rate and progress of a chemical reaction. In order to describe and understand the behavior of a reaction or kinetics, one wants to observe how the reaction rate varies as the reaction progresses and derive a rate law from the collected data. A rate law is a mathematical expression that depicts the reaction progress. In general, rate laws are determined from data and observation gained from experiments [34].

The reaction rate for a chemical reaction is the measurement of the change in concentration of the reactants or the change in concentration of the products per unit time.

The majority of the chemical reactions follow one of three “differential” rate laws. Each rate law contains a constant, k, know as the rate constant [34].

By applying these terms to biodiesel production, it’s accepted that the transesterfication reaction precedes via three consecutive reversible reactions.

$$TG + 3\,Methanol \overset{k}{\Rightarrow} Glycerol + 3\,Metylester \qquad (3.3)$$

$$\text{R1:}\,TG + Methanol \overset{k}{\leftrightarrow} DG + Metylester$$
$$\text{R2:}\,DG + Methanol \overset{k}{\leftrightarrow} MG + Metylester$$
$$\text{R3:}\,MG + Methanol \overset{k}{\leftrightarrow} Glycerol + Metylester$$

Where DG, MG and G represents diglycerides and monoglycerides respectively. Reactions R1 to R3 are first order with respect to the catalyst-alchol concentration in both forward and reverse directions. At each step, a glyceride molecule reacts with an alcohol molecule (methanol) to produce one molecule of glycerol and three molecules of fatty acid methylester. The esterfication reaction is given by the following reaction (3.4) [34]:

$$Free\ fatty\ acid\ (FFA) + Methanol \overset{k}{\leftrightarrow} Water + Metylester \qquad (3.4)$$

3.3 Activity of a catalyst:

An important tool in chemical engineering is the”Arrhenius equation”. It explains the dependence of the rate constant k of chemical reactions to the temperature T and activation energy E_a, as shown in equation 3.5.

$$k(T) = Ae^{-\frac{E_a}{RT}} \qquad (3.5)$$

$k(T)$is the rate constant, A is the frequency factor, $E_a$is the activation energy, R is the gas constant and T is the measured temperature in kelvin.

The Arrehenius equation has many application areas (modelling temperature-variance of diffusion coefficients). In the biodiesel research, this is applied to find the activity of a new catalyst based on experimental data.

3.4 Catalyst deactivation:

The total activity of catalyst or concentration of active sites on the catalyst surface will decrease over time. The rate of this loss of active sites is called catalyst deactivation or decay. Knowledge related to the deactivation of a catalyst can contribute to wider perspective when designing a reactor, optimization of a process and deciding rate law parameters etc [34].

The activity of the catalyst is depicted by equation (3.6):

$$a(t) = \frac{r\prime(t)}{r\prime(t_0)} \qquad (3.6)$$

a(t) is the acitivty of the catalyst, $r'(t)$ is reaction rate at a given time, $r'(t_0)$ is the initial reaction rate.

Deactivation to the catalyst can be caused by fouling, poisoning and sintering. An example of deactivation in the biodiesel process is swelling of the catalyst caused by water in the feedstock or produced in the esterfication reaction. To address the issue of deactivation, a larger amount of catalyst in the reactor may be considered to obtain a longer overall catalyst lifetime or f.ex provide sufficient pretreatment steps to reduce the amount of polluntants that accelerate the decay rate [34].

3.5 Comparisonment of heterogenous catalysts:

The purpose of this review is to identify a suitable catalyst for small-scale biodiesel production. There is a substantial amount of different catalysts that can catalyze the esterification and transesterfication, each with its own advantages and disadvantages. From Figure 3.1 the main genre and subgenre of the catalysis in biodiesel production are illustrated. In this review, the focus will be on the heterogenous base, acid and the ion-exchange resins.

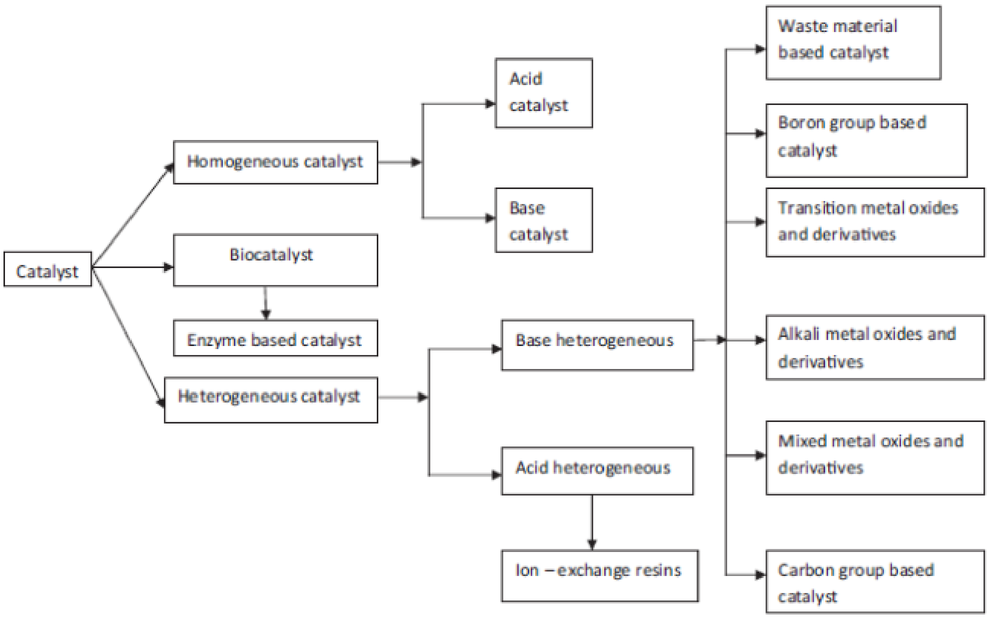


Figure 3.1: A categorization of catalysts [35].

There are many criteria to take in consideration when choosing a catalyst. The first consideration was whether the catalyst forms a homogenous or heterogeneous mixture with the reaction mixture to reduce total production time, a heterogeneous (solid) catalyst is hugely beneficial because the process avoids the washing step and the regeneration of the catalyst regenerated for use in later reactions, minimizing costs. Cost is one of the most important criterion when deciding on the most appropriate catalyst. Research from the last decade has led to the discovery of many catalysts that achieve high FAME conversion, but cost considerations alone severely limited the number of possible catalysts for prototype reactors [35].

An important property is the catalysts activity meaning its ability to catalyze the conversion of WCO to FAME. Each type of catalyst has different amount of active sites per unit of mass of the catalyst. Consideration was mainly the catalyst tolerance to FFAs, water, and other contaminants. The final consideration made when choosing a reactor catalyst was the solubility of the catalyst in the biodiesel product. Many solid metal catalysts under consideration have moderate solubility in biodiesel requiring additional purification processes that add significant costs.

Similar to homogeneous catalyst, heterogenous alkaline-catalysts are more active than their acid counterparts. In this review, the focus is on the most tested heterogenous alkaline and acid catalysts

3.5.1 Heterogenous alkaline catalyst:

In recent years, extensive research in the area of solid alkaline catalysts as direct replacements for current alkaline homogeneous catalysts has been conducted. However, to this day there are few commercial biodiesel production plants currently using solid alkaline in the transesterification step. The main groups of solid alkaline catalysts is [35]:

- **Alkaline earth metal compounds:** Oxides, carbonates,
- **Inorganic materials:** Zeolites
- **Transition metal compounds:** Oxides

There is a whole range of other solid alkaline catalysts wich is under a considerable research. However, these will not reviewed because of their availability or price. Alkaline earth metals such as Be (Beryllium), Mg (Magnesium), Ca (Calcium), Sr (Strontium) and Ba (Barium), and their oxides and derivatives has promising potential to be an good alternativ catalysts in biodiesel production. Among the more popular alkaline earth is the oxides CaO, MgO and SrO.

3.5.1.1 Solid calcium oxides:

Calcium oxides (CaO) is most widely used as catalyst for transesterification among the alkaline earth metal oxides. Some trials with CaO reports of an achievd yield of 98% FAME during the first cycle. The activity of such CaO is further determined by its calcinations temperature. The number of active sites can be increased by minimizing the individual crystal size of the catalyst by calcination; thermally pre-treating the catalyst at temperature ranging from 500-900°C this is related to calcium oxides. However, reusability of a CaO catalyst for subsequent steps is represents an uncertainty for effective application in biodiesel production, but CaO has higher activity, lower solubility, lower price, and is easier to handle than the conventional catalyst KOH, making it an interesting candidate for future research.

Interestingly CaO derived from waste eggshell by calcination as seen in Figure 3.2 has been reported as a very suitable catalyst for transesterification [36].

Figure 3.2: Eggshell are crushed into a powder and then calicinated to CaO [37].

During the test with CaO derived from eggshell, the reaction was set at 65 ◦C, with an oil/alcohol ratio 1:9, catalyst loading 10 wt%, for a FAME yield 97–98%. The CaO catalyst could be reused for 17-reaction cycle when using used palm oil [35].

A recent identification of the compound calcium glycerolate - "which notably surpasses calcium oxide and glyceroxide in stability." after the first reuse cycle, only calcium diglycerolate showed a good catalytic activity and structure maintenance. This compound also presented good activity until a third reuse cycle (82.8%) and after that, being completely decomposed into a mixture of inactive calcium carbonate and hydroxide. The decomposition after a third reuse cycle is not a great problem because the compounds formed could be calcined to reform the CaO and the glycerol synthesized as co-product in the transesterification of soybean oil can be used to react with calcium oxide to obtain a new batch of calcium diglycerolate. At the present time, the focus is to optimize the catalyst for potential industrial application [38].

3.5.1.2 Nano catalyst Calcium containing silicate mixed oxide-based catalyst:

Research on mixed metal oxides in confined spaces provided the necessary platform to custom design a new class of catalysts that can convert mixed feedstocks and work under milder conditions. The company “Catilin” recently launched the Nanocatalyst “GoBio T300” illustrated in Figure 3.3. This novel solid catalyst is nontoxic and is a direct replacement for conventional catalysts used in biodiesel production. It is a calcium-based solid catalyst with an average particle size of approximately 10-15 microns [39].

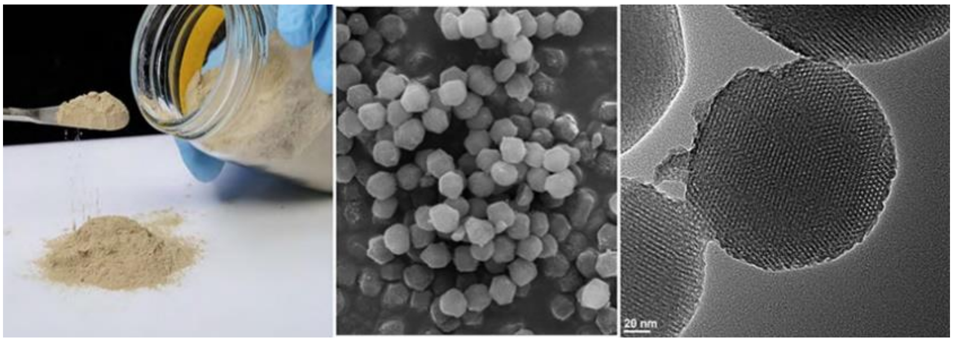


Figure 3.3: From left to right: (a) T300 catalyst, (b) scanning and (c) transmission electron microscopy images of catalytic nanoparticles *[40]*.

The T300 catalysts operate at industry standard pressures and temperatures (60 degrees and 1 bar), and can be removed by filtration. T300 has demonstrated effective transesterification using feedstocks containing up to 1% FFA. The maximum FFA percentage at which T300 is effective will vary depending on the overall composition of the feedstock used. In Figure 3.4

the kinetics of the T300 catalyst in the presences of methanol and oil with relative low content of FFA is illustrated [41]:

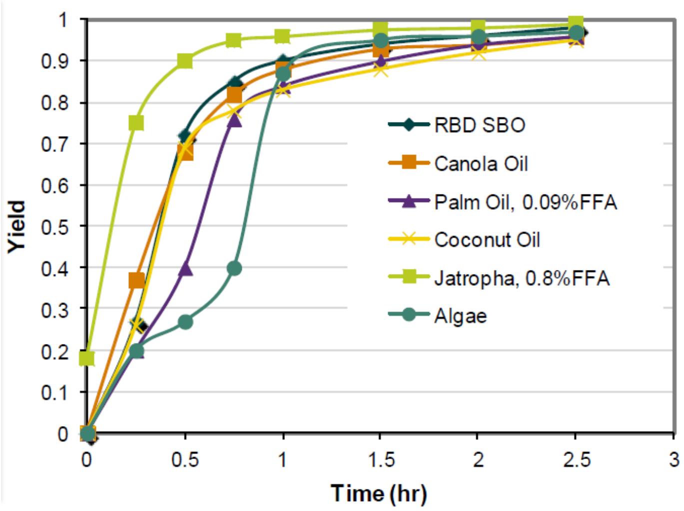


Figure 3.4: Kinetics of the T300 in methanol and different oil with low FFA content [41].

The catalytic activity is similar to Sodium Methoxide, with a residence time of 0.8 to 1 hour. In addition the T300 is recyclable and lab tests have shown a high catalyst activity for up to 16 cycles without the addition of fresh catalyst.

3.5.1.3 Solid Magnesium Oxide and Solid Strontium Oxide:

Investigation into Magnesium Oxide (MgO) as an inexpensive catalyst for the transesterification of waste vegetable oil to biodiesel led to the discovery that MgO has relatively high solubility in the FAME product. MgO has shown to possess catalytic activity for synthesis of biodiesel. It was observed 92% biodiesel yield with MgO catalyst, using a molar ratio of 12:1 methanol to oil with 5.0 wt % of the catalyst in 1 h. Data was obtain showing that MgO worked efficiently in batch reactor at ambient temperature during the transesterification reaction [35].

Strontium oxide (SrO) was studied as a potential heterogeneous catalyst for biodiesel production due to its strongly basic nature. It was found that SrO is far more active than its CaO neighbor. In 2006 researchers from the Department of Chemical Engineering Tsinghua University, Beijing observed that SrO displayed high activity and insolubility when mixed in with methanol and vegetable oil (soybean). They demonstrated that SrO could catalyze the transesterification of soybean oil and reported to achieve a yield of 90% FAME after a reaction time of 0.5 hr, a temperature of 65 °C, with methanol/oil molar ratio of 12 and 3 wt.% catalyst loading. Based on the results, SrO could be a suitable heterogeneous catalyst for biodiesel production [42].

3.5.1.4 Sodium silicat:

F. Guo et al tested Sodium silicate in the transesterification of soybean oil. During the thermal pretreatment or calcination, the temperature set to 400 °C for 2 h was observed to be optimum conditions when preparing the Sodium silicate catalyst. The researches observed that solid Calcined Sodium Silicate (CSS) was successfully applied to produce biodiesel from vegetable oil, The maximum biodiesel yield of around 98 wt% was achieved with 3.0 wt.% of sodium silicate catalyst, a molar ratio of methanol to oil of 7.5:1, and a reaction time of 1 hr at 60 °C. It was observed that the CSS displayed a higher activity then a traditionally homogenous alkaline in the first reaction cycle. However it was observerd a considerable loss in activity when the CSS was recycled for more than 5 times. In addition of being a low-cost solid alkaline catalyst to catalyze the transesterification of crude oil (some amount of water and FFA), the CSS functions as adsorbent to FFA and could therefor contribute to the purification of the final product [43].

3.5.2 Heterogenous acid catalysts:

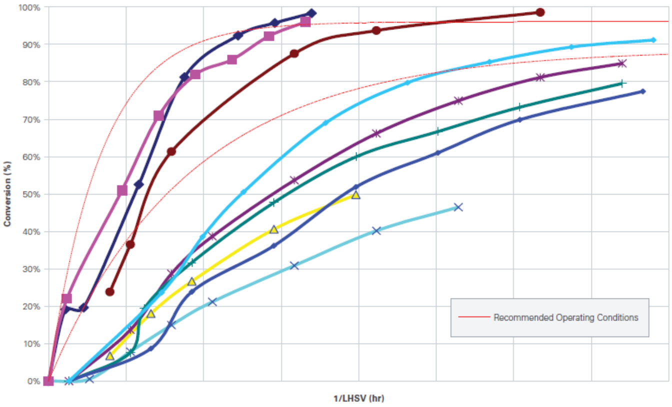
Like solid alkaline catalyst, solid acids is investigated in the search for solid catalysts in applications in the production of biodiesel to catalyze the esterification reaction. Solid acid catalysts have the potential to replace strong liquid acids and eliminate the corrosion problems and consequent environmental hazards posed by the liquid acids. Several recent studies have reported the technical feasibility of biodiesel production via heterogeneous acid-catalyzed transesterification. For a solid catalyst to be a promising candidate to replace sulfuric acid for the esterification of FFA, it must have a high concentration of strong acid catalytic sites (sulfonic acid groups) and have high thermodynamic stability. Also of interest is the number of weak acids that may alter the chemical environment near the active surface sites, which could possibly improve the catalytic swelling properties.

3.5.2.1 Functionalised Polymers (Ion Exchange Resins):

Functionalised polymers are known to be active catalysts in a number of esterification reactions. A large range of functionalized polymers is available from different chemical companies with a number of these trialed in the esterification of FFA present in low quality feedstocks. These resins have a high affinity for the long carbon chains of FFA because of the hydrophobic character of their polymer backbones. The acid sites are almost exclusively sulphonic acid groups grafted onto various types of polymer backbones (substrates).

The “Dow chemical company” offer a range of these industrial catalysts under the name Amberlyst and Dowex. Further development of these catalysts has resulted release of

AmberlystBD20, an esterification catalyst develop specifically for biodiesel production. Data gathered from a test plant resulted in porposed kinetic model as seen in figure 3.5. The test condition in this plant was: FFA content in feedstock = 1-40 %, MeOH: FFA-ratio= 5-20 and the temperature between 85 -105°C.



Figur 3.5: The resin Amberlyst BD20 and its kinetics during a residence time of 1 hour [44].

This catalyst reportedly outperforms all other currently available solid acid catalysts and at least matches the performance Sulfuric acid. Furthermore, in addition it has be observered that this catalyst does not deactivated by swelling, remaining stable in FFA, glycerol and triglycerides) [44]. The UMBio-group did an extensive project during the summer 2013, where several polymer catalyst were used for catalyzing the esterification reaction of oleic acid in the presence of ethanol. Of the catalystet tested, the Amberlyst BD20 proved to be the best alternative with an achieved conversion of 54.3% in six hours at 60 °C. From Figure 3.6, a comparrison between sulphuric acid and the amberlyst BD20 is illustrated.

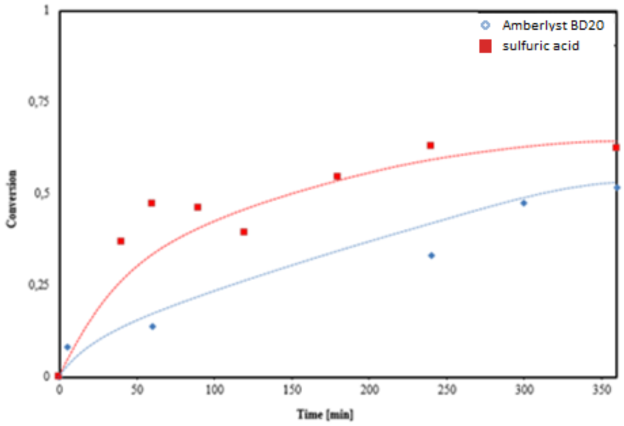


Figure 3.6: Comparison of the conversion of FFA for the Amberlyst BD20 and sulfuric acid. Fixed conditions at Temperature = 60°C; N=3:1, S= 5%; P = 1 bar [2].

One can observe that the sulfuric acid outperforms the Amberlyst BD 20 at the set conditions (six hours, 60°C). From the results gathered from the experiments preformed by the

UMBio group, this catalyst shows potential as ideal candidate for further testing with new operating-condition in order to optimize for achieving a higher conversion rate.

3.5.2.2 Zeolites:

Zeolites are naturally occurring crystalline aluminosilicates. They possess three-dimensional framework structures with molecular pores and channels of uniform sizes. These pores can absorb molecules that fit inside them while preferentially excluding larger ones; thus acting as molecular sieves. This property gives zeolites the ability to exchange ions. For instance, Al3+ replaces Si4+ within the crystalline silica (SiO_2) framework. This replacement produces negative charges within the catalyst framework; thus enhancing catalytic activity [45].

3.5.2.3 Carbon catalyst:

This type of catalyst was developed from a sugar source (sucrose), is inexpensive and is simple to produce. Sucrose was treated directly with sulfuric acid with molar ratio of 9:1 at 25°C. A carbon foam was immediately formed as see in in Figure 3.7 a. The foam was then washed until no sulfate was detected, dried, and sieved. Thermal treatment of the carbon was conducted for some samples under nitrogen at 155°C, 205°C, and 255°C. The finished pretreated carbon catalyst can be viewed in Figure 3.7 b.

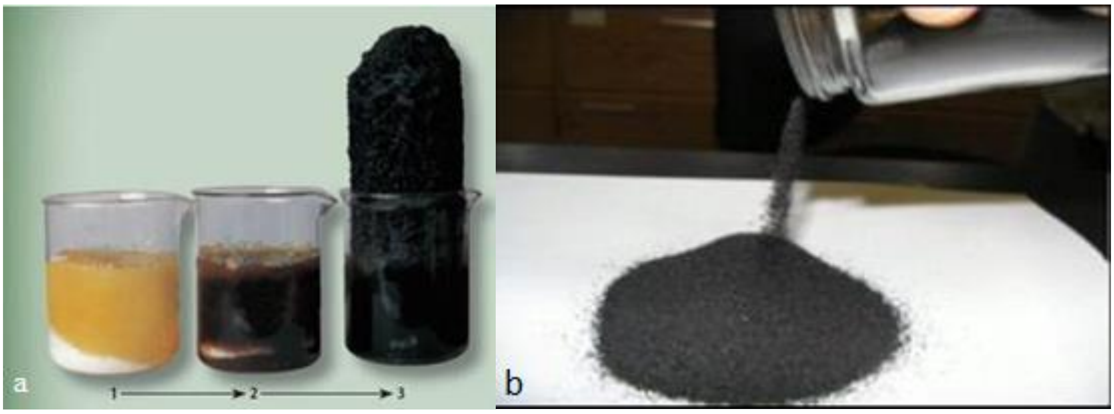


Figure 3.7: The sulphure/sugar mix forming the carbon foam (a) and the cranular carbon solid acid catalyst (b) [46, 47].

The researchers observered a large number of weak acid sites was detetected, ranging from 6-7 mmol/g and a number of strong acid sites was found to range from 0.8-1.2 mmol/g, which compares favorably to commercial solid acid catalysts. The catalysts was then evaluated to commercial polymer catalysts such as Amberlyst and Nafion, and the results illustrated in Figure 3.8. The feedstock used was a soy-based vegetable oil with a FFA content of 15 wt. % [47].

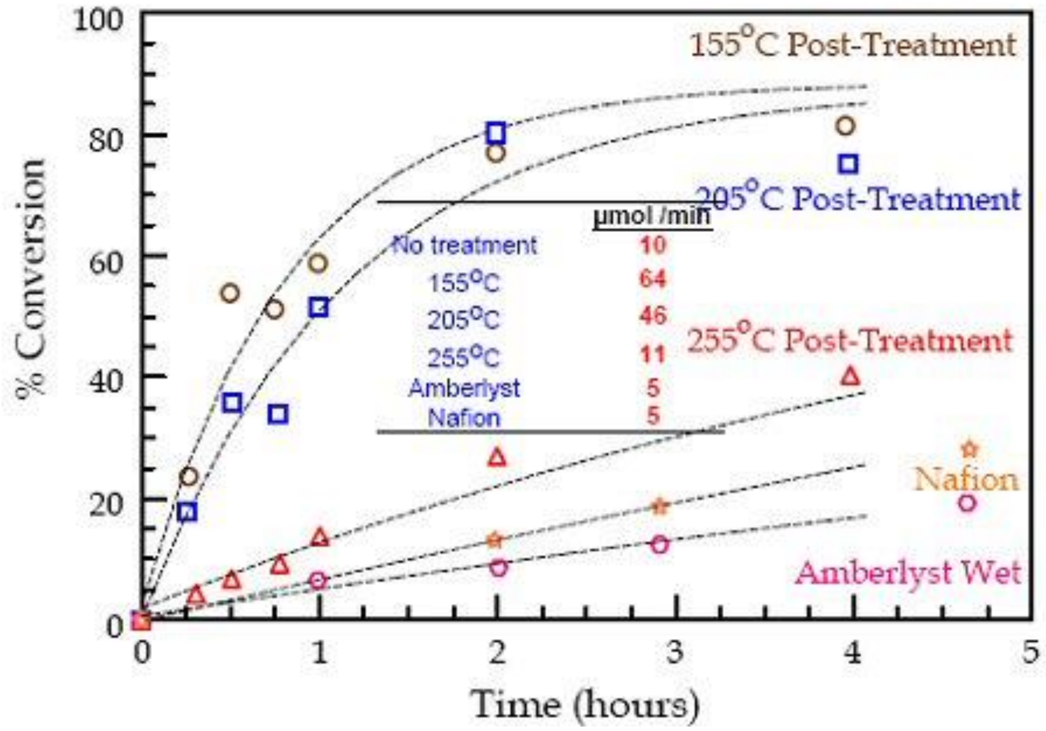


Figure 3.8: Percent conversion versus time for the kinetic studies of the carbon catalysts and commercial solid acid catalysts [47].

The catalyst post-treated at 155°C performed better than the other carbon based catalysts and outperformed Amberlyst and Nafion. The post-treated 255°C carbon had significantly lower catalytic activity than other carbon samples tested, possibly due to degradation. Even if the results shows the potential of the carbon catalyst, the need for further research and development is essential to fully evaluate carbon as a potential replacement for current technology. Several key areas of research were identified, but the most crital point is the Re-usability of the catalyst. A similar experiment observered that the conversion dropped significantly from 88.73% to 26.24% after the 1 st cycle of catalyst reusability test and the conversion continuously dropped to 22.39% after the 2nd cycle of catalyst reuse [48].

Acid catalysts shows a reduced activity in the transesterification reactions, compared to the alkaline catalysts. The lower activity is usually compensated by setting higher operation temperatures. Thus, the design of the solid acid catalyst with economic, versatile, efficient, and economically viable is the major challenge.

3.5.2.4 Solid Zirconium Oxide:

Recent research shows that it is possible that a heterogeneous catalyst could perform simultaneous esterification of FFA and transesterfication of oils in a “one step” reaction system. Solid zirconium oxide (ZrO_2) metal catalyst has recently proven to be a useful catalyst in biodiesel production. Not only does ZrO_2 function as an excellent heterogeneous catalyst for the transesterification reaction of triglycerides to FAME, it simultaneously functions as a catalyst for the esterification reaction. This property gives ZrO_2 a unique advantage over all other catalysts. ZrO_2 achieves high FAME conversion, 90+% at the planned ambient conditions. Furthermore, the effectiveness of ZrO_2 can be improved by modification with specific anions. Sulfated and tungstated zirconium oxides have been found to be most active for FAME conversion. ZrO_2 is moderately resistant to poisoning by water in the feedstock feed and can be heat treated to restore original catalytic activity. ZrO_2 and its modified derivatives have negligible solubility in the reaction mixture, which adds to their favorability as a catalyst for biodiesel production. The current market price for ZrO_2 is very low making a inexpensive option. Still there is one primary disadvantage to ZrO_2, a small particle size. Meaning the required particle size for ZrO_2 to work as an effective catalyst is quite small [49].

3.5.2.5 Evaluation of the heterogenous acid and alkaline catalysts:

A great variety of solid acid/alkaline catalysts have been reported in the literature with a high yield of FAME. However, it is not possible with any of the catalysts presented in this review to possess simultaneously a strong acid/base, high surface area and inexpensive catalyst production. There is need for a compromise in each case. Table 3.1 presents a comparison between the homogenous and heterogenous catalysts.

Table 3.1: Key factors for evaluating the heterogenous vs homogenous catalysts.

Key factors	Heterogeneous (Alkaline)	Heterogeneous (Acid)	Homogenous (Alkaline)	Homogenous (acid)
Reaction rate	Moderate	Moderate	Fast	Slow
Catalyst reuse	Possible	Possible	No	No
Presence of FFA	Moderate	Effective	Sensitive	Effective
Presence of Water	Moderate	Moderate	Effective	Effective
Equipment	Simple	Simple	Complex	Complex
Amount of catalyst	High	High	-	-
Methanol/oil ratio	High	High	Low	Low
Temperature	Low	High-low	Low	Low
Pressure	High	High	Low	Low

In heterogenous technology, there is numerous catalyst alternatives to choose between with only a small fraction mentioned in this thesis. There is also operating parameters such as catalyst loading, mixing method, presence of impurited in the feedstock and the reactiontime that is crucial when designing a biodiesel system. Each of the reviewed catalyst has it own advantages and disadvantages, in table 3.2 a comparison between the solid acids and in table 3.3 the different solid alkaline is presented. The basis for this evaluation is their abilty to be implemented in a small-scale plant. Therefore, factors like price, lifetime, regeneration, activity at lov temperature and water resitance plays a crucial part in the decision making.

The commercial Amberlyst BD20 is a well-tested catalyst that in addition to high activity also have superior resitance to watern making it a very good catalyst candidate. A downside is the price and availability, the price (see appendix D) and it can only be bought through the “Dow Chemical company”. It can also be regenerated with strong acids (hydrochloric, sulfuric, and possibly methane sulfonic). However, catalyst regeneration requires capital and operating expenditures for additional process units, but if the lifetime of the catalyst is several year this could be profitable option.

Impregnated zeolites has much of the same properties as the Amberlyst BD20, but shows lower activity. This could also be profitable in the long term because of a reported lifetime of 1-2 years. Altough carbon catalyst has not nearly the life span as the Amberlyst Bd 20 (hours compared to years) it is so inexpensive,very renewable and also the raw materials is very acessable making it a very a interesting option.

Table 3.2: Evaluation of the solid acids average properties.

Catalyst	Amberlyst BD20	Carbon	Zeolites
Price	High	Very low	Medium
Life time	Long	Low	Long
Regeneration	Complex	Possible	Possible
Operation temperature	Medium	Low	Low
Resistant to water	High	Medium	Medium

The ideal heterogeneous catalyst will have similar if not greater activity than current homogeneous catalysts at mild conditions, inexpensive, widely available and reusable. Of the reviewed solid alkalines catalysts, the commercial nano catalyst (GoBio T300) or calcium oxides shows promising signs of being a suitable catalyst. Similar to the Amberlyst, the commercial T300 represent an effective catalyst, but is a more expensive option. On the other hand it is economical viable in the long run. The primary benefit of using T300 is that the glycerin produced will be of higher purity and, with that, a higher value. For example, after methanol stripping, the glycerin has a nominal purity of at least 95%. The improved value is expected to provide the producer an additional revenue.

Calcium Oxide is the most inexpensive catalyst of the the ones reviewed and shows high activity. It is easy to synthesis and is easily be obtained. In addition, it is possible to regenerate it, but it could be more profitable to use the deactivated catalyst as fertilizer than regenerate it.

Table 3.3: Comparison of the solid alkaline catalysts average properties.

Catalyst	Calcium Oxide	Magnesium	Strontium	Nano catalyst	Sodium silicate
Price	Very low	Low	Low	High	Medium
Life time	Medium	Low	Low	High	Low
Regeneration	Possible	Possible	Possible	Possible	Possible
Operation temperature	Low	Low	Low	Low	Low
Resistant to water	Medium	Low	Low	High	High

By using a solid acid catalyst as pretreatment for reducing FFA content in the oil and a solid alkaline to catalyze the transesterification reaction a suitable system can be designed for producing biodiesel from waste vegetable oil.

4. Proof of concept and Aspen simulation:

4.1 Conceptual design:

To be economically viable the small-scale production plant must be efficient, able to producing high quality biodiesel and by-products as part of a biodesel system. The previous review in chapter 3 has identified that heterogeneous catalyzed production of biodiesel is a suitable approach for the small-scale plant. In this chapter the details for designing a system that filters WCO, converts it to form biodiesel, recovers and recycles un-reacted reagents, and purifies the biodiesel is presented.

4.1.1 System description:

The inability of standard catalysts to handle the FFA in waste vegetable oils is overcomed by developing a two stage heterogeneously catalyzed biodiesel production process. The first stage utilizing a solid acid catalyst like the commercial «Amberlyst BD20» or an inexpensive carbon catalyst to convert FFA to methyl esters and water in the esterification reaction. The second reactor uses a solid alkaline catalyst as the commercial T300 or calcinated CaO as catalysts for the transesterification. These alternative candidates provide good, repeatable conversion at low temperatures. In addition, the synthesizing of CaO is very inexpensive and can be modified to improve its activity [50].

Table 4.1 illustrates some key properties of the raw material that will affect the design.

Table 4.1: Average properties (at standard conditions) of the reactants and products in transesterfication and esterification reaction [51, 52].

Component	Densiy (kg/m3)	Molecular weight (g/mol)	Boiling point (℃)
Vegetable oil (sunflower)	**920**	**872.60 -900**	**176**
Oleic acid	**890**	**282.4**	**359.8**
Methanol	**791**	**32.04**	**64**
FAME	**875**	**292.20**	**>130**
Glycerol	**1126**	**92.09**	**>130**
Water	**1000**	**18.01**	**100**

The data gathered from table 4.1 can be used to formulate a model for the production of 50 kg/hr of biodiesel (see appendix B). This will give a good starting point for a simulation of the plant.

In addition, operation conditions for the esterification and transesterification reaction is crucial for developing and designing a model of the biodiesel plant. Data regarding these conditions is presented in Table 4.2 and 4.3. The data collected is based on experiments preformed with oils of different grades (0.1-20 wt% FFA).

Table 4.2: Operating conditions for the esterification reaction using Amberlyst BD20 [53].

Conditions	
Temperature	**<100 ℃**
Pressure	**<7 bar**
Weight ratio alcohol/oil into reactor	**5-10**
Flow rate (LHSV)	**0,7-1.7**
Residence time	**0.5 – 2 hours**

Table 4.3: Operating conditions for the transesterification reaction catalyzed by CaO [54, 55, 56].

Conditions	
Temperature	**60**
Pressure	**7 bar**
Catalyst density	**3.34 g/cm3**
ratio alcohol/oil into reactor	**7-13**
Residence time	**1 – 3 hours**

The operation data collected in Table 4.1, 4.2 and 4.3 will contributed to setting the ranges for the operation parameters, but also affect the type of equipment and material that is suitable in the biodiesel plant.

4.2 Small-scale plant: The prototype.

4.2.1 System housing:

The system components needs to be attached to an internal supporting framework for keeping the equipment set-up stable and easy to access. In order to provide mobile and rigid plant, a standard 20 ft shipping container is modified to hold the internal structure. The internal structure is evaluated by the following:

- **Able hold all of the components**
- **Easy access to all components**
- **Inexpensive**

The choice was based on a framework donated to project by the Machine section at NMBU seen in Figure 4.1 (a, b). This framework had previously been used to support a centrifuge for a separation lab and had the needed dimensions for the equipment in this project.

Figure 4.1: The framework prototype (a) with a centrifuge and the new framework (b).

From extensive testing of the mobility and weight capability of the rig, the need for improvements to this design was clear and extensive. Mainly the maneuverability was an issue, but it had the ideal dimensions. So an alternative framework design was constructed by NMBUs prototype workshop based on the older version as seen in Figure 4.1(b). The main improvements was a better wheels and powder coated metal frames instead of stainless steel to cut costs. This design can easily be adapted to hold the needed equipment.

4.2.3 Material Storage:

The reactor system will require some raw materials to be stored nearby such as methanol, WCO, waste glycerol, and biodiesel. The material storage must meet a few requirements for the purpose of the design.

- **Sufficient volume**
- **Safe to use**
- **Easily accessible**

After researching the properties of various materials, the result was three alternatives to consider for the design, High Density Polyethylene (HDPE), stainless steel, or glass. Of these alternatives, the HDPE seems like the only suitable candidate. The cost of this material and its ease of access making it a suitable choice. In addition, HDPE barrels are available in many sizes, providing a large range of storage capacity for our materials. The barrel as seen in Figure 4.2 was given by the company "Noreko" and has a volume of 250 liter. A total of three barrels was provided.

Figure 4.2: HDPE barrel provided by "Noreko".

Properties of HDPE [57]*:*

- **Withstands temperature up to 120** ℃
- **Moisture resistance**
- **Excellent chemical resistance**

4.2.4 Pre-Filtration:

In order to use waste vegetable oil filtering is a vital process for the design, because there is a high possibility of particles in the feedstock. This could affect the pumps and disturb the kinetics of the reaction. Therefore, the collected oil needs to be filtered.

Filtation process specs:

- **Remove all large particles.**
- **Easy to use.**
- **Low maintenace**
- **Handle large flow rates**

As a pre-filtration, the system will use a mesh filter when filtrating the oil. It has a high flow rate capacity necessary for the large quantities of oil available at a single time, and is easily replaced and cleaned. Additional pretreatment steps can implemented such as centrifuge filtration, acid pretreatment and degumming.

4.2.5 Dewatering and heating:

Dewatering the WCO is an essential step in the process because the water can deactivate the catalyst, by adsorbing to the catalyst sites. By removal of water the life of the catalyst can be prolonged and reduce operation cost. In this plant the dewatering step could be applied before and after the esterification reactor since the there is some amount of water that is produced during this step.

The dewatering system must:

- **Reduce the amount of water in the oil**
- **Remove water at a rate compatible with the required flow**
- **Sufficient capacity**
- **Small and inexpensive**

A well know technique for removal of water, is the use of absorbents such as silicate or zeolites. Zeolite molecular sieves are crystalline, highly porous materials, which belong to the class of aluminosilicates, Zeolite spheres contain billions of tiny pores of a known diameter as seen in Figure 4.3 on the next page.

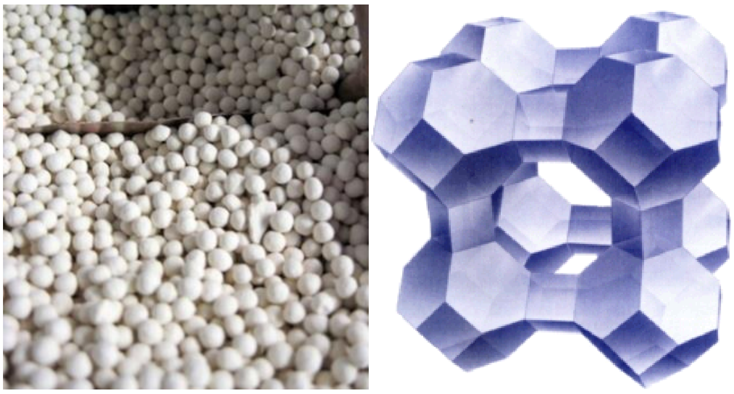


Figure 4.3: From left to right: Zeolite spheres and the structure of a zeolite [58, 59].

Zeolite function by selecting a bead with a pore size smaller than the carrier liquid, but larger than the liquid contaminant in that carrier liquid. For example, if one wishes to use the beads to remove trace water from Biodiesel, a molecule of water is 2.8 Angstroms, while a molecule of Biodiesel (Methyl Esters) is much greater, and so a Sphere of 3 Angstroms - 3A, would be used, this would capture all molecules below 3 Angstroms. Zeolite will adsorb 21% of its own weight in water before the need for regeneration [60].

The heater system works by heating the WCO to the wanted reaction temperature from table 4.2 and 4.3. The heating element could consist of an electric heating coil as seen in Figure 4.4 and has a capacity of 3.0 kW.

Figure 4.4: Heating coil [61].

These elements are operational throughout their length, so it is important to never install it in a position where the coil is not completely immersed or it may present a fire hazard. This can be avoided by installing a Level Control Switch (LCS) to prevent operation of the heater when the level of liquid is insufficient to cover the element. The heating elements that are available are inexpensive and have a broad range of power (3-12 kW).

A more safe approach for the heating system is the use of a jacket heater or a band heater illustrated in Figure 4.5. The band heaters has a range of 300 – 1200 watts with a max temperature of 218 ℃ at a reasonable cost. In this type of heater, the heating element is laminated between two layers of 20 mm fiberglass reinforced silicon rubber and has an adjustable thermostat as seen in figure 4.5 (b).

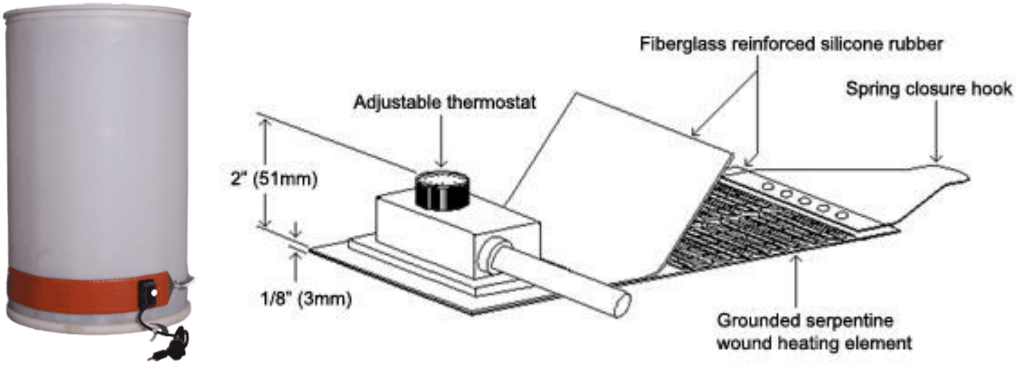


Figure 4.5: Band heater used for heating an oil drum (a) and it schematic (b) [62].

The band heater could be connected in series to give a uniform heating of the system. Other options such as Vacuum Evaporation was deemed too expensive and complex. Of the reviewed options the band heaters seems to be the best option to meet the required design requirements and scope of the project.

4.2.6 Reactor

As stated before the system will be using two packed bed reactors (PBR) in series. The criteria's for this system is that the reactor system must be able to:

- **Achieve high FAME conversion, 94-100%, at the required flow rates.**
- **Able to accommodate a heterogeneous catalyst**

Due to the limited budget, a simple PBR was investigated. As a result, a high-pressure vessel for dry wash will act as a reactor module. By modifying this module with a heat jacket or heat band, it could be used as a reactor. From Figure 4.6, the pressure vessel is shown next to mechanism that will hold the catalyst in place. The catalyst is held in place by two perforated steel plates.

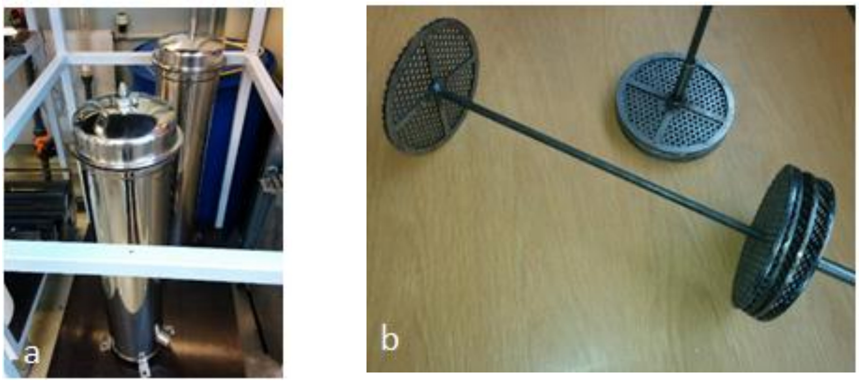


Figure 4.6: Pressure vessel (a) and perforated steel plates (b).

The reactor has an estimated catalyst capacity of 2 kg, is made of 316 Stainless Steel and has a volumetric flow rate of 3 l/min. Max pressure was given from the supplier to be 10 bar. An issue with the perforated steel plates, is that the hole width is bigger than the catalyst diameter. Therefore, in order to avoid loss of the catalyst, a smaller whole size mesh was used to keep the catalyst with in the reactor volume. This new modification is illustrated in Figure 4.7.

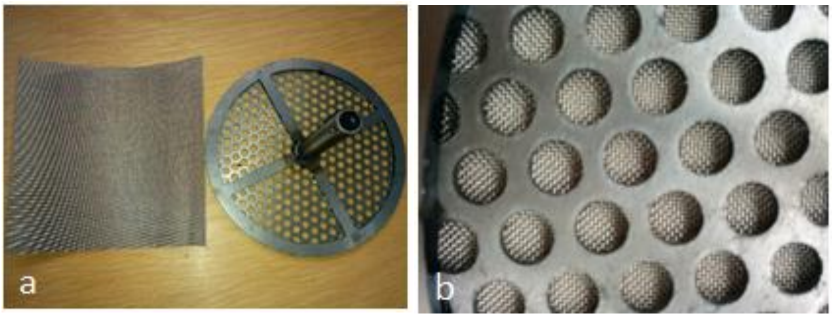


Figure 4.7: Modification of one of the steel plates with a mesh (300 μm).

4.2.7 Catalyst Recovery

A small but important part of the design is the ability for the system to reclaim the used catalyst for regeneration. By reclaiming the catalyst, the potential costs of the system can be reduced. A recovery system for the catalyst should:

- **Handle the required flow rate.**
- **Easy for the end user to use.**
- **Replace catalyst without shut down of the system.**

If the catalyst needs to be regenerated or replaced without shutting down the system, an option is to add several reactors in parallel. By doing this, it will allow the system to run continuously without stop when handling the catalyst. This will increase the fixed cost, but is a viable long term option used in the commercial reactor systems. Due to a limited budget, an alternative is developed. A mechanism is added to the reactors that will allow the reactors be tilted out of the framework and the catalyst to be removed. For example by a tilt mechanism as illustrated in Figure 4.8.

Figure 4.8: A reactor with a tilt-mechanism [63].

The best option for catalyst recovery system is perhaps a combination of the two methods mentioned, but due to the cost, a pressure vessel with a tilt function and a heat jacket will utilized as a reactor.

4.2.8 Methanol Recovery

As stated in the previous chapter, methanol recovery is a crucial step in the biodiesel process. The benefits of reusing the excess methanol is:

- **Removes toxic and flammable methanol from the fuel**
- **Simplifies safe handling of fuel and byproducts**
- **Save money and energy**

Figure 4.9 on the next page, the principle behind a simple methanol recovery system is illustrated. By adding heat to the system (at atmospheric pressure) the liquid methanol changes phase into methanol vapor (evaporation), a condenser then cools vapors returning methanol to liquid state (condensation). The recycled methanol can then be reused in the biodiesel process.

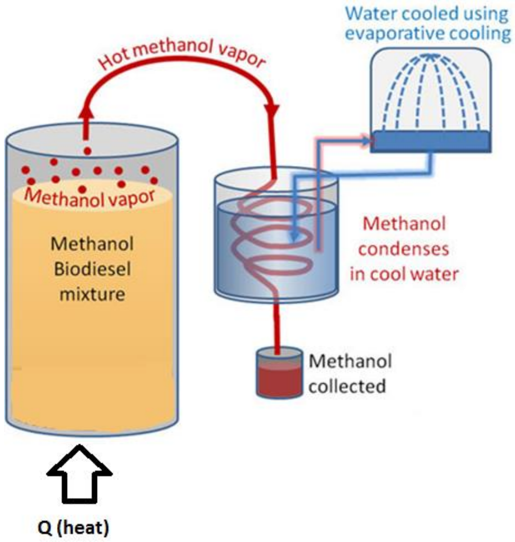


Figure 4.9: Methanol recovery system [64].

The system illustrated in Figure 4.9 is suitable alternative for an easy methanol recovery system, but requires a substantially amount of energy to evaporate the methanol under atmospheric pressure. By preforming the methanol, recovery under vacuum the amount energy required to separate out the methanol. This technique is called "Vacuum-Assisted Evaporative Distillation" [25].

By utilizing a vacuum distillation, ones uses that fact that the flash point (boling point) decreases with a decreasing temperature as illustrated in Figure 4.10 with water flash points.

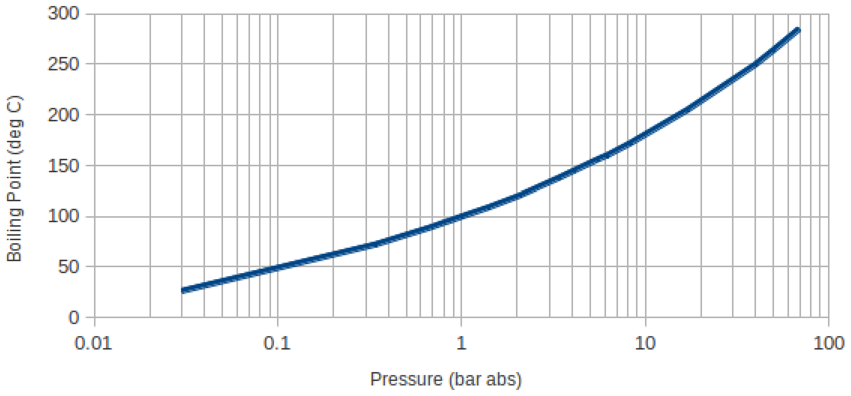


Figure 4.10: Flash point of water at different pressure [65].

As stated in Chapter 2.7: By using vacuum-Assisted Evaporative Distillation, the system requires less energy. As the reactor stream out is generally is warm, resulting in a fairly, energy-efficient separation that requires only some vacuum. As a sealed system, there is little risk of methanol evaporating and escaping into the atmosphere.

4.2.9 Biodiesel Purification:

After isolation of FAME from the product stream in the separator and subsequent removal of methanol, outlined in the previous sections, further purification is required to remove any remaining contaminants and fulfil the EN14214 specifications (see Appendix A). As stated before in chapter 2.7, the alternatives is the ion-exchange Resin Column or Water Wash. An ion-exchange resin column was determined for the final biodiesel and glycerol purification due to its ease of operation, excellent contamination removal, and simple integration into a continuous flow design.

4.2.10 Mixer:

For mixing the methanol and oil, a Low Density Polyethylene (LDPE) conic tank with electrical mixer will be used, as seen in Figure 4.11. This type of tank is widely used in the "Do It Yourself" (DIY) biodiesel community and is available in several different volumes from 60 liters to several thousands.

Figure 4.11: 200 liter conical tank and mixer [67].

Properties of LDPE [66]:

- **Maximum Temperature: 80°C**
- **Melting Point: 120°C**
- **Tensile Strength: 117 bar**
- **Good resistance to Vegetable oil, esters, alcohol and acids**

In processes where the operation conditions exceeds the properties of the LDPE, a stainless steel tank with mixer can be implemented if needed.

4.2.11 Separator:

While some of the methanol from the reactor feed (glycerol, biodiesel and unreacted methanol) will be removed by a methanol recovery system as outlined in the previous section the glycerol must be separated in the next step. The requirement in this plant is a separator that effectively separates the glycerol from the biodiesel. As mention in the previous chapter, the choice is mainly between a settling tank and a centrifuge. The need for a quick separation makes a centrifuge a good option. The selected centrifuge is a relative new developed centrifuge called the “Raw Power” from WVO designs and is illustrated in illustrated in Figure 4.12.

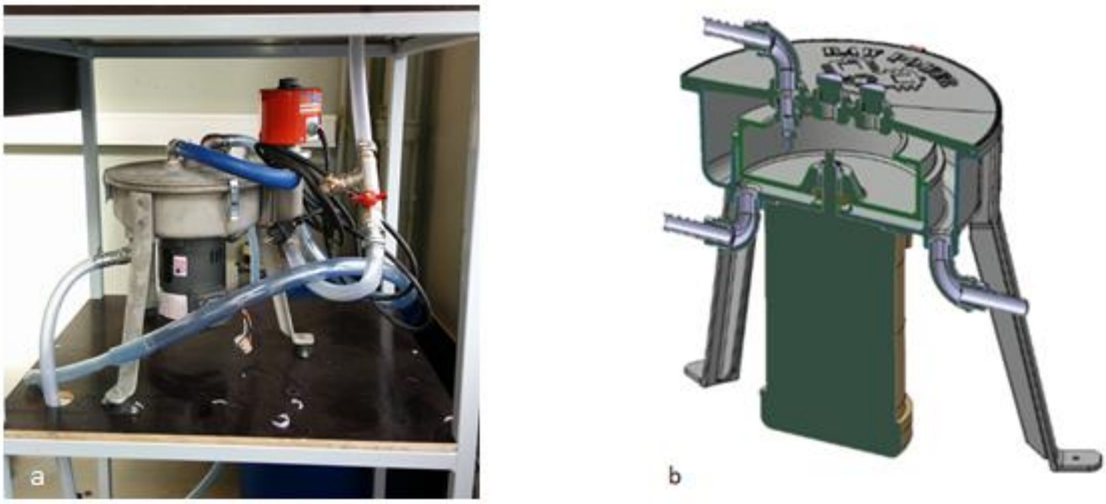


Figure 4.12: The centrifuge (a) and its schematic (b) [68].

The body is cast aluminum, the rotor speed is 6,000 rpms, and it is gravity feed. One of the main benefits with this type of centrifuge is that it can handle liquids up to 200 ℃ and it is constructed for small-scale biodiesel production. The reason for choosing this centrifuge is because of its simple design, gravity Fed, pumps, Single Pass - Designed so you only need to run the oil through once and it is very quiet. The centrifuge velocity is stated to be 6000 rpm that will generate roughly 3800 G of force. In addition, a 1000 watts heat filter was included; this will greatly affect the rate of flow in the centrifuge and help remove traces of water.

4.2.12 Transport of fluids:

There are several options and choices when it comes to transportation of fluids. In this case, the company OEM Automatic sponsored the pump. The pump is the UP3/AC Marco high-pressure gear pump as seen in Figure 4.13 and was recommended to this plant by “OEM Automatics” product supervisor Mikko Mannermaa.

Specifications:

- **Motor: 12 kW 0,91A.**
- **Volts 220V 50 HZ**
- **Max pressure 7 bar**
- **Flow (2m) 10 l/min**

Figure 4.13: The UP3 high-pressure pump [69].

Another gear pump from “Biltema” as shown in Figure 4.14 will be applied to the less critical transport steps:

Specifications:

- **Flow: 60 l/min.**
- **Motor: 0.35 kW**
- **Working pressure: 3 bar**

Figure 4.14: Gear pump from “Biltema”.

4.2.13 Piping and hoses:

The recommended flowrate in a process plant is between 1 and 5 m/s for liquids. The average temperature is 60 ℃ and 1 bar, but some of the pipes must have a requirement of withstanding a pressure of 7 bars and max 150 ℃.

For transport of fluids in the plant, a Merlett Armorvin, Polyurethane Lined Clear PVC hose, with Steel Spiral can be applied as seen in Figure 4.15. This hose has all the transparency advantages of clear PVC, but with the additional advantages of a Polyurethane (PU) lining, which is more resistant to vegetable oil based products.

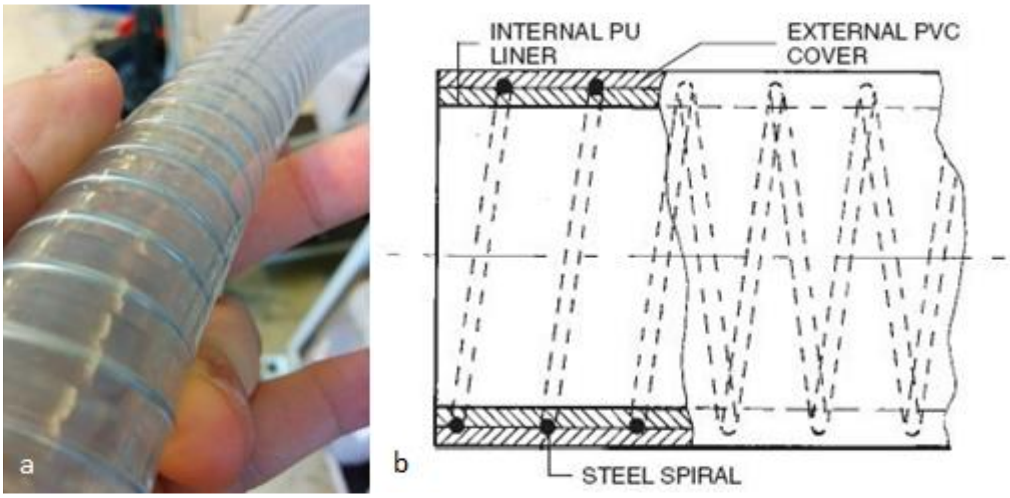


Figure 4.15: Polyurethane Lined Clear PVC Hose with Steel Spiral (a) and its schematic (b) [70].

The hose also has a very high working pressure of 20 Bar and temperature range of -20 to +90℃.

In the reactor system, specialty hoses seen in Figure 4.16 will be purchased to insure extra safety in the harsh conditions such as in the separation of water, where the temperature exceeds 100℃.

Figure 4.16: Steel hose from “Hydroscand” [71].

4.3 Process description:

Based on the previous equipment description a stoichiometric model was made in the simulation program “Aspen Plus” which is illustrated in Figure 4.17. In Aspen, the FFA is represented by Oleic acid and Vegetable oil by Triolein (a Triglyceride) due to a lack of thermodynamic properties library in the software. This model represents a schematic of a plant where the pre-filtered raw materials is stored in HDPE barrels at room temperature. In Figure 4.17, several sections have been colored over the flow sheet in order to separate the different areas of the production process. The first step (marked in a red square) is when the methanol and waste vegetable oil (1.4 wt% FFA) is mixed in the LDPE tank at 60 ℃ and atmospheric pressure to be afterwards pumped into the reactor with a discharged pressure of 7 bar into the esterification packed bed reactor. During a residence time of 2 hours in the reactor, the methanol has reacted with the Oleic acid with a molar ratio of 10, achieving a conversion of 95% of FFA into Biodiesel, this can be seen in the yellow are in Figure 4.17. The outlet of the first reactor is then heated up to 120 ℃ and undergoes a flash separation where the water and methanol is separated out of the stream (dark green area). Following the separation of water, the vegetable oil and biodiesel is cooled down to 42 ℃ and mixed with additional methanol achieving a molar ratio of 7 (methanol to FFA), this is represented with the blue square in the flow diagram. These components are mixed at 60 ℃ and transported at 7 bar into the next reactor. In this reactor, the transesterification occurs. Here methanol and Triolein reacts with a molar ratio of 9 methanol to Triolein with a residence time of 3 hours, producing biodiesel and glycerol (green area). The biodiesel, glycerol and the unreacted methanol exits the reactor and enters an additional separation step that is presented by the orange square. Where the glycerol, biodiesel and methanol (MeOH) is separated, by a heat and centrifuge combination. The glycerol exits at 70 ℃ and 1 bar with a minor trace of biodiesel, but some methanol and therefore must be sent to an external purification system (not included in flow chart due to not being the focus in this thesis). Crude biodiesel is therefore sent through a final purification step (dark blue area) to further improve the quality of the product by removing the traces of methanol in a distillation column at 131.5℃. The recycled methanol is then condensed in an external system and reused into the biodiesel system.

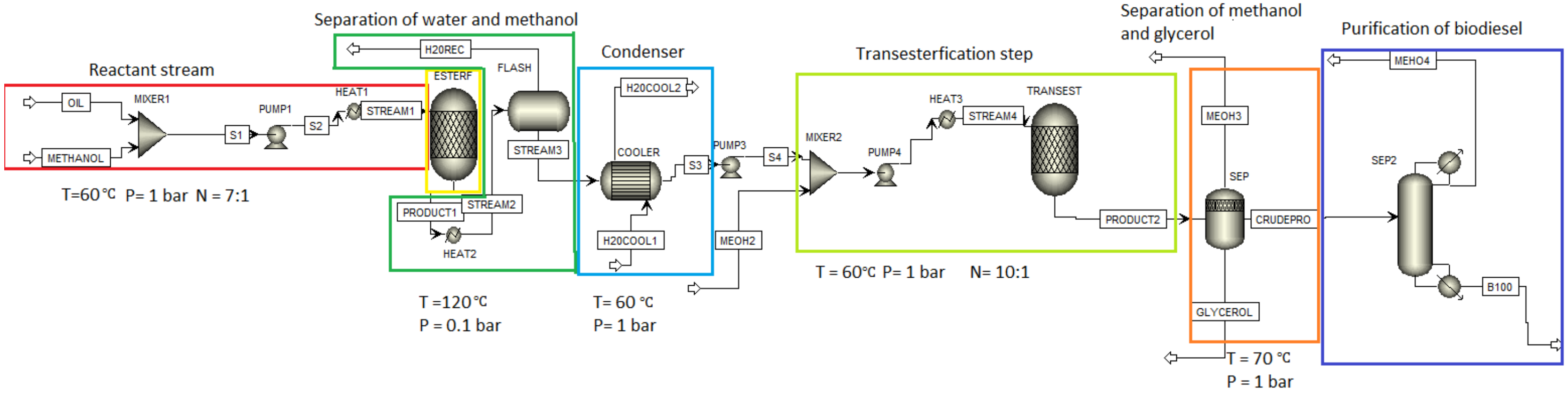


Figure 4.17: Aspen model of the small-scale plant.

Table 4.4: Results from the Aspen simulation related to Figure 4.17.

Heterogenous Biodiesel production											
Stream ID		STREAM1	STREAM2	H20REC	MEOH2	STREAM4	MEOH3	GLYCEROL	CRUDEPRO	MEOH4	B100
Temperature	C	60,0	100,0	120,0	20,0	60,0	100,0	100,0	100,0	31,0	131,5
Pressure	bar	1,000	7,000	0,100	1,000	7,000	1,000	1,000	1,000	0,200	1,000
Vapor Frac		0,000	0,000	1,000	0,000	0,000	1,000	0,000	0,000	0,000	0,000
Mole Flow	kmol/hr	0,064	0,064	0,013	0,432	0,483	0,242	0,055	0,185	0,019	0,167
Mass Flow	kg/hr	43,515	43,515	0,403	13,842	56,955	7,775	4,318	44,861	0,594	44,268
Volume Flow	cum/hr	0,056	0,056	4,378	0,018	0,080	7,424	0,004	0,055	0,001	0,055
Enthalpy	Gcal/hr	-0,027	-0,026	-0,001	-0,025	-0,050	-0,011	-0,007	-0,027	-0,001	-0,025
Mole Flow	kmol/hr										
METHY-01			0,002	trace		0,002	trace	trace	0,146	trace	0,146
OLEIC-01		0,002									
TRIOL-01		0,048	0,048	trace		0,048					
METHANOL		0,014	0,012	0,011	0,432	0,433	0,242	0,012	0,034	0,019	0,016
WATER			0,002	0,002		< 0,001	< 0,001	trace	trace	trace	trace
GLYCEROL							< 0,001	0,043	0,005	trace	0,005

Note: In appendix C a second simulation can be found, where the FFA content has been altered to 30 wt%.

4.4 Conceptual design:

Based on the following reviews and Aspen model (Figure 4.17), a concept was designed in the solid modeling program "Solidworks". The work is a result of a collaboration between the author and a student project related to the biodiesel plant and is illustrated in Figure 4.18.

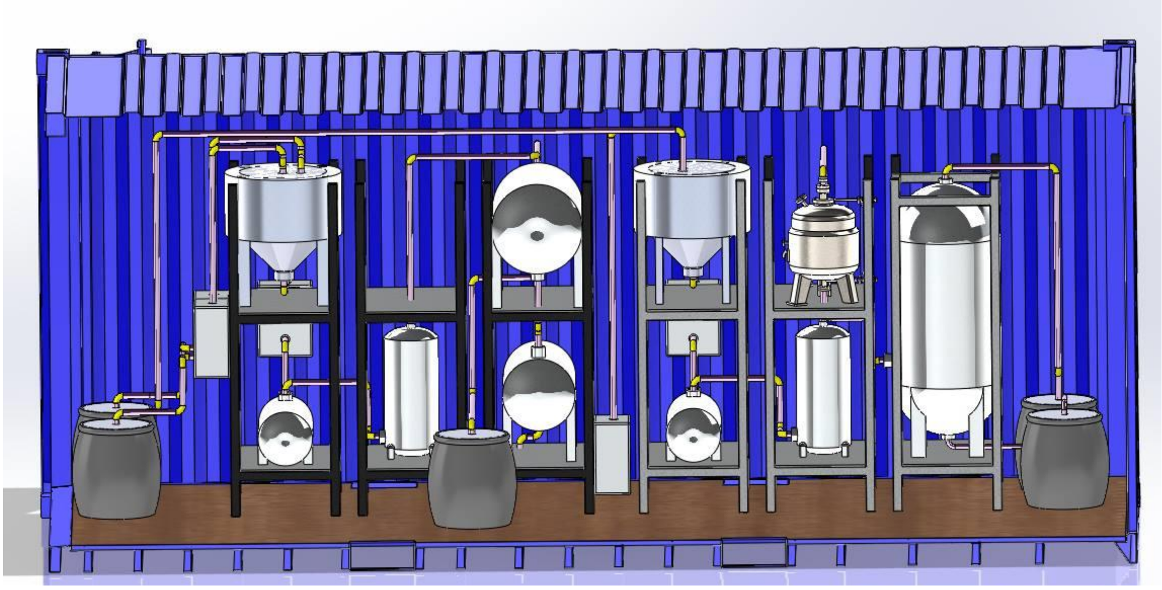


Figure 4.18: The finished concept of the biodiesel plant based on the Aspen model (Designed by Kristian Roderburg and Rene Boogaard).

The system has six separate subassemblies in addition to the storage vessels, resulting in system easy to maintain. The subassemblies, in Figure 4.18, is referred to as the *input (mixers)*, the *refinery (two reactors), separation (centrifuge and flash separation)* and the *Purification* assembly.

Table 4.5: Details for the concept art in Figure 4.18.

Left section	First module	Second module	Third module	Fourth Module	Fifth Module	Sixth module
Input Tanks	Mixers	Reactor (esterfication)	Flash separator	Mixer	Centrifuge (with flash separator)	Destilliation column
Feedstock tank	Pressure pumps	MeOH tank (in front)	Heat exchanger	Pump	Reactor (transesterfication)	Storage vessels for the product (to the right)
MeOH tank	Heater		Pump (between)	Heater	Reactor (transesterfication)	

Not seen in the figure is the sensor, instrumentation and valves.

More illustrations of the conceptual design done in solidworks can be found in Appendix E.

4.5 Construction of some of the modules:

Limited by the budget and time of the thesis, the construction of the entire plant was very difficult. Therefore, the focus turned against creating three modules less than half what needed. Two fully functional and one soon to be operational. Figure 4.19 shows the three modules that is constructed and invested in. The two modules, is a mixer stage with a 200 liter conical tank, a low-pressure pump, a static mixer and the second modules is the separator stage that consists of a 60 L conic tank and a centrifuge. This module is designed either to clean waste cooking oil as a standalone or separate glycerol from the biodiesel connected to the mixer. The third module is a reactor rig under development where the framework, reactors and a high-pressure pump is acquired. This meant to be attached to the mixer module when finished.

Figure 4.19: The part of the plant constructed (from left to right): HDPE barrel with a tank of WCO on top of it, mixer, separator with a 60 L conic tank above it and the reactor rig.

By constructing, the centrifuge module the short-term goal is to create purification set-up for WCO and use it in a simple modified pickup truck as seen in Figure 4.20.The long-term goal is to integrate this system into a future small-scale biodiesel plant.

Figure 4.20: Modified pickup truck that runs on WCO.

4.6 Benchmark of the centrifuge module:

The purpose of this part is to investigate the use of a centrifuge in the separation steps and as a pretreatment in a small-scale biodiesel system.

As stated in chapter 2, the centrifuge can remove residual amounts of glycerol and any particle that is denser than oil, or anything that will settle out. By applying g-force (around 3000 G) to a liquid, causing a "forced settling" of the denser particles and fluids such as water and dirt to occur.

The equipment used in this experiment is the "Extreme Raw Power" Centrifuge from "WVO designs". In figure 4.21 explains how the centrifuge works when cleaning waste cooking oil. A typical setup includes a feedstock-storage (to draw vegetable oil), a valve to control the flow, a container for the filtered oil, and storage for the sump/overflow.

Some relevant applications according the manufacture:

- **Filtration of used vegetable oil**
- **Filtration of used motor oil**
- **Harvest of algae**
- **Separation of glycerol**

This centrifuge was obtained from the company "Selko Motor" at reduced cost.

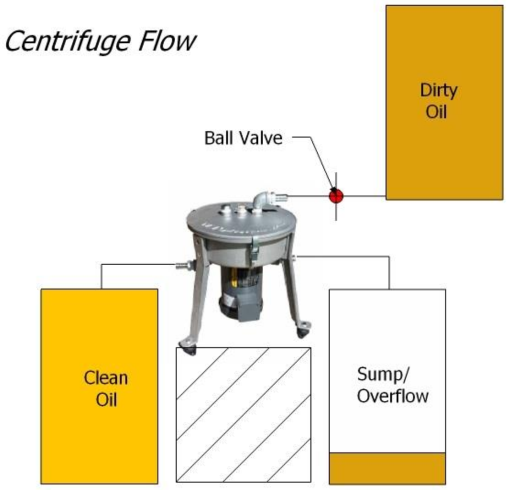


Figure 4.21: A standard centrifuge set-up [66].

From figure 4.22, the set-up of the centrifuge module is shown. Attached to a framework is a conical tank where waste cooking oil is gravity fed to a centrifuge below.

Figure 4.22: Centrifuge pre-treatment plant set up.

As initial simple test, measuring the flow at different temperature and rpm would be the most sensible place to start. During the test it was observed that temperature greatly affected the flow and the ideal temperature was 65 °C. The flow rate was 70 l/hr at 6000 rpm 3600G at oil temp of 65 °C. The use of a centrifuge as a pretreatment for waste cooking oil worked beyond expectation and managed to clean waste vegetable oil significant faster than using a conventional filter.

5. Economic evaluation:

An important issue regarding biodiesel production, is to determine the economic viability of the technology. In this chapter, the goal is to evaluate the economic constraints surrounding the sustainability of a small-scale plant.

5.1 Cost related to biodiesel production:

5.1.1 Marked in general:

From the year 2000 to the 2010, the global production of biodiesel has exploded illustrated Figure 5.1. In 2013 the production was estimated to 28.7 billions with the Europen Union (EU) as the world largest producer of biodiesel and also the largest importer of biodiesel (from USA, Malasya, Indonesia etc).

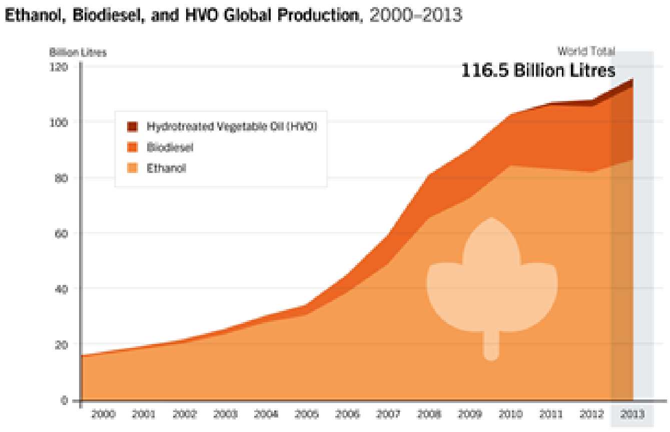


Figure 5.1: The global biodiesel production from 1998 to 2013 [72].

According to Organisation for European Economic Co-operation (OECD) the production of biodiesel will increase to 41.5 billion liter in 2021 [73].

5.2.1 Production cost:

As stated before in chapter 1 and 2, the dominating factor in conventional production of biodiesel is the cost of the feedstock. Based on canola/rapeseed oil cost of February 2015 an estimate of production cost is presented in Table 5.1:

Table 5.1: Conventional biodiesel production cost [74, 75].

Production cost pr liter ($):	
Feedstock (rapeseed)	0.66
Refining (degumming	0,062
Energy (kWh)	0,0062
Transesterfication	0,1
Logistic, transport	0,09
Total	0,92

After tax (road and CO_2) the retail price for biodiesel is $ 1.69 pr liter.

5.2 The heterogeneous biodiesel system:

By using collected data, an economical evaluation was preformed using the software "SuperPro designer". A new flowsheet was designed (based on the Aspen model) and can be viewed in Appendix D, Figure D.1. The main criterion for economic evaluation for the proposed small-scale concept is the rate of return after tax. The first step in this process is estimation of capital costs and the second, determination of operation costs and the value of the product. Several scenarios was simulated for achiving an estimated of the payback (break-even) time of the biodiesel plant.

5.2.1 System fixed cost:

The estimated total cost of the prototype plant was estimated with SuperPro to 67000 $, see Appendix D.2 for more detalied cost.

5.2.2 Operation cost:

The prices for products and feedstock will vary as the supply and demand in addition to global economy is continually changing. If the marked prices is reduced below a certain point, the production of biodiesel is no longer economical viable. If the product price becomes too low, a minimum production will be beneficial. The prices of feedstock's and products can be viewed in appendix D.3.

Table 5.2 presents the production cost pr liter biodiesel produced. Assumptions regarding the production cost is that the catalyst used is either very inexpensive (CaO) or it can be reused several times (Amberlyst BD20), both resulting in minimal catalyst cost pr kg biodiesel produced. In addition it is assumed that the cost of catalyst pr m^3 biodiesel produced is around $ 12.35. In this estimate, the catalyst price is included regeneration and energy used in the regeneration process. Another crucial assumption is that the feedstock is considered a waste and therefore free at the start of the analysis

Table 5.2: Heterogenous biodiesel production cost pr liter.

Component	Cost ($)
Waste cooking oil	Free
Methanol	0.045
Catalyst (included regeneration)	0,052
Energy (kWh)	0,006
Total	0.113

Transport cost is minimal because of an onsite trading of biodiesel.

5.2.3 Break-even and breaking point analysis:

Based on the production cost in table 5.2 and data collected in appendix D, an estimate of the downpayment time could be achived using "SuperPro". It is accepted to assume 7920 operating hours a year for a continuous production plant (approximately 90% of the total hours a year). For a 40-50 kg/hr production plant this results in a yearly production of 316 00 - 397 500 kg biodiesel, which will form the reference point for the two scenarios: A single producer, in this case a farmer and a more commercial scenario, use as supplement in a renovation company. In both cases, the plant has a project life of 15 years [76].

Scenario: Use of a small-scale biodiesel plant in Norwegian farming:

In this scenario, a Norwegian farmer produces biodiesel from WCO onsite. Either the farmer can sell or use (or both) the biodiesel to surrounding area, but in this case only retail will be considered for determining the downpayment time of a plant. In the SuperPro analysis, it is assumed that the excess methanol and produced glycerol is sold, but in real life, the methanol would be recycled and reused. Therefore, the focus is on how much biodiesel the farmer must produce to break even. Four production scenarios is presented in Table 5.3, 5.4, 5.5 and 5.6:

1. An ideal scenario where the farmer is a full-time producer and sells at retail price:

Table 5.3: Break-even analysis #1: 40% tax, Retail price of $ 1.75 pr. kg biodiesel.

Product:	Net profit ($):	Production cost($):	Payback time (year)
Biodiesel	326 462	42 061	0.2

2. A scenario where the full-time producer selles at roughly half price as competitive mean.

Table 5.4: Break-even analysis #2: 40% tax, Retail price of $ 0.83 pr. kg biodiesel.

Product:	Net profit ($):	Production cost ($)	Payback time (years)
Biodiesel	158 117	42 061	0.4

3. The farmer is part-time supplier of biodiesel that sells for half the retail price.

Table 5.5: Break-even analysis #3: 40% tax, Retail price of $ 0.83 pr. kg biodiesel.

Product:	Net profit ($):	Production cost ($):	Payback time (years)
Biodiesel	78 057	27 204	0.8

4. A more realistic scenario, where the production is season based for a period of 3 months with continuous production at has half the retail price of conventional biodiesel.

Table 5.6: Break-even analysis #4: 40% tax, Retail price of $ 0.83 pr. kg biodiesel.

Product:	Net profit ($):	Production cost	Payback time (years)
Biodiesel	48 534	20 466	1.9

Even if Table 5.5 presents the most realistic sceneario of the four, it still shows an attractive downpayment time of 1.94 years. For being a viable production model for a single producer with limited production capacity, a downpayment time should be comparable with f.ex the downpayment time of a car loan, meaning between 1-5 years.

Commercial scenario: Use of a small-scale biodiesel plant in a renovation company:

The main difference between the two scenarios is that in a commercial setting one-would need to pay a worker for operating the facilities meaning additional production cost. In addition, the run time of the plant could be affected, but it is assumed that the plant is operating continuous. One major benfit in this scenario is that a collection system for WCO most likely is already in place and the company receives payment for each liter of WCO collected.

It is assumed that the amount of hours to operate this plant during a year is 7920 hours and in a team of 7.5 (one 50% position) operators divided at different shifts of 8 hours during 24 hours run time. With a rate of $ 69 pr. hr this will result in total labor cost of $ 390 943 (salary of $ 52 000) resulting in an overall operation cost of $ 531 000. As a effect of labour cost a working capital will be included to the fixed cost leading to overall increase from $ 67 000 to $ 93 000 for Table 5.7 and $ 102 087 in Table 5.8.

The results from the SuperPro simulation, showed even if the production cost increased substantially, the payback time would be reasonable even if the biodiesel is sold at retail price or below ($ 1.25 pr. kg) shown in Table 5.7 and 5.8.

Table 5.7: Break-even analysis: 40%tax, Retail price of $ 1.75 pr kg biodiesel.

Product:	Revenues ($):	Production cost ($):	Net profit ($):	Payback time (year)
Biodiesel	641 045	429 917	110 673	0.7

Table 5.8: Break-even analysis: 40%tax, Retail price of $ 1.3 pr kg biodiesel.

Product:	Revenues	Production cost	Net profit:	Payback time (year)
Biodiesel	460 000	431 696	25 862	4,2

Of the two examples, Table 5.8 presents the most viable retail model, but it could also be interesting to use the produced biodiesel for fueling the companys transport fleet and reduce the fuel expenses.

In addition to the break-even analysis, a breaking point analysis was preformed on the commercial scenario. In other words, a SuperPro simulation was used to find the max purchase cost of WCO before the production is unprofitable. In table 5.9, the max purchase cost is depicted for a full retail price and Table 5.10 illustrates the maximum cost in minimum retail cost scenario.

Table 5.9: Breaking point analysis: 40%tax, Retail price of $ 1.75 pr. kg , price of $ 0.5 pr. kg WCO.

Product:	Revenues	Production cost	Net profit:	Payback time (year)
Biodiesel	460 000	431 696	25862	3,5

Table 5.10: Breaking point analysis: 40%tax, Retail price of $ 1.3 pr kg, price of $ 0.1 pr. kg WCO.

Product:	Revenues	Production cost	Net profit:	Payback time (year)
Biodiesel	498 600	463 696	25862	3,7

For being a viable production model for a commercial producer with a higher production capacity, a downpayment time should be comparable with f.ex the downpayment time related to the oil industry, meaning a payback time around 3-4 years.

More detalied results can be found in appendix D.3. Appendix D.3 displays the results from the “SuperPro” economic evaluation report of the scenarios presented in Tables 5.6 and 5.8.

6. Discussion:

6.1 System choice:

The production model proposed is a two-step catalytic processing system that focus on the use of unedible oils or waste vegetable oils as a feedstock. The system employs a heterogenous catalyst instead of the more conventional homogenous catalyst. Both technologies can be utilized in small-biodiesel system, but the heterogenous approach is more suitable for oils with high FFA content. A heterogenous catalyst in combination with mobile platform (shipping container), creates a small-scale plant that is economically feasible for the Norwegian case scenario.

As stated in previous chapters, the attractiveness of heterogeneous catalysts lies in their ability to simplify the biodiesel production and using waste as a feedstock. One of challenges presented by using a heterogenous catalyst lies in identifying a suitable catalyst in order to optimize the production.There is the commercial options that are expensive, but reliable and the non-commercial such as CaO and other experimental types (carbon catalyst, MgO etc) that represents a more inexpensive option. Of the two options, perhaps alternatives like the CaO incorporates the small-scale philosophy of on-site production and more labour intensive production. Perhaps this opens the possibility of synthesizing catalyst next to the biodiesel plant and either regenerate the catalyst on-site or finding alternative uses for the spent catalyst (for used CaO, fertilizer). Resulting in a viable and sustainable production model.

6.2 Small-scale biodiesel model viability in the Norwegian market:

To this day, a viable conventional biodiesel production in Norway is very difficult. This is because like any other places conventional biodiesel productions competes directly with food production, making refined feedstock many times more expensive than waste cooking oils. This along with the CO_2.tax and unstable marked with small profit margin pinpoints why biodiesel producers in Norway have gone bankrupt such as “Milvenn As”, “BV Energy” and now recently Norways largest producer of biodiesel “North Sea Biodiesel” (former “Uniol” and “Habiol”) is bankrupted for the third time since 2009 [77]. This results in a virtually none excisting production of biodiesel in Norway. Large-scale operations may have the advantage of spreading the fixed operating and capital costs across huge production volumes. On the other hand, the low capacity utilisation in most of these plants indicates that they cannot find markets for the majority of their biodiesel and biproducts. Furthermore, the high capital costs make commodity price spikes disastrous as seen in Norway. Small-scale plants do not face these problems [32]. By employing small-scale production units spread around in Norway instead of centralized large-scale production one can easier gather the dispersed sources of feedstock. A typical end user of small-scale plant could be farmer or a community of farmers as seen in Figure 6.1 and presented in chapter 5. A small-scale system generates a market for local feedstock and agricultural producers in its ability to selectively process a range of feedstock.

Figure 6.1: Raw material delivered to a biodiesel plant on farm.

As shown in chapter 5, the plant could also be considered a profitable supplement to the municipal renovation service, but it could also be good PR.

An issue with biodiesel sales is that it is still very difficult to sell it (taxation etc). Therefore, a new retail model should be developed parallel to the designing of a small-scale biodiesel plant. Instead of selling the product, the plant can be rented out for hourly rate to a costumer on f.ex a farm or on a landfill. Where the costumer pays an amount for using the plant for f.ex 1 hour resulting in 40-50 kg of biodiesel.

6.3 Availability of waste feedstock:

WCO is a hazardous waste, should be disposed off correctly against a fee (see Appendix D, Table D.1), and is mandatory for companies in the food industry. In the Oslo area, it’s estimated that each person disposes of 1 kg of fat to the sewers each year and is a growing concern. Resulting in major cost for the community and stress to seweage system [78, 79]. A small-scale plant placed in central location by the municipality own renovation system can contribute to reduce amount WCO ending up in the sewers and instead beoming a green fuel.

If the availabilty of waste feedstock is reduced and creating competition for raw material. An option is to import WCO from abroad, which could less expensive than using refined vegetable oils. See appendix D, Table D.3 for cost of waste cooking oil from oversea from f.ex Scotland or Estonia

7. Conclusion:

In this thesis, a small-scale model for biodiesel production based on heterogenous technology was purposed.

Chapter one identified biodiesel as an important measure to reduce GHG emissions. Despite the advantages with using biodiesel, chapter one also presented the limitations of large-scale production of biodiesel. These limitations were identified as feedstock availability and cost. As a result an evaluation of large-scale biodiesel-production was performed in chapter two in addition to a comparison of heterogenous and homogenous processes. Result of the evaluation was the development of a new production consept, focusing on small-scale biodiesel production from waste cooking oil (WCO). To increase the process-efficiency, the focus of this thesis shifted towards finding a heterogenous catalytic system suitable for using WCO as feedstock. After a review of different heterogenous/solid catalyst, a two-step catalytic process was presented in the simulation software "Aspen plus", employing a solid acid (Amberlyst BD20 or a carbon catalyst) and alkaline catalyst (CaO) for handling feedstock containing more than 1wt% FFA. The simulation in Aspen showed that the biodiesel produced satisfied the product-standard for biodiesel.

The economic evaluation of the small-scale plant showed that the combination of a heterogenous technology and a small-scale system is viable. The result of the SuperPro simulation showed lower production costs and a reasonable payback time for the purposed system. For a single user the downpayment time was 1.94 years in the most realistic scenario (3 months of operation time). In a commercial scenario the downpayment was 4.2 years for the most realistic scenario. In addition, a breaking point analysis was preformed in order to investigate the constraints of the commercial "SuperPro" model. By changing the cost of feedstock and retail price, the results from the breaking point analysis showed that the model was viable if the feedstock cost rose to $ 0.5 pr. kg at full retail price ($ 1.75 pr. kg) and $ 0.1 pr. kg at reduced retail cost ($ 1.25 pr. kg). From the SuperPro simulation one can see that this production method is a viable option for Norwegian conditions both for a single producer and in commercial scenario.

As a supplement to the thesis, some modules of a future prototype plant was constructed and designed. The short-term goal is to create purification set-up for WCO and use the end-product as fuel for a modified pickup-truck.The long-term goal is to integrate this system into a commercial small-scale biodiesel plant at NMBUs campus.

8. Future work:

A future goal of this thesis is to serve as a foundation for other master thesis, where students gain knowledge about biodiesel for their own thesis or to be inspired to continue the construction and further developing of the concept. In order to complete the construction and development of the plant, more funding is needed as well as kinetic data and modelling through experimental research using the proposed feedstock.

8.1 Catalyst research and kinetic data:

Obtaining experimental data is crucial in the understanding the dynamics of the proposed system by viewing the deviation in the collected literature, could lead to a wider understanding of the kinetics. A part of the basic research is to find other catalyst options that can used in the reactors, since there is an abundance of catalyst options such as "*Titanium niobate nanosheet*", "*12-tungstophosphoric acid"* or other zeolites etc [80, 81]. By examination of other catalyst with similar properties to the catalyst reviewed, it could lead to an improvement in the operating conditions and performance of the biodiesel plant. Resulting in a reduced cost and an improved efficiency.

The heterogeneous catalyst will deactivate with time and therefore new data might result in an optimized reactor design. With more kinetic data in place, a reactor-configuration with different size volume could be an alternative. Modification to the catalyst to resolve poor reusability of some of the catalyst like the CaO by investigating the potential leaching of calcium. The CaO catalyst reviewed was in the form of powder. It would be worth investigating if different forms of the catalyst such as pellets could resolve the the issue related to reusability.

8.2 Constraints of the process and modified Aspen models:

The constraints regarding the different parameters in the purposed Aspen model should be explored when optimizing the operational limits of the process. To find operational limits, the operation temperature related to the degradation of glycerol should be known exactly at the operation parameters for the model. When the optimized data for the purposed model are available, a more detailed thermodynamic model of the small-scale plant can be preformed. A in-depth Aspen model could be designed based the kinectic and thermodynamic data obtained. This could help to provide a detailed energy and mass balance.

8.3 Sizing and optimization of equipment:

With the proper data, the distillation column could be investigated in search of; the bottom composition, optimized reflux ratio and feed stage. In addition, finding the number of distillation stages required for the purification of the FAME product or an optimization of the separation stages of the plant could be preformed.

There is also a substantial amount of work related to the building phase. The most critical component is the reactor module, but also the separation stages should be the focus in future. For solving the regeneration issue with some of the more inexpensive catalyst, a catalyst recovery system could be designed in order to easily replace the deactivated catalyst. For achiving a longer lifetime for catalyst, a purification module could be designed based on the use of dry-wash method f.ex with Amberlite resin.

A control system should be designed to operate the plant, something that could be arranged as a project in the automation course “Tel240” at NMBU.

Further development of the plant could also be designing a larger module based plant based on the shipping container approach as a continuation of this work. Instead of having all components are in one container, one container could f.ex be the reactor module and another container is the separation step etc together all the modules form a large-capacity plant. This could contribute to have a wider marked appeal beyond the border of Norway.

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10. Appendices:

Appendix A: The EU biodiesel standard (EN 14214).

Table A.1: The EU biodiesel standard [10].

EN 14214 - Property	Units	Lower limit	Upper limit	Test-Method
Ester content	% (m/m)	96,5	-	EN 14103
Density at 15°C	kg/m³	860	900	EN ISO 3675 / EN ISO 12185.
Viscosity at 40°C	mm²/s	3,5	5,0	EN ISO 3104
Flash point	°C	> 101	-	ISO 3679
Sulfur content	mg/kg	-	10	-
Tar remnant (at 10% distillation remnant)	% (m/m)	-	0,3	EN ISO 10370
Cetane number	-	51,0	-	EN ISO 5165
Sulfated ash content	% (m/m)	-	0,02	ISO 3987
Water content	mg/kg	-	500	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Copper band corrosion (3 hours at 50 °C)	Rating	Class 1	Class 1	EN ISO 2160
Thermal Stability	-	-	-	-
Oxidation stability, 110°C	Hours	6	-	EN 14112
Acid value	mg KOH/g	-	0,5	EN 14104
Iodine value	-	-	120	EN 14111
Linolic Acid Methylester	% (m/m)	-	12	EN 14103
Polyunsaturated (>= 4 Double bonds) Methylester	% (m/m)	-	1	-
Methanol content	% (m/m)	-	0,2	EN 14110
Monoglyceride content	% (m/m)	-	0,8	EN 14105
Diglyceride content	% (m/m)	-	0,2	EN 14105
Triglyceride content	% (m/m)	-	0,2	EN 14105
Free Glycerine	% (m/m)	-	0,02	EN 14105 / EN 14106
Total Glycerine	% (m/m)	-	0,25	EN 14105
Alkali Metals (Na+K)	mg/kg	-	5	EN 14108 / EN 14109
Phosphorus content	mg/kg	-	10	EN 14107

Appendix B: Aspen model basis.

The basis of the Aspen model was a wanted biodiesel production of ca 40-50 kg/hr. From this basis the molar flow of vegetable oil can be estimated. The amount of moles of FAME produced can be calculated in Equation B.1for a 50 kg/hr production.

$$F_i = \frac{50.0\ [\frac{kg}{hr}]}{292.2\ [\frac{kg}{kmol}]} = 0.17\ [\frac{kmol}{hr}] \tag{B.1}$$

From the chapter 3.2, the stoichiometric coefficient of the transesterification is 3, therefore in Equation B.2 the molar flow must be divided by three.

$$F_i = \frac{0.17\ [\frac{kmol}{hr}]}{3} = 0.05\ [\frac{kmol}{hr}] \tag{B.2}$$

In order to obtain feedstock flow that contains 98.6 wt% triglyceride (Triolein) the mole fractions must be calculated. The equation for mole fraction is depicted by Equation B.3.

$$X_i = \frac{\frac{w_i}{M_i}}{\sum_i^1 \frac{w_i}{M_i}} = \frac{\frac{0.986}{890\ [\frac{kg}{kmol}]}}{\frac{0.986_i}{890\ [\frac{kg}{kmol}]} + \frac{0,014}{282.4[\frac{kg}{kmol}}} = 0.96 \tag{B.3}$$

By dividing the obtained flow with mole fraction the final total flow can be calcuated by Equation B.4.

$$F = \frac{F_i}{X_i} = \frac{0.05}{0.96} = 0.052[\text{kmol/hr}] \tag{B.4}$$

This will act as a reference when creating the Aspen models for 1.4 wt% and 30 %wt FFA.

Appendix C: Equipment and material data for Aspen and SuperPro simulation.

Table C.1 depicts the operation parameters collected from the articles presented in Table 4.2 and 4.3. The articles will assist in setting the boundary condtion for the parameter ranges.

Table C.1: Equipment size, parameters and assumptions.

Equipment	Parameter	Specification
Reactor 1		
	Inlet temperature	60◦C
	Inlet pressure	7 bar
	Volume	0.018 m3
Reactor 2		
	Inlet temperature	60◦C
	Inlet pressure	7 bar
	Volume	0.018 m3
Flash tank Data		
	Temperature	120 ◦C
	Pressure	0.1 bar
Heat exchanger		
	Water inlet temperature	10 ◦C
	Flow	12.6 kg/hr
	Product temperature	From 120 to 60
	Pressure	1 bar
Glycerol-Methanol flash separation		
	Pressure	1 bar
	Temperature	80 ◦C
Biodiesel-Methanol distillation Specification (DSTWU)		
	Pressure (boiler, condenser)	1bar, 0,2 bar
	Temperature	131.5 C
	Number of stages	3
	Feed stage	2
	Reflux ratio	2
	Bottom purity	>0.95

Note: mixing of reactants occurs at standard conditions.

Stream inlet specification and assumptions for the Aspen model and SuperPro simulation can be viwed in Table C.2.

Table C.2: Feedstream data.

Component	Specification	Assumption
Oil		
Flowrate triglyceride	50 [mol/hr]	Steady state
Water	0 - 0.1 wt%	Negligible
FFA	Oleic acid 1.4 wt%	1
Pressure	1 bar	atmospheric
Temperature	293 K	room
Methanol		
Water content	0.1%	Negligible
Pressure		atmospheric
Temperature	293 K	Constant
Feedstock flow to reactor 1	64 [mol/hr]	Steady state

The amount of oil is found from the models basis in appendix B.

Aspen simulation #2: Biodiesel production from a non edible oil containing 30% FFA can be seen in Figure C.1. The purpose of the second simulation is to check to wich extent the changes affect the mass flow in the Aspen model when altering the level of FFA, f.ex change in the methanol flow and to see if the operational conditions for the model holds.

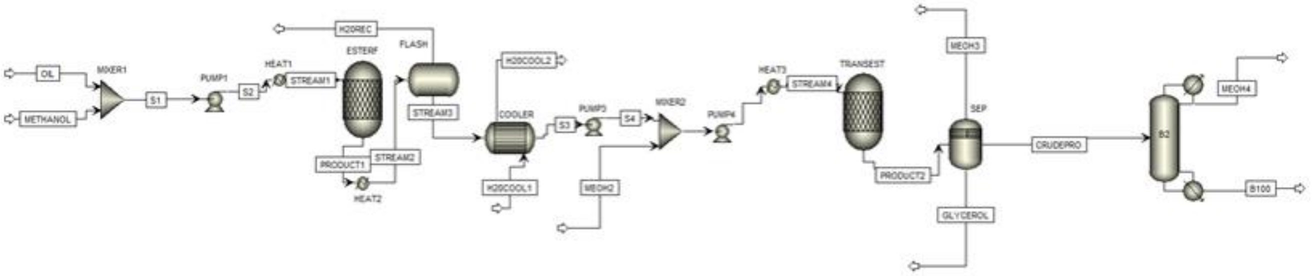


Figure C.1: Aspen simulation of biodiesel production from oil containing 30 wt% FFA.

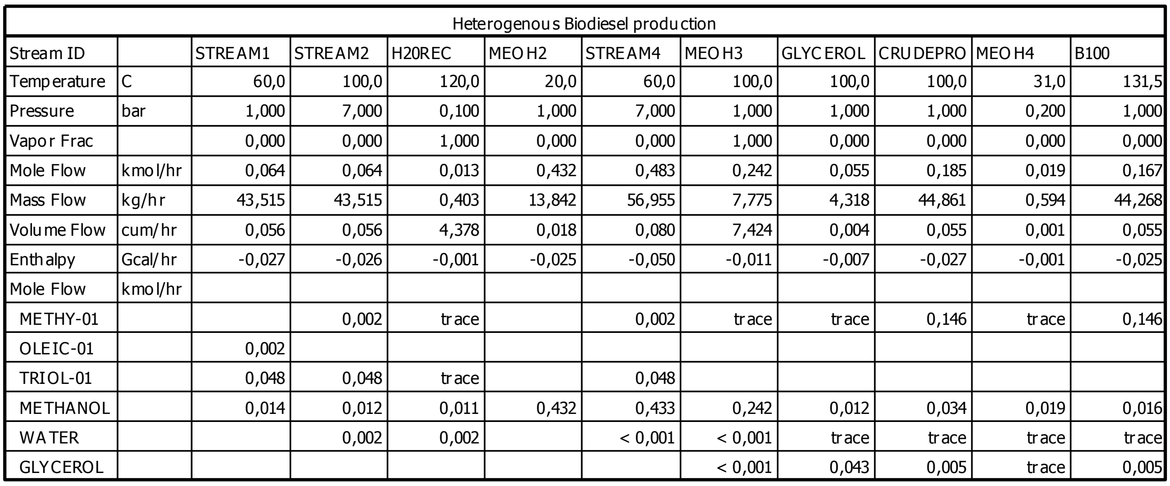
In Table C.3 the results of the second Aspen simulation is presented.

Table C.3: Results from the the second Aspen simulation with 30wt% FFA.

Heterogenous Biodiesel production											
Stream ID		STREAM1	STREAM2	H20REC	MEOH2	STREAM4	MEOH3	GLYCEROL	CRUDEPRO	MEOH4	B100
Temperature	C	60,0	100,0	120,0	20,0	60,0	100,0	100,0	100,0	21,2	131,3
Pressure	bar	1,000	7,000	0,100	1,000	7,000	1,000	1,000	1,000	0,100	1,000
Vapor Frac		0,502	0,000	1,000	0,000	0,000	1,000	0,000	0,000	0,000	0,000
Mole Flow	kmol/hr	0,390	0,390	0,311	0,360	0,439	0,218	0,036	0,185	0,025	0,160
Mass Flow	kg/hr	52,399	52,399	9,379	11,535	54,555	7,005	2,854	44,696	1,423	43,273
Volume Flow	cum/hr	5,384	0,073	101,474	0,015	0,074	6,688	0,002	0,054	0,002	0,053
Enthalpy	Gcal/hr	-0,043	-0,042	-0,015	-0,021	-0,046	-0,010	-0,005	-0,027	-0,002	-0,024
Mole Flow	kmol/hr										
METHY-01			0,045	< 0,001		0,044	trace	trace	0,145	0,001	0,144
OLEIC-01		0,045	< 0,001	trace		< 0,001	trace	trace	< 0,001	< 0,001	< 0,001
TRIOL-01		0,034	0,034	trace		0,034					
METHANOL		0,312	0,267	0,266	0,360	0,361	0,218	0,008	0,034	0,019	0,015
WATER			0,045	0,045		< 0,001	< 0,001	trace	trace	trace	trace
GLYCEROL							< 0,001	0,028	0,005	0,004	0,001

On the following page Table C.4 shows the data collected from the first simulation where the feedstock had 1.4 wt% of FFA (Oleic acid). This table will act as a reference to the second simulation to verify the change of mass flow across the model.

Table C.4: Results from the the first Aspen simulation #1 with 1.4wt% FFA.



Heterogenous Biodiesel production

Stream ID		STREAM1	STREAM2	H20REC	MEOH2	STREAM4	MEOH3	GLYCEROL	CRUDEPRO	MEOH4	B100
Temperature	C	60,0	100,0	120,0	20,0	60,0	100,0	100,0	100,0	31,0	131,5
Pressure	bar	1,000	7,000	0,100	1,000	7,000	1,000	1,000	1,000	0,200	1,000
Vapor Frac		0,000	0,000	1,000	0,000	0,000	1,000	0,000	0,000	0,000	0,000
Mole Flow	kmol/hr	0,064	0,064	0,013	0,432	0,483	0,242	0,055	0,185	0,019	0,167
Mass Flow	kg/hr	43,515	43,515	0,403	13,842	56,955	7,775	4,318	44,861	0,594	44,268
Volume Flow	cum/hr	0,056	0,056	4,378	0,018	0,080	7,424	0,004	0,055	0,001	0,055
Enthalpy	Gcal/hr	-0,027	-0,026	-0,001	-0,025	-0,050	-0,011	-0,007	-0,027	-0,001	-0,025
Mole Flow	kmol/hr										
METHY-01			0,002	trace		0,002	trace	trace	0,146	trace	0,146
OLEIC-01		0,002									
TRIOL-01		0,048	0,048	trace		0,048					
METHANOL		0,014	0,012	0,011	0,432	0,433	0,242	0,012	0,034	0,019	0,016
WATER			0,002	0,002		< 0,001	< 0,001	trace	trace	trace	trace
GLYCEROL							< 0,001	0,043	0,005	trace	0,005

By compairing the two Tables (C.3, C.4), one can detect some alteration in the mass-flow espesically regarding the methanol flow. The comparison of the two Tables, shows an overall methanol increase from 446 mol/hr (simulation #1) to 672 mol/hr, roughly a 50% increase of methanol. Interestingly, one can observe that the methanol content in the final product is lower than the first simulation with little change in the operation conditions. However, one can observe that the final mass flow of biodiesel is almost 1kg/hr less than the first simulation. This could a result in a different economical outcome than the one presented Chapter 5 in this thesis if the all the feedstock used in the plant contains more than 30 wt% of FFA. This scenario however is not crucial to this thesis, but could prove useful in further work when an optimalization of the plant is preformed.

Appendix D: Economical data.

D.1 Budget for the thesis:

The student organization TEKNA graciously provided the team with a $ 3191 (25 000 NOK) grant that will be the economic frame for this thesis. This will not be sufficient for a whole plant but will contribute to the finishing some of the key modules. Private investors and sponsors contribute to the remaining equipment. The totale budget of this thesis can be viewed in Table D.1.

Table D.1: Budget for the thesis.

Equipment	Quantity	Cost ($)
Framework	3	1 659
Conical tank (200 l)	1	447
Conical tank (60 l)	1	127
Pressure vessels	2	893
Pipework		383
Centrifuge (Raw Power)	1	1915
High pressure pump	1	Sponsored
Low pressure pump	1	217
Heating element	2	38
HDPE tank	3	sponsored
Total		5 680

D.1 The fixed cost of the prototype plant:

Based on literature and data collected during the run of the thesis, an economic analysis was preformed in the software “SuperPro designer”. The purpose of the simulation is to decide the payback time of an investment in the plant. Assumption surrounding the simulation is that the producer pays 40% tax of the revenue. However, in real life the taxation will reduced. This is because of subsidies and support-programs for bioenergy solutions from “Innovation Norway”,”Enova” and “Skattefunn” that could in theory reduce the own investment and increase the overall revenue.

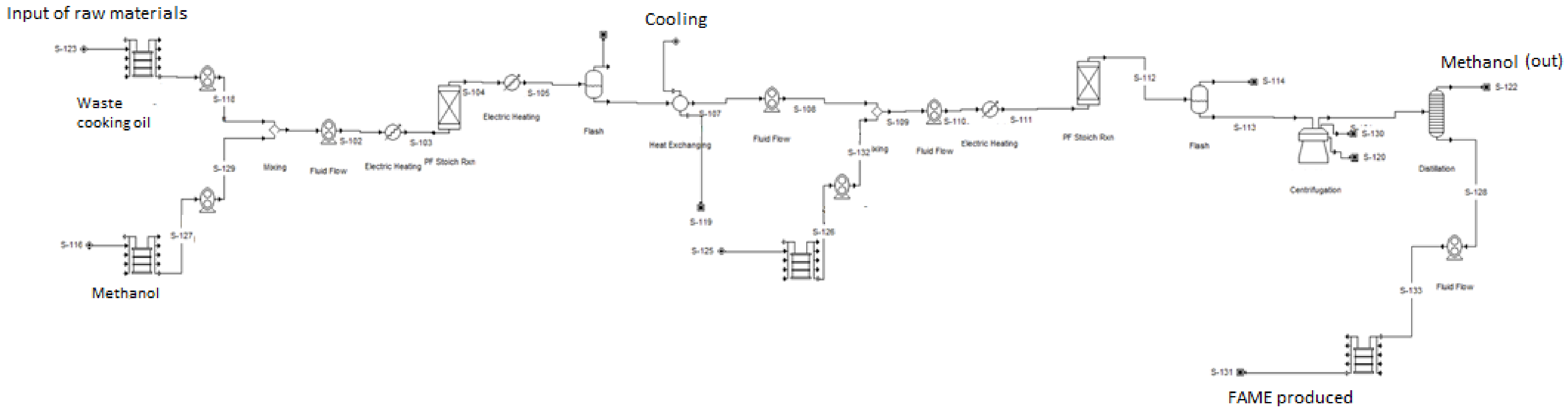


Figure D.1: Flowsheet from the SuperPro Simulation.

Note: one difference between the Aspen model and the SuperPro model, is the use of a centrifuge and flash separator in the SuperPro model. In the Aspen model this same step is represented with just the flash separator which separate the stream into three different streams (methanol, glycerol and crude biodiesel).

From the “SuperPro” analysis, a fixed capital cost of a future plant was determined and can be viewed in Table D.2. However, the fixed cost for a pilot-plant could possible be more than the estimated capital cost from “SuperPro”.

Table D.2: Estimated cost of a future small-scale plant.

Equipment	Quantity	Cost ($)
Conical tank (200 l)	3	1340
Flash drum	2	2042
Destillation column	1	7148
Conical tank (60 l)	5	638
Pressure vessels	2	2276
Centrifuge	1	2042
High pressure pump	5	2042
Low pressure pump	7	1583
Heating element	2	38
Heat element band	8	1276
HDPE tanks	8	382
Mixer	3	1915
Heat Exchanger		3829
Framework	6	4084
Pipework		6127
Electrical		2042
Container	1	8680
Insulation		1021
Auxillary facilitys		2042
Installation		5106
Control system		7148
Sensors		4199
Total		67 000

In addition to the fixed cost, an estimation of the catalyst and material (sulfuric acid) cost must be preformed. The catalyst is viewed as fixed cost as it can be regenerated. The data related to material cost is gathered in Table D.3.

Table D.3: Catalyst and some basic material cost [82, 83].

Type	Price pr. kg ($)
Amberlyst BD20	112
GoBio T300	Around 50
Carbon catalyst	Less than 12
Calcium oxide	Less than 12
Sulfuric acid	61
Zeolites	19

Note: Regarding the Amberlyst BD20, the change frequency depends on the impurities level and can be renewed every 180 days [84].

D.2 Cost of feedstock and products:

The prices for the reactants and the products can be located in Table D.4. The prices of the glycerol given is for food grade. The data is based for a Norwegian scenario regarding the feedstock such as WCO. WCO can cost the user $ 0.58 pr liter when disposed off [85].

Table D.4: Prices of feedstock and products [86, 87, 88].

Feedstock and products	Cost pr ton ($)
Methanol	370
Waste vegetable oil	no cost to minimal
Biodiesel	2000 (1.75 pr. liter)
Glycerol (refined)	1225
Glycerol (waste)	112

Table D.5: Cost of waste cooking oil from overseas [89, 90].

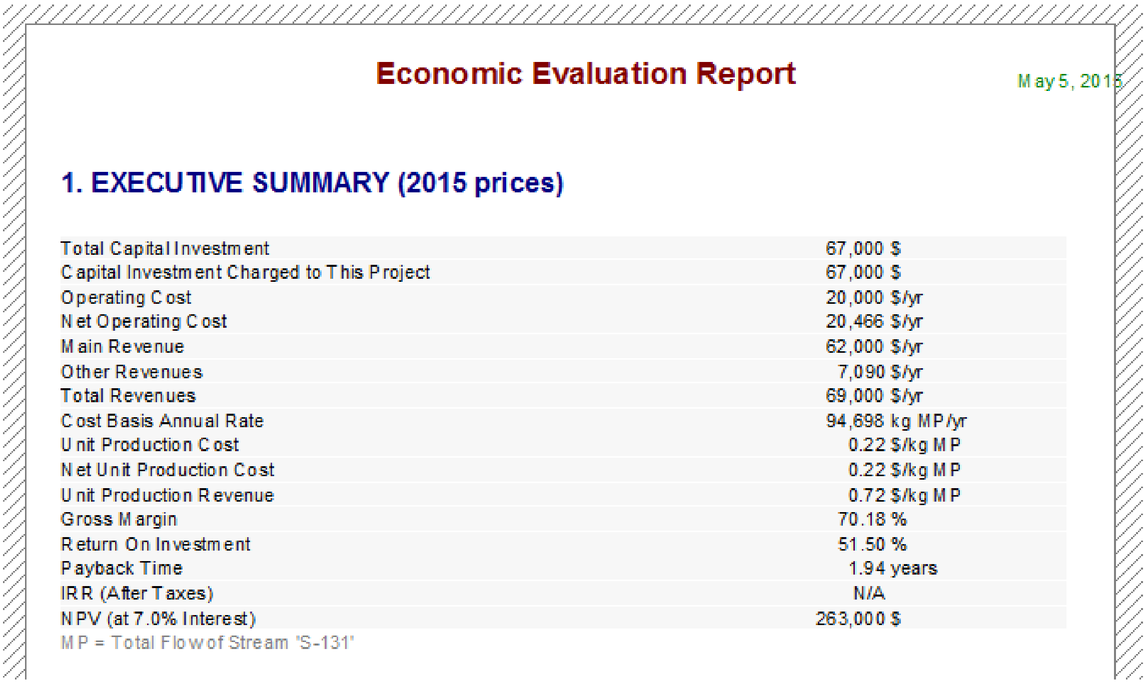
FFA-content (wt%)	Origin	Cost pr ton ($)
3.0	Malaysia	255-370
3.75	China	510-1123
1-20	South Africa	408-765
3.0	Indonesia	242-384
3.0-5.0	Tunisia	714
< 1	Estonia	363
1.5	Scotland	102

Note: The references in Table D.5 are from the Chinese e-commerce company “Alibaba”.

D.3 Results from the "SuperPro" simulation:

Displayed in Tables D.6 and D.7 is a more detailed economic report from the SuperPro simulations regarding the two most viable scenarios simulated in this thesis.

Table D.6: Results from the "3 months" production for single producer, 40% tax, $ 0.83 pr. kg biodiesel.



Economic Evaluation Report

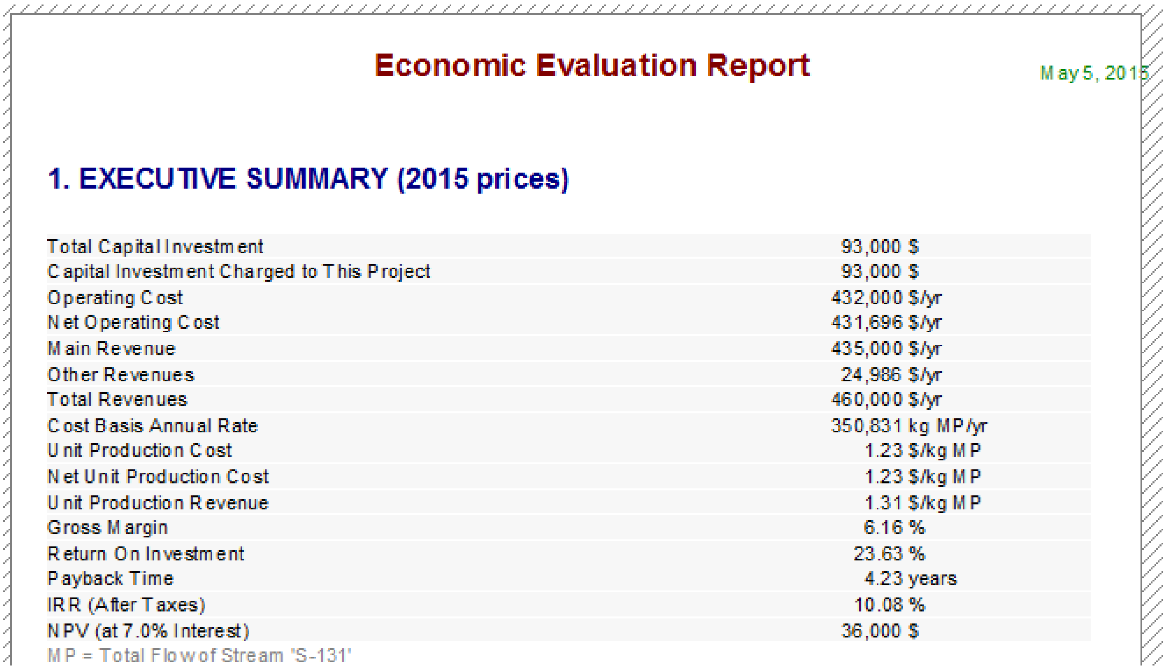
May 5, 2015

1. EXECUTIVE SUMMARY (2015 prices)

Total Capital Investment	67,000 $
Capital Investment Charged to This Project	67,000 $
Operating Cost	20,000 $/yr
Net Operating Cost	20,466 $/yr
Main Revenue	62,000 $/yr
Other Revenues	7,090 $/yr
Total Revenues	69,000 $/yr
Cost Basis Annual Rate	94,698 kg MP/yr
Unit Production Cost	0.22 $/kg MP
Net Unit Production Cost	0.22 $/kg MP
Unit Production Revenue	0.72 $/kg MP
Gross Margin	70.18 %
Return On Investment	51.50 %
Payback Time	1.94 years
IRR (After Taxes)	N/A
NPV (at 7.0% Interest)	263,000 $

MP = Total Flow of Stream 'S-131'

Table D.7: Commercial scenario for a renovation company, 40% tax and retail price of $ 1.3 pr. kg biodiesel.



Economic Evaluation Report

May 5, 2015

1. EXECUTIVE SUMMARY (2015 prices)

Total Capital Investment	93,000 $
Capital Investment Charged to This Project	93,000 $
Operating Cost	432,000 $/yr
Net Operating Cost	431,696 $/yr
Main Revenue	435,000 $/yr
Other Revenues	24,986 $/yr
Total Revenues	460,000 $/yr
Cost Basis Annual Rate	350,831 kg MP/yr
Unit Production Cost	1.23 $/kg MP
Net Unit Production Cost	1.23 $/kg MP
Unit Production Revenue	1.31 $/kg MP
Gross Margin	6.16 %
Return On Investment	23.63 %
Payback Time	4.23 years
IRR (After Taxes)	10.08 %
NPV (at 7.0% Interest)	36,000 $

MP = Total Flow of Stream 'S-131'

Appendix E: Concept art from Solidworks.

The final conceptual design of the biodiesel plant done in “solidworks” can be viewed in the Figure E.1, E.3 and E.3.

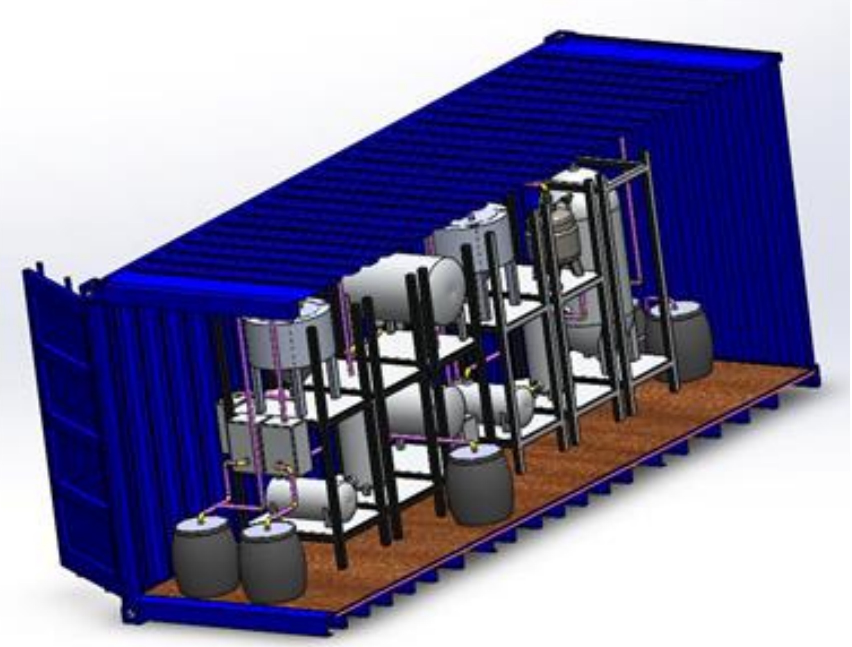


Figure E.1: Small-scale biodiesel plant concept #1.

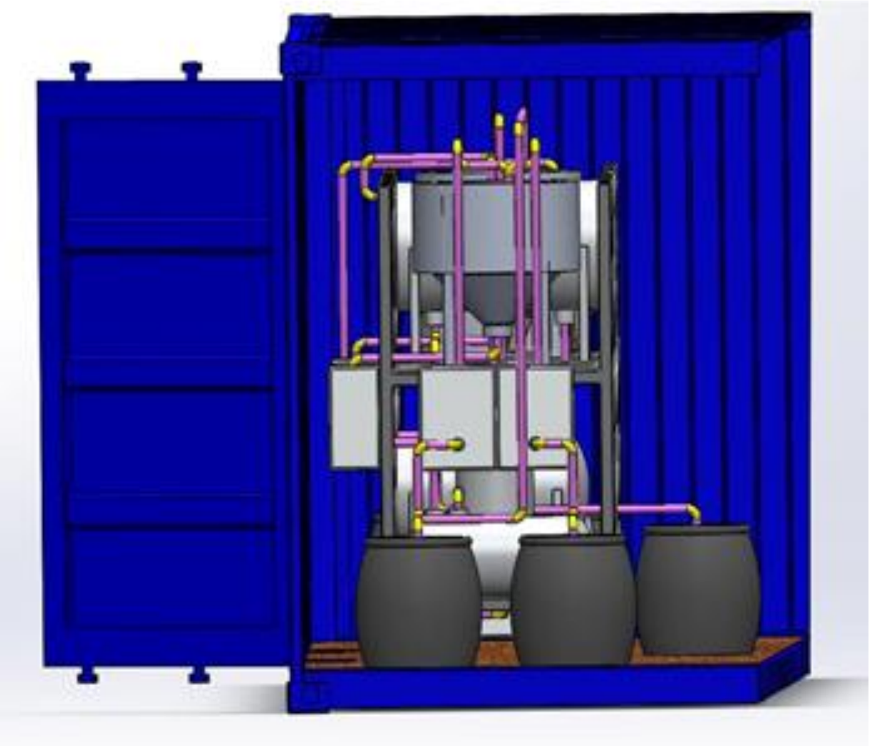


Figure E.2: Small-scale biodiesel plant concept #2.

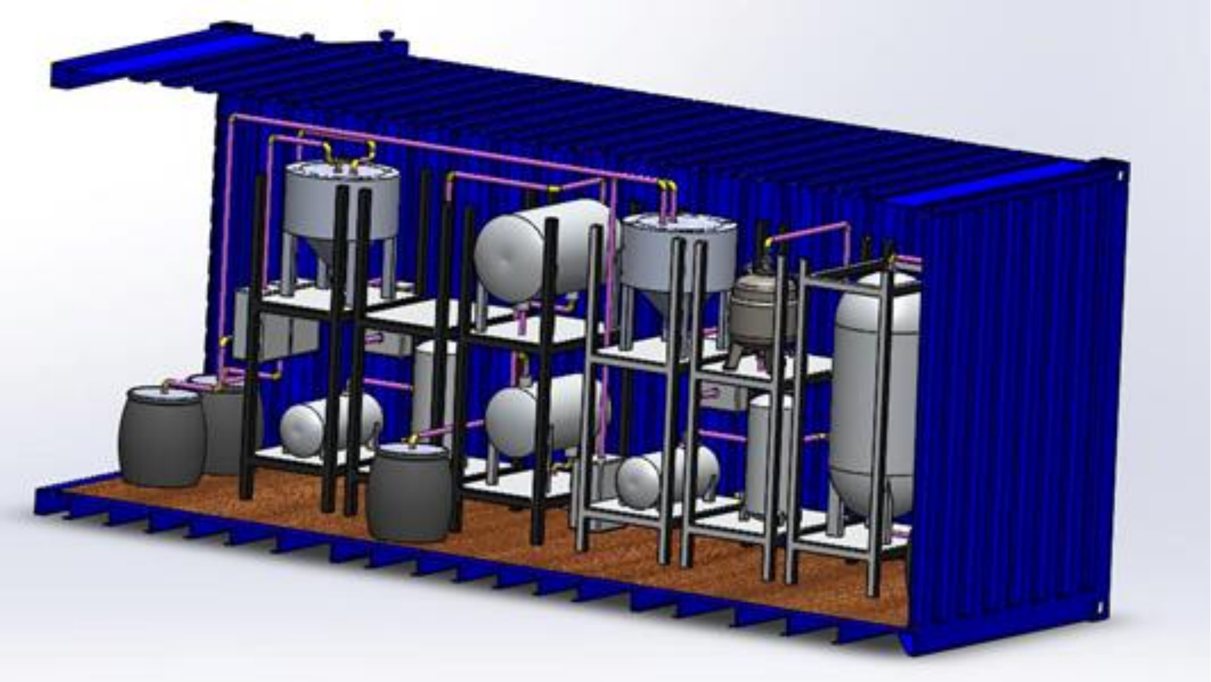


Figure E.3: Small-scale biodiesel plant concept #3.

For a short animation film showing a simplified small-scale plant based on the solidwork model, please visit: https://www.youtube.com/watch?v=DyV_RGYjwC8

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