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Biodiesel Production by the Esterfip-H Process

Modelling, Optimization and Control Structure

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Abstract

For this master's thesis the Esterfip-H process for biodiesel production from rapeseed oil have been modelled in Chemcad. Esterfip-H is a two fixed-bed reactor system using a heterogeneous catalyst of zinc aluminate oxide at high pressure and temperature. Literature and patent information have been collected and merged for a model basis. The original model was optimized with respect to the inlet temperature at the reactors and the methanol to oil and methyl oleate weight ratios. A control structure has been suggested based on placement of throughput manipulator, consistency rule and degrees of freedom.

The model has been found to produce biodiesel satisfying the European standard requirement of 96.5wt% ester. The glycerol product is purer than the literature value of 98wt%, with a purity of 99.8wt%. The model production of biodiesel is 99.95% of the model basis, 20000 kg/hr, with a purity of 99.7wt% methyl oleate. The biodiesel production is optimized at the active constraints of reactor inlet temperature and the total glycerine including glycerol, tri-, di-, and monoglyceride of 0.25wt% in the biodiesel product.

It was found that the optimum is flat, giving good opportunities for controllability, but making it sensitive to model convergence noise. The model noise was found to be of a scale affecting the optimal point, resulting in the built-in optimization sequence giving in a bit different solution after each run, but within a methanol flow rate of ±0.9%.

Modification of the original model by the use of three reactors have been found economically beneficial with a profit increase of 129% from the original profit, 1074 $/hr. Profit increase by a factor of 140% when implementing simple improvement suggestions found under the study of the original model.

The model has been found to imitate the Esterfip-H process well, as far as can been seen from available literature. The model can be developed further for optimization of the process.

Sammendrag

I denne masteroppgaven har det blitt laget en modell av Esterfip-H prosessen for produksjon av biodiesel fra rapsolje ved bruk av Chemcad. Esterfip-H er en prosess der det benyttes to reaktorer med stasjonær heterogen katalysator bestående av oksid av sink og aluminium ved høy temperatur og trykk. Litteratur og patent informasjon har blitt samlet inn og fusjonert til en modell basis. Den opprinnelige modellen har blitt optimalisert i henhold til reaktor innløps temperatur og vektforhold metanol til olje og metyl oleate. Deretter har det blitt foreslått en kontrollstruktur basert på produksjonskapasiteten, konsistens og frihetsgrader.

Modellen tilfredstiller de europeiske kravene til biodiesel på 96.5wt% ester. Glyserolen som blir produsert har en høyere renhet enn litteraturverdi på 98wt%, med en renhet på 99.8wt%. Produksjonen i modellen er på 99.95% av modell utgangspunktet på 20000 kg/time, med en renhet på 99.7vekt% metyl oleate. Produksjonen er optimalisert med aktive restriksjoner på reaktor innløps temperatur og den totale glyserin vekt prosenten i biodiesel på 0.25wt% som inkluderer glyserol, tri-, di-, og monoglyceride.

Optimumet ble funnet til å være flatt, noe som gir gode muligheter for kontrollbarhet, men også gjør modellen sensitiv for forstyrrelser fra modellen når den konvergerer. Modellforstyrrelsene er funnet til å være av en størrelsesorden som vil påvirke det optimale punktet. Dette gir utslag ved at det optimale punktet, gitt av den innbygd optimaliserings sekvensen, gir litt ulike resultater ved hver gjennomkjøring, men med en metanol strøm på ±0.9% av det benyttede optimumet.

Modifikasjon av den opprinnelige modellen ved bruk av tre reaktorer er funnet økonomisk fordelaktig med en økning i fortjeneste på 129% av den opprinnelige profitten på 1074 $/time. Ved implementering av forbedringspotensialene funnet ved modell analyse kan profitten økes med 140%.

Modellen etterligner Esterfip-H prosessen godt så langt den lar seg validere mot tilgjengelig litteratur. Modellen kan utvikles videre for optimalisering av prosessen.

Preface

This thesis is the final part of my integrated Master of Science degree in Chemical Engineering at the Norwegian University of Science and Technology.

A great thanks to supervisor Sigurd Skogestad and Chriss Grimholt for all help, support, guidance and inputs. Especially thanks to Chriss Grimholt my co-supervisor, for all his help. I appreciate the open door for question and discussion and their willingness to help. I would also like thank to Johannes Jäschke for interest in my thesis.

I am grateful for Magne Hillestads help in getting the license to Chemcad and Magnar Hole at ED service for making the license available for more users. A great thanks to Karoly Moser at Norpal for giving an introduction course in Chemcad, making the introduction to a new program as smooth as possible. And for giving me the possibility to ask questions related to Chemcad and input on approaches for solving arising problems.

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Declaration of compliance

I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU).

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Contents

1 Introduction

The scope of this thesis has been to create a model for biodiesel production by the Esterfip-H process, and optimization of the model. A control structure has also been suggested.

In the following introduction the focus is on why biodiesel is produced in the first place and general interest in biodiesel. Norway is a country rich in oil and gas, why should there be any interest in biodiesel as a fuel? What are the benefits with biodiesel, and how could this become an economical feasible operation competing with petroleum fuel?

1.1 Biodiesel

Vegetable oil for engine gain its place as a result of the energy crises of the 1970's, [1], but was already used as emergency fuel during World War II. The interest for vegetable oil as fuel has increased since and keep on increasing since fossil fuel reserves are limited. Several nations have long-term national goals in energy policy where the increased use of biodiesel is included in the targets, [2]. Already in 1938 Walton recommended that glycerol should be removed from the oil, being the practice in today's biodiesel (esters) production. Ester formation is an important class of reactions for adding value to oil, and some of the typical ways for doing this today are given in Equation 1.1-1.3 where R, R' and R" are alkyl groups, [2, 3].

Esterification

$$\text{ROH+R'COOH} \rightarrow \text{R'COOR+H}_2\text{O} \tag{1.1}$$

Transesterification

$$\text{RCOOR'+R''OH} \rightarrow \text{RCOOR''+ R'OH} \tag{1.2}$$

Acidolysis

$$\text{RCOOR'+R''COOH} \rightarrow \text{RCOOH+R''COOR'} \tag{1.3}$$

This study will only cover the transesterification. Independent of the production method the main characteristics of the transesterification reaction is the same when introducing alcohol:

$$\begin{aligned} \text{Triglyceride} &\rightarrow \text{Diglyceride} \rightarrow \text{Monoglyceride} \\ &\rightarrow \text{Glycerol} + 3 \cdot \text{Methyl Oleate} \end{aligned} \tag{1.4}$$

1.2 Biodiesel versus Petroleum fuel

There are benefits and disadvantages with biodiesel compared to competitive products. Comparison of biodiesel and petroleum diesel shows the benefits with the renewable energy, but also points out some of the disadvantages, see Table 1.1, [4, 5]. B100 is pure biodiesel, while B20 is 20% biodiesel.

Table 1.1: Biodiesel emissions compared to petroleum diesel in %, pointing at advantages and disadvantages, [4, 5].

Emission	B100	B20
Carbon monoxide	-48	-12
Total unburned hydrocarbon	-67	-20
Particulate matter	-47	-12
Nitrogen oxides	+10	+2
Sulfates	-100	-20
Air toxics	-60 to -90	-12 to -20
Mutagenicity	-80 to -90	-20

The main disadvantage is the emission of nitrogen oxide. It has recently been discovered that the amount of nitrogen oxides from diesel engines are higher than previously predicted, possibly creating negative focus around biodiesel production, [6].

1.3 Energy gain

A triglyceride such as rapeseed oil is a natural way of storing energy, and the energy content is naturally high. A 1 to 3.24 positive life cycle energy balance has been reported, and recent data is suggesting 1 to 4.5, [1]. Other sources are operating with a range of 2.8-4.2 energy balance, [2, 7]. From these literature values it could be concluded that the process could be made beneficial as long as the energy consumptions are minimized, feedstock prices are low and product prices are high enough.

Cetane number (CN) is similar to the octane number for petroleum fuel and indicate the performance and quality of the biodiesel. The cetane number is a dimensionless description of the ignition quality. CN is affected by branching and chain length, where a decreasing chain and increased branching lead to a lower CN. The CN should not be to high or low, because it would cause incomplete combustion or other operational problems, [1, 2]. The CN for rapeseed methyl ester have been reported as 47.9-56.0 by, [1, 2], and should extend 51 as a minimum limit by biodiesel standard EN 14214, see Appendix A.

Heat of combustion for rapeseed methyl ester (RME) is reported as 37.8 [MJ/kg], [8], in the range 37.3-39.9 [MJ/kg], [1], and 38 [MJ/kg] by Perstorp, [9]. Heat of combustion is a measurement of the energy content in biodiesel, the energy released as heat under complete combustion, [1].

1.4 Feedstock

The choice of feedstock depends on the availability, price, governmental policy, and food use in the area, [1]. The oil can be divided into the main parts vegetable-based, animal-based or waste oils. Some different types of vegetable-based oil are sunflower oil, soybean oil, coconut, corn, palm, peanut, tallow, lard, yellow grease and brown grease, [10]. One ethical aspect with the biodiesel production is the competition of raw material for fuel production contra being food for the humans. The use of waste oil will reduced this competition, but contain more impurities than the vegetable-based oil and processing will be more difficult and require more pretreatment. Impurities will have effect on the reaction conditions and side reactions will have larger significance.

Rapeseed oil is considered the main feedstock in biodiesel production in Europe, while in USA soyabean oil is the main feedstock, [1, 2]. Rapeseed oil contains several fatty acid chain as given in Table 1.2, but will for simplicity be assumed based one the dominant component oleic acid, [2, 11]. When the triglyceride is breaking up into three methyl esters, three methyl oleate will be formed.

1.4.1 Physical properties

When creating pseudo components for the triglyceride based on oleic acid the physical properties were taken from a patent by the French Institute of Petroleum, [12], given in Table 1.3.

Table 1.2: Composition of fatty acid chains in rapeseed oil, [11].

Fatty Acid Chain	Chain formula	Composition by weight %
Palmitic	C16:0	5
Palmitoleic	C16:1	< 0.5
Stearic	C18:0	2
Oleic	C18:1	59
Linoleic	C18:2	21
Linolenic	C18:3	9
Arachidic	C20:0	< 0.5
Gadoleic	C20:1	1
Behenic	C22:0	< 0.5
Erucic	C22:1	< 1

Table 1.3: Physical data for the reactants, intermediates and products in the transesterification reaction from patent, [12].

Component	Molar mass [kg/kmol]	Normal boiling temperature [°C]	Density at 15°C [kg/m^3]
Water	18	100	998.6
Methanol	32	65	795.65
Glycerine	92.1	290	1265.1
Ester	296.5	344	876.9
Monoglyceride	356.6	358	941.1
Diglyceride	621.1	367	928.1
Oil (Triglyceride)	885.5	375	915.6
Oleic acid	282.5	370	892.1

1.5 Biodiesel production methods

For large scale plants producing more than 4 million litres/year the process is operating continuously, [13], while smaller plants often operate on batch basis. Smaller batch processes are often used for home production of biodiesel, and can be bought on-line. In addition to the chosen process for study, Esterfip-H, there exists several others processes, some are more conventional today. Some of the other methods are given briefly in Table 1.4. The thesis has been done for the Esterfip-H process due to more recent technology and a starting establishment as a design alternative to the conventional plug flow reactor, possibly being the process for the future.

Table 1.4: Biodiesel production methods in use and in research phase.

Method	**Advantages**	**Disadvantages**
Supercritical methanolysis, [2]	• Treats both triglyceride and free fatty acids so it will be both esterification and transesterification simultaneous. • No catalyst is required. • The reaction time is shorter than in the common used method. • The operating process is simplified due to now catalyst. • No soap formation.	• More expensive than conventional transesterifacation. • The process operates at high temperature and pressure, hence increased safety issues. • The necessary amount of methanol is in the molar ratio 40:1 with the oil. • Increased cost.
Batch processes, [14]	• High flexibility in feedstock.	• Uses catalyst. • Low production compared to continuous.
Enzymatic processes, [14]	• Low energy requirement • Ambient operating conditions.	• Reduced yield. • Increases reaction time. • Little research for industrial use.
Multi step processes, [14]	• High purity of glycerol. • No need for catalyst and thereby reduction of washing and neutralisation.	*–contiune*

Method	**Advantages**	**Disadvantages**
Reactive separation, [14]	• Single unit. • Improved production. • Reducing energy demand. • Reactants in stoichiometry.	• Difficulties with temperature and pressure for both reaction and separation simultaneously.
Hydro-pyrolysis, [14]	• Mixture of hydrocarbons.	• Complex equipment. • Requires hydrogen.
Continuous processes, [14]	• Ambient operating conditions. • Widely used method in industry.	• Homogeneous catalyst.

1.6 Biodiesel in engines

Biodiesel can be used in engines in its pure form (B100) or usually mixed with traditional petrodiesel. Biodiesel is meant to be used in a standard diesel engine. The chemical group for biodiesel is ester, and the alkyl group attached will depend on the alcohol used for conversion. The length of the chains will be given by the original triglyceride composition. Biodiesel is now in use in cars, buses, trains, and is also tried in aircrafts, [1].

1.7 Storage

One of the main critical factors with biodiesel is the storage capacity and the production should mainly reflect the demand, [3]. Often the demand will have fluctuations in amount, but also in specifications. A plant could produce one type of biodiesel for mixing with petroleum diesel and another for use in pure form, giving different demands for purity. In the northern part of Europe the specification will depend on season and temperature. At winter when the temperature falls below zero degrees Celsius, it must be avoided that the biodiesel cloud and plug the engine.

1.8 Glycerol

A benefit with the Esterfip-H process compared to conventional processes is the high glycerol purity. With a high world production of glycerol, a high purity glycerol will be a benefit. Due to reducing customer purification requirements on a closely saturated market.

Due to oversupply of glycerol worldwide new applications of glycerol have been introduced. The more traditional uses of glycerol are in cosmetics, food, and pharmaceutic applications, [15, 16]. Glycerol can also be used in tobacco, explosives, drug and plastics, [16]. Figure 1.1 illustrates the distribution of the applications of glycerol, [16].

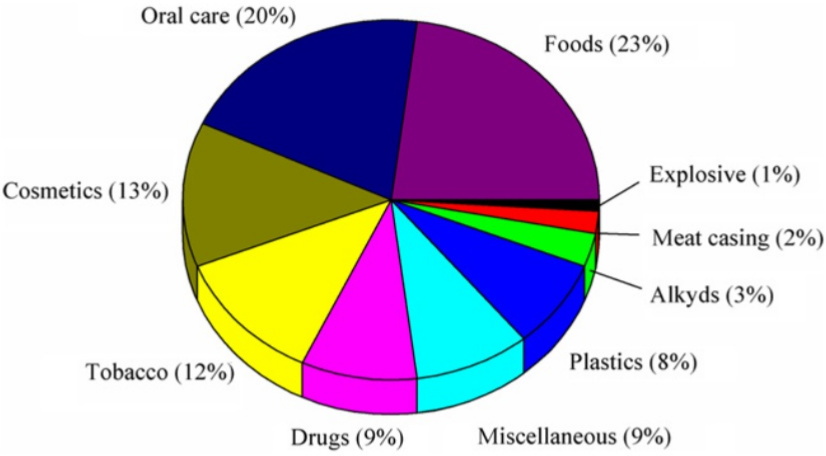


Figure 1.1: Glycerol applications, [16].

1.8.1 Free and bounded glycerol

Biodiesel product will contain both free and bounded glycerol and the product specifications will be related to these amounts individually and in total. Bounded glycerol is the portion of glycerol molecule unreleased from triglyceride, diglyceride and monoglyceride. Free glycerol is the amount of glycerol in the finished biodiesel phase. Alcohol can operate as a co-solvent and increase the amount of free glycerol in biodiesel and the amount of methanol in separation unit should be controlled.

1.9 Life Cycle Assessment

Some producers sell biodiesel as CO_2 neutral, but when considering the whole life cycle it will not be neutral, but it will have a lower CO_2 emission than petroleum fuel due to closed carbon cycle, [2].

The saving effects are greatest when rapeseed oil or sunflower oil is used for production of biodiesel, [2]. Some aspects of the analysis will be site dependent, like transport of the feed and product, [2]. Table 1.5 gives some of the positive and negative aspects with biodiesel production, [2].

Table 1.5: Some of the aspects with biodiesel production compared to petroleum, [2].

Advantages	**Disadvantages**
• CO_2 reduction • Saving fossil energy • Organic waste reduction • Less transport	• Land use • Acidification of water • Water pollution by pesticides

When applying the Esterfip-H process compared to the conventional biodiesel process some of the disadvantages will be removed or reduced. Like the acidification of water and the water pollution as the catalyst is fixed-bed and less water will be used at the production site. Water will still be used in cooling and heating, but will not be mixed with products in a washing step.

1.10 Biodiesel in cold environment

Verdis Polaris is a biodiesel developed for the cold northern environment by the Perstorp concern. The cold filter plugging point, CFPP, for Verdis Polaris is -11/-20°C for summer and winter respectively. Compared to normally CFPP of -10°C reported by, [1]. This makes it a more suited biodiesel in the nordic climate. It is still sensitive to extreme temperatures, and is not applicable in northern and inland Norway in the hardest winter season. To produce the winter friendly biodiesel some more posttreatment to the Esterfip-H process will be necessary, [17]. Exactly what treatment is not available yet, due to patent application, [17].

2 Process

Patents are used as the basis for process description and choice of necessary equipment. As stated in literature patents can be used as source of information, but with some care, [18]. It is informed that examples given in patents often give an indication of the process conditions used. The examples are not always for industry, but could be for laboratory scale, [18]. “The best conditions will usually be at or near the upper or lower end of the narrowest range”, [18] .

2.1 Esterfip-H process

The process used as basis for the model is the Esterfip-H process patented by the French Institute of Petroleum commercialised by Axens, [2, 19, 20, 21]. The flow scheme is based on patents and extraction of information under the guideline cited above, together with some conditions from the more conventional processes, [2]. Figure 2.1 gives the flow scheme of the process taken from literature, [1, 2, 22, 23]. The Esterfip-H process is an improvement of the Esterfip process using a heterogeneous catalysts for elimination of neutralization and washing steps compared to conventional operation, [20, 22].

The main invention of the Esterfip-H process is two fixed-bed reactors with a catalyst of zinc and aluminium oxide. By the use of a heterogeneous catalyst problems related to formation of salt with catalyst, and thereby emulsion between the methyl ester and glycerol phase and the phase separation complexity will be reduced or removed, [23].

2.1.1 Process outline

Figure 2.1 shows a draft of the Esterfip-H process principles from literature, [1, 2, 22, 23]. This outline only indicates the main actions of the process and the choice of more exact equipment must be based on other sources.

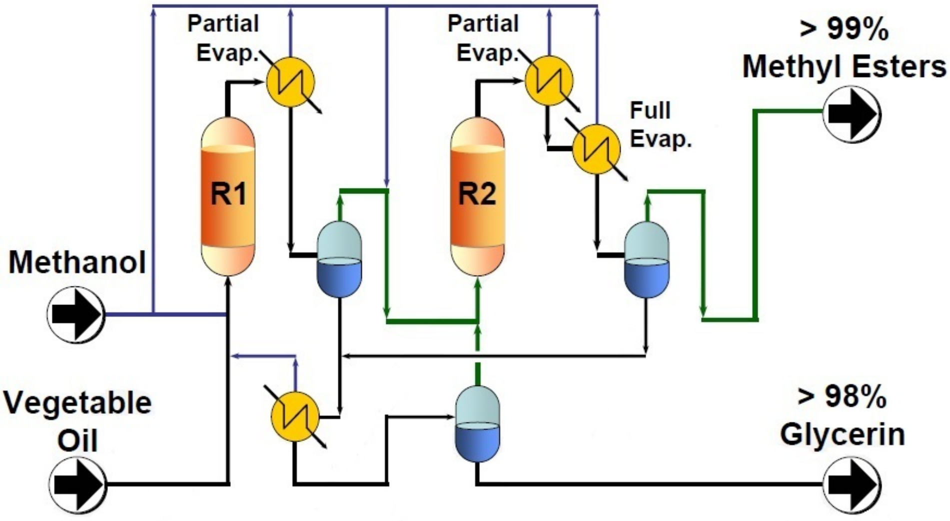


Figure 2.1: The principal of the Esterfip-H process scheme from article sources, [1, 2, 22, 23].

2.1.2 Process flow scheme

Figure 2.2 gives a flow diagram of the designed process containing pumps, heat exchangers, reactors, decanters and purification units. Pumps and heat exchangers are necessary to satisfy the required reactor conditions. There are two reactors in series with intermediate removal of methanol by pressure reduction and separation of glycerol and methyl phase.

Figure 2.2 is generated based on comparison and connection of all the patents, [12, 24, 25, 26, 27, 28, 29, 30]. It is desired that the process generated is close to the real process, but in lack of more real data the aberration from industrial data and behaviour could be large.

The pressure after reaction is released in two steps and methanol is flashed off. When the pressure is reduced the boiling temperature of the components will be reduced and due to the difference in boiling point between methanol and glycerol, methyl ester, triglyceride, diglyceride, and monoglyceride, methanol will be removed. The removed hot methanol is used for pre-heating of inlet streams to the reactors.

The intermediate removal of glycerol is for driving the reaction in the desired direction and avoiding undesired reverse reaction in according with the principle of Le Chatelier. The separation of glycerol and methyl ester in a decanter will be based on the difference in density, see Table 1.3. When the phases have been separated the reaction could be pushed further in the desired direction

After glycerol has been removed, new or recycled methanol is reintroduced in the methyl ester phase before compression and temperature increase back to reactor conditions. The two-step flash procedure is repeated after the second reactor and followed by vacuum distillation. Last purification of methyl ester phase after vacuum distillation is done in a decanter followed by a coalescer for final removal of fine glycerol droplets.

Glycerol from the first decanter is passed through one column for removal of methanol, being the most energy consuming step in the process. This is due to methanol and glycerol being closer in boiling temperature than methanol and methyl ester. The glycerol phase is then passed through a smaller column for water removal before a final decanter unit to achieve high purity specification. In the decanter unit the remaining biodiesel and intermediates are removed and could be sent to the second reactor.

For the heat exchanger units the methanol leaving the flash unit is used to pre-heat the inlet streams to reduced energy consumption, [12]. The configuration of the heat exchanger between hot methanol stream leaving the flash and cold inlet streams can be taken as heating the methanol inlet stream, the oil inlet stream or the mixed stream, taken as heating the mixed stream.

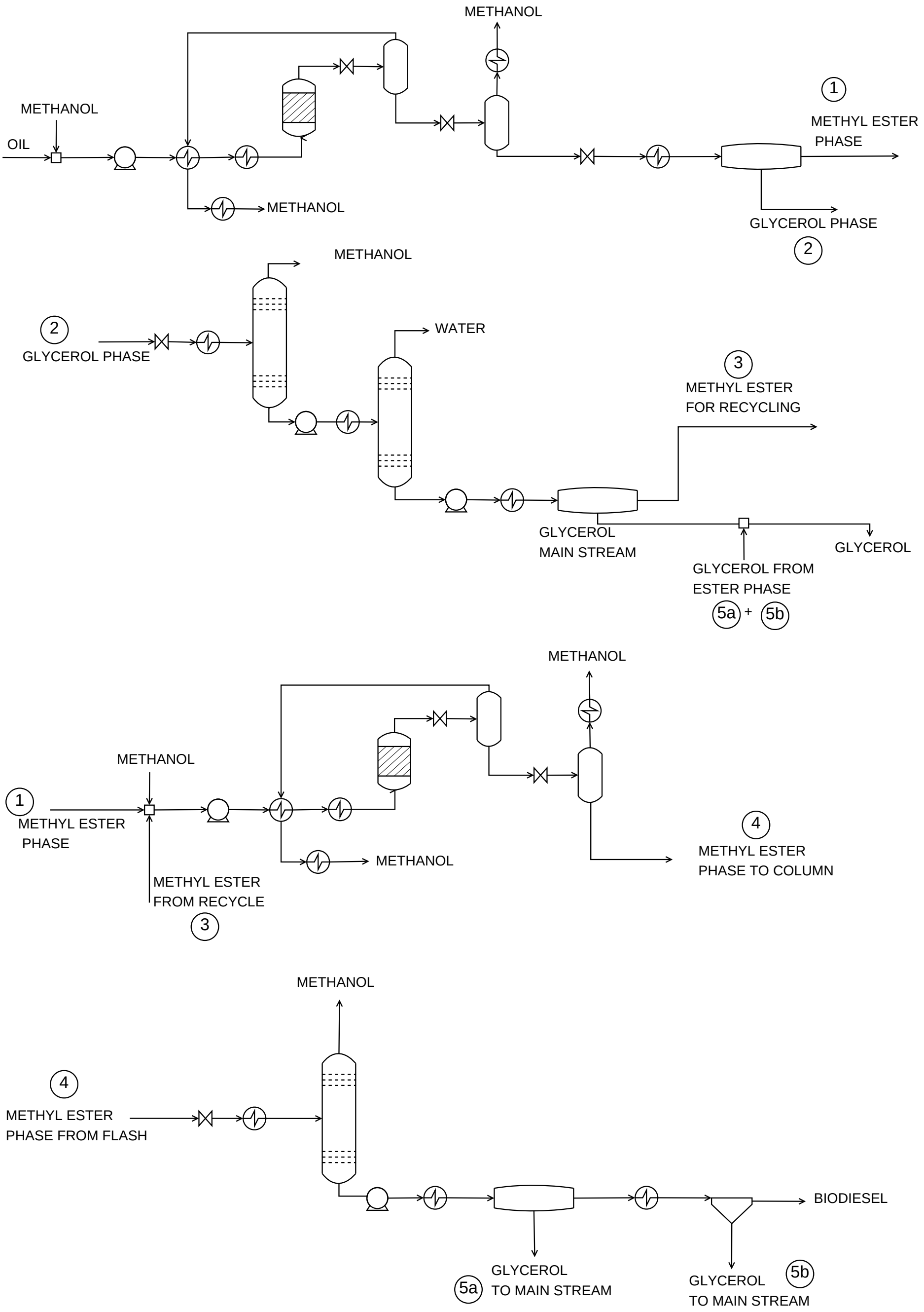


Figure 2.2: Simplified process flow scheme of the basic process divided into sections.

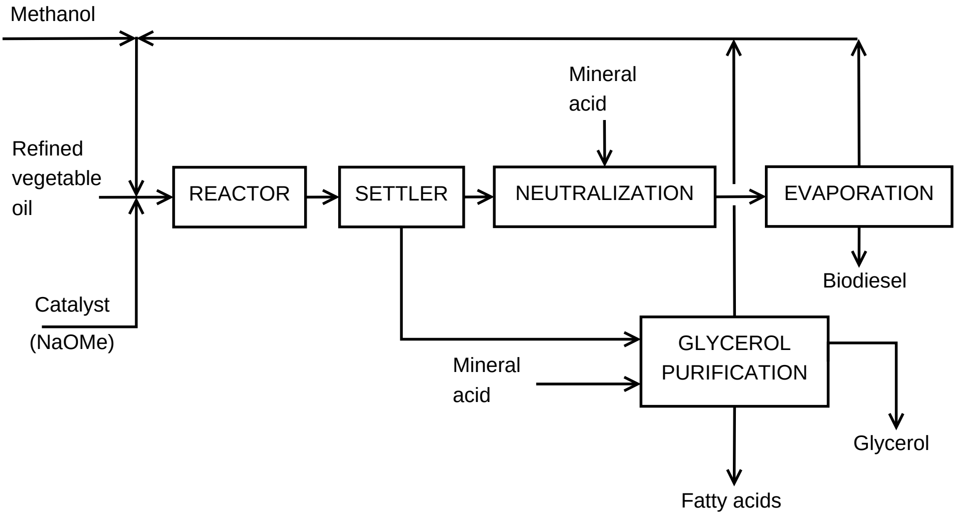
2.1.3 Esterfip-H versus conventional operation

Compared to the conventional process the high purity of the glycerol generated without the need for neutralization and washing will be economical beneficial for the Esterfip-H process. The investments related to the Esterfip-H process could be higher than the conventional operation due to higher temperature and pressure which give more restrictions to equipment and safety, [31].

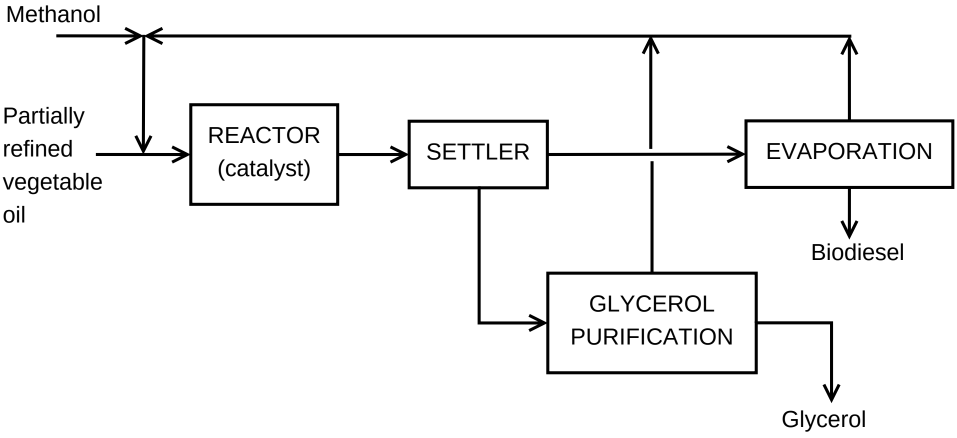
The two next Figures (2.3a, 2.3b) illustrates some of the benefits mentioned above and in Table 2.1, [2, 31]. Table 2.1 give some of the highlights with the Esterfip-H process.

Table 2.1: Highlights with the Esterfip-H process, [2].

Esterfip-H process highlights
• Simplified process scheme • High biodiesel yield • High glycerol purity • High biodiesel purity • No soap formation • No need for catalyst recovery and washing step • No hazardous acid/base chemicals • High temperature and pressure • Two step fixed-bed process • Continuous technology based on solid catalyst



(a) Process flow diagram for the conventional technology.



(b) Process flow diagram for the Esterfip-H technology.

Figure 2.3: Process flow diagram comparison between Esterfip-H process and conventional operation, [2, 31].

2.1.4 Process behaviour

Some literature values have been found for the products of the transesterification after removal of glycerol, [11, 22]. These values are given in Table 2.2 and can be used in model validation. This information is also published by researchers at the French Institute of Petroleum and compliance with patents used can be taken as satisfying.

Table 2.2: Main characteristics of biodiesel from rapeseed oil with catalyst consisting of a mixed oxide of zinc and aluminium from literature, [22].

Weight composition (%)	**Methyl ester phase reactor 1**	**Methyl ester phase reactor 2**
Methyl esters	94.1	98.3
Monoglyceride	2	0.5
Diglycerides	1.1	0.1
Triglyceride	1.6	0.1
Free glycerol	-	-

2.1.5 Where to find the Esterfip-H process

The Esterfip-H process has been applied at Sete in France, Stenungsund in Sweden, Kuantan Port in Malaysia and several more plants worldwide, [32]. Table 2.3 gives more places using the Esterfip-H proces in operation or planned use for the production, [33, 34].

2.1.6 Biodiesel production in Norway

Biodiesel is not produced in Norway at the moment. But due to requirements in emission reduction for planes, some norwegian plane companies are looking into the possibilities to start production of biodiesel in Norway again, [35]. The Esterfip-H process is used in Sweden, so this may be of consideration in Norway as well.

Table 2.3: Some of the plants in operation, under building or in the design phase using the Esterfip-H process by IFP, [32, 33, 34].

Year	Company	Country	Capacity [tonne/year]	Status
2006	Diester	France	160 000	In operation
2007	Perstorp Oxo	Sweden	160 000	In operation
2007	Confidential	Southern Europe	50 000	Ordered
2007	Beatrice Biodiesel, LLC	USA	165 000	Ordered
2008	NaturOil	Brazil	200 000	Under engineering
2009	Mission Biofuels	Malaysia	250 000	Under design
2009	Confidential	Canada	100 000	Under engineering

3 Model basis

The basis for the model will be a production of 160 000 tonnes/year of biodiesel, [19, 33, 34]. The product should fall within the standard specifications stated later.

It is normal to assume 8000 operating hours a year for a continuous production unit, which is approximately 90% of the total hours a year, [36]. The non operating hours could be due to revision, changing catalyst and unexpected events. This will give a production of approximately 20000 kg/hr of biodiesel as give in Equation 3.1. From the molar weight of ester, [12] and the stoichiometric coefficient between triglyceride and methyl oleate the molar feed of triglyceride can be found under the assumption of 100% yield and purity. Resulting in a molar flow of 23.59084 kmol/hr oil as calculated in Appendix B.

$$\frac{160000[\text{tonne/year}]}{8000[\text{hr/year}]} = 20[\text{tonne/hr}] = 20000[\text{kg/hr}] \tag{3.1}$$

3.1 Pseudo components

The pseudo components are created on basis of the rapeseed oil containing only one fatty acid, oleic acid, [1]. When included in Chemcad the components are generated by UNIFAC model, with group contributions. Triglyceride will contain three oleic acid chains, diglyceride two and monoglyceride one. The methyl ester will following only contain methyl oleate. The different intermediate components are taken as containing the given groups and numbers given in Table 3.1.

Table 3.1: UNIFAC groups for the pseudo components of the glycerides.

UNIFAC group	Triglyceride	Diglyceride	Monoglyceride
CH_3	3	2	1
CH_2	41	28	15
CH	1	1	1
CH=CH	3	2	1
OH	0	1	2
CH_2COO	3	2	1

3.2 Thermodynamics

The global K-value model is taken as UNIFAC, while the decanters are using UNIFAC-LLE.

3.2.1 Universal Quasi-Chemical Functional-group Activity Coefficient (UNIFAC)

In conversation with Karoly Moser providing the Chemcad license and supervisor Sigurd Skogestad it was decided to use UNIFAC and UNIFAC-LLE. The UNIFAC-LLE is a result of the original UNIFAC model not predicting the liquid-liquid eqilibrium satisfyingly. Since physical properties are available for the components and kinetics are found a rigours model can be built, [37]. For the UNIFAC model all the necessary parameters are already available for all of the groups. Chemstation is stating that the choice of thermodynamic model is tricky and then suggesting UNIQUAC, NRTL, MARGULES as K-value methods for an alkali-catalysed production of biodiesel, [37, 38].

The UNIFAC model has several successful application, but also some limitations that are listed below, [38, 39]:

- Does not distinguish between isomers
- The γ limits the pressure to below 10-15 atm ($\approx$ 10-15 bar)
- Temperatures in the range 275-425 K
- Noncondensable gases, electrolytes and polymers are not included
- The UNIFAC-LLE should mainly be used in the range 10-40°C, [39]

The reactors will be the only equipment operating outside the UNIFAC range and thereby the UNIFAC thermodynamic model can be used. If using NRTL for the reactor the results becomes the same and the use of UNIFAC is fine.

3.2.2 Literature and Chemcad boiling temperatures

When the components had been included in Chemcad by the UNIFAC groups their boiling temperatures at atmospheric pressure were compared to patent values, [12].

Tri-, di-, and monoglyceride all have a boiling temperature 4-5 K lower than the literature value in Table 3.2, [12]. The boiling temperature of glycerine is approximately 2 K lower, but when comparing this Chemcad value to the normal boiling temperature given by Dippr, ([40]) 287.9 K, the deviation is 0.1 K. Deviation from the literature and supplied boiling temperature could origin from the coefficients generated. The coefficients are then used for calculating the vapour pressure. The boiling temperatures from literature are included in the Chemcad model for the pseudo component, and the coefficients are generated based on the input information. When comparing coefficients for water and triglyceride, water include several more coefficients and are thereby able to predict the boiling temperature more accurate. Some of the deviation for the pseudo components could also origin from the assumption of the triglyceride only containing oleic acid while the literature oil could contain a combination of several different acids. In main feature the boiling temperatures in Table 3.2 fits well.

Table 3.2: Boiling temperature for the reactants, intermediates and products in the transesterification reaction from literature and Chemcad.

Component	**Normal boiling temperature literature[°C], [12]**	**Normal boiling temperature Chemcad [°C]**
Water	100	100
Methanol	65	64.5
Glycerine	290	287.7
Ester	344	344.3
Monoglyceride	358	353.3
Diglyceride	367	362.7
Oil (Triglyceride)	375	371.3

4 Pumps

4.1 Theory

Several pump units will be necessary to achieve the required inlet condition for the reactor. Typical efficiency factor will be 0.8 due to friction, [36], resulting in a temperature increase. Process industries commonly use centrifugal pumps and this will be used in this model, [41]. From normal operating range of pumps the centrifugal pump has the highest capacity range of $0.25 - 10^3$ m^3/h, [18], and the given operation falls within the given range.

For an incompressible fluid the reversible pump work will be given by Equation 4.1. Where the density, ρ, is assumed constant, which normally holds for a liquid with moderate temperature increase.

$$w_\mathrm{s}^\mathrm{rev} = \frac{\mathrm{P_2 - P_1}}{\rho}[\mathrm{J/kg}] \tag{4.1}$$

The pump effect is found by multiplication with mass flow, as given in Equation 4.2.

$$\mathrm{W_s^{rev}} = \frac{\mathrm{P_2 - P_1}}{\rho} \cdot \dot{\mathrm{m}} = (\mathrm{P_2 - P_1}) \cdot \dot{\mathrm{V}}[\mathrm{J/s}] \tag{4.2}$$

As stated above the efficiency, η, will not be 1 and the real pump work is given in Equation 4.3.

$$\mathrm{W_s} = \mathrm{W_s^{rev}}/\eta \tag{4.3}$$

The temperature increase as a result of pumping for an adiabatic process (Q=0) with constant heat capacity, is given in Equation 4.4 and 4.5, [36].

$$\dot{\mathrm{m}} \cdot \mathrm{cp} \cdot (\mathrm{T_2 - T_1}) = \mathrm{W_s} \tag{4.4}$$

or

$$\dot{\mathrm{n}} \cdot \mathrm{Cp} \cdot (\mathrm{T_2 - T_1}) = \mathrm{W_s} \tag{4.5}$$

The heat capacity of the mixture is taken as 112 $\left[\frac{\mathrm{kJ}}{\mathrm{kmol \cdot K}}\right]$ from Chemcad. The heat capacity for the mixture can be calculated from the component heat capacity and the mole fractions in Equation 4.6 giving approximately the same number 110 $\left[\frac{\mathrm{kJ}}{\mathrm{kmol \cdot K}}\right]$.

$$\mathrm{Cp_{mix}} = \sum_{1}^{\mathrm{N}} \mathrm{x_i} \cdot \mathrm{Cp_i} \tag{4.6}$$

4.2 Results

Table 4.1 gives pump work and temperature increase for the first pump by Chemcad and calculated values, the pump work only have small deviations, see Appendix C for calculations. The deviation between the temperatures are higher possibly due to heat capacity change and non-ideality.

Table 4.1: Comparing pump calculations against Chemcad results.

Condition	Calculated	Chemcad
Work [kW]	148.45	148.53
Temperature increase [K]	3.18	3.95

The pressure should be high enough to keep the fluid in the reactor in liquid state. Methanol flashing off is indicated by increased triglyceride fraction in the liquid phase as shown in Figure 4.1. Methanol starts to flash off at approximately 49 bar when the temperature is 483 K, making this the limit for the inlet reactor pressure. As the reaction is endothermic and the temperature decreases throughout the reactor the necessary pressure to keep all the components in liquid phase at the outlet will be lower than at inlet. Avoiding conflict between the necessary inlet and outlet pressure. The same pressure limit will be used for the second reactor now mainly containing methyl ester and methanol instead of triglyceride and methanol. A reduction of the pressure from 62 bar to 50 bar, will only give small savings as pumping of liquid requires little energy, and only is 0.1% of the original costs.

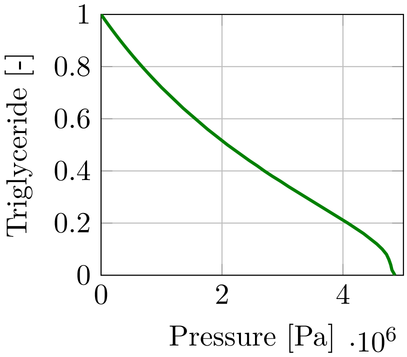


Figure 4.1: Triglyceride mole fraction in liquid as a function of pressure at 483K.

5 Heat exchangers

For heating up the reactants heat exchangers will be placed in series. In the first step the hot methanol stream from the flash will be used to increase the temperature, and the second exchanger will be used to reach reactor inlet conditions. The heat exchangers between reactant and hot methanol are taken as operating countercurrent. The choice of the configuration using hot methanol for heating is related to energy consumptions and cost savings. The first is a shell and tube exchanger, where the high pressure reactants are placed on the tube side, [18]. The high pressure flow is placed on the tube side to avoid a thick and expensive shell. The hot methanol will be at lower pressure than the reactant and will condense, making shell side the choice for the methanol. In which extent the hot methanol will condense depend on the flow rate. The second heat exchanger before the reactor inlet will use steam at 500°C to reach the reactor inlet condition, [42].

The material for the exchanger should be able to cope with the high pressure, and stainless steel is taken as the material, [18].

The required energy received for the reactant stream is given by Equation 5.1.

$$\mathrm{Q} = \dot{\mathrm{m}} \cdot \mathrm{Cp} \cdot \Delta\mathrm{T} \tag{5.1}$$

The amount of steam necessary is calculated from this by assuming ΔT when Q is given from Chemcad and heat capacity from Dippr ([40]), see Appendix D.

For the heat exchanger the dimensions of the tubes are taken as the standard outer diameter 19.05 mm and a wall thickness of 1.65 mm, [41]. With tables for pressure rating this is within workable limits, [43]. The tube size (19 mm) is given as a good trial for starting the design, [18] and as default values in Chemcad if not otherwise is specified, [38].

The preferred length of the tubes for heat exchangers are: 1.83, 2.44, 3.66, 4.88, 6.1, 7.32 meters, [18]. Where Chemcad has 6.1 meter as the maximum length. The longer tubes will reduce the shell diameter, but will lead to increased pressure drop. The heat exchanger area is approximated to 500 m^2 from Chemcad being in the area range of 10-1000 m^2 given by, [18].

TEMA- American tubular exchanger manufacturers association is the applied standard in Chemcad, with classes R (petroleum and related industries), C (moderate duties in commercial and general process applications), and B (chemical process industries), [18].

The tube pattern in Chemcad could be triangular, square or rotated square. The triangular and rotated square patterns give higher heat-transfer rates, but they do also give higher pressure drop, [18]. The pattern is taken as rotated triangular being the Chemcad default value.

Baffles are placed in the shell for directing the fluid to increase the rate of transfer. The most common type of baffles are the single segmental baffle. Baffles in horizontal shell side condensation could use a dam baffle, [18].

For heat to be exchanged a minimum temperature difference must be maintained between the two streams. The practical minimum temperature difference will be 5-30 K, if the temperature difference becomes lower it is no driving force in the system. For the first shell and tube heat exchanger ΔT_{min} is 14 K, see Figure 5.1.

When looking at the energy balance of the system it should be avoided to mix streams at very different temperature because this will give loss of heat, [18]. Streams at different pressures should not be mixed as the outlet stream will be at the lowest pressure. The high pressure stream will undergo cooling as a result of the adiabatic expansion and total heating could become less than if operating separately, [18]. Therefore only the hot methanol from the flash unit operating at 5 bar and 387.9 K is used for heating as the temperature of the mix at 2.5 bar is 371.8 K.

5.1 Condensers

Four different configurations possible for condensers are listed below:

- Horizontal with condensation in shell
- Horizontal with condensation in tubes
- Vertical with condensation in shell
- Vertical with condensation in tubes

The most common configurations used are the horizontal shell side condensation and the vertical tube side condensation. When the heating medium is the condensing steam the horizontal condensation in tubes could be used.

The shell and tube heat exchanger is taken as a horizontal with condensation at shell side as the reactants have a high pressure and therefore should be placed on the tube side, [18]. At the optimal condition with a large methanol stream, the steam is only partly condensed. The exchanger must then have a vent for the cooled methanol vapour or another configuration should be considered. Pressure drop in condensers is only of major consideration in vacuum condensers and will not be a problem in this case, [18].

5.2 Heat exchanger profile

For the shell and tube heat exchangers, the maximum heat recovery is reached when the hot and cold curves touches each other on a Temperature-Enthalpy plot. At this point the driving forces are zero. The stream will not cross as this will violate the 2nd law of thermodynamics, [18]. In practice the temperatures will not touch each other, but reach a minimum temperature difference where the driving forces are small.

From the temperature enthalpy profile for the first exchanger, see Figure 5.1, it can be seen that the temperature in the cold stream increases linearly. While the hot stream has a range without temperature change, when vapour is condensing and no temperature change occurring. For the heat exchanger profile for the second shell and tube exchanger see Appendix E.

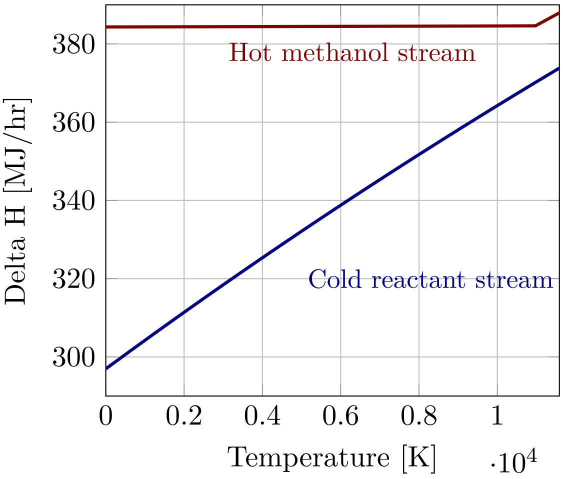


Figure 5.1: Temperature-Enthalpy plot for the first shell and tube exchanger using hot methanol for heating of the reactants.

When the first flash tank is operating at 5 bar the methanol vapour flow holding 387.9 K has a flow rate of 431 kmol/hr.

6 Kinetics

The most common used alcohol for biodiesel production is methanol, which will result in methyl ester. Other alcohols used are ethanol, isopropanol and butanol. The choice between methanol and ethanol are often related to price and availability on site. The transesterification reactions are given below, where Equation 6.1 is the overall reaction, [2, 44] and Eqaction 6.2 - 6.4 are the first order reversible reactions for biodiesel production.

$$\begin{aligned}\text{Triglyceride(TG)} + 3\cdot\text{Methanol(MeOH)} \leftrightarrow \\ \text{Glycerol(GL)} + 3\cdot\text{Methyl ester(ME)}\end{aligned} \tag{6.1}$$

$$\begin{aligned}\text{Triglyceride(TG)} + \text{Methanol(MeOH)} \Leftrightarrow \\ \text{Diglyceride(DG)} + \text{Methyl ester(ME)}\end{aligned} \tag{6.2}$$

$$\begin{aligned}\text{Diglyceride} + \text{Methanol(MeOH)} \Leftrightarrow \\ \text{Monoglyceride(MG)} + \text{Methyl ester(ME)}\end{aligned} \tag{6.3}$$

$$\begin{aligned}\text{Monoglyceride(MG)}+ \text{Methanol(MeOH)} \Leftrightarrow \\ \text{Glycerol(GL)} + \text{Methyl ester(ME)}\end{aligned} \tag{6.4}$$

The kinetics for the transesterification of rapeseed oil is taken from Pugnet et al. ([45]) for zinc aluminate catalyst, $ZnAl_2O_4$. This article is published by researchers from the same institute as researchers having the patent for the Esterfip-H process, giving compliance between literature. The article is based on a batch process, the industrial process is a fixed-bed reactor while the Chemcad reactor will be a plug flow. The conversion between reactor types is done under the assumption of catalyst density, catalyst void fraction, and catalyst filling grade in the reactor. For calculations of catalyst density assumption see Appendix F.

Based on the studies done by Pugnet et al. in relation with patents on the field, the start operating conditions for the reactor have been taken as given in Table 6.1, [12, 20, 24, 25, 26, 27, 28, 29, 30].

The equilibrium constant is given by the forward and reverse reaction constant as given in Equation 6.5, [46]:

$$K = \frac{k_{\text{reaction}}}{k_{-\text{reaction}}} \tag{6.5}$$

The equilibrium constant will contain information about the preferred direction of the reaction. A strong preference for the undesired direction, indicated by a small value of K, could be compensated for by driving forces.

Table 6.1: Operating conditions for transesterification of rapeseed oil by zinc aluminium oxide catalyst at originally assumed conditions.

Condition	Value
Temperature [°C]	210 [26, 45]
Pressure [bar]	62 [26]
Catalyst density	1540 g/L
Weight ratio methanol/oil into reactor 1	2
Weight ratio methanol/methyl ester into reactor 2	2

The driving forces will be temperature and a significant excess of methanol, reactant, by Le Chateliers principle. Le Chaterliers principle says that if an equilibrium is disturbed by a change in the conditions like temperature and concentration, the position of the equilibrium moves to counteract the change and a new equilibrium is established.

Table 6.2 gives the literature values for the kinetics, [45]. The equilibrium constant below 1.0 for reaction 1 and 3 indicate drive in the undesired direction. The reactions are driven towards methyl oleate and glycerol formation by the large methanol/oil mass ratio given in Table 6.1 together with a high temperature. The k_{cat}/k_{tot} gives the relation between the catalytic drive and the total drive containing catalytic and thermal drive. A higher k_{cat}/k_{tot} indicate a larger need for catalyst to drive the reaction.

Table 6.2: Equilibrium constant for transesterification with zinc aluminate catalyst over the temperature range of 180-210°C, [45].

Reaction number	Equilibrium constant K	k_{cat}/k_{tot}[%]
1	0.27	37.3
2	1.21	64.8
3	0.87	100

For the calculations and implementation in Chemcad, the data in Table 6.3 is used. By implementation of the filling grade of the reactor, 70% volume catalyst/volume reactor, assumed from Figure 7.6.

Table 6.3: Kinetics for the three equilibrium of the transesterification reaction at $180-210°C$ and 4wt% $ZnAl_2O_4$/oil with molar ratio 6/1 to 40/1, [45]. Achieved by modifications shown in Appendix F.

Reaction	k°[L/kmol · s]	Activation energy [kJ/kmol]
1	$2.618 \cdot 10^8$	82000
2	$1.4476 \cdot 10^{11}$	103000
3	$5.698 \cdot 10^9$	88000

The kinetic data for the reverse reactions have been found from the natural logarithm of the Arrhenius equation, see Table 6.4.

Table 6.4: Kinetics for the three reverse equilibrium reactions of the transesterification reaction at $180-210°C$ and 4wt% $ZnAl_2O_4$/oil with molar ratio 6/1 to 40/1. Achieved by Arrhenius plot shown in Appendix G with units for Chemcad.

Reaction	k°[L/kmol · s]	Activation energy [kJ/kmol]
1	$9.6922 \cdot 10^8$	82000
2	$1.1967 \cdot 10^{11}$	103002
3	$6.5518 \cdot 10^9$	88004

6.1 Arrhenius equation

The kinetics of the reactions will be temperature dependent and the Arrhenius equation (Equation 6.6) is often used, [46]. The kinetic parameters given previously are taken over the temperature range 180-210°C. These data are considered to be valid for the whole operating range since the temperature range coincide with the recommended range from patent 170-210°C, [12].

$$k(T) = k^\circ \cdot e^{-E_a/(R \cdot T)} \tag{6.6}$$

k° is originally given as $\left[\frac{L^2}{mol \cdot g \cdot s}\right]$ and the density of the catalyst is assumed and given in Table 6.1. When taking the natural logarithme of Equation 6.6, Equation 6.7 is achieved, [46].

$$\ln(k(T)) = \ln(k^\circ) - \frac{E_a}{R} \cdot \frac{1}{T} \tag{6.7}$$

Plotting ln(k(T)), k(T) found from equilibrium constant, against 1/T will give a straight line with interception ln(k°) and slope of -E_a/R. This could be used for finding the kinetic parameters of the reverse reactions. Figure 6.1 is the Arrhenius plot for the first reaction with the belonging natural logarithmic equation given. The preexponential factor and activation energy for the first reverse reaction can be found, given in Table 6.4, calculations are shown in Appendix G. The plots for the two last reactions and constant values are given in Appendix G.

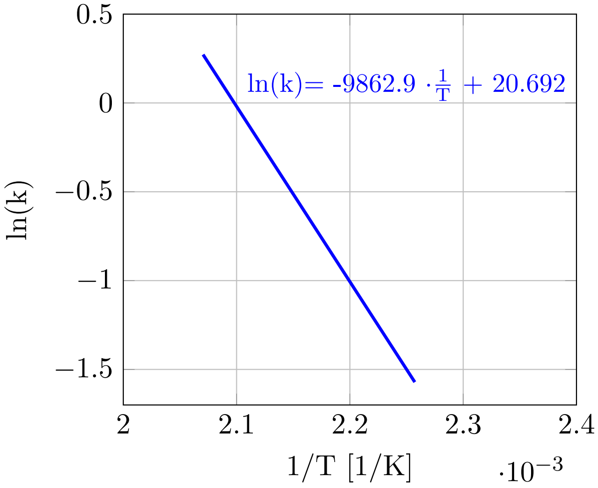


Figure 6.1: Arrhenius plot for the first reverse equilibrium reaction.

6.2 Heterogeneous catalysis

The use of heterogeneous catalysis in transesterification of rapeseed oil is not a new discovery, but has only lately been economical efficient, [47]. From Peterson et al. ([47]) looking at heterogeneous catalysis, mentioning $ZnO \cdot Al_2O_3$ being supported by ZnO (26.2%) and Al_2O_3 (73.8%) it is assumed that the catalyst is Al_2O_3 supported. The related density of 4.0 [g/cm^3] for Al_2O_3 is used, [48]. Other metal oxides have also been studied for biodiesel production by heterogeneous catalysis. $LiNO_3/CaO$, $NaNO_3/CaO$, KNO_3/CaO, MgO, $LiNO_3/MgO$, $MgO \cdot MgAl_2O_4$ and $\gamma - Al_2O_3$ are some of the catalyst studied, [49, 50, 51]. A modification to the Esterfip-H could be to use another catalyst with similar properties as zinc aluminium oxide.

A heterogeneous fixed-bed reactor eliminates the catalyst removal step from the process flow scheme, see Figure 2.3a and 2.3b. Advantages and disadvantages with the heterogeneous catalyst process are given in Table 6.5, [2].

Table 6.5: Advantages and disadvantages with the heterogeneous catalyst process compared to conventional process, [2].

Advantages
• Simplified separation downstream of reactor
• Low catalyst losses
• No product contamination
• No corrosion
• Reducing foaming
Disadvantages
• Large amount of catalyst
• High methanol/oil ratio
• High temperature and pressure

6.2.1 Catalyst deactivation

The total concentration of active sites in a catalyst will decrease with time. The deactivation adds more perspective to the available catalyst, rate law parameters and the decay of the catalyst could adjust the reactor design. The activity of the catalyst is given by Equation 6.8.

$$\mathrm{a(t)} = \frac{-\mathrm{r}_\mathrm{i}'(\mathrm{t})}{-\mathrm{r}_\mathrm{i}'(\mathrm{t{=}0})} \tag{6.8}$$

Deactivation can happen due to sintering, fouling and poisoning, [46]. Sintering is loss of active sites due to exposure to high gas-phase temperature, [46], and will probably not be a problem here as the reactions are taking place in liquid phase. Fouling is a common mechanism for reactions involving hydrocarbons and results from material being deposited on the surface of the catalyst. Deactivation by poisoning occurs when molecules become irreversibly chemisorbed to active sites and the number of active sites thereby are be reduced. Sulfur coming in with the oil could poison the catalyst slowly over time. In packed-bed reactors the deactivation process will move like a wave front, see Figure 6.2, [46]. A larger amount of catalyst than first predicted may be considered to get a longer operating time for the reactor before the catalyst must be changed, [46].

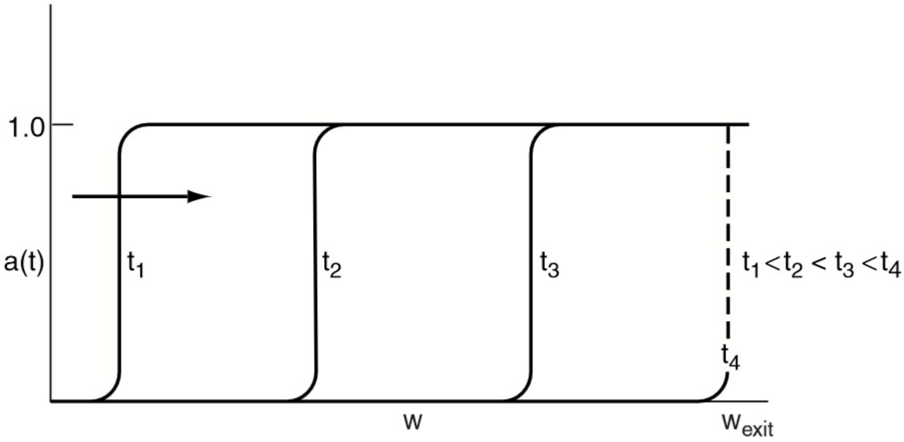


Figure 6.2: Movement of activity front in a packed bed from Elements of chemical reaction engineering, [46].

No details about the Esterfip-H catalyst lifetime are available, [2]. When information about deactivation is available it could be of consideration to increase the reactor size and catalyst amount for prolonging the operating time. The consideration should also include the operation time for other equipment and their need for revision. It is most desirable if the need for revision on equipment occur at the same time. There are no need for a larger reactor making the operating longer if shut down time will occur anyway due to revision on other equipment. A solution for prolonging the operating time could be to inter change reactor one and two. The final reactor design will also depend on cost of catalyst, cost of changing catalyst, and downtime due to change of catalyst.

7 Reactor

Some articles are proposing to introduce the methanol at different levels in the conventional reactor to get the best performance, [24]. This can also be done in a similar way by the use of a configuration with several reactors in a series. For the operating conditions with a large excess of methanol, as in the given case, the introduction of methanol at different levels in the reactor probably looses some of its benefits.

The large excess of methanol is in order to displace the thermodynamic equilibrium in the right direction, [12]. The reaction can in addition be displaced by temperature, but degradation of glycerol will limit the temperature operating range, [52]. Degradation meaning that the molecule break up into its elements. Because of the need of displacement of the thermodynamics the process is carried out in two reaction steps, [12]. Since nothing is specified in literature, the reactors are taken as operating adiabatically. The isothermic performance compared to the adiabatic is looked at later. The general mass balance for a unit or plant is given in Equation 7.1. This is the basis for all the specific design equations for the different reactors.

$$\text{In - Out + Generation = Accumulation} \tag{7.1}$$

Figure 7.1 illustrates that if the amount of glycerol in the reactor inlet increases the reactions will be pushed in the reverse direction. Glycerol increase in the inlet could origin from recycling or poorly phase separation in decanter.

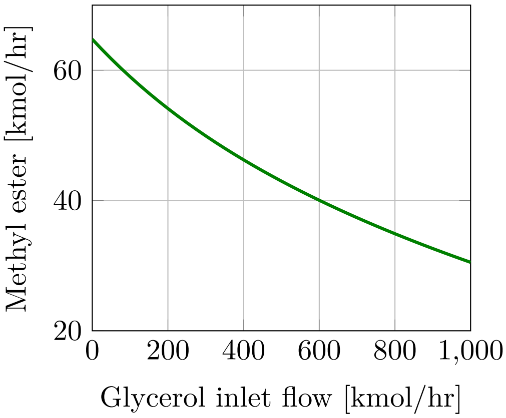


Figure 7.1: Methyl ester outlet flow from a reactor of 60 m^3 at 62 bar, 483 K and a weight ratio of 2 methanol/oil as a function of inlet glycerol flow.

By increasing the temperature further than the limit given by the patent, [12], the reactor behaviour will not improve dramatically, (see Figure 7.2), but degradation of glycerol might take place.

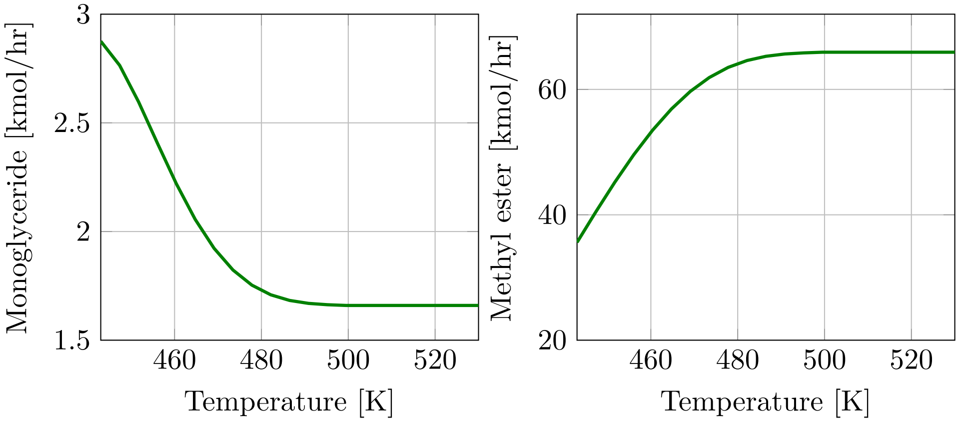


Figure 7.2: Amount of methyl ester and monoglyceride for optimal oil and methanol inlet at 62 bar by increased reactor inlet temperature.

Even at the highest reactor inlet temperature the profile for monoglyceride leaving the first reactor is stagnating at a minimum value above zero. Meaning that for a given flow of oil and methanol it is a maximum conversion of the intermediate even if the temperature is increased further. If the situation is changed and the methanol flow could be changed for a given temperature it will be a maximum conversion before the hourly space velocity becomes too high.

Hourly space velocity (HSV) is a flow rate expression, expressed as volume of oil/volume of catalyst/hour. Patents are operating with HSV limits from 0.5-1.5 to 0.1-3, while the value for the process is 0.54 which fall within the wide range from patents, [12, 26, 29]. The lower hourly space velocity the longer residence time and possibly better conversion.

7.1 Batch reactor

Batch reactor is normally used for small-scale operation and lab experiments. The kinetic data for the transesterification of rapeseed oil with zinc aluminate oxide was performed in batch reactor and conversion between the different types of reactors would be necessary, [45]. The design equation for the batch reactor is given in Equation 7.2, [46]. The dimensions for kinetic data from literature will be converted to plug flow reactor parameters before being implemented in Chemcad, see Appendix F.

$$\frac{\mathrm{dN_i}}{\mathrm{dt}} = \mathrm{r_i} \cdot \mathrm{V} \tag{7.2}$$

Where $\mathrm{r_i}$ has units [moles/(time · volume)] and is a function of the rate constant and concentrations.

7.2 Plug flow reactor (PFR)

Figure 7.3 is a simplified drawing of a plug flow reactor.

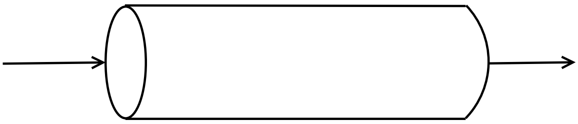


Figure 7.3: Plug flow reactor.

The reactor volume is calculated from Chemcad to be approximately 60 $\mathrm{m^3}$, with the given kinetics and conversion of glyceride (85-90%), [26]. At the operating conditions being a temperature of 473 K and the weight ratio between methanol/oil of 2, [12, 45]. If the operating conditions here were taken differently the necessary reactor volume for achieving the desired conversion would be higher or lower. A different reactor volume could be an improvement to the given model. The conversion of 85-90% in the first reactor is given by patents, [24, 26, 27, 29, 30, 53, 54]. The plug flow reactor in Chemcad is a rigorous model under the assumptions of no axial mixing or axial heat transfer.

A plug flow reactor would illustrate the packed-bed behaviour best when catalyst is included in the kinetics, with the design equation given in Equation 7.3.

$$\frac{\mathrm{dF_i}}{\mathrm{dV}} = \mathrm{r_i} \tag{7.3}$$

Where the rate of reaction is given by the reaction constant and the concentrations of reactants in Equation 7.4.

$$\mathrm{r_i}\left[\frac{\mathrm{kmol}}{\mathrm{L \cdot s}}\right] = \mathrm{k}\left[\frac{\mathrm{L}}{\mathrm{kmol \cdot s}}\right] \cdot \mathrm{C_k}\left[\frac{\mathrm{kmol}}{\mathrm{L}}\right] \cdot \mathrm{C_j}\left[\frac{\mathrm{kmol}}{\mathrm{L}}\right] \tag{7.4}$$

The reactor profile of tri-, di-, and monoglycerides over the reactor volume is shown in Figure 7.4. Shown for a weight ratio between methanol and oil of two for the first reactor, but the optimal weight ratio is 1.9. Monoglyceride stabilizes at an earlier and higher flow in the reactor and will limit the conversion. Monoglyceride is produced from diglyceride and methanol, and glycerol and methyl ester, see Equation 6.3 and 6.4. As the glycerol concentration increases, reaction three Equation 6.4, is driven in the left direction possibly stabilising the monoglyceride flow rate at a higher level.

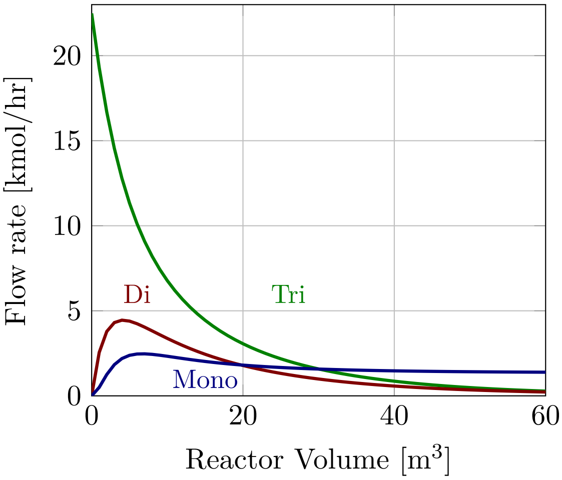


Figure 7.4: Plug flow reactor profile for tri-, di-, and monoglyceride at 62 bar, 483 K and 2 in weight ratio between methanol and oil.

7.3 Packed-Bed reactor (PBR)

Figure 7.5 illustrates the packed-bed reactor in a simple outline.

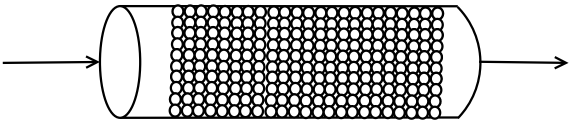


Figure 7.5: Packed-Bed reactor.

PBR's are plug flow reactors filled with catalyst particles. For a PBR the rate of reaction is given by the mass of the catalyst. The units for the rate of reaction is $\left[\frac{\text{mol}}{\text{time}\cdot\text{weight}_{\text{catalyst}}}\right]$ for a PBR. For the packed-bed reactor the design Equation 7.5, will be as given below:

$$\frac{\mathrm{dF_i}}{\mathrm{dW}} = \mathrm{r_i'} \tag{7.5}$$

And in terms of conversion, Equation 7.6.

$$\mathrm{F_{i,0}} \cdot \frac{\mathrm{dX}}{\mathrm{dW}} = \mathrm{r}'_\mathrm{i} \tag{7.6}$$

Due to high operating pressure the pressure drop could be assumed small and possibly neglected. In reality there will be a pressure drop over the reactor due to catalyst and height differences as the reactor operates upflow.

Two basic types of packed-bed reactors are one in which the bed is a reactant and one where the bed is a catalyst, [18]. The fixed-bed for this process will be catalyst with upflow, and the velocity of the fluid must not fluidizate the bed. The catalyst could be randomly or structured packed, but no information about the given catalytic process configuration is found, [18]. An outline of the reactor with two catalytic sections is given in the simplified frame in Figure 7.6, from the French Petroleum Institute, [55].

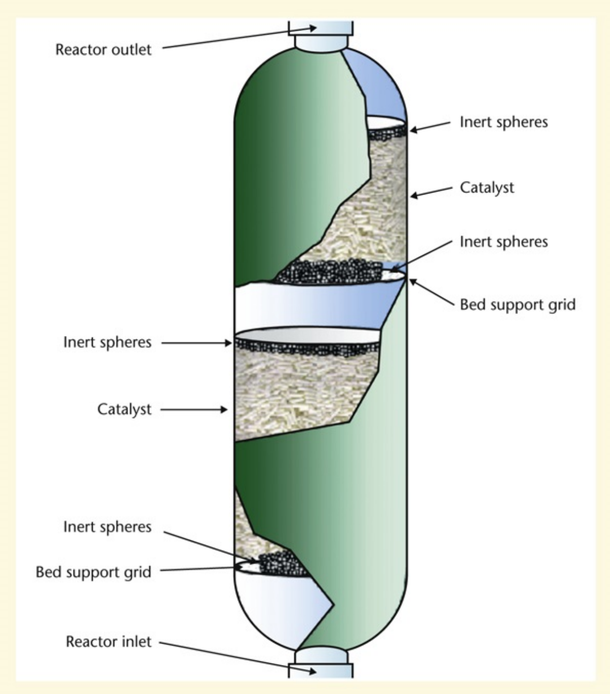


Figure 7.6: Simplified diagram for the production unit FAME (Fatty acid methyl ester) for heterogeneous catalyst, [55].

The catalyst is not dense packed and the void fraction and porosity are defined in Equation 7.7 and 7.8 respectively:

$$\phi = \frac{\text{Volume of void}}{\text{Total bed volume}} \tag{7.7}$$

The void fraction was assumed to be 0.45, [46], giving a porosity of 0.55.

$$1 - \phi = \frac{\text{Volume of solid}}{\text{Total bed volume}} \tag{7.8}$$

7.4 Conversion and yield

7.4.1 Conversion

Conversion is a measurement of the fraction of the reactant that has reacted to the product, Equation 7.9 and 7.10, [18, 46]. For an irreversible reaction the maximum conversion is 1, while for a reversible reaction the maximum conversion will be given by the equilibrium conversion. For the transesterification reactions the maximum conversion will be given by the three reversible reactions, Equation 6.2-6.4, [41].

$$\mathrm{X} = \frac{\text{Moles of i reacted}}{\text{Moles of i in feed}} \tag{7.9}$$

$$\text{Conversion} = \frac{\text{Amount of reagent consumed}}{\text{Amount of reagent supplied}} \tag{7.10}$$

At the optimal solution from the advanced profit function the conversion over the first reactor is 91.2% and the second 99.5% when including all the glycerides. If only looking at the triglyceride amount the respective numbers are 98.7 and 100%. The difference being a result of unconverted intermediates. Showing that the reaction extent is larger in the first than the second reactor. Since the overall reaction is endothermic this is indicated by a lower temperature fall over the second reactor.

7.4.2 Yield

Yield is a measurement of the performance of a plant, [18]. Based on the supplied amount of triglyceride, the amount of methyl ester is the product of interest. It tells how much of the reactant that gives the desired product instead of intermediates or undesired products, see Equation 7.11. When no side reactions are considered the abbreviation from complete yield is due to intermediate of di- and monoglyceride and unconverted triglyceride. If part of the products or reactants leave in other streams the yield will be reduced.

$$\text{Yield} = \frac{\text{Moles of methyl oleate formed}}{\text{Moles of triglyceride supplied} \cdot \text{ Stoichiometric factor}} \tag{7.11}$$

The yield of the heterogeneous catalyst is referred to as close to 100%, [11, 26, 56]. This number for the created model is 99.7%.

7.5 Water in the system

The presence of water is harmful due to formation of soap and thereby emulsion between glycerol and methyl ester phase making the separation difficult. Water could be introduced to the system through the oil, methanol or leaks. The amount of water in vegetable oil is below 0.1wt% and the water content in methanol stream is also below 0.1wt%, [2, 15]. Water amount in the feed streams is included at the highest level from literature to assure that the model can be applied for as many cases as possible. When recycling is introduced water is a typical component accumulating, leading to the snowballing effect and a water removal step is necessary. Side reactions with water is not included in the reactors, but hydrolysis reaction of esters lead to formation of fatty acids and loss of yield as a result, [45]. Water in the system is able to affect the nature of the catalyst active sites and the adsorption of reactants and products on the catalyst surface. A slight favour of the ester hydrolysis at higher water fractions is reported by Pugnet et al.([45]).

7.6 Adiabatic or Isothermic reactor

The reactor could be operating under isothermic or adiabatic conditions. At isothermic conditions the temperature is kept constant, while under adiabatic conditions the heat exchange with the surroundings is zero. By operating isothermic the reactors could be smaller than under adiabatic conditions, but the energy consumption would be higher. The isothermic reactor would have a more complex configuration and higher operating cost due to an endothermic reaction.

Figure 7.7 shows the outlet profile of mono- and triglyceride in the reactor under adiabatic and isothermic operation. When operating isothermic the necessary volume to achieve the same conversion is smaller than under adiabatic operation in the beginning. As the reactor becomes large the adiabatic reactor approaches the isothermic reactor and at sufficient reactor size the benefits with the isotherm reactor is removed.

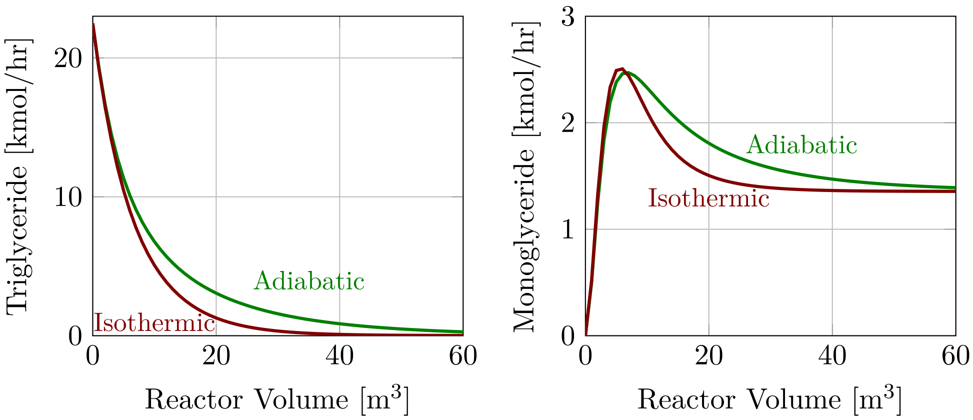


Figure 7.7: The reactor behaviour for adiabatic and isothermic reactor at inlet conditions 483 K, 62 bar and weight ratio methanol/oil 2.

Indicating that the reverse reactions limits the extent and phase separation is necessary. The reactors should operate adiabatically with sufficient size.

7.7 Reactor behaviour

A couple of cases were performed on the reactor to study the behaviour for change in conditions.

7.7.1 Case 1: Constant temperature, disturbance in methanol flow

A case study is performed where the methanol feed stream is increased while the inlet temperature is kept constant at 483 K. Figure 7.8 illustrates the reactor response to the increased methanol inlet flow. When the methanol flow becomes too high the residence time in the reactor is reduced to a level where the velocity constraints the conversion. The hourly space velocity becomes too high and the contact time with the catalyst is too low.

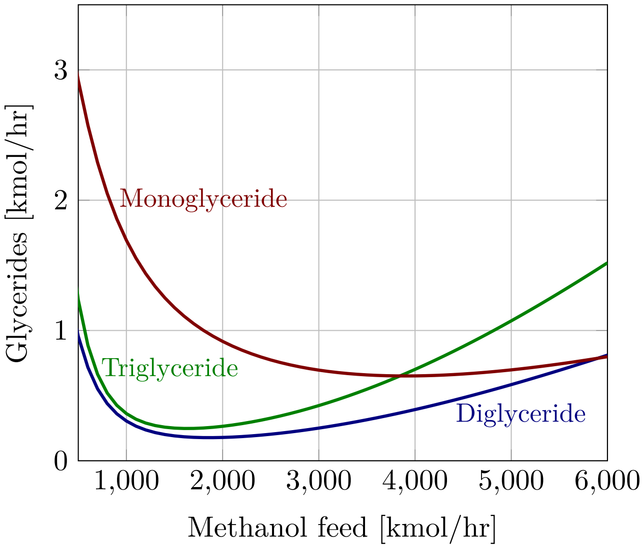


Figure 7.8: Tri-, di-, and monoglyceride outlet flow profiles as a function of methanol flow at 483 K and 62 bar.

7.7.2 Case 2: Triglyceride and methyl ester profiles at 443 and 483 K

A case study is performed where the methanol flow at the outer limits of the temperature range from the patent is increased for the reactor, [12], see Figure 7.9. A higher temperature will give a larger drive and the reactions will go to a higher extent in the desired direction. The reactor behaviour follow Le Chateliers principle for an endotherm reactions. At a higher temperature the system is less sensitive to increases in the methanol flow as the driving forces are already high. At the constraint of 483 K the gradient for changes in triglyceride amount will be low over a larger range of methanol. A lower methanol flow is more economically as the downstream energy is lower. The minimum triglyceride amount leaving the first reactor at a given temperature occurs at higher methanol feed as the temperature increases. Explanation of this behaviour could be that the reverse reactions are slightly more temperature sensitive than the forward reactions due to slightly higher activation energy.

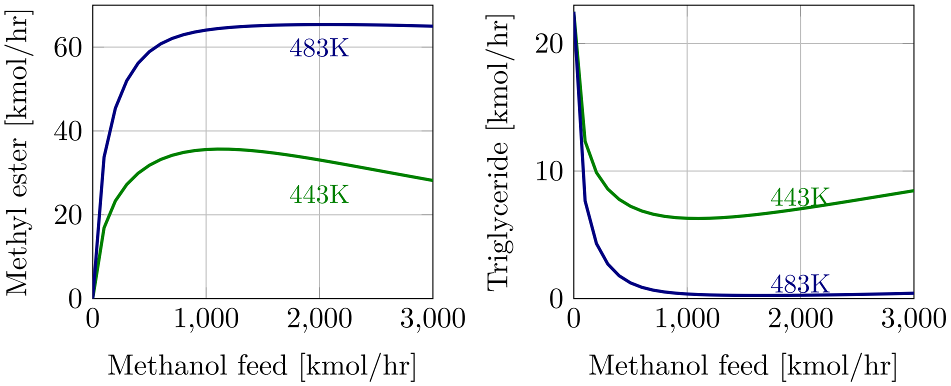


Figure 7.9: Methyl ester and triglyceride profiles at 443 K and 483 K with increasing methanol inlet flow.

7.7.3 Case 3: Methanol need for a given conversion of triglyceride as a function of reactor volume

If the reactor volume increases then residence time will increase and the conversion of triglyceride for a given methanol flow will be increased. If the reactor volume is taken larger than in the original case (60 m^3) the required amount of methanol could be decreased. The flow of methyl ester would still be the same and energy will be saved, see Figure 7.10. The maximum reactor size will be limited by catalyst cost and weight compared to methanol and energy costs. When the methanol flow is reduced the reactor volume need to increase to keep conversion constant. A methyl ester flow of 64.7 kmol/hr is achieve in the first reactor for a methanol flow of 1200 kmol/hr and reactor volume of 60 m^3. When decreasing the flow to 1000 kmol/hr the volume must be 71 m^3 to keep the methyl ester flow constant. If decreasing further to 800 kmol/hr of methanol the corresponding volume is 108 m^3. Indicating that even if the reactor volume is increased there will be a limit for how much the methanol flow can be reduced and simultaneously keep the purity specifications fulfilled.

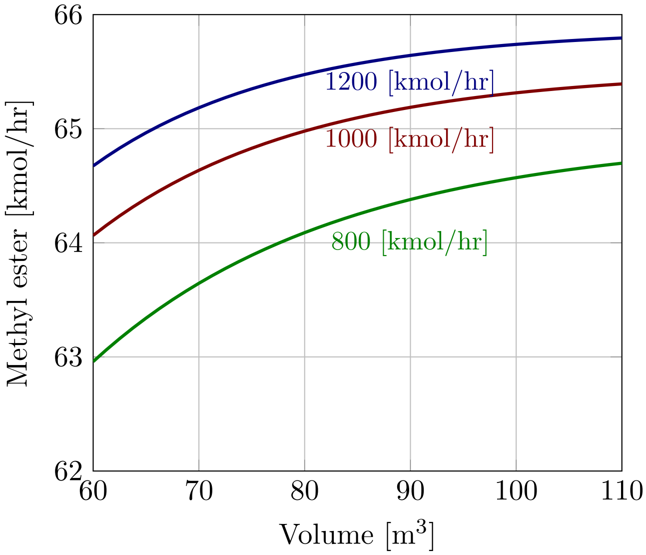


Figure 7.10: Methyl ester outlet for reactor one volumes with different methanol inlet flows at 483 K and 62 bar.

7.8 Number of reactors in series

In the original patent there are two reactors in series. A consideration for changes could be one larger reactor or several smaller reactors in series. The necessary volume of the first reactor under adiabatic conditions was found to be 60 m^3. The volume of the second reactor was taken as the same since the patents not are distinguishing between the reactors. This total volume of the two reactors (120 m^3) is used for all the cases with different number of reactors. Since the reactors are of same size the sequence of the reactors could be changed when the first reactor have deactivated in larger extent than the second.

7.8.1 One reactor

The behaviour for one reactor with a volume of 120 m^3 is studied. If the methanol inlet flow was unconstrained the conversion with one reactor would not become as high as the two reactor system as illustrated by Figure 7.11. The maximum yield of the one reactor system is 99.1% when unconstrained methanol flow, but the methanol flow is constrained.

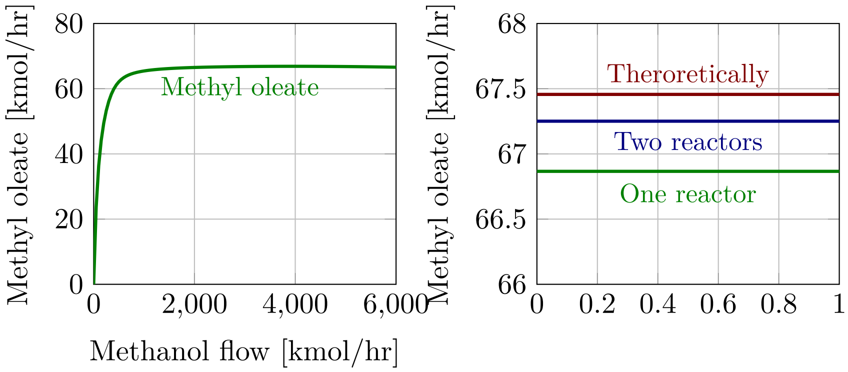


Figure 7.11: Flow of methyl oleate in one reactor system (120 m^3) as a function of methanol inflow is shown to the left. To the right a zoomed result of the methyl oleate flow theoretically achieve able, the two reactor result from the optimization and the maximum for one reactor at high methanol flows.

Even if the reactor volume is taken as infinite one reactor would not be enough to get the desired conversion of triglyceride with a weight ratio of 2. As the reactor volume reaches 100 m^3 the reaction can not be driven further in the desired direction as the amount of glyceride provides the extent of the reverse reactions to be too high, see Figure 7.12. A two reactor system with intermediate removal of glycerol will make sure the reactions can be pushed further in the desired direction.

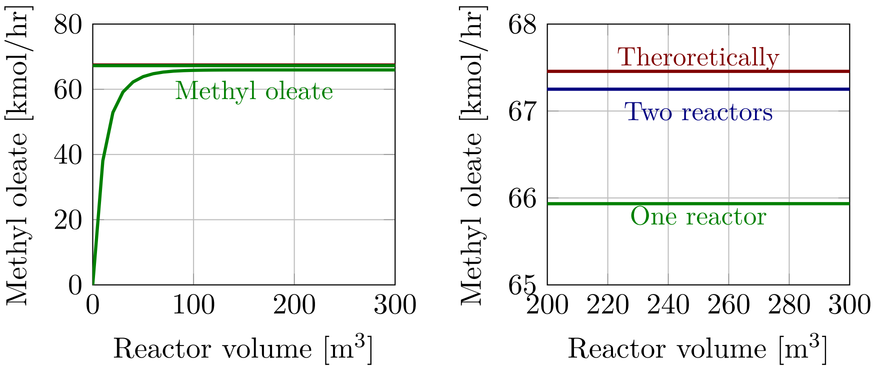


Figure 7.12: Product flow rate in a one reactor system for different reactor volumes at 483 K, 62 bar and a weight ratio methanol/oil of 2.

7.8.2 Three reactors in series

A study of the change in performance of the system when the total reactor volume is divided over three reactors instead of two, 40 m^3 per reactor. The inlet temperature is kept at 483 K. The evaporation after the second reactor is now the same as after the first reactor in the two reactor system including two flash units and a decanter. The equipment after the third reactor is the same as the one originally after the second reactor.

By having three reactors instead of two the amount of necessary equipment is increased. The total amount of methanol is reduced to 63% of the original amount. By a reduction in methanol stream the energy usage is also reduced giving a high profit. The profit is compared to the optimal profit of the original two reactor system from the modified advanced profit function, see Appendix D. The original profit of approximately 1074 $/hr is increased by a factor 129% for the three reactor system with the same equipment. The profit increase will be lower when the two reactor system is modified in accordance with a suggestions from system equipment study. If increasing the number of reactors further problems related to convergence occurs and the profit ends at a lower profit than the three reactor system before the problems happen. More reactors might be beneficial if equipment sizing to the operation is introduced, but then it can not be directly compared to the given model.

8 Flash

The required amount of evaporation of methanol is higher after the second reaction step due to purification requirement, [11, 19, 22, 23]. As can be seen from process flow scheme in Figure 2.1. After the first reactor the removal of methanol is only necessary to achieve separation between the glycerol and methyl ester phase. When the transesterification is completed in the second reactor the removal of methanol must be done in an extent to satisfy fuel properties given by standards, 0.2wt% methanol.

Mass balance over the flash unit is given in Equation 8.1 illustrated in Figure 8.1. For the components, methanol will leave in the vapour stream and the remaining components and non-evaporated methanol will leave in the liquid stream. This is consistent with literature values under the assumption that the reactor product contains mainly methanol, methyl oleate and glycerol, [57].

$$F = V + L \tag{8.1}$$

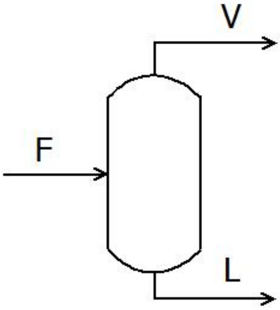


Figure 8.1: Flash unit.

Methanol is removed intermediate to avoid emulsion between glycerol and methyl ester for easy phase separation and better conversion.

Pressure is relieved over a valve to the desired conditions of 5 and 2.5 bar given by patents, [12, 26]. Pressure temperature profile for methanol would indicate the necessary temperature to evaporate of methanol at the given pressures, see Figure 8.2. The pressure of 5 and 2.5 bar are indicated in the pressure temperature diagram to show the minimum temperatures for evaporation of methanol.

From the Antoine coefficients the vapour pressure [Pa] at the given temperatures in [K](Figure 8.2) can be found from Equation 8.2, [40].

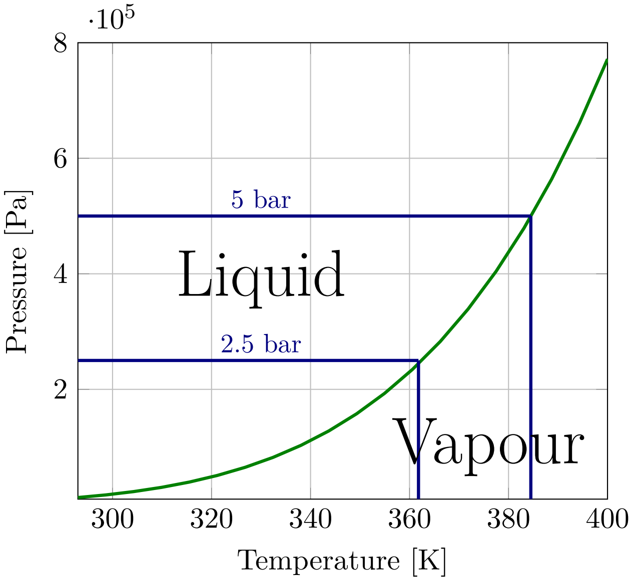


Figure 8.2: Pressure as a function of temperature for methanol indicating the minimum temperatures for methanol to be flashed off.

$$\log_{10} P = \text{Aant} + \frac{\text{Bant}}{\text{T}} + \text{Cant} \cdot \ln(\text{T}) + \text{Dant} \cdot (\text{T})^{\text{Eant}} \tag{8.2}$$

Antoine coefficients for methanol are given below in Table 8.1, [40].

Table 8.1: Antoine coefficient for methanol for vapour pressure calculations.

Antoine coefficient	**Value methanol**
Aant	$8.2718 \cdot 10^{1}$
Bant	$-6.9045 \cdot 10^{3}$
Cant	$-8.8622 \cdot 10^{0}$
Dant	$7.4664 \cdot 10^{-6}$
Eant	$2 \cdot 10^{0}$

The boiling temperature for methanol at the given pressures found in Chemcad, given in Table 8.2 and Figure 8.2, was checked by Equation 8.2. By applying the temperatures the vapour pressures have a deviation of less than 0.2%, indicating good agreement between literature and Chemcad. How tightly each component is bonded to the mixture depend on the mixture composition and conditions.

Table 8.2: Boiling temperatures for the different components at 5 and 2.5 bar from Chemcad.

Component	**Boiling temperature at 5 bar [K]**	**Boiling temperature at 2.5 bar [K]**
Triglyceride	722.4	686.1
Diglyceride	712.6	677.1
Monoglyceride	701.1	666.2
Methanol	384.6	362.5
Methyl oleate	701.9	662 .1
Glycerol	633	598.7
Water	425.1	400.6

At 0.5 MPa, the boiling temperature is >384.6 K for methanol, which is significantly lower than the boiling temperature of glycerol and methyl oleate at the given pressure, see Table 8.2. The vapour will therefore contain mainly methanol, 99.9wt%.

Under the pressure reduction before the flash unit a portion of the sensible heat is converted into latent heat for the state change of the methanol. The conversion of the sensible heat into latent heat results in temperature reduction over the valve, [12]. The vapour temperature will therefore be lower than the temperature at the reactor outlet.

8.1 Retention and surge time

For sizing of the flash tanks in Chemcad the input parameters could be the retention and surge time as stated below in Equation 8.3 and 8.4 taken as 8 and 4 minutes respectively.

$$\text{Retention time} = \frac{\text{Volume}}{\text{Flow}} \tag{8.3}$$

$$\text{Surge time} = \text{Time to empty} \tag{8.4}$$

When the volume of liquid is small compared to the vapour volume a vertical vapour-liquid separator will normally be used. Due to the large excess of methanol all the flash units in the biodiesel model is taken as vertical, [38].

8.2 Flash behaviour

The pressure conditions for the flash units were taken from patent to be 5 and 2.5 bar, [12, 26].

8.2.1 Case I. Flash unit one

When reducing the inlet pressure to the first flash, lower pressure will give a higher amount of methanol to be flashed off. Figure 8.3 shows that more methanol is flashed of at lower pressure as the vapour flow increase and the liquid fraction of methanol decrease. The same behaviour goes for the rest of the flash units. For the improved model a third flash operating at 1 bar is included for more methanol removal due to Figure 8.3.

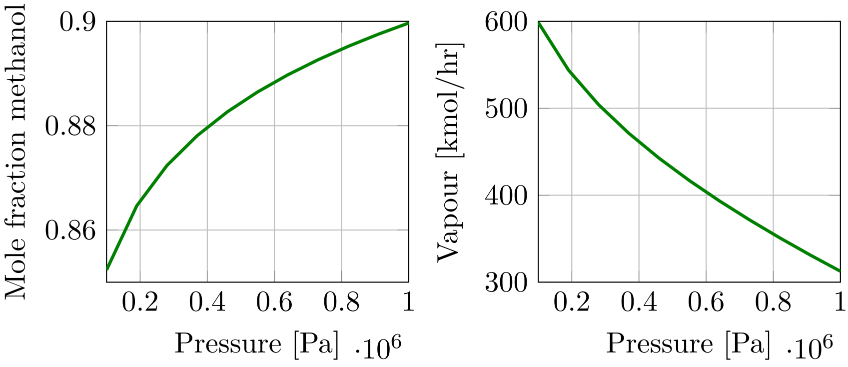


Figure 8.3: Vapour flow and liquid mole fraction of methanol leaving the flash as a function of the pressure.

9 Distillation

Distillation is based on differences in relative volatility, α. The greater the difference in relative volatility is, the easier will the separation be and less stages will be necessary. The total mass balance over the column is given in Equation 9.1. See Figure 9.1 for an illustration.

$$\mathrm{F} = \mathrm{D} + \mathrm{B} \tag{9.1}$$

The component balance is given in Equation 9.2.

$$\mathrm{x_{i,F}} \cdot \mathrm{F} = \mathrm{y_{i,D}} \cdot \mathrm{D} + \mathrm{x_{i,B}} \cdot \mathrm{B} \tag{9.2}$$

Due to larger difference in boiling temperature between methanol and methyl ester than methanol and glycerol this separation will be easier.

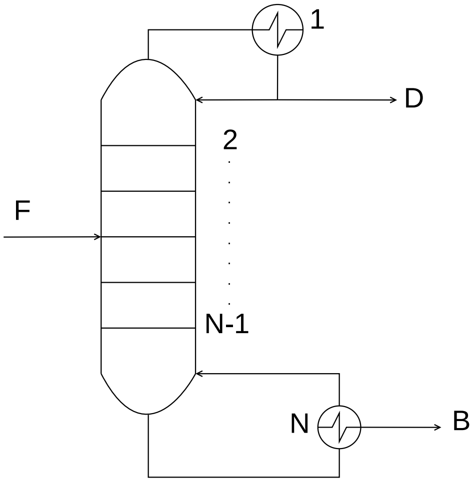


Figure 9.1: Distillation column with normal nomenclature and Chemcad numbering.

A distillation column could be checked by the mass balance over each stage. The flows given by Chemcad for a stage are the flows leaving that stage. The main principle of the mass balance when no accumulation or generation is taking place is given in Equation 9.3.

$$\mathrm{In} = \mathrm{Out} \tag{9.3}$$

The mass balance for each of the stages in the column must also be fulfilled as given in Equation 9.4 over stage i.

$$L_{i-1} + V_{i+1} = L_i + V_i \tag{9.4}$$

Figure 9.2 illustrates the balance given in Equation 9.4. This apply for all stages with some modifications for the stages with in- or outputs, Equation 9.5-9.7.

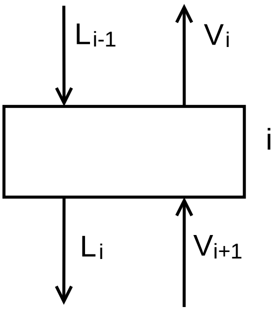


Figure 9.2: Balance over stage *i*.

For a total condenser:

$$V_2 = L_1 + D \tag{9.5}$$

For the reboiler unit:

$$L_{N-1} = V_N + B \tag{9.6}$$

With the feed entering at stage n, being taken as the middle stage for all of the columns:

$$L_{n-1} + V_{n+1} = L_n + V_n + F \tag{9.7}$$

The feed entering the column could be vapour, liquid or a mixture. The mass balances have been checked for all the columns over all the stages by the equations stated above, all being fulfilled. For practical packed columns flooding should be avoided, but that has not been considered here. Flooding occur when the vapour velocity becomes too high and liquid is transported with the vapour, [41].

Tray or packing

A benefit with plate column is that it is easier to provide internal heating or cooling. “The pressure drop per equilibrium stage (HETP) can be lower for packing than plates, and packing should be considered for vacuum columns”, [18]. Packing should always be considered for columns with diameter less than 0.6 m since plates could be difficult to install and expensive, [18]. The columns are all taken as packed due to low pressure operation. Packed columns are not suitable for very low liquid rates.

Vacuum distillation

Vacuum distillation need a low pressure drop per tray and packings are often the preferred column fill for vacuum service, [18]. Vacuum distillation is more expensive than conventional steam distillation, but they can be used for compounds that are miscible with water, like glycerol.

9.1 Biodiesel purification

Downstream the first reactor the biodiesel and glycerol phase is purified by partial evaporation by two flash in series. After the second reactor the requirements to methanol removal is significantly higher and the partial evaporation will be followed by a full evaporation, see Figure 2.1. The full evaporation is done by a distillation column. It was tested with several flash units in series and the product was not satisfying the requirements given in Table 11.2. Two flash tanks were kept as the partial evaporation part followed by a vacuum distillation column, [2]. The operating conditions for this column were taken from a more conventional acid-catalysed process, [2], see Appendix H. The design of the column was taken from the acid-catalysed process with 10 stages and a reflux ratio of 2, [58]. The feed is assumed entering at the middle stage in this case and for the two other columns as well. The bottom specification of the methanol mole fraction was taken at a very low level (0.0001) due to the high methanol purities (99.9-100%) stated by West et al., [58]. The bottom specification could possibly be higher without large aberration from the EN 14214 specifications since it at the moment is 0.001wt% methanol in the biodiesel product and the limit is 0.2wt%, [1].

After decanting between methyl ester and glycerol phase followed by distillation the purity of the biodiesel phase should be above 96.5 wt% ester to fulfil the EN 14214 standard given in Europe, [1], but above 99% by Figure 2.1, [11, 56].

9.1.1 Original biodiesel column behaviour

By studying the profiles under the initial assumptions improvements of the given model can be pointed out.

Feed enter at stage 5 and the sharp change in flow of methyl ester between stage 4 and 6 indicates a high relative volatility between ME and MeOH, see Figure 9.3. Methyl ester goes mainly straight into the liquid phase and methanol in the vapour phase as a result of the easy separation.

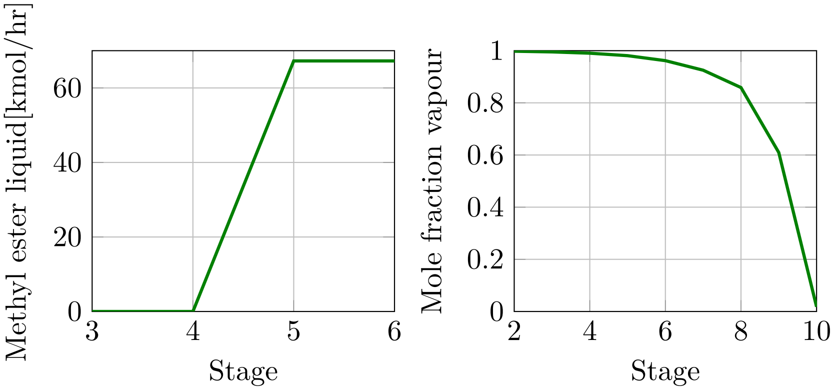


Figure 9.3: Stage profiles for methanol vapour fraction and methyl ester liquid flow over the feed stage.

By studying the mole fraction of methanol in the vapour phase it can be pointed out that all the stages are necessary. Several stages are necessary even though the relative volatility is high to make sure methyl ester is not leaving with the vapour phase due to large amounts of methanol being removed.

The sharp change in the temperature profile in Figure 9.4 is due to the large difference in boiling temperature between biodiesel and methanol, see Table 1.3. This will create a sudden changes in liquid and vapour flow in the bottom of the column as hot reboil meet colder and more methanol enriched downflow resulting in methanol flashing off.

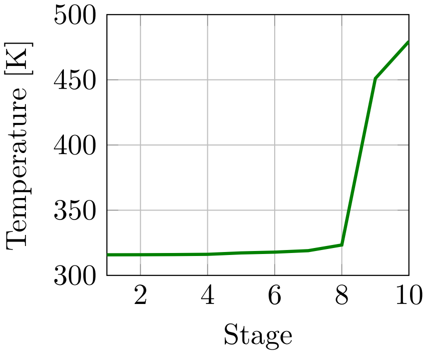


Figure 9.4: Temperature profile over the column.

9.1.2 Sensitivity of biodiesel column

The reflux ratio was taken as the literature value 2 given by, [58]. If the reflux ratio could be reduced the energy consumption for reboiler and condenser will be reduced. If the reflux ratio become low, approximately below 0.4 methyl ester will start to follow the distillate, see Figure 9.5. The column will still keep the bottom composition specification but it will result in product give away, lower production rate of biodiesel and possibly accumulation of products by recycling. In lack of industrial information a reflux ratio of 0.5 was used in the improvement to keep the possibility for disturbances rejection.

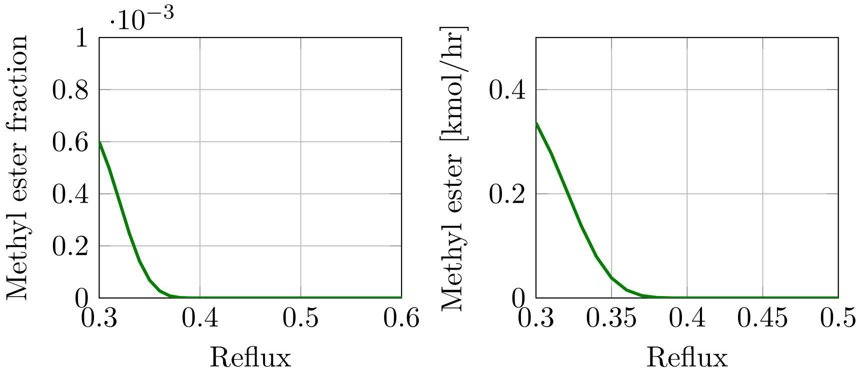


Figure 9.5: Distillate mole fraction and flow of methyl ester for different reflux ratios.

From the plot of energy use for condenser and reboiler as a function of the reflux ratio it can be seen that the lowest reflux ratio is the most energy efficient, see Figure 9.6. It can be observed that the slope changes if the reflux ratio becomes too low due to methyl oleate in vapour flow.

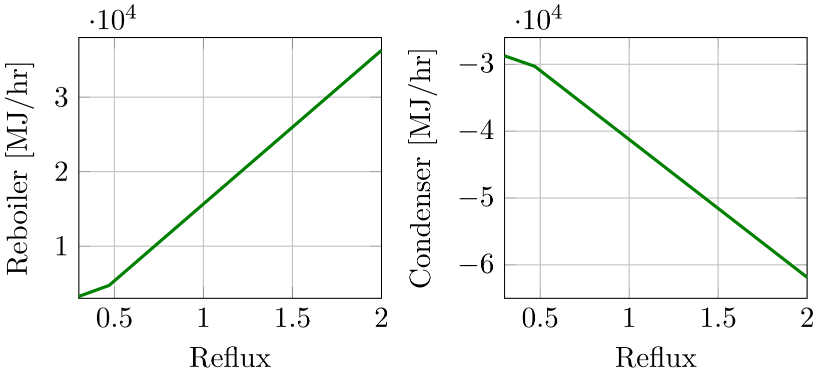


Figure 9.6: Energy use for reboiler and condenser for different reflux ratios.

This behaviour could be clarified by a profit plot for the advanced profit function disregarding the methanol and oil flow. If the reflux ratio becomes low and methyl oleate leave with vapour the profit will be reduced, see Figure 9.7.

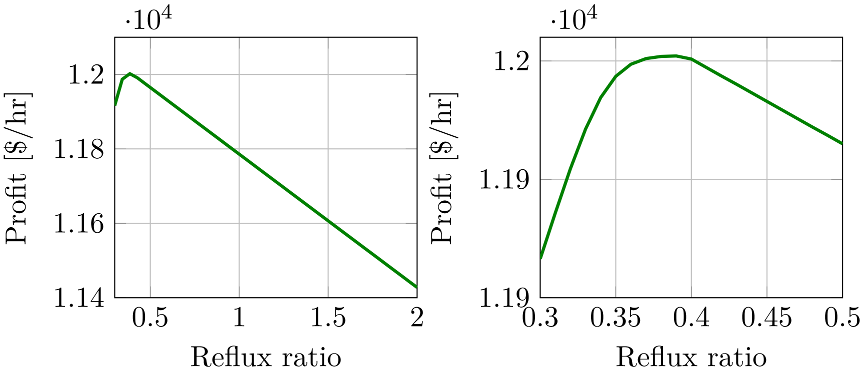


Figure 9.7: Profit as a function of the reflux ratio. The figure to the right is an enhanced view of part of the figure to the left.

Given maximum energy load

When a system have a finished design and reboiler and condenser size are given, it will be a maximum possible energy access. In these cases the maximum energy is taken as + and - 20% of the original use for the reboiler and condenser, respectively. The maximum feed load is then 754 kmol/hr with mass fraction of methanol of 0.47, see Figure 9.8.

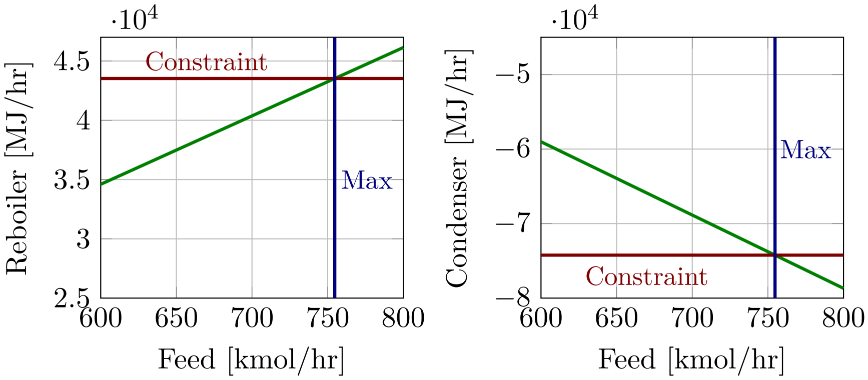


Figure 9.8: Total feed into biodiesel column, with constraint on reboiler and condenser energy, max inlet is 754 kmol/hr. The energy constraint and the maximum inlet flow is drawn.

Another alternative for process disturbances is the feed composition, if the mass fraction of methanol increases more energy is necessary to achieve the desired result with the original operating conditions. The maximum mass fraction of methanol entering the column under the assumption of a maximum reboiler and condenser energy of + and - 20% respectively is 0.6, see Figure 9.9.

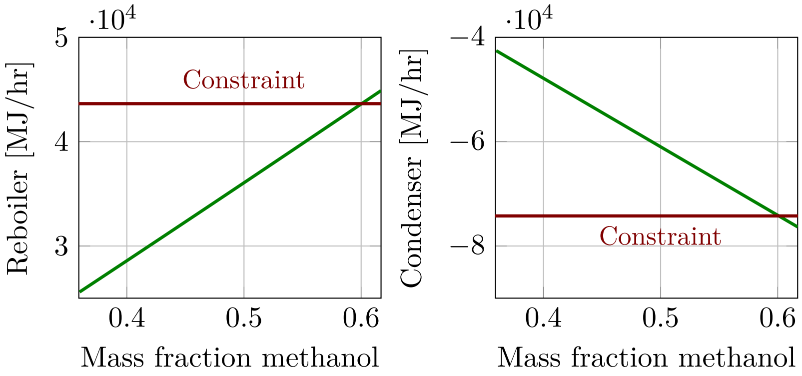


Figure 9.9: Mass fraction methanol into the biodiesel column with constant total mass and the constraint on the reboiler and condenser energy of 20% of now, resulting in max 0.6.

9.2 Glycerol purification

For glycerol purification a two column configuration with one methanol and one water removal column was used, [52].

9.2.1 Methanol removal column

Based on relative volatility between glycerol and methanol the removal of methanol is easy. A flash could be used if the purity specification was less strict and the methanol flow lower. Due to the high specification of both the biodiesel and glycerol phase the distillation columns must be specified to remove large amounts of methanol. The operating conditions for the column was taken as those used in glycerol purification with acid-catalysed process, [2]. Design and operating parameters were taken as a rough estimate and combination with data taken from Kiss et al. ([52]) and West et al. ([58]). The number of stages taken as 20, [52], and the reflux ratio as 2, [52, 58].

The feed stream into the model column contain a higher fraction of methanol and a larger total stream than the column optimized by Kiss et. al ([52]) and the number of stages and reflux ratio were rounded up. The column is operating under vacuum conditions which seems normal for methanol removal, [52, 59, 60].

When introducing control configuration of the process, the bottom product will be the main focus of the distillation columns since these will contain glycerol and methyl oleate. The distillate is mainly containing methanol which will be recycled, but if containing products or intermediates the equilibrium can be affected. With the given process configuration without methanol recycle introduced, it must be avoided that the desired product is removed with vapour. By looking at Figure 7.1 the conversion of methyl ester in the reactor will be affected by recycled glycerol even at small traces.

Even if the main focus is the removal of methanol it is not desired that valuable product recycle, a product give away should be avoided. A higher purification than required should also be minimized if it is not beneficial from other process aspects.

The water removal column could be considerably smaller than the methanol column due to smaller amounts of water in the system. The separation of glycerol and methyl ester is affected by the water within the system, because an emulsion is created and water accumulation should be avoided.

Kiss et al. is suggesting a divided-wall column for the separation of methanol and water from glycerol, and reporting of reduced energy consumption, [52]. As the methanol removal from glycerol is the most energy requiring unit in the process, a reduction of the energy use here would give a high contribution to the biodiesel production profit.

Column profile The number of trays and reflux ratios were first taken as rough number from literature, [52, 58], see Appendix H. Over several of the stages there are no change in the phase composition indicating that the column is larger than necessary. The number of stages could be reduced to half without any effect on the column behaviour, see Figure 9.10. The resulting number of stages from this, 10, is the same as the number of active stages in the methanol removal column from the compositional plot for the direct distillation sequence given by Kiss et al., [52]. This number should have been used in the first place instead of a higher number taken as a rough estimate due to a higher flow and methanol fraction in the feed stream. With the given configuration the reflux could be reduced dramatically without any effect on purity, but energy is saved.

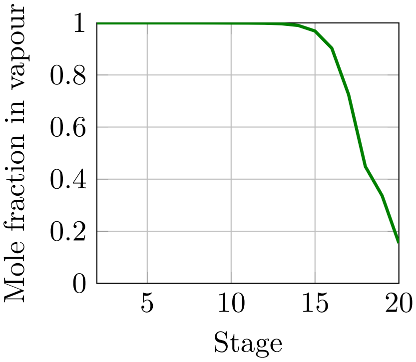


Figure 9.10: Mole fraction of methanol in vapour at the stages in the glycerol column.

9.2.2 Water removal column

The water removal column was mainly included in the model considering that recycling of methanol shall be included. This recycle stream will contain water and to avoid accumulation and snowballing of a component each component need to have its own exit, giving a need of a water column. The number of stages for the water column was taken as the number of active stages excluding reboiler and condenser, 4, given by the composition plot for the water removal column by [52]. At the original operation the column was taken at atmospheric pressure and with a feed temperature of 380 K. The temperature was taken as a value being higher than the boiling temperature of methanol and water, but lower than the boiling temperature for the other components, see Table 1.3, [58]. The pressure was taken from the value used for several methanol recovery columns by, [58], but the column could preferably operate under vacuum (40/50kPa), [42, 52]. Since the operating condition should avoid glycerol degradation vacuum operation could be preferable to keep column temperature low. Changing the operating conditions of the water column have little affect on the profit of the system since the energy use here is small compared to biodiesel column, glycerol column and heating before reactors. From the given operation the reboiler duty and energy duty are 3% and 0.5%, respectively, of the biodiesel column energy requirements.

Water in the conventional process is mainly due to pre-treatment and water washing. In the Esterfip-H process the water washing step is removed, and compared to conventional process the need of water removal is smaller.

10 Decanter

The separation between the glycerol and methyl ester phase is due to the density differences, see Table 1.3. The decanter principle with the ester phase at top and the glycerol phase in the bottom is shown in Figure 10.1.

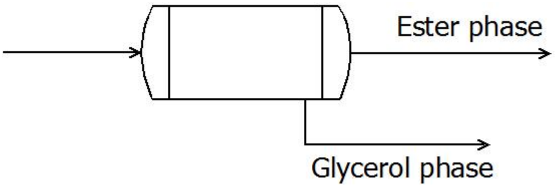


Figure 10.1: Decanter.

The liquid-liquid separation will take place at 50°C and atmospheric pressure, [26, 28]. Some patents operate with a temperature range of 50-70°C, [12], but the given value is the most common. Liquid-liquid separation could be enhanced by a centrifuge. From literature on the ternary system of methyl oleate, glycerol and methanol it can be extracted that methanol mainly will stay in the glycerol phase, [57], which is the result in the Chemcad simulation as well.

From literature the value is reported as 8.5-10.9 weight percentage methanol in glycerol phase divided by weight percentage methanol in biodiesel phase, [61]. The lower value is for a higher methanol molar ratio, [61]. From the given model this number is 15.9. The literature values are for KOH catalyst, which could create more emulsions and possible bind up methanol. The number for the model, with a fixed-bed catalyst, might be high due to no catalyst following the streams to create more emulsions or the use of rapeseed oil instead of soybean oil. The fraction of methanol leaving with the glycerol phase is reported as being higher with a lower temperature, [61], and the choice of 50°C would thereby be better than 70°C. Other literature is operating with values of 1-3.6 ratio being significantly lower than the values stated above, but still indicating that methanol mainly follows the glycerol phase, [62].

In conventional operation the problems related to the separation are mainly due to soap and dispersed water. The amount of water in the Esterfip-H process is less than in conventional process due to fixed-bed removing the neutralization and water washing step. The only water within the process is the water introduced with the oil and methanol stream, and the probability of emulsion is reduced.

The settling velocity must be low enough to allow time for the smallest droplets to move towards the interface and coalesce, [41]. By more information about droplet size distribution the decanter could be configured better.

10.1 Decanter in Chemcad

Three-phase flash, the first outlet stream will be vapour (non in this case), the next the less dense liquid phase (methyl ester) and the last output is the more dense phase (glycerol), see Figure 10.1. A normal flash unit could also be used for a LLV flash if the K-value setting is set to three phase option and the units will provide identical results, [38].

The LLV units in Chemcad are sensitive to the water amount in the feed for solutions of two phases. Phase inversion sometimes take place if switching between the horizontal and vertical LLV-flash units. Figure 10.2 shows that if the water flow becomes too large the phases will invert in Chemcad. A possible suggestion for the phase inversion could be change between water in liquid and liquid in water dispersion, where the liquid could be biodiesel or glycerol.

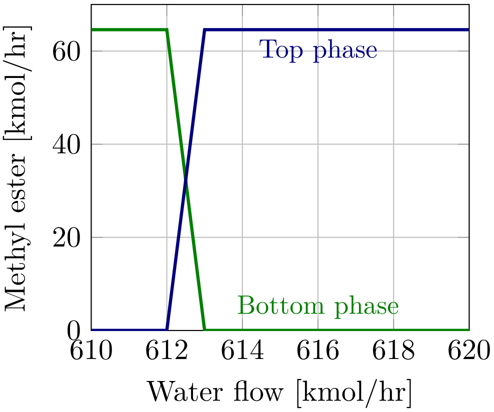


Figure 10.2: Methyl ester flow in the upper and lower liquid flows from the decanter unit as a function of the inlet water amount to the reactor.

Literature values point out that at higher temperature the fraction of methanol in biodiesel phase relative to glycerol phase increases, [61], this is also the case for the Chemcad model illustrated in Figure 10.3.

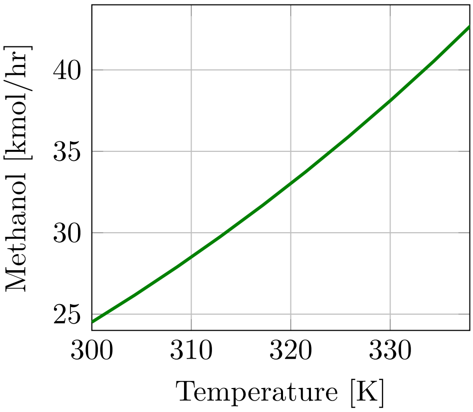


Figure 10.3: Methanol flow in the biodiesel phase as a function of the temperature at constant inlet flow.

10.2 Coalescer

For the coalescer the retention time must be high enough so the droplets have time to coalesce and move vertically. The coalescer is modelled as a three phase separation after conversation with Karoly Moser.

11 Optimization

For the optimization the focus has been on the economic aspect, by looking at the energy conservation. The objective function is the parameter to optimize for, which could be minimized or maximized. This could often be to minimize the energy consumptions and cost, or maximize the production and profit. It is here desired to maximize the profit while keeping the production of biodiesel above a given level and of a certain quality. If the energy consumption could be minimized while the product requirement is kept within range the economical benefits will be largest. A typical profit function is given in Equation 11.1, with purity and operational constraints always being considered, [63].

$$\begin{aligned} \text{J} = \text{Value products} \cdot \text{Product flows} - \text{Cost feeds} \cdot \text{Feed flows} \\ - \text{Cost energy} \cdot \text{Energy consumption} \end{aligned} \tag{11.1}$$

Equation 11.2 gives a cost function more specific for the given production. Energy requirement can origin from pumps, heating, and cooling and thereby be divided into electricity, steam consumption and cooling water respectively.

$$\begin{aligned} \text{J} = \text{Price biodiesel} \cdot \text{Biodiesel flow} + \text{Price glycerol} \cdot \text{Glycerol flow} \\ - \text{Price methanol} \cdot \text{Fresh methanol flow} - \text{Price oil} \cdot \text{Oil flow} \\ - \text{Price energy} \cdot \text{Energy requirement} \end{aligned} \tag{11.2}$$

The optimization is done for a given feed stream of oil and the cost of the oil will be fixed for all optimization functions and could therefore be disregarded in the profit function. Assuming that the required amount of fresh methanol is stoichiometrically given by oil as the excess methanol will be recycled. The cost of methanol will then be the same in all optimization cases as the total flow will be given by fresh and recycled methanol. A fixed cost will only shift the total cost function vertically and not change the optimal point, so methanol cost could also be disregarded. By having a good recycle loop for the methanol the cost of the methanol feed could be minimized compared to using mainly fresh methanol. When running cases where the methanol and oil flow will change these costs must be included in the profit function.

11.1 Optimization with different functions

The given process was tried optimized based on two different profit functions and one energy function, for detailed functions see Appendix D. In the simplest profit function all energy used as electricity, cooling water, and heating steam are covered in one post, Equation 11.3, as both the hot steam and cooling water will require electricity for heating and pumping.

$$\begin{aligned}\text{Profit} = \text{Biodiesel flow} \cdot \text{Biodiesel price} + \text{Glycerol flow} \cdot \text{Glycerol price}\\ -\text{Energy use} \cdot \text{Energy price}\end{aligned} \tag{11.3}$$

The more advanced profit function is separating between electricity, cooling water and heating steam with prices as given in Table 11.1 by Equation 11.4:

$$\begin{aligned}\text{Profit} = \text{Biodiesel flow} \cdot \text{Biodiesel price} + \text{Glycerol flow} \cdot \text{Glycerol price}\\ -\text{Cooling water} \cdot \text{Cooling water price} - \text{Heating} \cdot \text{Steam price}\\ -\text{Electricity} \cdot \text{Electricity price}\end{aligned} \tag{11.4}$$

For the advanced cost function several assumptions have been done for calculating the steam and cooling water flow.

- Steam at 500°C and 27 bar is used for all heating, [64]
- Cooling water at 6°C and 4 bar is used for all cooling, [64]
- Steam is cooled to 230°C, a bit above the boiling temperature for water at 27 bar, 228°C
- Cooling water is heated to 140°C, a bit below the boiling temperature at 4 bar, 144°C
- No phase transition take place

If a phase transition takes place more energy will be released per unit of flow and the cost could thereby be reduced. It is not always the case that the end temperature will be as assumed due to pinch point with process stream and the flows used in the profit results will change. If the cooling water is to be introduced back into the environment, lakes or rivers, the temperature increase should only be small to not effect the ecology.

Necessary treatment for removal of water and glycerides from methanol flow might give some drawbacks with the high methanol flows. It is decided to only included the drawback by cooling of the methanol flow to 293 K, which is the surrounding temperature.

Third objective function, Equation 11.5, minimize the energy use.

$$\text{Cost} = \text{Energy consumption} \tag{11.5}$$

The energy function is at minimum for the lowest methanol flow amounts, but the purity constraint will be leading the methanol flows to be above a certain level. All three objective functions gave the same range for the optimum when the purity constraint is active.

The optimization results are for the given system, if the system is changed the optimum can change. In the start case the reflux ratio for methanol removal columns are taken as 2. If the reflux ratio for the biodiesel column is doubled while the reflux ratio for the glycerol column is halved it will be optimal with a larger methanol flow in the first column and a smaller in the second. If the reflux ratio changes are done in the opposite direction a larger portion of methanol should be feed into the second reactor. This is a result of a change in which of the columns being the main economical drawback.

11.2 Prices

The prices for the reactants and the products are all taken from the same article to get the right relation between the costs and incomes, see Table 11.1, [64]. The prices of the glycerol given in articles is for a 92wt% purity and in the Esterfip-H process the purity is higher and the price for the glycerol could be higher giving a better income from the glycerol, [58, 64]. The data is of older date, but for finding the most optimal point these data give a good relation between cost and income.

Table 11.1: Basic prices for the cost function, [64]. Canola oil is bred from rapeseed.

Item	**Price**
Biodiesel	600 $/tonne
Glycerol	1200 $/tonne
Virgin canola oil	500 $/tonne
Methanol	180 $/tonne
Cooling water	0.007 $/m^3
Electricity	0.062 $/kWh
High pressure steam	10 $/tonne

11.3 Constraint values

The biodiesel from the Esterfip-H process is said to fall within the EN 14214 standard or exceed the requirements. EN 14214 is the standard for biodiesel for automotive fuel, [1, 2], and it is given in complete form in Appendix A.

Due to simplification only some of these are included as constraints in the optimization shown in Table 11.2. The total glycerine content of 0.25wt% will be the active constraint together with the reactor temperatures. Some publications are operating with only the constraint of the individual components being fulfilled, [11, 22]. To assure the largest cover of the model, the most strict constraint with the total glycerine weight fraction is included. If the model gives profit at the most strict purity constraint, the profit will be larger if operating with less strict constraints due to reduced methanol use.

Table 11.2: Main aspects of the constraints on the biodiesel product requirement by EN 14214, [1]. The complete EN 14214 can be found in Appendix A.

EN 14214 requirement to biodiesel product
· Methanol content < 0.2 wt%
· Triglyceride < 0.2 wt%
· Diglyceride < 0.2 wt%
· Monoglyceride < 0.8 wt%
· Total glycerine < 0.25 wt%
· Free glycerine < 0.02 wt%

Different patents are utilizing different constraint range for operation making it difficult to know what the operation constraints will be without industrial data. It can be discussed if the constraints are reasonable, but to be able to eliminate the wrong constraints more data for the kinetics and component behaviour in the system are necessary. The temperature range for the operation is taken as one of the narrowest, given by the newest of the patents under the assumption of more studies showing that a wider operating range is of no interest. The temperature should be kept low to avoid glycerol degradation taking place, [52]. The mass ratio constraints are taken as a value within the range for all the top and bottom limits provided by the studied patents, [12, 24, 25, 26, 27, 28, 29, 30, 53, 54, 65]. The operating constraints used for the model are given in Table 11.3.

Due to the high operating pressure and temperature secondary reaction like intermolecular dehydration is favoured, [65]. In addition to the sever

Table 11.3: Operational constraints given by the patents used as background for the Esterfip-H process.

Operation constraints given by patents	
· Weight ratio methanol/oil 3>Ratio>0.3	[25, 27, 53, 54]
· Weight ratio methanol/methyl ester 3>Ratio>0.3	[25, 27, 53, 54]
· Temperature 483 K > T > 443 K	[12, 24]

operating condition the catalyst must contain a Brønsted acid site, [65]. Tri-, di-, and monoglycerides contains three, two and one fatty acid chains of oleic acid respectively. Equation 11.6 - 11.8 gives the possible intermolecular dehydration, [65]:

$$\text{Glycerol} + \text{Alcohol} \rightarrow \text{Glycerol ether} + \text{Water} \tag{11.6}$$

$$\text{Glycerol} + \text{Glycerol} \rightarrow \text{Diglycerol ether} + \text{Water} \tag{11.7}$$

$$\text{Alcohol} + \text{Alcohol} \rightarrow \text{Ether} + \text{Water} \tag{11.8}$$

From the reactions above it can be seen that too high methanol concentration is undesired as this will drive the intermolecular dehydration. Exactly what the maximum ratio of methanol/oil is will depend on the oil and the alcohol choice, and the patent constraint will be assumed counting here. Literature is also stating that if the alcohol ratio becomes higher than a certain level the yield will be reduced as glycerol begin to stay in the ester phase, [66]. This information is for a homogeneous catalysts, but is is assumed that the same problem can occur for a heterogeneous catalyst.

A high molar ratio between alcohol and vegetable oil will also interfere with the separation of the phases due to increased solubility, [3]. Emulsion is partly created by the mono- and diglyceride which have both a polar hydroxyl groups and hydrocarbon chains, [3]. Emulsion problems are normally a larger problem when using ethanol than methanol due to higher stability, [3].

11.4 Brute Force method

In the brute force method each candidate set of CVs is evaluated. This is the most general and exact method, but also the most time consuming, [63]. The optimal operation for the biodiesel process was found by trial and error as a first approach. The model was checked for combinations between the controlled variables temperatures and methanol flows to find the optimal operation.

11.5 Procedure for optimization

The procedure used for the optimization is by changing one variable and then checking the profit function. When a step is performed in one direction and the profit increases the steps are continuously performed in the same direction until profit starts decreasing or constraints are meet. Then a step is performed in one of the other variables and profit is observed. This is repeated for all of the parameters. After finding a good value for the second parameter, the first one is checked again. This is repeated for all of the parameters to avoid problems were they are influencing each other to give a decrease in profit. An example of the procedure is: Increase the inlet temperature of reactor one, then changing the inlet feed to the same reactor observing the trend in profit in the different directions. The results after the trial and error procedure, followed by the Chemcad optimization routine are given in Appendix I.

11.6 Local and global optimum

When moving in different directions for the methanol flow and reactor inlet temperatures, several local maximum could be found. If applying the optimization routine at a point far from the global maximum the routine can stop at the local maximum. For the built-in optimization routine to work the initial values must be close to the global optimum to avoid ending in the local optimum.

11.7 Flat or steep optimum

For the given case the optimum is flat related to the methanol flow meaning that the objective function changes little with the flow parameters around the optimum. After the trial and error procedure, the system was optimized by Chemcad and the values here were used as the optimum. Since the optimum is flat, other inlet conditions could give the same result for the profit function with some noise in the model under calculations for convergence of the system. The range for good combination of methanol flow is 1165-1185 kmol/hr into the first reactor and related 1255.2-1234.4 kmol/hr for the second reactor. These outer points give a profit of 11427.5479 and 11427.5996 \$/hr from the advanced cost function disregarding oil and methanol flow with a maximum between the two outer points above.

Figure 11.1 shows that the model contain some program noise. With this in mind it can be pointed out that the optimal point can depend on each run as the optimum is flat and the model noise is in the range affecting the optimum. This is the disadvantage with the flat optimum compared to a steep optimum. The optimum returned after one optimization routine is likely to be another than the one from the previous run. When moving too far away from the optimal solution the model noise will stop affecting the result and optimization routine will move the result back within to optimal solution range. This lead to the result from the optimization sequence ending within the same range each time even though model noise exist.

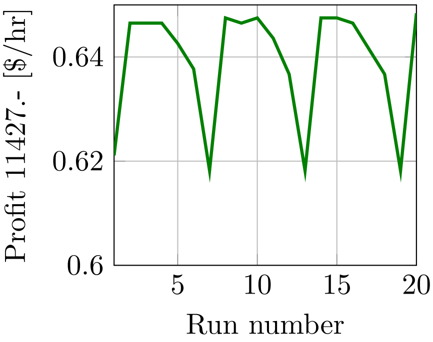


Figure 11.1: The model was ran twenty times and the advanced profit function result was observed to be in the range 11427.6182-11427.6484 $/hr. This shows that the results include some program noise.

If changing the methanol flow into the first reactor, this could be compensated for by the methanol flow in the second reactor to achieve the product specifications. One advantage is that the system is easy controllable as the range of the optimum is flat. Measurement noise will have little effect if operating with some extra methanol related to the required by product specifications, having little effect on profit as the optimum is flat.

11.8 Optimization Chemcad

Optimization in Chemcad could be done by Generalized Reduced Gradient, Successive Quadratic Programming(SQP) and Simultaneous Modular SQP. It was performed with SQP as used in the two column system by Kiss et al., [52]. SQP uses a quadratic approximation to the objective function. It is an iterative method for nonlinear problems. If the problem is unconstrained the method is reduced to Newtons method.

Forward difference or central difference can be used for calculating the slope of the function. Forward difference uses one point forward and calculate the slope between this point and the given point. The central difference uses one forward and one backward point for calculation of the slope. The central difference method is slower, but could be more accurate, [38].

It tries to minimize the objective function, Equation 11.9,

$$\min_{\mathrm{x}} \mathrm{f(x)} \tag{11.9}$$

it is being implemented as the profit function. Under constraints given previously by patents and European standard.

When finding the optimal operation the temperature is at the upper constraint given in the patents and as stated in Chemical engineering design "The best conditions will usually be at or near the upper or lower end of the narrowest range". The active constraints from the optimization routine will be the temperatures and the product purity. To check the optimization routine the initial temperature values to the optimization routine were taken a bit below the constraint to see if the routine moved and stopped at the constraint, which it did. The results after the trial and error procedure, followed by the Chemcad optimization routine are given in Appendix I. The temperatures will be 483 K, the methanol flow to the first reactor 1175 kmol/hr and to the second reactor 1244.7 kmol/hr giving a profit of 1074 $/hr.

11.9 Profit sensitivity to price changes in feed and products

The prices for feedstock and products will vary as the demand and world economy are changing. At given price drops the production is no longer economical beneficial. If the product price becomes too low a minimum production will be the beneficial. Normally the price of the feed and the price of the product will fluctuate in some of the same trends, but in the cases below only one of the prices are changed at the time. All the cases below have been done for a fresh methanol flow of 1500 kmol/hr and 1200 kmol/hr to reactor one and two respectively. The oil flows used are 15, 20 and 25 kmol/hr all making sure the product is within the given purity constraint. A higher oil flow will give a less pure product, but still within limits. The modified advanced profit function including oil and methanol cost have been used, see Appendix D.

11.9.1 Case I: Changes in product price

There will be change in the price of the biodiesel product while all the other parameters are kept constant. By looking at the change in profit at different oil flows as the price change it can be observed that as the product price falls below a certain level it is no longer beneficial to produce as much as possible for a given methanol flow. In Figure 11.2 this point falls at around 389 \$/tonne, but the operation is anyway not beneficial at this point since the profit is negative. When operating labour, salary, maintenance, insurance and taxes are included in the profit equation the profit will shift to the right, and a higher product price is necessary to achieve the same profit.

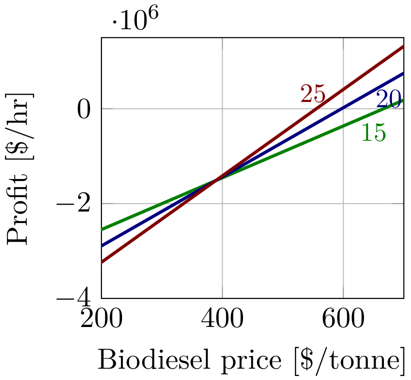


Figure 11.2: Profit as a function of biodiesel prices at different oil flows [kmol/hr] at constant methanol flows.

The benefit with a high production rate becomes smaller as the biodiesel(product) price falls.

In the case of the glycerol price the highest production is always best for realistic prices as the intersection point between the oil flows falls at a negative price, see Appendix J. The price of glycerol changes from 750 to 1200 \$/tonne when the purity increase from 85 to 92wt%, [64]. The glycerol price for the given model purity, 99.8wt%, could be assumed to be higher than the applied literature value due to a higher purity.

11.9.2 Case II: Changes in feed price

When the feed price increases the slope of the profit function will be negative. As the prices of the feedstock increases the economical study changes from being economical beneficial to give losses. If the feed costs become high, 712 $/tonne, the operation change from highest to lowest product. For a higher oil flow the oil price can increase more before the profit function goes in zero, 545 $/tonne for 25 kmol/hr, than for a 15 kmol/hr oil where the intersection happens at 435 $/tonne, see Figure 11.3. Indicating that for a given methanol flow under the given prices the oil flow must exceed a level to be economically feasible and that the methanol flow for a given oil flow should be kept low. The oil cost for the original model accounts for 74% of the production cost considered, being lower than the reported 88% in literature, [21], but indicating that the process costs are most sensitive to changes in the oil price.

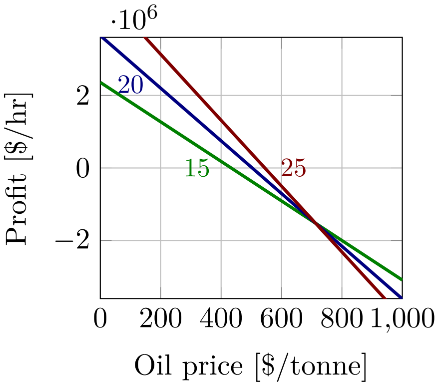


Figure 11.3: Profit as a function of oil prices at different oil flows [kmol/hr] at constant methanol flows.

11.10 Energy cost

For a given oil flow it is originally beneficial to not use more methanol than necessary, but if the energy costs becomes low the disadvantage with the excess methanol is reduced. Energy fraction 1 is with the original cost, and at a fraction of 0.5 the energy cost is half of the original while at a fraction of 2 the costs are doubled.

A higher methanol flow for a given oil flow will give increased purity, but also increased costs. Under all practical energy costs the lowest methanol

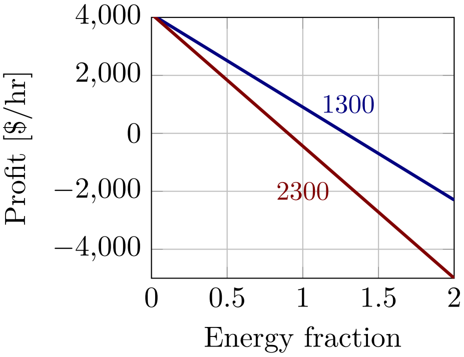


Figure 11.4: The profit function for the originally given oil flow and optimal methanol flow into the second reactor as response to the energy fraction of original. Tested for two different methanol flows [kmol/hr] to the first reactor.

flow is the most economical, see Figure 11.4. Indicating that the best operation is at the purity constraints given by EN 14214, avoiding over purification. If the product restrictions were taken for the individual components instead of the total less methanol would be required and thereby less energy which make the process more economically beneficial.

11.11 The given process

For the chosen optimal operation with given oil and methanol flows as given in Appendix I the response to price changes is reported. In the profit function here only operation costs and incomes are included and the graphs will move downwards as labour cost, salary, maintenance, taxes are included. Oil and methanol costs are included in the advanced profit function giving the modified advanced profit function to give the actual profit of 1074 $/hr.

The response to changes in product and feed prices is showed in Figure 11.5 where the slope of the profit function against product and feed price is opposite. The highest product price and the lowest feed price are preferable.

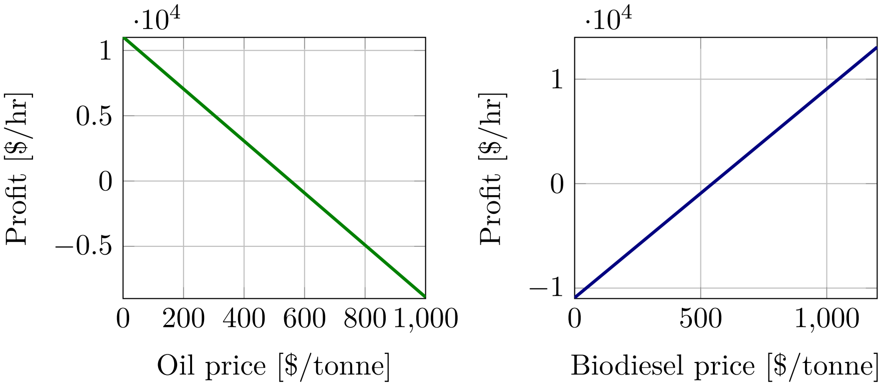


Figure 11.5: Response in profit function for the given optimal process conditions to disturbances in oil and biodiesel prices.

It has earlier in the cases been assumed that a stoichiometric amount of methanol is paid for under the assumption of total recycling of methanol. In the same way as the price cases previously, when the required amount of fresh methanol paid for becomes too high, the operation is no longer beneficial, see Figure 11.6. A good recycle loop for methanol is necessary to make the plant profitable.

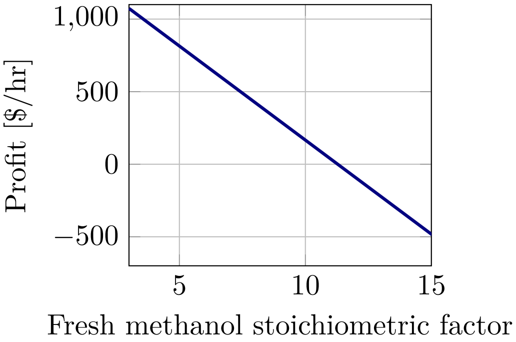


Figure 11.6: Profit as a function of the methanol stoiciometric factor being paid for.

11.12 Cooling water and steam

The cooling water and steam amounts have been calculated by assuming the final temperature of the steam and cooling water. These amount can become larger or smaller if the possible temperature intervals are larger or smaller, or phase change occurs.

The price of the cooling water (0.007 $\$/\text{m}^3$) is significantly lower than the steam price (10$/tonne $\approx$ 10 $\$/\text{m}^3$), illustrated in Figure 11.7. The profit changes little with the required cooling water amount thereby indicating that the reboiler/heater units are the main economical drawback for the energy use. The amount of necessary cooling water might increase dramatically if the maximum temperature increase is given by the environment if released back into the lake or river. If to be returned without ecological consequences the temperature increase should be low giving a need of a high cooling water flow rate and increased costs.

The costs of the steam could be reduced if steam at lower pressure and temperature can be used for some of the heaters. The cost of steam will also be reduced if the steam is condensed at the operating pressure, releasing the heat of condensation.

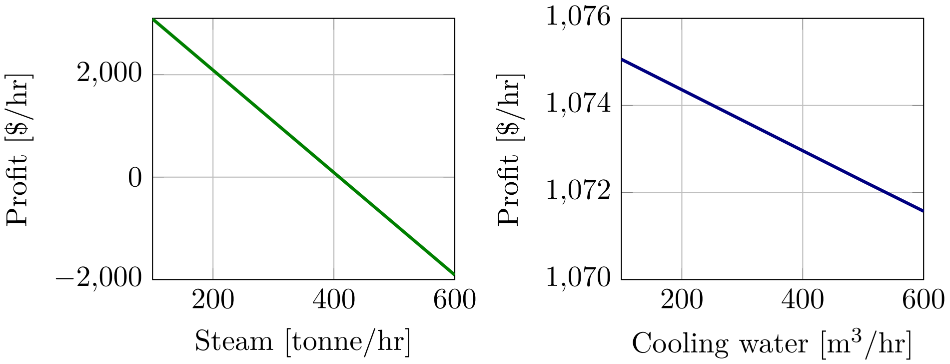


Figure 11.7: Profit as a function of required steam and cooling water.

12 Control

The main tasks with the control structure are to achieve the desired purity and production of biodiesel and glycerol and to maintain safe and stable operation.

12.1 Economic plantwide control

Plantwide control is the design of a control structure for a whole plant, [67]. The control structure will be layered based on time, the need of tight and smooth control.

The procedure for achieving a plantwide control is using the top down and bottom up procedure, which puts focus on structural decisions like selections of the parameters given below:

- Controlled variables (CV)
- Manipulated variables (MV)
- Extra measurement
- Control configuration
- Controller type

Only parts in the top down procedure like choice of control configuration, production rate, degrees of freedom, controlled and manipulated variable are considered here.

12.1.1 Top down

The first step in the top down procedure is to define the operational objectives and constraints, see the section on optimization. Finding the optimal operation is often more extensive than firstly assumed and was time consuming. Operational constraints like safety and product requirement should be included as constraints in the control configuration. The biodiesel plant is partly operating at high pressure leading to safety constraint to avoid pressure built-up.

Next on the agenda is to identify the degrees of freedom, manipulated variable, primary controlled variables and production rate, [67].

12.2 Throughput manipulator (TPM)

The throughput manipulator is the gas pedal of the system and where the production rate is set. Traditionally this is set at the feed, and for the biodiesel production at the oil flow. For maximum production the TPM should be set at the production bottleneck. “A TPM is a degree of freedom that affetcs the network flow and which is not directly or indirectly determined by the control of the individual units, including their inventory control”, [68, 69]

12.3 Consistency

Consistency means that the individual and overall mass balance at steady state are satisfied, [68]. Consistency in control structure makes sure that the process have no internal accumulation. Depending on the location of the throughput manipulator (TPM) the control units should be placed thereafter and a shift in TPM is not desired as this will change the control configuration to get consistency.

The inventory control must ”radiate” from the throughput manipulator, as illustrated in Figure 12.1, [67, 68, 69]:

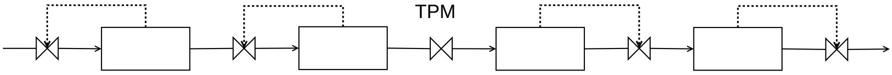


Figure 12.1: Illustration of the radiating consistency rule.

“A local-consistent inventory control structure must be radiating around the location of a given flow (TPM)” as the radiating rule given in Figure 12.1, [68].

12.4 Degrees of freedom (DOF)

To find all operational degrees of freedom (DOF) the valve counting method could be used, where valves also includes adjustable compressor power, and heating energy. The degrees of freedom determines the number of variables to manipulate. When applying the valve counting method some of the valves will have no steady state effect and should be subtracted, like liquid levels.

Some units have a potential number of DOF and this method in compliance with the valve counting method will eventually lead to the correct answer for the degrees of freedom. Potential number for some of the process units used in biodiesel production is given in Table 12.1, [70]:

Table 12.1: Potential number of degrees of freedom for some of the operational units with steady state effect, [70] .

· Each external feed stream: 1 (rate)
· Splitter: n-1 (split fractions) (n= number of exit streams)
· Compressor, turbine, pump: 1 (work/speed)
· Adiabatic flash tank: 0 (when pressure is assumed given by the surrounding process, if not 1 as here)
· Liquid phase reactor: 1 (Holdup reactant)
· Pressure: Add one DOF at each extra place where the pressure is set
· Heat exchanger: 1
· Column (excluded heat exchangers): 0 (Resulting in 2 = 1 heat exchangers + 1 split, when feed and pressure is given and two liquid levels)
· Split: 1
· Mixer: 0

12.5 Control configuration

The choice of the control configuration must be taken in relation with consistency of the system.

12.5.1 Feedback

In a feedback configuration the output is measured and then adjustments upstream are done as a response to this deviation from setpoint. In the same way as the units to the left of TPM in Figure 12.1 are illustrating. Advantage with feedback control is that it compensates for all disturbances disregarding origin. A disadvantage with this configuration is that a disturbance is not detected before after deviation from set point, [71].

12.5.2 Feedforward

The feedforward configuration measure the disturbance and compensate before the disturbance is able to move through to sensitive equipment and create deviation from set point. In compliance with the units to the right of the TPM in Figure 12.1. A disadvantage with the feedforward control is the need to know in which parameters the disturbance will occur, and in which extent this will affect.

12.5.3 Cascade control

The master controller keeps the primary variable at set point, and the secondary variable is kept at set point by the slave controller also called the inner or secondary controller, [71]. The setpoint for the inner controller is given by the master controller. A cascade control can be used between concentration and temperature for the bottom purity in the distillation columns.

12.5.4 System configuration

As the throughput manipulator is placed at the oil feed all the flow, pressure, and level control units will be feedforward, to the right in Figure 12.1. As the temperature controllers have no affect on the consistency as they are adjusting steam and cooling water in the biodiesel system these are suggested as feedback controllers, see Appendix K.

12.6 Tight and smooth control

Within tight control the object is to keep the output to its set point and the control will be as fast as possible. Tight control is typically used for active constraints since it reduces the backoff. With tight control it is a disadvantage of input disturbances continue throughout the process. In smooth control the controller is made slower, but still with acceptable control of the system. Even if the control is smooth it should not reject disturbances, [72].

12.7 Control units

For a suggestion for control structure see Appendix K. The control structure suggested is based on the degrees of freedom and consistency.

12.7.1 Level control

Level controllers (LC) will be used for decanters, flashes, distillation condensers and the liquid level in the bottom of the distillation columns. A smooth level controller at the decanter would smooth out upstream disturbances for sensitive downstream equipment like distillation columns. An example of level and pressure controllers are shown in Figure 12.2 on a decanter unit.

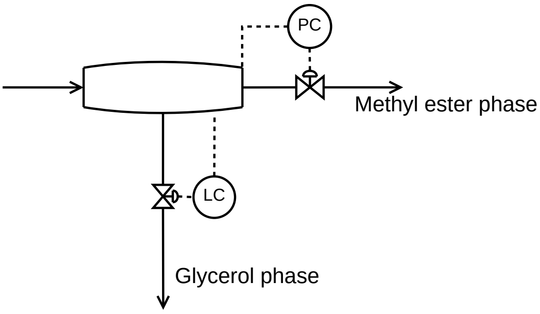


Figure 12.2: Decanter unit with pressure and level controllers.

12.7.2 Pressure control

Pressure control (PC) devices will be necessary for flash tanks for vapour flow control and to avoid pressure build-up possibly leading to rupture. These valves should for safety reasons be fail open, to avoid pressure build-ups at energy failure. The control valve actions indicate if the valve fully opens or closes if the energy supplies fails, [71]. The pressure in the distillation columns and the decanter units should also be controlled. The pressure over the reactor is controlled to keep the operating conditions within the limits. The pressure in the reactor must be high enough for the components to stay in liquid phase at the given temperature, see Figure 4.1.

In processes with a high pressure reaction section and a low pressure separation unit, the pressure in the high pressure section is usually controlled by expansion over a control valve, [18]. If no phase change occur over the control valve a turbine or turbo-expander will be introduced for a more economical benefits, [18]. For pressure reduction before the flash and decanter units there will be a phase change as methanol evaporate and a valve is used.

12.7.3 Flow control

There will be flow control (FC) on the feed streams, and the flow of methanol must be adjusted to give the desired outlet purity. If the methanol flow into the first reactor is reduced this could be compensated for by an increase in the methanol flow into the second reactor to achieve the necessary product purity. The flow of methanol into the second reactor should be controlled based on the product purity as the methanol/oil and methanol/methyl ester ratios are not constant for oil flow disturbances. The temperature control of process streams will be done by a flow controller for steam and cooling water, the utilities.

12.7.4 Temperature control

The outlet temperature from the steam heat exchanger must be kept close to set point to get the optimal conversion and reaction conditions, Figure 7.2 shows the trend. The temperature will be actively constrained to a maximum of 483 K. Here it is a balance to get a low as possible energy use, while the conversion should be satisfying at the same time. Control units over the reactor are shown in Figure 12.3.

There will also be a temperature control (TC) before the decanter to achieve ideal conditions for phase separation. If the temperature in the decanter is too high methanol will start to flash off. Temperature controller could be used in the distillation column for bottom purity specifications. For storage of the flashed methanol, it need to be cooled and temperature controllers should be used.

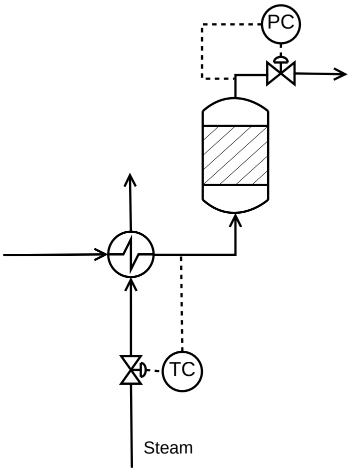


Figure 12.3: Reactor unit with temperature and pressure control of the reactant stream.

12.8 Distillation control

The configuration of the control units for the distillation column could be placed in several different configurations. The most common configuration is the LV-configuration where D and B are used for level control while L and V remains as degrees of freedom for purity control, see Figure 12.4. The column pressure should be controlled and the valve at the condenser duty could be applied for this. Then there are two degrees of freedom left as given in Table 12.1 to control the flow composition. If the reboiler duty is used to control the temperature in the column it should be made sure that it avoids saturation. If the control parameter saturate the control will be lost. The reflux ratio could be controlled by a ratio controller with the inlet feed, and the bottom purity by a cascade controller between concentration(master) and temperature(slave).

For the columns for biodiesel production the bottom products are of main interest since these are glycerol and methyl ester flow while the distillate mainly is methanol or water to be recycled.

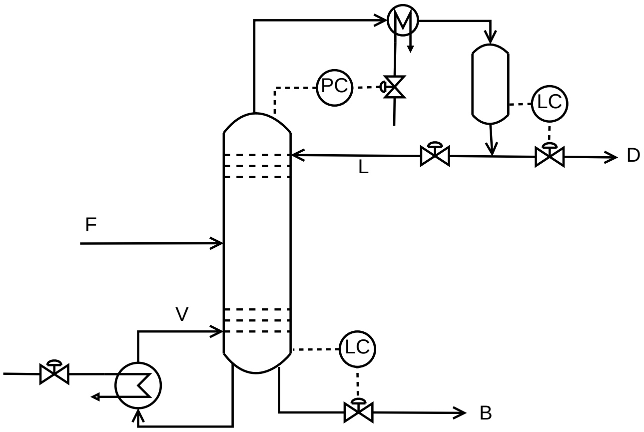


Figure 12.4: Distillation column with liquid levels controlled by D and B and pressure by condenser duty indicating two degrees of freedom left.

13 Discussion

13.1 Overarching discussion

Even though it has been used a critical view on the information and data applied, which mainly are from the French Institute of Petroleum, the data will include aberration. A large amount of information have been collected and tried processed in a good matter. Sorting of information might have gone wrong in the process and interesting information can have been left out and uninteresting or unrepresentative information been included. Rapeseed oil will have some small differences in composition due to natural variation of the feedstock, this is disregarded here. As the model is being based on patents the amount of information available is significantly lower than in more established process where research have been performed from several contributors. The range of the operational constraints are large by the different patents and more certain values are desirable, [12, 24, 25, 26, 27, 30, 53, 54, 65]. The values implemented in Table 11.3 are given after collection and merging of values from the patents above. As the patents used as background information for this thesis are an assortment of all patents on the Esterfip-H process, values are taken within the separate range for the top and bottom limits given by the patents. A weakness with the model and results are the large amount of assumptions and sometimes thin foundations. This can be improved with access to operative data from a process plant.

13.2 Production

The starting values for the original case are rough numbers from literature and the possibility of default or out of range values are high. It is an uncertainty in every element of the model. The model result in a yield of 99.7% and a total conversion of 99.5% leading in a product of 99.7wt% methyl oleate purity. The product purity is above the standard limit of 96.5wt% ester (Appendix A) giving a satisfying product. The yield is approximately 100% as stated by literature values, [11, 26, 56]. The production rate of biodiesel is 19990 kg/hr relative to the model basis of 20000 kg/hr. A production rate of 99.95% of the theoretical value can be said to be satisfying. The glycerol product have a purity of 99.8wt%, well above the stated literature value of 98wt%, [1, 2, 22, 23]. The high purities of the product could origin from the strict bottom specifications for the columns, see Appendix H. The production is partly lower than theoretical value as a result of some methyl oleate and mono-, di-, and triglycerides leaving with the glycerol phase and some with the methanol and water vapour phases. The components leaving with the vapour phase can enter the system again when the complete recycle loop is included.

For the purity constraint the most conservative value, the total amount of glycerine, is used rather than the individual values for each of the components. By using the constraints for the separate components as done by Hillion et al. ([11]) instead the restrictions become slack and less methanol is required resulting in a higher profit.

The cetane number for the biodiesel product is 51.7 and within the reported values for RME, [1, 2], and slightly above the EN 14214 specification of 51, Appendix A. The heat of combustion 37.5 and 40.1 MJ/kg(net and gross) is also in the reported range 37.3-39.9 MJ/kg, [1, 8, 9].

13.3 Profit

The profit of the production with the original assumptions is positive 1074 $/hr, but can be made higher by including the improvement suggestions from the previous sections. In the modified advanced profit function no other costs than the production cost is included and the profit will decrease as for example the fixed costs and salary of production are included. Literature is reporting of a negative after tax rate-of-return indicating a need for governmental subsidies, [58, 64]. One article is reporting of a positive after tax rate-of-return for a heterogeneous acid-catalyzed process making it a competitive alternative for the traditional processes, [58]. One of the reasons that only the process using heterogeneous catalyst is reported with a positive values could be the reduced need for post-treatment, see Figure 2.3.

13.4 Model versus Literature

If comparing the methyl ester phase after the first reactor and methanol removal from the model and literature values, [22], the distribution of tri-, di- and monoglycerides has some differences. A study of the results given in Table 13.1 could indicates a smaller extent of the reactions in the model compared to the literature, [22].

Reasons for the deviation could be the kinetics, the size of the reactor, assumptions done for finding the reactor size, operating conditions and the catalyst used. The generated model gives a lower weight fraction for all components after the first reactor and decanting than from literature containing no methanol, [22]. This could partly be due to a higher amount of methanol being in the methyl ester phase. It should be pointed out that literature percentages are not summing up to 100. The literature values

Table 13.1: Weight composition of the methyl ester phase after the first decanter from literature and model.

Weight composition (%)	**Methyl ester phase reactor 1, [22]**	**Methyl ester phase reactor 1, model**
Methyl esters	94.1	92
Monoglyceride	2	0.51
Diglycerides	1.1	0.74
Triglyceride	1.6	1.29
Methanol		5.44
Free glycerol	-	-

in Table 13.1 are from 2005, [22], but four of the same writers contributed to an article in 2003 ([11]) operating with a weight% of methyl ester of 94.5 indicating deviation depending on rapeseed oil composition, kinetic, equipment and operating conditions.

Literature have the highest fraction monoglyceride and thereafter tri-, and diglyceride, while the sequence for the model is tri-, di-, and monoglyceride indicating a lower conversion of triglyceride to intermediates in the model than literature. Even though it contains methanol and the relation between the glycerides is different the model seem to cope reasonably well with literature values. Indicating that the specifications are not too far away from the real operating values. For proper comparison the operating conditions should be the same and the model should be validated against industrial data.

13.5 Kinetics

The literature for the process refer to using a catalyst consisting of mixed oxide of zinc and aluminium, [11, 20, 21, 22, 31, 50]. This is not necessarily exactly the same catalyst as the one used for the kinetics, $ZnAl_2O_4$, [45], even though they are mainly given by IFP. The results so far are indicating that the model can be used for imitation of the Esterfip-H process and biodiesel production.

13.6 Optimum

The optimum is found to be flat and calculation noise from Chemcad could lead to some deviations. The result from the optimization sequence will be different for each run as the program noise will affect the result and any values within the flat range are satisfying. A consideration for a better model could be to optimize for the equipment sizes and parameters together with temperature and methanol flow. Parameters like the number of stages in the column, reflux ratio, the reactor volume, heat exchanger area will effect the profit.

Eventually if nominal values for flows and equipment sizes for a production facility are included a desired study of control system and optimization can be performed. When having an understanding of the existing control configuration suggestions for new and possibly improved configurations can be studied from a plantwide view.

13.7 Improved model

The values for the improved model is given in Appendix H together with the original values. In addition to the changes in Appendix H an extra flash unit operating at atmospheric pressure is included with the two-flash unit system. For even better profit increase the bottom specification could probably be less strict. Increasing the allowed methanol flow in the bottom could lead to the introduction of the methanol constraint by EN 14214, see Appendix A. This results in less energy consumption and reduced methanol requirement. The profit increase by 140% giving a profit of 2571 $/hr. Profit improvements can also be done by a three reactor model, giving a profit increase of 129%.

13.8 Proposals for further work

The suggestions for further work, improvements and possibilities for what to study next are many as building and validation of the model have been a learning process. New aspects and possibilities have been discovered giving an opportunity for new approaches. Decisions made have been found to give results deviating from the most profitable operation and suggestions for improvements are considered. When the recycle loop is included in the model some of the model behaviour might change and should be investigated to find improvements.

Since the process is quite new, the first plant was built in 2006, more information is continuously being published and it is likely to find literature updates. With a quite new process there are often many aspects which have not been looked at yet. Only one article for kinetic for a mixed zinc and aluminium oxide was found and an interesting study could be, if possible, to find more kinetic data for the same and other similar catalyst. By looking at deviation in literature the certainty of the kinetics could be established. Oxide of zinc and aluminium is the only catalyst reported used, [11, 20, 21, 22, 31, 50], but others are mentioned of possible options, [49, 50, 51]. To look into other catalyst with similar properties or different distribution of the components could possibly improve the performance and operating conditions. The heterogeneous catalyst will deactivate with time and data for zinc aluminium oxide deactivation might put new light on the reactor design.

UNIFAC is the thermodynamic model used, but other thermodynamic models are suggested and used for conventional operation, [37, 38]. When operating data for the Esterfip-H process are available an in-depth study of a good thermodynamic model can be performed. As the conditions for part of the Esterfip-H process is harsher than conventional operation other thermodynamic models might be more predicative of flow behaviour. With industrial data the model predictions for different thermodynamic models could be compared to the real behaviour.

At the moment the heat recovery is done by the hot methanol heating the mixed inlet reactants, but for energy saving more heat recovery between units should be considered. Suggestions possibly of interest are using the energy from condenser units for heating elsewhere. Hot methanol leaving the flash tank at 2.5 bar could possibly be used for heating of columns or other equipment or streams, giving more preheating. Other heat configurations for heating the reactants separately or partly separately could be studied more closely hoping to find a lower total energy consumption.

If reactive distillation could be combined with the extreme conditions of the Esterfip-H process, as both reaction and separation need to take place, this could be a possibility. And if glycerol could be removed at several levels in a reactive column or reactor this could give a higher conversion. If the reactor is a two section unit, see Figure 7.6, then glycerol could be removed intermediate if allowed by the flow profile.

A quick study of process including several smaller reactor with intermediate glycerol removal have been studied and found possibly advantageous from the original model. For finding out if this is a realistic improvement industrial data should be used. The investment and operational cost for several smaller reactors must be compared with few large reactors. With the given configuration including two reactors of similar size the sequence could be changed. With the reaction mainly taking place in the first reactor it is not necessarily required to change the catalyst at the same time in both reactors and interchanging could prolong the operating time. With catalyst deactivation data in place a configuration of two reactors of different size could be considered as an option.

The values of the constraints should be investigated more deeply for finding the operational constraints. To find the best operation the degradation temperature for glycerol should be known exactly at given pressures, to know the operational limits.

Kiss et al. is mentioning the use of divided-wall column for removal of methanol and water from glycerol phase with positive conclusions related to energy reduction and cost savings. If looking at this for a system containing more methanol in the glycerol stream this could be of consideration for the process.

The lighter phase leaving the decanter after the glycerol and water column mainly containing methyl ester, mono-, and diglyceride is recycled back into the second step in the process for conversion in the second reactor. This stream should also be considered recycled into the first reactor step for improved conversion.

The distillation columns could be investigated further for finding the optimal reflux, bottom composition and feed stage with plant data and known disturbances range. The number of stages required for the separation could be optimized. The bottom fraction of methanol could be increase until a level constrained by the European standard for the known disturbances with methanol recycle applied. For the methanol to be recycled all the necessary treatment of the methanol stream should be included and known in a further extent than at the moment.

If getting access to industrial data and thereafter modifying the existing model with the new data it could be validated against operating data. The model should then be checked for expected disturbances to get better knowledge of the model behaviour. If in compliance with the industrial process the model could possibly be used to predict process behaviour.

14 Conclusion

The model was created for an Esterfip-H process in Chemcad by collection and merging of literature and patent information in the best extent. From the original optimal model 19990 kg/hr of biodiesel was produced with a satisfying purity of 99.7wt% methyl oleate. The biodiesel product satisfies the European standard for biodiesel for automotive fuels, 96.5wt% ester. The production is marginally smaller than the model basis of 20000 kg/hr of biodiesel with a yield of 99.7%. The glycerol product has 99.8wt% of glycerol, well above the 98wt% limit. The cetane number of the produced biofuel exceed the specification of 51 by 0.7. The model hereby seems to imitate the process pretty well under the assumptions done.

The optimum was found to be flat, giving good opportunities for controllability, but making it sensitive to model convergence noise. The built-in optimization sequence give a bit different solution after each run as a result of the model noise being of a scale affecting the optimal point. The methanol flows will be of a range ±0.9% of the applied optimum due to the model noise. The active constraints for the model are reactors inlet temperature, 483 K, and product purity, total glycerine limit of 0.25wt%.

The production profit when including oil, biodiesel, glycerol, methanol, cooling water, steam and energy consumption is 1074 $/hr. The original model was studied and equipment and process parameter improvements giving a profit increase of 140% was suggested. A three reactor system was investigated giving an increase in the profit of 129%, indicating that several different approaches can be used for improvements although the model is operating well as it is.

Nomenclature

Symbol	**Meaning**
α	Relative volatility
ΔT	Temperature difference
γ	Activity coefficient
η	Efficiency
ρ	Density, [kg/m^3]
ϕ	Void fraction
a(t)	Catalyst activity of time
Aant	Antoine coefficient
B	Bottom liquid flow, [mole/time], [mass/time]
Bant	Antoine coefficient
Cant	Antoine coefficient
$\mathrm{C_i}$	Concentration, [kmol/L]
cp	Heat capacity mass basis, [J/K·kg]
Cp	Heat capacity mole basis, [J/K·mole]
$\mathrm{Cp_i}$	Heat capacity component i, [J/K·mol]
$\mathrm{Cp_{mix}}$	Heat capacity of mix, [J/K·mol]
D	Distillate flow, [mole/time], [mass/time]
Dant	Antoine coefficient
Ea	Activation energy, [J/mole]
Eant	Antoine coefficient
f(x)	Function of x
F	Feed stream/stream, [mole/time], [mass/time]
$\mathrm{F_i}$	Moles/time of component i
J	Profit function, [$/hr]
k	Rate constant, [L^2/mole·g·s], [L/mole·s]
k°	Preexponential factor, [L^2/mole·g·s], [L/mole·s]
$\mathrm{k_-}$	Rate constant reverse reaction,[L^2/mole·g·s],[L/mole·s]
K	Eqilibrium constant *−continue*

Symbol	Meaning
L	Liquid stream, [mole/time], [mass/time]
$\mathrm{L_i}$	Liquid stream component i, [mole/time], [mass/time]
$\dot{\mathrm{n}}$	Mole flow, [mole/Time]
$\dot{\mathrm{m}}$	Mass flow, [mass/time]
$\mathrm{M_i}$	Molar mass of component i, [mass/mole]
n	Feed stage
N	Number of stages
N	Number of components
$\mathrm{N_i}$	Number of moles of component i
P	Pressure, [Pa], [Bar]
$\mathrm{P_i}$	Pressure of component i/ at state i, [Pa], [Bar]
Q	Heat, [J/hr]
r	Rate of reaction, [kmol/L·s]
$\mathrm{r'}$	Rate of reaction for catalytic reactor, [mole/g·s]
$\mathrm{r_i}$	Rate of reaction of component i, [kmol/L·s]
$\mathrm{r'_i}$	Rate of reaction for of component i (catalytic), [mole/g·s]
R	Gas constant, [J/K·mol]
t	Time
T	Temperature, [K]
$\mathrm{T_i}$	Temperature at in or outlet, [K]
V	Vapour stream, [mole/time], [mass/time]
V	Volume, [L], [$\mathrm{m^3}$]
$\mathrm{V_i}$	Vapour of component i, [mole/time], [mass/time]
$\dot{\mathrm{V}}$	Volume flow, [volume/time]
$\mathrm{w_i}$	Mass fraction
$w_{\mathrm{s}}^{\mathrm{rev}}$	Reversible pump work, [J/kg]
W	Catalyst weight
$\mathrm{W_s^{rev}}$	Reversible pump effect, [J/time],[W]
$\mathrm{W_s}$	Real pump effect, [J/time],[W]
$\mathrm{x_i}$	Mole fraction
X	Conversion

Glossary

Abbreviation	**Meaning**
B100	Pure biodiesel
B20	20% biodiesel
CFPP	Cold filter plugging point
CN	Cetane number
CV	Control variables
DG	Diglyceride
EN 14214	Biodiesel standard
FAME	Fatty acid methyl ester
FC	Flow controller
GL	Glycerol
HETP	Height of equivalent theoretical plate
HSV	Hourly space velocity
IFP	The French Institute of Petroleum
LC	Level controller
LCA	Life cycle assessment
LLV	Liquid-liquid-vapour
LV	Liquid-vapour
MeOH	Methanol
ME	Methyl ester
MG	Monoglyceride
MV	Manipulated variables
PC	Pressure controller
PBR	Packed-bed catalytic reactor
PFR	Plug flow reactor
RME	Rapeseed methyl ester
SQP	Successive quadratic programming
TC	Temperature controller

–*continue*

Abbreviation	Meaning
TEMA	Heat exchanger standard
TG	Triglyceride
TPM	Throughput manipulator
UNIFAC	Thermodynamic model
UNIFAC-LLE	Modified UNIFAC for liquid liquid equilibrium

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Appendices

A EN 14214

The European standard “Automotive fuels - Fatty acid methyl esters (FAME) for diesel engines - Requirements and test methods”, [1]. The standard entered in 2003.

Property	**Limits**		**Units**
	min	**max**	
Ester content	96.5		%(m/m)
Density; 15°C	860	900	kg/m^3
Viscosity; 15°C	3.5	5	mm^2/s
Flash point	101		°C
Sulfur content		10.0	mg/kg
Carbon residue		0.3	%(m/m)
Cetane number	51		
Sulfated ash		0.02	%(m/m)
Water content		500	mg/kg
Total contamination		24	mg/kg
Copper strip corrosion (3hr,50°C)	1		
Oxidative stability, 110°C	6.0		hr
Acid value		0.50	mg KOH/g
Iodine value		120	g iodine/100 g
Linolenic acid content		12	%(m/m)
Content of FAME with 4 or more double bonds		1	%(m/m)
Methanol content		0.20	%(m/m)
Monoglyceride content		0.80	%(m/m)
Diglyceride content		0.20	%(m/m)
Triglyceride content		0.20	%(m/m)
			–continue

Property	**Limits**		**Units**
	min	**max**	
Free glycerine		0.02	%(m/m)
Total glycerine		0.25	%(m/m)
Sodium and Potassium		5.0	mg/kg
Calcium and Magnesium		5.0	mg/kg
Phosphorus content		4.0	mg/kg

B Molar model basis

From a basis of 20000 kg/hr of biodiesel the molar flow of oil containing 99.9wt% oil can be calculated. The molar biodiesel production is given in Equation B.1

$$\cdot\frac{20000[\mathrm{kg/hr}]}{296.5[\mathrm{kg/kmol}]} = 67.45362563[\mathrm{kmol/hr}] \tag{B.1}$$

Giving the molar flow of triglyceride from the stoichiometric coefficient, 3, in Equation B.2.

$$\frac{67.45362563[\mathrm{kmol/hr}]}{3} = 22.48454188[\mathrm{kmol/hr}] \tag{B.2}$$

To get the total oil flow containing 99.9wt% triglyceride the mole fractions is found from Equation B.3.

$$\mathrm{x_i} = \frac{\frac{\mathrm{w_i}}{\mathrm{M_i}}}{\sum_{\mathrm{i}} \frac{\mathrm{w_i}}{\mathrm{M_i}}} = \frac{\frac{0.999}{885.5[\mathrm{kg/kmol}]}}{\frac{0.999}{885.5[\mathrm{kg/kmol}]} + \frac{0.001}{18.015[\mathrm{kg/kmol}]}} = 0.9531047 \tag{B.3}$$

Resulting in a total molar flow of oil of 23.59084 kmol/hr from Equation B.4

$$\mathrm{F} = \frac{\mathrm{F_i}}{\mathrm{x_i}} = \frac{22.48454188[\mathrm{kmol/hr}]}{0.9531047} = 23.59084147[\mathrm{kmol/hr}] \tag{B.4}$$

C Pump work

The pump work for the inlet stream is calculated for the first pump to check the consistency with the Chemcad model. Inlet parameters for the calculations are given in Table C.1.

Table C.1: Flow parameters for pump calculations from Chemcad.

Parameter	**Value**	**Unit**
Mass flow	57562.891	kg/hr
Molar flow	1198.5918	kmol/hr
ρ	821.2789	kg/m^3
Cp	112280.96	J/kmol ·K

The calculations of the work is given in Equation C.1 while the temperature increase is given in Equation C.2.

$$\begin{aligned} \mathrm{W_s^{res}} &= \frac{\mathrm{P_2 - P_1}}{\rho} \cdot \dot{\mathrm{m}} = \frac{(62-1)\cdot 10^5[\mathrm{Pa}]}{821.2789[\mathrm{kg/m^3}]\cdot 3600} \cdot 57562.891[\mathrm{kg/hr}] \\ &= 118762.4823[\mathrm{J/s}] \\ \mathrm{W_s} &= \mathrm{W_s^{rev}}/\eta = 118762.4823/0.8 = 148453.1029[\mathrm{J/s}] = 148.45[\mathrm{kW}] \end{aligned} \tag{C.1}$$

$$\begin{aligned} \dot{\mathrm{n}} \cdot \mathrm{Cp} \cdot (\mathrm{T_2 - T_1}) &= \mathrm{W_s} \\ 1198.5918[\mathrm{kmol/hr}] \cdot 112280.96[\mathrm{J/kmol \cdot K}] \cdot (\mathrm{T_2 - T_1}) & \\ &= 118762.4823 \cdot 3600[\mathrm{J/hr}] \\ (\mathrm{T_2 - T_1}) &= 3.1769[\mathrm{K}] \end{aligned} \tag{C.2}$$

D Profit functions

Energy function

Energy cost function is given in Equation D.1.

$$\begin{aligned}\text{Cost} =&\text{Pump energy [kW]} + \\ &\text{(Heat exchanger, Condernser, Reboiler) [MJ/hr]}\end{aligned} \tag{D.1}$$

Conversion of the heat exchanger, condenser and reboiler units to kW, Equation D.2

$$\begin{aligned}\text{Cost [kW]} =&\text{Pump energy [kW]}+ \\ &\text{(Heat exchanger, Condernser, Reboiler)} \cdot 1000/3600 \text{ [kW]}\end{aligned} \tag{D.2}$$

Simple profit function

Simple profit function where all the energy use is weighted the same by using the electricity price, Equation D.3.

$$\begin{aligned}\text{Profit [\$/hr]} = &\text{ Biodiesel price [\$/tonne]} \cdot \text{Biodiesel flow [tonne/hr]} + \\ &\text{Glycerol price [\$/tonne]} \cdot \text{Glycerol flow [tonne/hr] -} \\ &\text{Pump work [kW]} \cdot \text{Electricity price [\$/kWh] -} \\ &\text{Reboiler energy [MJ/hr]} \cdot 1000/3600 \cdot \text{Electricity price [\$/kWh] -} \\ &\text{(-Condenser energy [MJ/hr])} \cdot 1000/3600 \cdot \text{Electricity price [\$/kWh] -} \\ &\text{Total heating need [MJ/hr]} \cdot 1000/3600 \cdot \text{Electricity price [\$/kWh] -} \\ &\text{(-Total cooling need [MJ/hr])} \cdot 1000/3600 \cdot \text{Electricity price [\$/kWh]}\end{aligned} \tag{D.3}$$

Advanced profit function

The different prices for steam, electricity and cooling water are included in the profit function. As the process is optimized for a given oil flow and the amount of fresh methanol is assumed to be stoichiometric factor of oil, 3, from Equation 6.1, these are not included in the profit function as they will not change the optimal point, Equation D.4. The advanced profit function is used for the optimization.

$$\begin{aligned}\text{Profit [\$/hr]} =& \text{Biodiesel price [\$/tonne]} \cdot \text{Biodiesel flow [tonne/hr]} + \\ & \text{Glycerol price [\$/tonne]} \cdot \text{Glycerol flow [tonne/hr] -} \\ & \text{Pump work [kW]} \cdot \text{Electricity price [\$/kWh]} - \\ & \text{Sum cooling [m}^3\text{/hr]} \cdot \text{Cooling water price [\$/m}^3\text{]} - \\ & \text{Sum heating [tonne/hr]} \cdot \text{Steam price [\$/tonne]}\end{aligned} \tag{D.4}$$

Heat capacity of water at the given initial temperature for cooling water (6°C) is 75900 $[\frac{\text{J}}{\text{kmol K}}]$, [40]. It is assumed that the cooling water is heated to 140°C, which is a little below the boiling temperature for water at 4 bar, [40]. The heat and cooling requirements, Q, for the different heat exchangers are taken from Chemcad. Equation D.5 gives the needed cooling water flow under the assumptions above.

$$\text{Sum cooling}\left[\frac{\text{m}^3}{\text{hr}}\right] = \frac{\text{Q[J/hr]}}{75900[\frac{\text{J}}{\text{kmol}\cdot\text{K}}] \cdot 55.5[\frac{\text{kmol}}{\text{m}^3}] \cdot \text{(413-279) K}} \tag{D.5}$$

The heating steam is taken as high pressure steam at 27 bar and 500°C, [64]. The heat capacity for this steam is 38387 $[\frac{\text{J}}{\text{kmol K}}]$, [40]. It is assumed that the steam is cooled to 230°C a bit above the boiling temperature to find the necessary steam flows, flow of steam is then given in Equation D.6.

$$\text{Sum heating}\left[\frac{\text{kg}}{\text{hr}}\right] = \frac{\text{Q[J/hr]}}{38387[\frac{\text{J}}{\text{kmol}\cdot\text{K}}] \cdot \frac{1}{18[\frac{\text{kg}}{\text{kmol}}]} \cdot \text{(773-503) K}} \tag{D.6}$$

$$\text{Sum heating}\left[\frac{\text{tonne}}{\text{hr}}\right] = \frac{\text{Sum heating}\left[\frac{\text{kg}}{\text{hr}}\right]}{1000} \tag{D.7}$$

Modified advanced profit function

When studying for a given methanol inlet flow, but different oil flow, the function is modified to include the oil price and the stoichiometric methanol flow which will change as the oil flow changes. This function is also used for finding the process profits for the optimal point stated in the report as methanol and oil will be a cost in the process, Equation D.8.

$$\begin{aligned}\text{Profit [\$/hr]} =& \text{Biodiesel price [\$/tonne]} \cdot \text{Biodiesel flow [tonne/hr]} + \\ & \text{Glycerol price [\$/tonne]} \cdot \text{Glycerol flow [tonne/hr] -} \\ & \text{Pump work [kW]} \cdot \text{Electricity price [\$/kWh]} - \\ & \text{Sum cooling [m}^3\text{/hr]} \cdot \text{Cooling water price [\$/m}^3\text{]} - \\ & \text{Sum heating [tonne/hr]} \cdot \text{Steam price [\$/tonne]} - \\ & \text{Oil price [\$/tonne]} \cdot \text{Oil flow [tonne/hr]} - \\ & \text{Methanol price [\$/tonne]} \cdot 3 \cdot \frac{32\text{[kg/kmol]}}{885.5\text{[kg/kmol]}} \cdot \text{Oil flow [tonne/hr]}\end{aligned} \tag{D.8}$$

E Heat Exchanger profile

Heat exchanger profile for the second shell and tube reactor with a ΔT_{min} of 14 K is shown in Figure E.1. Methanol from the flash operating at 5 bar is condense at the shell side, while the reactants are heated on the tube side.

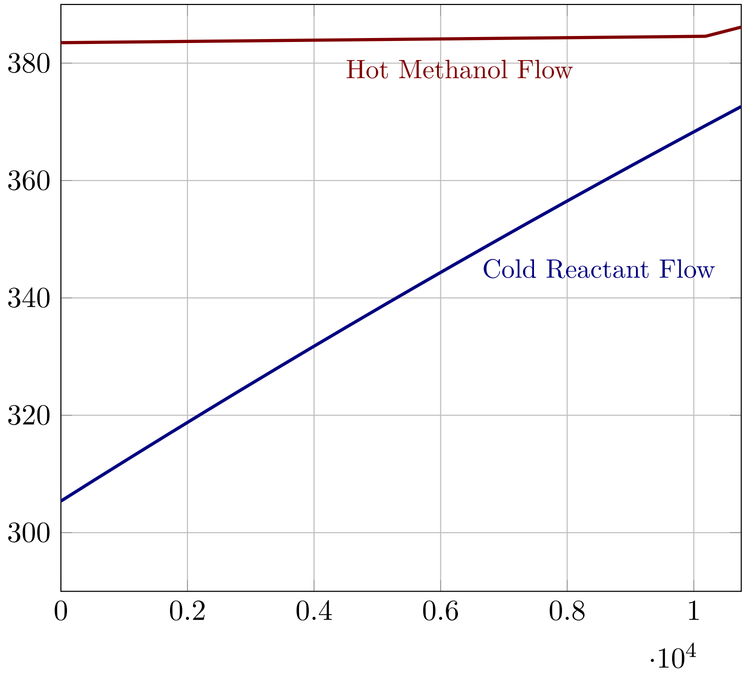


Figure E.1: Heat exchanger profile for the shell and tube exchanger before the second reactor.

F Kinetic parameter conversion

Density of Al_2O_3 being the main material supporting the $ZnAl_2O_4$ catalyst in Equation F.1.

$$\rho_{\mathrm{Al_2O_3}} = 4.0\mathrm{g/cm}^3 = 4000\mathrm{g/L} \tag{F.1}$$

Assumed void fraction of the catalyst in Equation F.2.

$$\text{Void fraction} = \phi = 0.45 \tag{F.2}$$

Assuming that the reactor is not completely filled with catalyst at the inlet, outlet and possibly in a middle section, Equation F.3:

$$\text{Filling of reactor} = 70\% \tag{F.3}$$

Which is the volume of catalyst per volume of reactor. Table F.1 gives the kinetic parameters for the three transesterification reactions given by Pugnet et al. [45].

Table F.1: Kinetics for catalytic part of transesterification reaction at 180-210°C and 4wt% catalyst/oil, [45].

Reaction	**k°[L^2/mol · g · s]**	**Activation energy [J/mol]**
1	$1.7 \cdot 10^2$	82000
2	$9.4 \cdot 10^4$	103000
3	$3.7 \cdot 10^3$	88000

The density of the catalyst is given in Equation F.4.

$$\rho_{\text{catalyst}} = \rho_{\text{metal}} \cdot (1 - \phi) \tag{F.4a}$$

$$\rho_{\text{catalyst}} = 4000 \cdot (1 - 0.45) = 2200\mathrm{g/L} \tag{F.4b}$$

With fraction of the reactor filled with catalyst the fixed-bed could be taken as a plug-flow reactor, since the kinetics now are over reactor volume instead of catalyst volume, in Equation F.5 .

$$\rho_{\text{catalyst,in plug-flow reactor}} = \rho_{\text{catalyst}} \cdot \text{Filling fraction} \tag{F.5a}$$

$$\rho_{\text{catalyst}} = 2200 \cdot 0.7 = 1540\mathrm{g/L} \tag{F.5b}$$

Table F.2: Preexponential factor for plug-flow reactor in Chemcad.

Reaction	**k°[L/mol · s]**	**k°[L/kmol · s]**
1	$2.618 \cdot 10^5$	$2.618 \cdot 10^8$
2	$1.4476 \cdot 10^8$	$1.4476 \cdot 10^{11}$
3	$5.698 \cdot 10^6$	$5.698 \cdot 10^6$

k°$[\mathrm{L}^2/\mathrm{mol} \cdot \mathrm{g} \cdot \mathrm{s}] \cdot 1540\mathrm{g/L}$ for conversion to plug flow reactor operation, per volume of reactor. And then to make the parameter in the right units for Chemcad, see Table F.2.

G Arrhenius plots

Calculations for finding the preexponential factor and activation energy for the first reverse reaction. Gas constant = 8.314 [J/K mol]
Input data for reactions in Chemcad k° in [L/mol · s] and activation energy E_a in [J/mol] from Table 6.3.

For the first reaction, the Arrhenius equation is given in Equation G.1.

$$\mathrm{k} = 261800000 \cdot e^{-82000/(8.314 \cdot \mathrm{T})} \tag{G.1}$$

At 443 and 483 K the resulting k values are 0.05609266 and 0.35453296 respectively. Then the reverse reaction rate constant can be found from the equilibrium constant, Table 6.2, in Equation G.2.

$$\mathrm{k}_{-} = \mathrm{k}/\mathrm{K} = 0.05609266/0.27 = 0.207750592 \tag{G.2}$$

When taking the natural logarithm, Equation G.4:

$$\ln(\mathrm{k\_}) = \ln(0.207750592) = -1.571416998 \tag{G.3}$$

Plotting the two points found at 443 and 483 K, in a ln(k) against 1/T diagram and finding the linear function, Equation G.4:

$$\ln(\mathrm{k\_}) = -9862.9 \cdot \frac{1}{\mathrm{T}} + 20.692 \tag{G.4}$$

Preeexponential factor in Equation G.5

$$\mathrm{k}^\circ = e^{20.692} = 96921217884.9 = 9.692 \cdot 10^8 \tag{G.5}$$

Activation energy from Equation G.6

$$\begin{gathered}
\mathrm{Slope}[1/\mathrm{K}] = -\frac{\mathrm{E}_a}{\mathrm{R}} \\
-9862.9[1/\mathrm{K}] = -\frac{\mathrm{E}_a}{8.314[\mathrm{J/K} \cdot \mathrm{mol}]} \\
\mathrm{E}_a = 9862.9[1/\mathrm{K}] \cdot 8.314[\mathrm{J/K} \cdot \mathrm{mol}] = 82000.1506[\mathrm{J/mol}]
\end{gathered} \tag{G.6}$$

Arrhenius plot for reaction two and three are given in Figure G.1 and G.2. With results shown in Table G.1 calculated in the same way as above.

Table G.1: Kinetics for the three reverse equilibrium of the transesterification reaction in units for Chemcad.

Reaction	**k°[L/kmol · s]**	**Activation energy [J/mol], [kJ/kmol]**
1	$9.6922 \cdot 10^{8}$	82000.1506
2	$1.1967 \cdot 10^{11}$	103002.146
3	$6.5518 \cdot 10^{9}$	88003.69

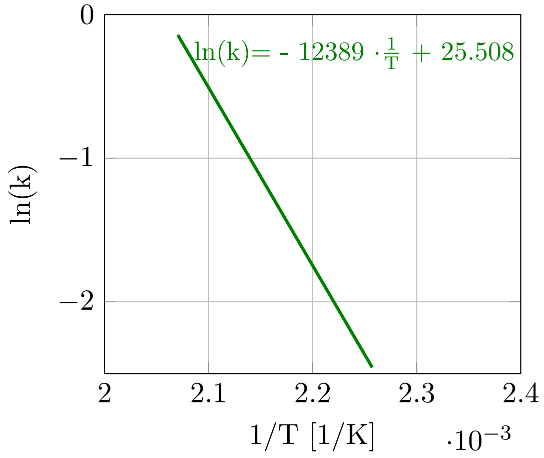


Figure G.1: Arrhenius plot for the second reverse equilibrium reaction.

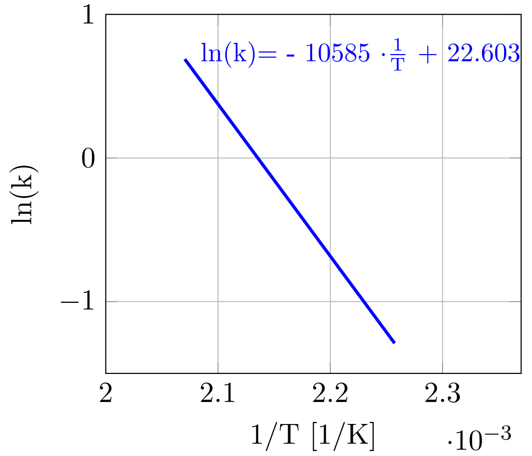


Figure G.2: Arrhenius plot for the third reverse equilibrium reaction.

H Equipment information

For the references at the specification the articles are used as inspiration and indication of the parameter ranges. This have often been done when the range of the values are large. While the references for the data the numbers are taken directly from the main part of the article or the examples as the literature range is small or consistent. The parameters used for the improved model are given in parenthesis in the value column. In addition to the improvements given here is it included an extra flash tank in addition to original two operating at atmospheric pressure.

Unit	**Data or Specifications**	**Parameter**	**Value**
Pump			
	Specification	Outlet Pressure, [26]	62 bar (50)
		Efficiency, [36]	0.8
Heat exchanger			
	Specification	Hot methanol from 5 bar flash, [18]	
		Shell and tube type	
		Tube flow, [18]	High pressure stream, reactant
		Material for high pressure, [18]	Stainless steel
		Shell side, [18]	Condensation of methanol
		Design parameters, [18], [38]	Chemcad default giving 500 m^2
Heat exchanger			
	Specification	Outlet temperature, [12]	170 – 210°C *–continue*

Unit	Data or Specifications	Parameter	Value
Reactor			
	Specification	Inlet temperature, [12]	170 – 210°C
		Inlet pressure,[26]	62 bar (50)
		Kinetic data, [45]	
		Catalyst material density, [47]	4.0 g/cm^3
		Void fraction, [46]	45%
		Filling, [55]	70%
		Volume from Chemcad	60 m^3 (100)
Flash tank			
	Data	Pressure, [12]	5 bar
	Assumption	Residence time	8 min
		Surge time	4 min
Flash tank			
	Data	Pressure, [12]	2.5 bar
	Assumption	Residence time	8 min
		Surge time	4 min
Decanter			
	Data	Pressure	Atmospheric
		Temperature, [26]	50°C
Coalescer			
	Specification	Modelled as three phase separation	*−continue*

Unit	**Data or Specifications**	**Parameter**	**Value**
Glycerol-Methanol distillation			
	Specification	Operating conditions as acid-catalysed/ base-catalysed process, [2]	
		Pressure, [2]	0.04 MPa
		Temperature, [2]	326 K
		Number of stages, [58]	20 (10)
		Feed stage	10 (5)
		Reflux ratio, [58]	2 (0.08)
		Bottom purity, mole fraction methanol, [58]	0.008
Glycerol-Water distillation			
	Specification	Pressure, [58]	0.1 MPa (0.04)
		Temperature	380 K (353)
		Number of stages, [52]	6
		Feed stage	3
		Reflux ratio, [58]	3
		Bottom purity, water mole fraction	0.0005 *−continue*

Unit	**Data or Specifications**	**Parameter**	**Value**
Biodiesel-Methanol distillation			
	Specification	Operating conditions as acid-catalysed/ base-catalysed process, [2]	
		Pressure, [2]	0.04 MPa
		Temperature, [2]	468 K
		Number of stages, [58]	10
		Feed stage	5
		Reflux ratio, [58]	2 (0.5)
		Bottom purity, methanol mole fraction, [58]	0.0001

I Feedstream information

Stream specification and assumptions given for the model. The oil flow is found from the model basis see Appendix B with the methanol flows found from optimization of the model.

Stream	**Specification or Assumption**	**Parameter**	**Value**
Oil			
	Specification	Water content, [2], [15]	0.1%
		Flowrate triglyceride, [19], [33], [34]	22.4845 [kmol/hr]
	Assumption	One acid, [1]	Oleic acid
		Temperature	293 [K]
		Pressure	Atmospheric
Methanol			
	Specification	Water content, [2], [15]	0.1%
	Assumption	Temperature	293 [K]
		Pressure	Atmospheric
		Flowrate to reactor 1	1175 [kmol/hr]
		Flowrate to reactor 2	1244.7 [kmol/hr]

J Glycerol price change

The profit from the advanced profit function as a function of the glycerol price is shown in Figure J.1.

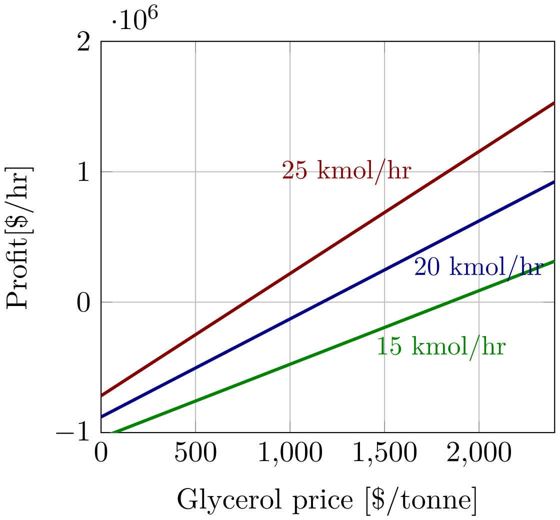
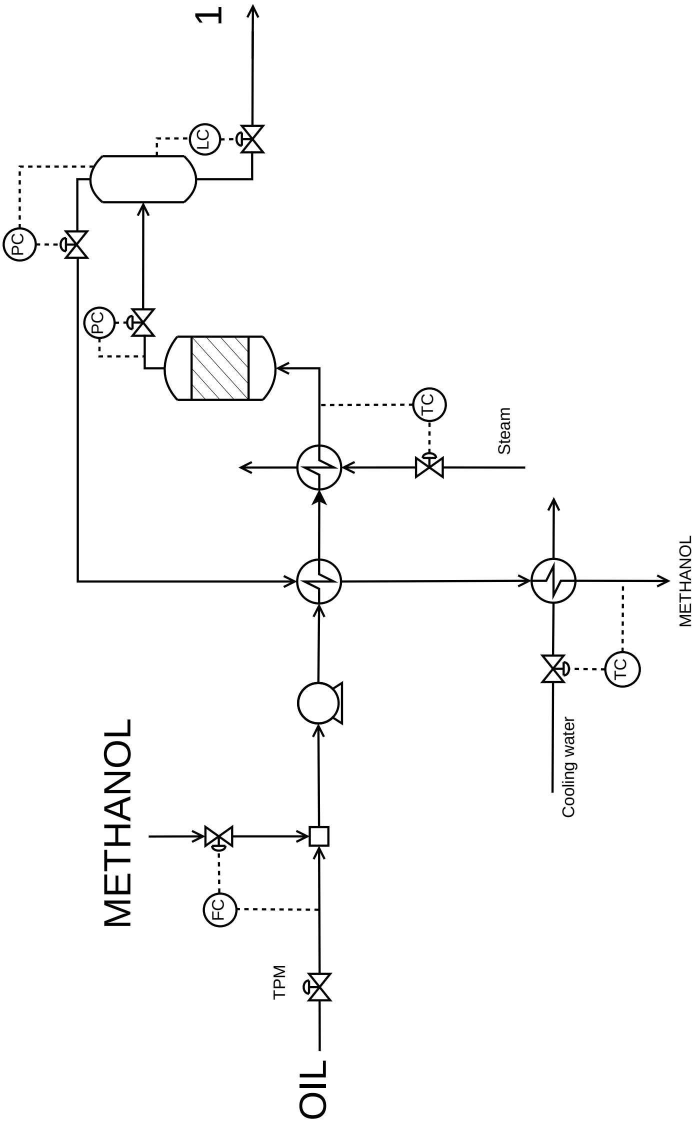
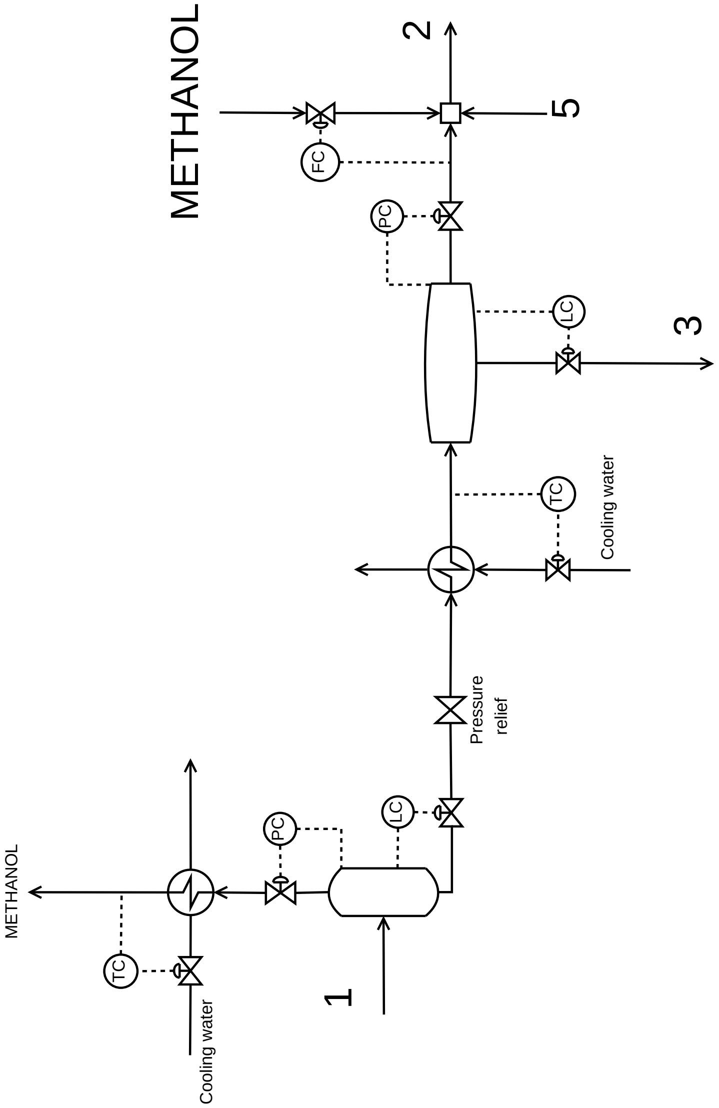


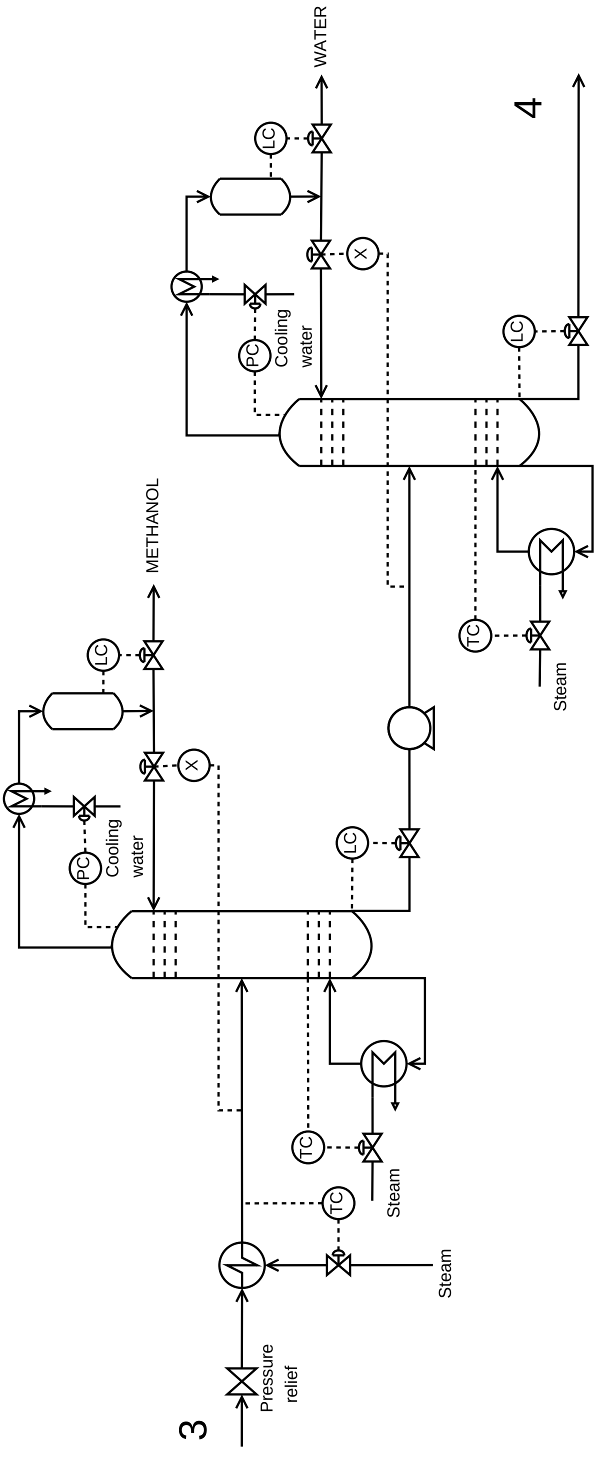
Figure J.1: Profit as a function of glycerol prices at different oil flows.

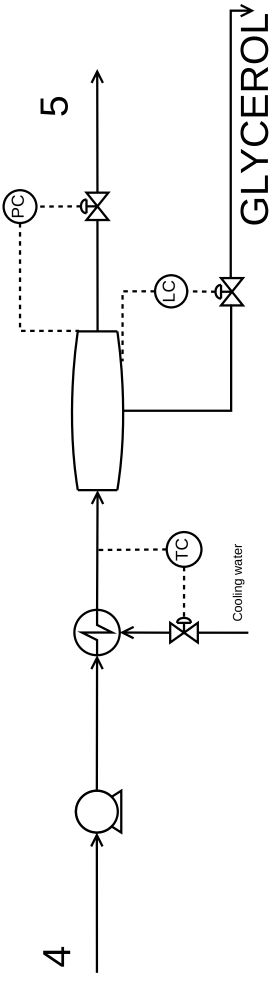
K Control structure suggestion

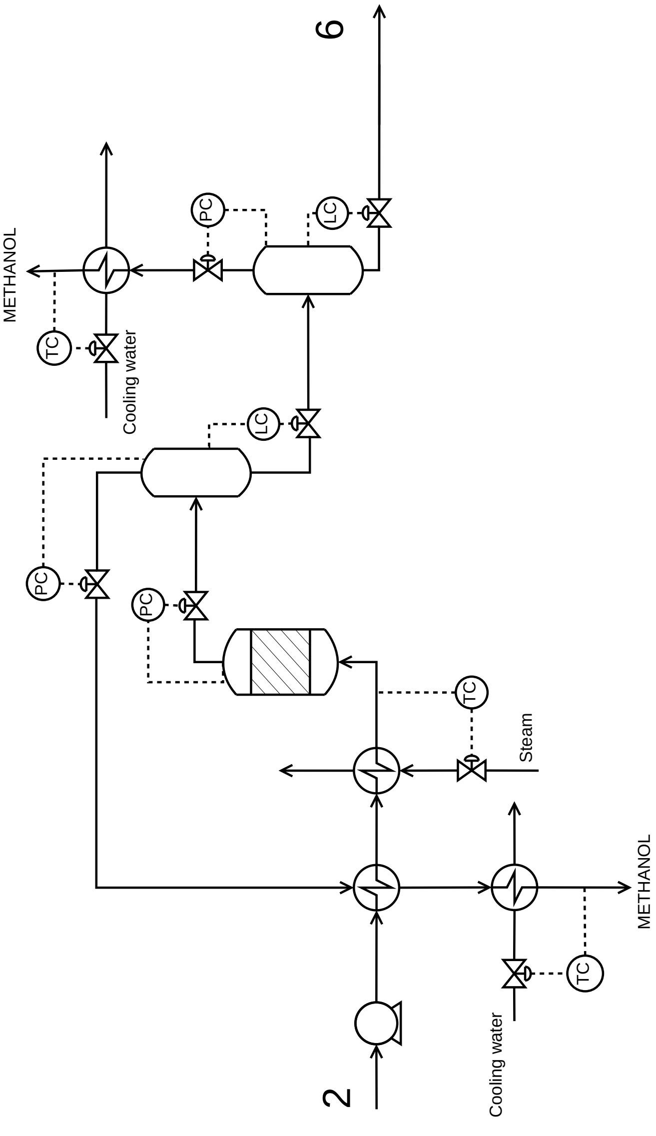
A control suggestion for the model is drawn below with level (LC), flow (FC), pressure (PC) and temperature controllers (TC). The large block letters is the introduced reagent and the products, the small block letters are the methanol and water leaving the system. The small letters are the utilities, cooling water and steam. The numbers are included to be able to follow the streams between the pages.

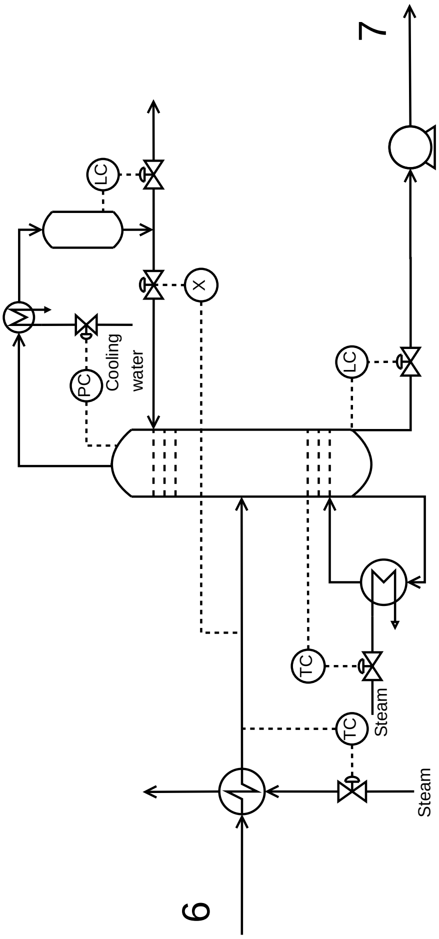


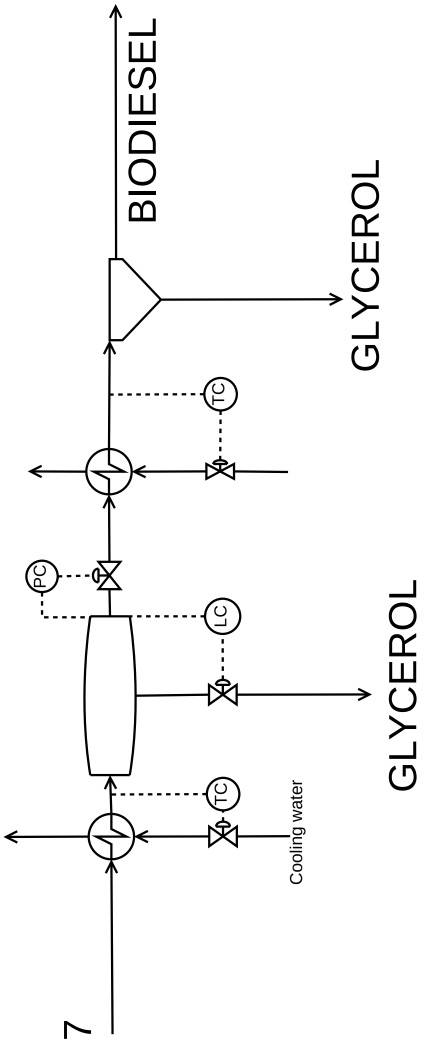

1
Cooling water
TC
METHANOL
PC
LC
Pressure relief
TC
Cooling water
LC
3
PC
FC
METHANOL
5
2


3
Pressure relief
Steam
TC
TC
Steam
LC
PC
Cooling water
X
LC
METHANOL
TC
Steam
LC
PC
Cooling water
X
LC
WATER
4


4
TC
Cooling water
LC
PC
5
GLYCEROL


2
6
METHANOL
METHANOL
Cooling water
Cooling water
Steam
TC
TC
TC
PC
PC
PC
LC
LC


6
7
LC
LC
X
PC
Cooling water
TC
TC
Steam
Steam


BIODIESEL
GLYCEROL
TC
PC
LC
GLYCEROL
TC
Cooling water
7