

Conversion of a batch biodiesel plant from homogeneous to
heterogeneous catalysed process: modelling, optimisation and techno-
economic analysis

by

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ABSTRACT

Most biodiesel plants operate batch-wise using homogeneous alkali catalysts. Recently, several heterogeneous catalysts have been suggested in literature, as they have shown potential for overcoming most of the challenges associated with the application of homogeneous catalysts. Previous published techno-economic comparisons of the two technologies on large-scale processes located in the developed world, have revealed the economic superiority of heterogeneously catalysed processes. Hence, prospect exists for current homogeneously catalysed process plants to be converted to heterogeneously catalysed ones.

The objective of this research was to investigate the actual cost benefit of converting a small-scale batch biodiesel plant from homogeneous to heterogeneous catalysed process. For this purpose, a small-scale batch biodiesel plant located in South Africa was taken as the base case homogeneous process. Aspen Batch Process Developer[®] software was used to perform the process simulations. The homogeneous process was converted to the heterogeneous one and results from process simulation were used to evaluate the economics of both processes, which were compared in terms of fixed capital cost, total manufacturing cost and profitability indicators. During economic evaluation, two types of cost factors were used: one prevailing in developed world and the other one relevant to South Africa. The sensitivity analysis of both processes was further performed in order to investigate the impact of some uncertain parameters on their profitability. Finally, a debottlenecking study was carried out.

Results obtained from this study showed an increase in the annual throughput of biodiesel as well as significant savings in the total capital cost for the heterogeneous catalysed process relative to the homogeneous one. As regards the estimation of the total unit manufacturing cost of biodiesel, significant differences arose when using the two types of cost factors. Results of economic analyses estimated using cost factors relative to South Africa suggest an increase in the unit manufacturing cost of biodiesel while using the developed world's cost factors suggests the opposite. This is due to the higher raw material and energy requirement for the CaO process, while knowing that the direct costs are a bigger proportion of the manufacturing costs estimated using the South African cost factors. Profitability and sensitivity analyses only provided positive results when estimated using the South African cost factors. In all cases, the heterogeneous catalysed process was found to be more promising than the homogeneous one over the prescribed project life. The study showed the importance of using cost factors relevant to a particular economic environment during techno-economic assessment of a process. It was

also shown that there are economic benefits when replacing settling with centrifugation in biodiesel production processes.

In summary, this thesis makes some important contributions. It presents the first process simulation for biodiesel production using Aspen Batch Process Developer[®] software and thereby proposes a methodology that is currently scarce in the literature. It also reports the first techno-economic analysis applied to the biodiesel field in South Africa and provides a preliminary insight to owners of biodiesel plants as regards the decision to convert or not their homogeneous catalysed plant to heterogeneous one.

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GLOSSARY

Acid:	An aqueous solution that has an excess of hydrogen ions (H^+).
Base:	An aqueous solution that has an excess of hydroxide ions (OH^-) in aqueous solution.
Batch process:	Process characterised by a discontinuous production of chemicals. The process units are frequently shut down and started and the process operation occurs over a finite period.
Biodegradable resource:	Resource capable of being decomposed by bacteria or other living organisms through biological processes.
Biodiesel:	A biodegradable transportation fuel for use in diesel engines that is produced through the transesterification of organically-derived oils or fats.
Biofuels:	Biomass converted to liquid or gaseous fuels such as ethanol, methanol, methane, and hydrogen.
Catalyst:	A substance that increases the rate of a chemical reaction, without being consumed or produced by the reaction.
Continuous process:	Industrial process that has steady flow rates of inputs and outputs.
Debottlenecking:	The process of increasing the production capacity of existing facilities through the modification of existing equipment to remove throughput restrictions.
Depreciation:	A noncash expense that reduces the value of an asset as a result of wear and tear, age, or obsolescence.
Enzymes:	A protein or protein-based molecule that speeds up chemical reactions. Enzymes act as catalysts for reactions

	converting a specific set of reactants into specific products.
Ester:	Compound formed from the reaction between an acid and an alcohol.
Fatty Acid:	A fatty acid is a carboxylic acid (an acid with a -COOH group) with long hydrocarbon side chains.
Fixed capital cost:	Portion of the total capital outlay that is invested in fixed assets such as land, buildings, vehicles, plant and equipment. It represents the total cost of the plant ready for start-up.
Fossil fuel:	Non-renewable carbon or hydrocarbon fuel formed in the earth's crust from the remains of dead plants and animals over the course of millions of years. Oil, natural gas, and coal are fossil fuels.
Free fatty acid:	Fatty acids not attached to alcohol molecules like glycerine in vegetable oil or methanol in biodiesel.
Global warming:	A term used to describe the increase in average global temperatures due to the greenhouse effect.
Glycerine:	A liquid by-product of biodiesel production. Glycerine is used in the manufacture of dynamite, cosmetics, liquid soaps, inks, and lubricants.
Heterogeneous catalyst:	Catalyst, usually solid, that exists in a different phase from the reaction mixture.
Homogeneous catalyst:	Catalyst that acts in the same phase as the reaction mixture.
Hydrolysis:	The chemical breakdown of a compound due to reaction with water.
Internal rate of return:	The discount rate often used in capital budgeting that makes the net present value of all cash flows from a particular project equal to zero. The higher a

	project's internal rate of return, the more desirable it is to undertake the project.
Monte Carlo analysis:	A problem solving technique used to approximate the probability of certain outcomes by running multiple trial runs, called simulations, using random variables.
Net present value:	It is the worth of the project at the end of the project life. It is the sum of all inflows and outflows cash flow discounted to the present value by the given interest rate. A positive NPV indicates a project that is acceptable and the higher the NPV the more profitable the project.
Non-renewable resource:	Finite energy resource that cannot be replaced as it is used.
Renewable energy resource:	Energy resource that can be naturally replenished or is theoretically inexhaustible. Renewable energy resources include solar, wind, geothermal, hydro and biomass.
Saponification:	Process that produces soap, usually from fats and lye.
Sensitivity analysis:	Analysis of how changing an input variable in a financial model affects the value, performance, or solvency of a given project.
Total manufacturing cost:	Costs associated with the day-to-day operation of the plant.
Transesterification:	A chemical process that involves reaction between alcohol and triglycerides contained in vegetable oils and animal fats to produce biodiesel and glycerine.
Triglycerides:	Naturally occurring ester of three fatty acids and glycerol, that is the main constituent of natural fats and oil.
Working capital cost:	It is the additional investment required over the fixed capital cost for starting and operating the plant to the point when income is earned.

CHAPTER 1: INTRODUCTION

1.1. GENERAL BACKGROUND

Over the past century, the world has been dependent on fossil fuels as its main sources of energy. Currently, due to the imminent depletion of these resources and the serious environmental concerns raised by their production and use, particular attention is being paid to new sustainable and environmentally-friendly sources of energy. Biodiesel fuel, derived from biomass is believed to be an attractive substitute for petroleum-based diesel fuel, as it is renewable, readily biodegradable, non-toxic and has a low sulphur and aromatic content (Dermibas, 2007). Furthermore, biodiesel is believed to reduce the net carbon emissions by 78% on a life cycle basis in comparison to conventional diesel fuel (West *et al.*, 2008), and does not therefore significantly contribute to global warming.

The traditional method employed in the production of biodiesel is via the transesterification of triglycerides contained in vegetable oil or animal fat, with an alcohol, in the presence of a catalyst. Glycerol, which is obtained as a by-product, finds its application and use in the food, cosmetic, pharmaceutical and plastic industries (Vicente *et al.*, 1998). Conventionally, methanol is the alcohol used in the reaction, due to its low cost (Ma & Hannah, 1999). A homogeneous base catalyst such as NaOH or KOH is commonly used as catalyst to increase the reaction rate and the transesterification reaction yield.

According to Gui *et al.* (2008), 95% of the biodiesel currently produced is made from edible oil. However, due to the food vs. fuel competition and the high price of virgin oil, which considerably affects the total production cost (Marchetti *et al.*, 2008), there is a current shift toward the use of waste vegetable oil (WVO) as feedstock (Zhang *et al.* 2003a). The problem encountered when using WVO is its high free fatty acid (FFA) and moisture content, which in the presence of homogeneous alkali catalyst causes undesired saponification reaction. This consequently results in the following: consumption of the alkali catalyst to saponification, significant reduction of the ester yield and inhibition of the subsequent purification process of biodiesel, including biodiesel separation and water washing (Borges & Díaz, 2012; Lam *et al.*, 2010; Kulkarni & Dalai, 2006).

The homogeneous catalysed transesterification on a large-scale suffers from techno-economic limitations. This has motivated intensive research on new approaches for the production of biodiesel. Increased interest is being given to the use of heterogeneous catalysts as they are known to be able to improve the biodiesel production process (Di Serio *et al.*, 2007). Heterogeneous catalysts are relatively cheap and are easily separated from the reaction mixture, making the purification step easier (Semwal *et al.*, 2011). Furthermore, the process provides

higher quality esters and glycerol which can be more easily separated, thus obviating expensive refining operations (Kondamudi *et al.*, 2011; Chouhan & Sarma., 2011; Atadashi *et al.*, 2013). Heterogeneous catalysts can be reused several times before they need replacement (Lam *et al.*, 2010; Atadashi *et al.*, 2013).

Based on the advantages of heterogeneous catalyst, there are potential techno-economic merits of converting already existing homogeneous catalysed plant to heterogeneous ones. This is the rationale of the current study, which aims to provide baseline information that will serve as a useful reference for future decision-making.

1.2. PROBLEM STATEMENT

Most biodiesel plants currently operating are batch process plants employing homogeneous catalysts. This technology faces some challenges such as expensive downstream separation processes, unsuitability of the catalyst toward low cost feedstock and non-renewability of the catalyst. While the conversion of existing homogeneous catalysed plant to heterogeneous has potential techno-economic advantages, there is currently no practical or experimental data to substantiate this claim. This research seeks to provide a basis for comparison, using existing experimental data to assess the economic feasibility for such conversion.

1.3. HYPOTHESIS AND RESEARCH QUESTIONS

It can be hypothesised that converting a biodiesel plant from homogeneous to heterogeneous catalysed process is economically advantageous.

In order to validate this hypothesis, the following research questions were developed:

1. What will be the change in the total manufacturing cost associated with the production of biodiesel for the new heterogeneous process relative to the initial homogeneous process?
2. What will be the change in investment cost resulting from the conversion of a biodiesel plant from homogeneous to heterogeneous catalysed process?
3. What are the factors that will affect the profitability of the new heterogeneous process and what will be the magnitude of these effects?

1.4. OBJECTIVES OF THE RESEARCH

Based on the hypothesis and research questions described above, the following objectives were developed for the current study:

- 1- To develop a process model of a batch homogeneous catalysed process plant for biodiesel production and to perform an economic analysis.
- 2- To convert the homogeneous catalysed process model to heterogeneous.
- 3- To perform the economic evaluation of the new heterogeneous model and to compare it with that of the homogeneous model.
- 4- To perform the sensitivity analysis of the new process in order to determine the major factors that will affect the profitability.

1.5. DELINEATION OF THE RESEARCH

The research will be conducted on a case study of a South African batch biodiesel plant using waste vegetable oil as feedstock. Therefore the results of this study may not be generalisable to continuous plants using virgin oils. As regards the type of catalyst to be used, the focus will be on already known catalysts with established optimum conditions.

1.6. THESIS OUTLINE

The approach for fulfilling the aim of this study is reflected in the thesis outline represented in Figure 1-1.

In **Chapter 1**, a general introduction to the thesis topic is provided with a description of the research problem, hypothesis and the objectives of the study.

Chapter 2 elaborates a background and introduces the theory necessary for understanding the research carried out in this thesis. A review of prior related academic works is also presented.

Chapter 3 describes the adopted methodology associated with process models development, and discussed the performances of the homogeneous and heterogeneous catalysed processes for biodiesel production.

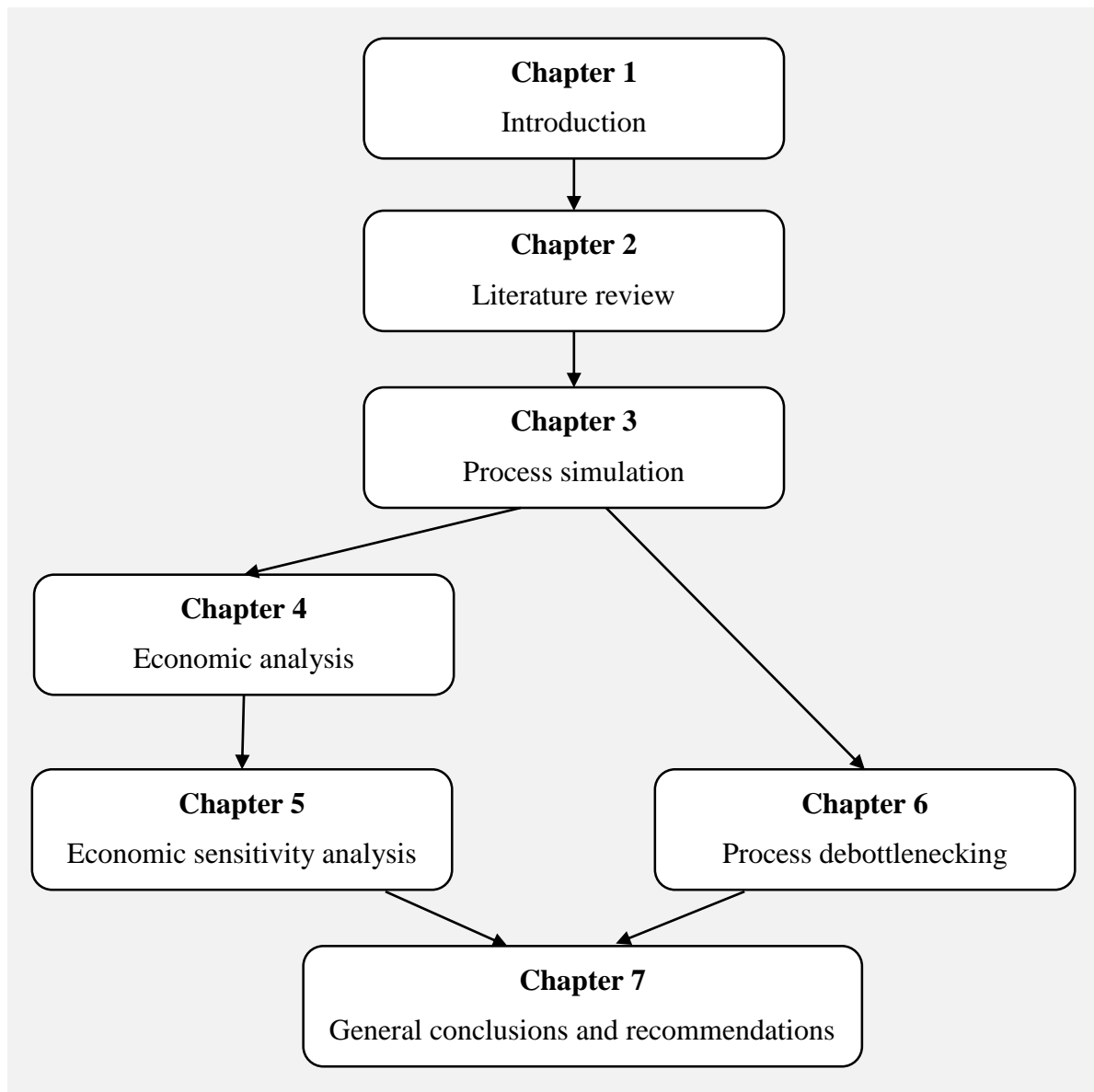


Figure 1-1: Thesis outline diagram

Using the simulation results obtained in **Chapter 3**, an economic analysis is performed in **Chapter 4**. The processes are compared in terms of fixed capital costs, total manufacturing costs and profitability indicators.

Chapter 5 investigates the impact of uncertain and variable parameters on the profitability of the processes under investigation.

In **Chapter 6** a debottlenecking study is performed. The purpose is to investigate the profitability of process scenarios alternative to the ones developed in **Chapter 3**.

Based on the findings of this study, conclusions are drawn, implications of the research are stated and recommendations for further studies in this field of research are presented in **Chapter 7**.

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CHAPTER 2: LITERATURE REVIEW

Highlights

- Different feedstock and technologies for biodiesel production are discussed.
- Heterogeneous catalysts proved to be a promising alternative to conventional homogeneous catalyst.
- Heterogeneous catalysed processes are economically superior to other processes.
- No previous study reported the impact of converting from homogeneous to heterogeneous catalysed process.

2.1. INTRODUCTION

This chapter provides the background necessary to understand the research carried out in this thesis. It first presents the general background around biodiesel such as its history, properties, chemistry and the factor affecting its production (Section 2.2). The advantages and disadvantages of the different feedstock employed in biodiesel production as well as the descriptions and comparison of the different catalytic technologies applied are presented in Section 2.3 and 2.4. Finally, prior studies relevant to the economics of homogeneous and heterogeneous catalysed processes for biodiesel production are reviewed in Section 2.5.

2.2. GENERAL BACKGROUND ON BIODIESEL PRODUCTION

2.2.1. BRIEF HISTORY ON BIODIESEL

The first record of the use of vegetable oil as fuel for automobile engines occurred in 1900, when Rudolf Diesel who developed an engine capable of using a variety of fuels in 1895, exhibited the performance of his engine running on pure peanut oil at the Paris World's fair (Knothe, 2001). In the subsequent years, due to widespread availability and low cost of mineral oils at that time, the design of diesel engines was altered in such a way as to only use petroleum oil (Schmidt, 2007), which is characterised mainly by a much lower viscosity when compared to virgin vegetable oil.

Despite the fact that petroleum oil was widely used in diesel engines, there was still a growing interest in using vegetable oil as fuel especially in the 1920's and 1930's and later during World War II (Thipse, 2010). Unfortunately, as mentioned previously, the newer diesel engine design was no longer suitable for vegetable oils. Hence, there was a need to lower the viscosity of vegetable oil, so that it could be properly combusted in the modified engine type (Thipse, 2010).

Several methods have been proposed to perform this task, including blending with solvent, pyrolysis and even emulsifying the fuel with water or alcohol. None of these methods have proven to be suitable (Knothe, 2001). The most suitable method for reducing the viscosity of vegetable oil appeared to be that of a Belgian inventor (Chavanne) in 1937, who first proposed using transesterification to convert vegetable oils into fatty acid alkyl esters and used them as diesel fuel replacement (Knothe, 2001; Thipse, 2010). The transesterification reaction is the basis for the production of modern biodiesel which is the trade name for fatty acid methyl esters (Knothe, 2001).

2.2.2. PROPERTIES OF BIODIESEL

To be called biodiesel, the product from the transesterification of triglyceride must conform to certain specifications given by standards such as the EN 14214 in the European Union and the ASTM D 6751 in the USA (Mittelbach and Remschmidt, 2005). The characteristics of biodiesel fuel as compared to diesel fuel are given in Table 2-1.

Table 2-1: Comparison of the ASTM standards for Diesel and Biodiesel (Adapted from Chopade *et al.*, 2012)

Properties	Biodiesel	Diesel
Standard number	ASTM D6751	ASTM D975
Composition	Fatty acid methyl ester (C ₁₂ -C ₂₂)	Hydrocarbon (C ₁₀ -C ₂₁)
Specific gravity (g/ml)	0.88	0.85
Flash point (K)	373-443	333-353
Cloud point (K)	270-285	258-278
Pour point (K)	258-289	243-258
Carbon (wt. %)	77	87
Water (Vol. %)	0.05	0.05
Cetane number	48-60	40-45
Sulphur (wt. %)	0.05	0.05
Hydrogen (wt. %)	12	13
Oxygen (wt. %)	11	0

2.2.3. CHEMISTRY OF BIODIESEL

Biodiesel is typically produced by a process called transesterification or alcoholysis (Figure 2-1). In the process of transesterification, the triglycerides contained in the oil, react with an alcohol in the presence of a catalyst (Ma & Hannah, 1999). Glycerol, obtained as a by-product of this reaction, finds its application in the food, cosmetic, pharmaceutical and plastic industry (Vicente *et al.*, 1998).

The transesterification reaction consists of a sequence of three consecutive reversible reactions as shown in Figure 2-2. The triglyceride is converted step wisely into diglycerides,

monoglyceride and finally glycerol, releasing each time a molecule of ester per molecule of alcohol consumed (Ma & Hannah, 1999).

Biodiesel can also be produced by a similar reaction called esterification, which consists of reacting free fatty acids with an alcohol in the presence of an acid catalyst (Issariyakul & Dalai, 2014). Water is obtained as a by-product of this reaction (Figure 2-3).

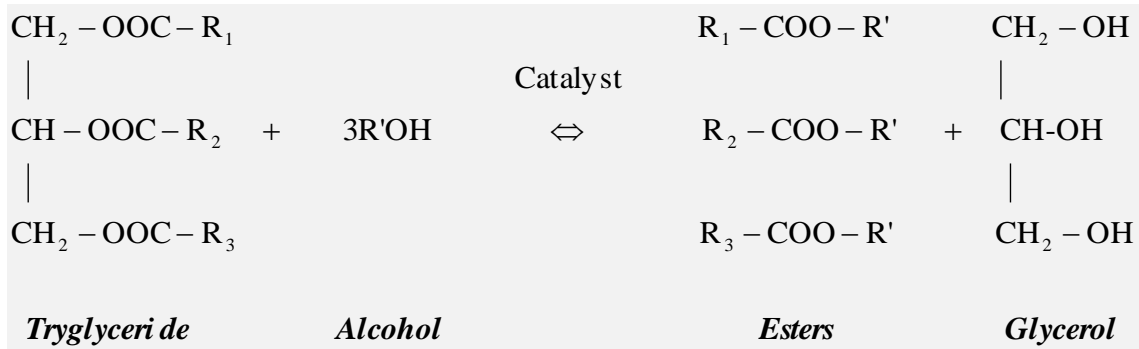


Figure 2-1: Transesterification reaction (R_x represent the hydrocarbon chains of the fatty acid triglyceride and R' the hydrocarbon chain of the alcohol)

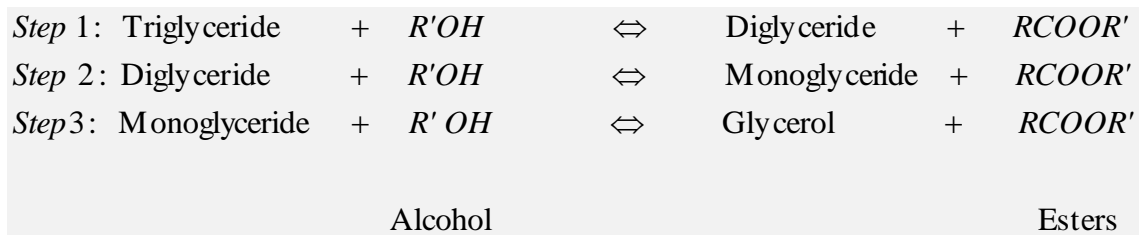


Figure 2-2: Stepwise transesterification of triglycerides

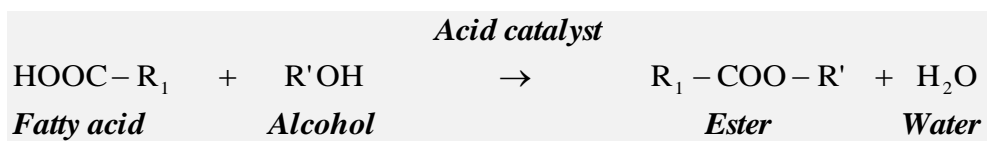


Figure 2-3: Esterification of free fatty acid

In general, the performance of the transesterification or esterification reactions is influenced by various parameters such as feedstock quality, alcohol to oil ratio, alcohol type, reaction temperature, reaction time, catalyst type and concentration and mixing intensity (Ma & Hannah, 1999; Gupta & Dermibas, 2010; Issariyakul & Dalai, 2014). These parameters will be briefly discussed in the following section.

2.2.4. FACTORS AFFECTING BIODIESEL PRODUCTION

2.2.4.1. FEEDSTOCK QUALITY

The quality of the feedstock oil, which is determined by its FFA and moisture content, significantly affects the performance of the transesterification reaction. In the presence of conventional homogeneous alkali catalyst, FFA and water have negative effects on the reaction. The presence of FFA causes saponification while the presence of water causes hydrolysis. Both undesired reactions result in the reduction of the yield of biodiesel (Gupta & Dermibas, 2010; Issariyakul & Dalai, 2014). A more detailed discussion on the different types of feedstock for biodiesel production as well as their characteristics is given in section 2.3.

2.2.4.2. ALCOHOL TO OIL MOLAR RATIO

Theoretically, an alcohol to oil ratio of 3:1 is needed for the reaction to complete. Since the transesterification reaction is a reversible reaction, excess alcohol is required in order to drive the equilibrium in the direction of the products. This enhances the solubility of methanol and increases the contact between the triglycerides and alcohol molecules (Ma & Hannah, 1999; Kumar *et al.*, 2010).

In general, 98% conversion can be achieved using a 6:1 alcohol to oil molar ratio for the alkali-catalysed reaction (Encinar *et al.*, 2005; Meher *et al.*, 2006; Agarwal *et al.*, 2012). However, an optimum alcohol to oil ratio can differ depending on the type of oil and the type of catalyst used. Leung and Guo (2006) reported a 98% ester yield from the transesterification of canola oil using a 6:1 alcohol to oil ratio while transesterification of used cooking oil required an alcohol to oil ratio of 7:1 to achieve 94% yield. Agarwal *et al.* (2012) reported a 98.5% yield of biodiesel from the homogeneous catalysed transesterification of waste cooking oil using an optimum alcohol to oil ratio of 6:1. However, the heterogeneous catalysed transesterification of the same oil required a 9:1 alcohol to oil ratio in order to achieve 96.8% yield.

The former study (Agarwal *et al.*, 2012) also showed the effect of increasing the alcohol to oil ratio beyond the optimum level. For the homogeneous catalysed transesterification, the yield of biodiesel was decreased from 98.5% to 94.1% with an increase of the alcohol to oil ratio from 6:1 (optimum) to 10:1. In another study, Rashid and Anwar (2008) also reported that further increase in the alcohol to oil ratio in transesterification reaction of rapeseed beyond the optimum level (from 6:1 up to 21:1) resulted in the reduction in the ester yield (from 96% to \approx 80%). These observations can be attributed to the fact that excess alcohol increases the polarity of the reaction mixture which results in an increase of the solubility of glycerol back into the ester

phase. This promotes the reverse reaction between glycerol and esters or glycerides, therefore reducing the ester yield (Issariyakul and Dalai, 2014).

2.2.4.3. TYPE OF ALCOHOL

The type of alcohol involved in the transesterification reaction can also affect the reaction performance. Methanol and ethanol are the most commonly used alcohols for biodiesel production. Methanol is relatively cheaper and more readily available (Ma & Hannah, 1999; Borges & Díaz, 2012). Its use results in higher equilibrium conversion due to the formation of higher reactive intermediate methoxide (Issariyakul *et al.*, 2007). Unlike methanol, ethanol has better solvent properties and can be produced from renewable sources. Its lower polarity allows a better miscibility of the triglycerides in the alcohol and vice versa, which results in a better mass transfer when compared to methanol, hence an increase in the rate of reaction (Issariyakul & Dalai, 2014). However, the lower polarity of ethanol also favours the mutual miscibility of ester and glycerol, which therefore inhibits their easy separation, consequently reducing the yield of biodiesel (Issariyakul & Dalai, 2014). Kulkarni *et al.* (2007) proposed as an alternative, the use of a mixture of ethanol and methanol in order to use the better solvent property of ethanol and the rapid equilibrium conversion property of methanol.

2.2.4.4. REACTION TEMPERATURE

Temperature strongly influences the rate of transesterification reaction, such that the higher the temperature, the higher the rate of reaction and the shorter the reaction time. This can be attributed to the reduction in the viscosity of oil at higher temperature (Mathiyazhagan & Ganapathi, 2011). However, according to Lung *et al.* (2006) and Eevera *et al.* (2009), when the temperature increases beyond the optimal level, the yield of the biodiesel product decreases because a higher reaction temperature accelerates the saponification reaction of triglycerides. This was also observed by Patil and Deng (2009), who investigated the effect of reaction temperature for the transesterification of four different types of oil (Karanja, Jatropha, canola and corn oil) in the temperature range of 40 to 120°C. The maximum yield was obtained at 80°C for corn oil and 60°C for the other three. Beyond the optimum temperature, a decrease in the ester yield was observed in all cases. Besides saponification, Patil and Deng (2009) also attributed the decrease in the ester yield to the excessive loss of methanol due to its evaporation at temperature greater than its boiling point (65°C). Usually, the reaction temperature should be kept below the boiling points of the corresponding reacting alcohol (65°C for methanol and 78°C for ethanol). In the case where extreme reaction temperatures are required e.g. transesterification in supercritical alcohol, pressure needs to be applied to the reaction mixture in order to maintain the reacting alcohol in the fluid state (Issariyakul & Dalai, 2014). By this

means, Ghoreishi and Moein achieved a 95% yield of ester by supercritical methanol transesterification of waste vegetable oil at 271.1°C in 20 min by applying a pressure of 23.1 MPa.

2.2.4.5. REACTION TIME

In general, the longer the reaction time, the higher the conversion. However, once the maximum conversion is reached, a further increase in the reaction time will not affect it anymore. In biodiesel production, a reaction time longer than the optimal level leads to the reduction of biodiesel yield. Eevera *et al.* (2009) investigated the effect of increasing the reaction time of the transesterification of several feedstock oils. The transesterification reactions were conducted at the following optimum conditions: 55°C, 1.5 wt. % NaOH concentration and 6:1 alcohol to oil ratio. The results indicated that complete conversion was achieved after 90 min. However, further increase in the reaction time from 90 to 150 min had no effect on the conversion of triglycerides but led to a reduction in the product yield from ≈99.5% to between 92 and 96 % depending on the type of oil. The authors attributed this decrease in the ester yield to the fact that longer reaction time enhanced the hydrolysis of esters (reverse reaction of transesterification) and causes more fatty acids to form soap.

2.2.4.6. CATALYST TYPE

The type of catalyst to be used in biodiesel production is the most important factor that influences the performance of the transesterification reaction, since its purpose is to improve the yield and the reaction rate. The selection of the catalyst is greatly dependent on the type and quality of feedstock (Issariakul & Dalai, 2014). Different types of catalyst are employed in biodiesel production: homogeneous catalysts (alkali and acid), heterogeneous catalysts (alkali, acid and bi-functional) and enzymes (Issariakul & Dalai, 2014). For virgin oil or feedstock oil having FFA and moisture content as low as 0.5-1 wt. % and 0.06 wt. % respectively, alkali-catalysed reaction provide a high conversion in relatively short reaction time (Ma & Hannah, 1998; Abbaszaadeh *et al.*, 2012). For higher FFA containing oils (≥ 0.5 wt. %), acid catalysts can be used to catalyse esterification and transesterification simultaneously. The use of acid catalyst (both homogeneous and heterogeneous) is characterised by a relatively slow rate of reaction and it requires higher reaction temperature as compared to alkali-catalysed transesterification (Drapcho *et al.*, 2008). Enzymes can be effectively used for the transesterification of low quality oils, since they are insensitive to the FFA and moisture content of the feedstock (Hama *et al.*, 2004; Abbaszaadeh *et al.*, 2012; Nouredini *et al.*, 2005). Nevertheless, enzymatic transesterification which is generally carried out at moderate temperature (20-50°C) with high yield (Semwal *et al.*, 2011), is characterised by a rate of

reaction relatively lower than alkaline and acidic processes (Bajaj *et al.*, 2010; Gog *et al.*, 2012). It is also possible to produce biodiesel in the absence of a catalyst. This is achieved using supercritical alcohol transesterification and it is characterised by very high pressure and temperature (>8 MPa and >239°C) (Kusdiana & Saka, 2001; Semwal *et al.*, 2011; Abbaszaadeh *et al.*, 2012). These different types of catalysts will be further discussed in section 2.4.1.

2.2.4.7. CATALYST CONCENTRATION

The effect of catalyst concentration on the transesterification reaction is dependent on the type of catalyst used. In a review of several studies, Atadashi *et al.* (2013) demonstrated how the reaction yield of biodiesel depends on homogeneous catalyst concentration. Homogeneous catalyst concentration ranging from 0.5 to 2 wt. % provided high yield up to 99.6%. The study indicated that an increase in homogeneous catalyst concentration above the optimum level does not affect the performance of the reaction, but could add extra costs of production (Jain *et al.*, 2011). As regards heterogeneous catalyst, increasing the catalyst loading increases the surface area for the reaction to proceed, leading to a greater yield of ester. Nonetheless, increasing the catalyst loading beyond the optimum level makes the slurry formed by the reactant mixture and the catalyst too viscous, giving rise to mass transfer problem during mixing. This results in a lower reaction performance (Kim *et al.*, 2004). Increasing the enzyme catalyst concentration increases the percentage conversion. Yet beyond the optimum limit, an agglomeration of enzyme will take place and decrease the active site available to the substrate (Kumari *et al.*, 2009; MacEiras *et al.*, 2010).

2.3. FEEDSTOCK FOR BIODIESEL PRODUCTION

Many sources have been investigated and used as raw materials for biodiesel production. These raw materials can be categorised into three main groups: vegetable oils (edible and non-edible), animal fats and waste cooking oils. According to Sivasamy *et al.* (2009), the source of feedstock for biodiesel production should fulfil two main requirements: price and ready availability. The cost of feedstock oil accounts for 75 % of the total manufacturing cost of biodiesel as depicted in Figure 2-4. Therefore, in order for biodiesel to remain competitive compared to conventional diesel, the feedstock used for the production of biodiesel should be available at the lowest price possible and in abundance.

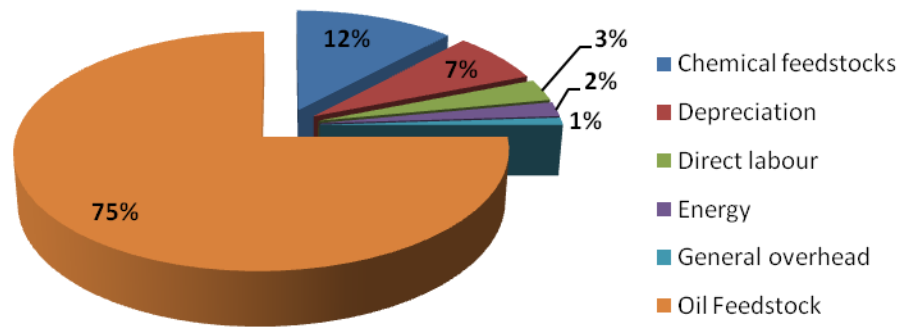


Figure 2-4: General cost breakdown for the production of biodiesel (Adapted from Lim & Teong, 2010)

In the following sub-sections, the advantages and disadvantages of each of the different sources for biodiesel production previously mentioned will be discussed.

2.3.1. EDIBLE VEGETABLE OIL

Currently, more than 95% of the world biodiesel is produced from edible oils extracted from oilgeneous plants like sunflower, soya, canola and palm (Christopher *et al.*, 2014), because they have the advantage of being easily available on a large-scale from the agricultural industry (Gui *et al.*, 2008; Balat, 2011). Furthermore, the properties of biodiesel produced from them are suitable to be used as diesel substitute (Leug *et al.*, 2010).

Nevertheless, the use of edible oil as feedstock for biodiesel production has raised several concerns. The first one termed as “food vs. fuel controversy which concerns the fact that the production of biodiesel from edible oils has potential to increase food scarcity. Currently, 60% of the world population is malnourished (Balat, 2011; Pimentel & Burgess, 2013). It is further believed that prolonged dependence of edible oil for biodiesel production will result in future competition for arable land as well as significant increase of basic food price. This will inevitably affect destitute populations’ access to food (Balat, 2011; Bankovic-Illic *et al.*, 2012) and exaggerate world hunger.

Recently, environmentalists have risen what is termed as the “energy vs. environment” debate. They claim that the production of biodiesel from edible oil has a negative impact on our planet since it promotes deforestation which disturbs the ecosystem. Indeed, more and more forests are being felled for plantation purposes (Gui *et al.*, 2008; Yaakob *et al.*, 2013).

Another major concern with the present use of edible oil as feedstock for biodiesel production is its conventionally high price which has caused the production cost of biodiesel to be approximately 1.5 times higher than that for diesel (Phan & Phan, 2008; Math *et al.*, 2010).

Following the disadvantages of edible oil as feedstock for biodiesel production, recent research has shifted toward the search for alternative feedstock that are expected to benefit the commercialisation of biodiesel, by lowering its cost and alleviating the ethical issues involved in its production. These alternative feedstock are described in the subsequent sections.

2.3.2. NON-EDIBLE VEGETABLE OIL

Non-edible oils are vegetable oils that are not suitable for human consumption due to the presence of some toxic compounds (Bankovic- Illic *et al.*, 2012). Some of the non-edible oils sources that have been investigated as potential feedstock for biodiesel production are: Jatropha, tobacco, jojoba and castor oils. These oils have been recognised as potentially good sources for biodiesel production since, while producing relatively good quality biodiesel, they also eliminate the food vs. fuel competition (Gui *et al.*, 2008; Bankovic- Illic *et al.*, 2012). Besides, non-edible plants can be grown on barren land unsuitable for edible crops. The cost of cultivation is much lower because these crops can sustain reasonably high harvest without intensive care (Gui *et al.*, 2008; Leug *et al.*, 2010; Borrugada & Goud, 2012). Jatropha can grow on waste, sandy and saline soils under a wide variety of climatic conditions (severe heat, low and high rainfall and frost) and it can produce up to 60% oil in its seed and kernels (Christopher *et al.*, 2014). Non-edible oils such as Jatropha are for this reason regarded as promising feedstock for biodiesel production. Nevertheless, as for most non-edible oils, crude Jatropha oil contains high level of FFA ($\approx 14\%$) which makes it unsuitable for the conventional alkali-catalysed process of production of biodiesel since it is far beyond the acceptable limit of 1% FFA (Koh *et al.*, 2011). Several studies have focused on the pre-treatment of the high FFA of Jatropha oil. Among others, Patil and Deng (2009) successfully reduced the FFA content of Jatropha oil from 14 to 1% by esterification under the following conditions: 60°C, 2h reaction time, 0.5 wt. % H₂SO₄ concentration and 6:1 methanol to oil molar ratio. They could then achieve 90-95% ester yield by the transesterification of the treated oil, using 2 wt. % KOH concentration and 9:1 methanol to oil ratio at a temperature of 60°C. Other studies achieved high yield up to 99% using this two steps process (Tiwari *et al.*, 2007; Syam *et al.*, 2009; Sahoo and Das, 2009).

2.3.3. ANIMAL FAT

Animal fats used as feedstock for biodiesel production include tallow, pork lard and chicken fat (Balat, 2011; Bankovic-Illic *et al.*, 2014). When compared to vegetable oils, animal fats have the advantage of being priced favourably for a cost efficient conversion to biodiesel (Leug *et al.*, 2010; Christopher *et al.*, 2014). Bhatti *et al.* (2008) investigated the production of biodiesel

from both chicken and mutton tallow. After 24 hours, 99.01 and 93.21% ester yield for chicken and mutton tallow respectively, were achieved under the following reaction conditions: 50°C, 30:1 methanol to oil ratio, 25 wt. % H₂SO₄ (chicken tallow) and 60°C, 30:1 methanol to oil ratio, 50 wt. % H₂SO₄ (mutton tallow). Animal fat methyl esters are characterised by high cetane number, non-corrosiveness, clean and renewable properties (Balat, 2011). Nonetheless, the use of animal fats as feedstock for biodiesel production present several issues. Animal fats contain higher saturated fatty acids which cause them to become solid wax at room temperature (Bankovic-Ilic *et al.*, 2012). Another problem is the limited availability of animal fat which according to Bankovic-Ilic *et al.* (2014) will never be able to meet the world's fuel needs.

2.3.4. WASTE COOKING OIL

Waste cooking oil (WCO) is defined as any oil-based substance consisting of vegetable and/or animal matter that has been previously used for frying or cooking and which is deemed unhealthy to reuse for human consumption (Gui *et al.*, 2008; Nurfitri *et al.*, 2013).

The amount of waste cooking oil available worldwide is huge and varies accordingly to the quantity of edible oil consumed. It is even expected to increase rapidly due to the tremendous growth of human population (Yakoob *et al.*, 2013). It is reported that the amount of waste cooking oil generated in the United States alone is approximately 10 million tons per year (Gui *et al.*, 2008), while for the EU countries, it lies in the range of 0.7 to 1 million tons (Kulkarni and Dalai, 2006; Gui *et al.*, 2008). In the South African context, 0.2 to 0.3 million tons of waste cooking oil is estimated to be generated annually as stated by First in Spec Biofuels (2009) and The green cab (2009). Even though some of this used cooking oil is used in the manufacture of soap, the major quantity of it is still being illegally dumped into landfills and rivers, causing environmental pollution (Chhetri *et al.*, 2008; Balat, 2011). Hence, using waste cooking oil as feedstock for biodiesel production is not only a way to give a value to it, additionally, due to its abundant availability, it has the potential to provide plentiful feedstock for biodiesel production.

Waste cooking oil is 2 to 3 times cheaper than conventional virgin oil (Table 2-2), which gives it the potential to reduce the total processing cost of biodiesel by 60-70 % (Math *et al.*, 2010). This makes it a promising alternative for overcoming the principal obstacle to biodiesel commercialisation: high production cost. Besides, the use of waste cooking oil eliminates any possible controversy about food resources and arable lands being used for fuel production, while contributing to solving waste disposal problem.

Table 2-2: Price comparison of different feedstock for biodiesel production

Feedstock	Price (\$/ton)
Rapeseed ^a	815-829
Soybean ^a	735
Palm oil ^a	610
Jatropha ^b	410
Waste cooking oil ^a	360
Animal Tallow ^a	245

^a Source: Lim & Teong (2010)

^b Source: Jatropha World. (2013)

Nevertheless, the main challenge with the production of biodiesel from WCO is the presence of unwanted contents such as FFA, water and solid impurities (Nurfitri *et al.*, 2013). The high amount of FFA results from the exposure of the oil to high temperatures for a long period, while water and solid impurities are from the food product cooked. These contents can have a negative effect on the performance of the conventional alkali transesterification reaction, since the presence of water in the oil leads to hydrolysis and high FFA content leads to saponification (Yakoob *et al.*, 2013).

Several authors have investigated the alkali-catalysed transesterification of WCO and have compared its performance with that of the virgin oil. Dias *et al.* (2008) compared the conversion efficiency of both WCO (1.64 % FFA and 0.05 wt. % H₂O) and virgin oils in the presence of different alkali catalysts for the production of biodiesel. It was shown that virgin oils resulted in higher conversion as compared to WCO (97% vs. 92%) under similar reaction conditions. These findings were corroborated by Dmystryshyn *et al.* (2004) where virgin canola oil and waste fryer grease (composition unspecified) were employed as feedstock and reacted with methanol in the presence of KOH alkali catalyst. It was reported that the conversion efficiency was 87% and 58% for virgin canola oil and yellow grease respectively. Furthermore, investigation by Refaat *et al.* (2008) showed that transesterification of virgin oil and two used sunflower oils of different qualities (the first one used 2 to 3 times at 120-130°C and the other used 2-3 times at 150-200°C) resulted in a higher yield from the virgin oil as opposed to the used sunflower oil (95% vs. 90%). It was observed further that the yield of biodiesel decreased with a decrease in the quality of waste cooking oil. On the contrary, Alcantara *et al.* (2000) showed that conversion was not affected by the use of virgin or used oil, provided that appropriate amount and type of alcohol and catalyst is used. Nevertheless, the requirement of the amount of catalyst is generally higher in case of used oil as compared to virgin oil (Issariakul & Dalai, 2014).

In order to overcome the above-mentioned drawbacks of using waste cooking oil as feedstock for biodiesel production, several techniques have been proposed. One of them refers to the pre-treatment of the waste oil by reducing the FFA content and removing the moisture and solid impurities (Yakoob *et al.*, 2013). To reduce the FFA content of the oil, different methods have been explored, such as acid esterification with sulphuric acid (Otadi *et al.*, 2011; Boffito *et al.*, 2013) esterification with ion exchange resin (Ozbay *et al.*, 2008), neutralisation with alkalis followed by soap separation by a decanter, and extraction with polar liquids along with acid esterification and distillation of FFA (Cvengros *et al.*, 2004). In order to eliminate the water content in the oil, the sample is usually heated over 100°C (Demirbas, 2009; Banerjee & Chakraborty, 2009). Alternatively, vacuum distillation (0.05 bar) is used on the industrial scale (Felizardo *et al.*, 2006). As for the solid impurities, they can easily be removed by centrifugation (Demirbas, 2009) or filtration (Cheng *et al.*, 2009).

Besides the pre-treatment of the waste oil, researchers have also focused on exploring different catalysed transesterification processes that would be insensitive to the FFA and water content of the oil so that it would not require pre-treatment. The main catalysed processes investigated for this purpose are: acid, bi-functional, enzyme and supercritical catalysed processes. These approaches are discussed in the following sections.

2.4. TECHNOLOGIES FOR BIODIESEL PRODUCTION

2.4.1. CATALYSTS FOR BIODIESEL PRODUCTION

Most process routes for the production of biodiesel requires the presence of a catalyst in order to increase the reaction rate and the transesterification reaction yield. The different types of catalyst largely investigated are homogeneous catalyst, heterogeneous catalyst and enzymes. The transesterification can also be achieved via supercritical process.

2.4.1.1. HOMOGENEOUS CATALYST

Homogeneous catalysts are defined as any catalysts that act in the same phase as the reaction mixture. Homogeneous catalysts for biodiesel production can be classified as base and acid.

2.4.1.1.1. HOMOGENEOUS ALKALI CATALYST

To date, homogeneous base catalysts such as sodium hydroxide and potassium hydroxide are the most commonly used catalysts in the biodiesel industry (Sharma *et al.*, 2011; Borges & Díaz, 2012). Other alkaline catalysts include sodium ethoxide, potassium methoxide, sodium propoxide and sodium butoxide (Atadashi *et al.*, 2013). Sodium and potassium hydroxide are

preferred over the others mainly because they are able to achieve high conversion and high yield ($\geq 97\%$) under mild conditions ($25-70^\circ\text{C}$) in a short reaction time (10 min to 2h) (Lam *et al.*, 2010; Borges & Díaz, 2012; Issariyakul & Dalai, 2014). Besides, they are widely available and economical (Loterio *et al.*, 2005). However, the use of alkali homogeneous catalyst is only limited to high purity feedstock, characterised by low FFA and moisture content. These impurities react with the alkaline catalyst to form soap (Figure 2-5). Different acceptable levels of FFA have been recommended in several literatures for basic transesterification, but they mostly range from less than 0.5 wt. % to 2 wt. % (Ramadhas *et al.*, 2005; Sahoo *et al.*, 2007; Zhang *et al.*, 2003a) with a maximum acceptable value of 6 wt. % as suggested by Loreto *et al.* (2005). Above this range, the excessive soap formation significantly affects the process. The reaction consumes the alkali catalyst, decreases drastically the ester yield and inhibits the subsequent purification process of biodiesel, including biodiesel separation and water washing (Kulkarni & Dalai, 2006; Lam *et al.*, 2010). Furthermore, according to Felizardo *et al.* (2006), the soaps of saturated fatty acid tend to solidify at ambient temperature, forming therefore a semi-solid mass which is difficult to recover. The moisture content in waste vegetable oil can hydrolyse triglycerides to glycerol and form free fatty acids (Figure 2-6), which in the presence of the base catalyst will cause the undesired saponification reaction.

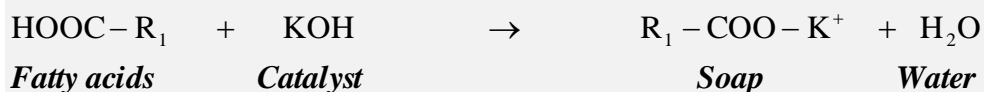


Figure 2-5: Saponification reaction

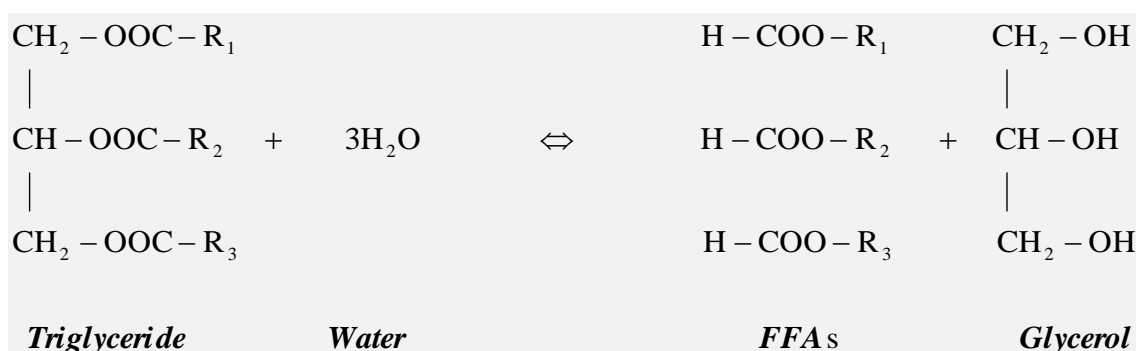


Figure 2-6: Hydrolysis of triglycerides

2.4.1.1.2. HOMOGENEOUS ACID CATALYST

In contrast to alkali catalysts, acid homogeneous catalysts are shown to be suitable for low quality feedstock as they convert the FFAs in the oil into fatty acid alkyl esters, improving the biodiesel yield (Hideki *et al.*, 2001). Homogeneous acid catalysts are able to catalyse both

esterification and transesterification simultaneously, with a higher efficiency when the amount of FFA in oils exceeds 1 wt. % as reported by Zhang *et al.* (2003a). Yield as high as 99% were reported by several authors from the homogeneous acidic transesterification of oils with FFA content higher than 1% (Freedman *et al.*, 1984; Zheng *et al.*, 2006). However, their use is associated with some disadvantages as compared to alkali catalysts. They are characterised by a weak catalytic activity causing a very slow reaction rate which according to Hideki *et al.* (2001) is 4000 times slower than that of alkali catalyst. Furthermore, acid-catalysed transesterification requires more severe reaction conditions such as high reaction temperature, high alcohol to oil ratio and long reaction time (Lam *et al.*, 2010). This is illustrated by Wang *et al.* (2006) study in which 90% conversion was achieved for the acid-catalysed transesterification of waste cooking oil ($\approx 38\%$ FFA) after 10h by using a methanol to oil ratio of 16:1 and 4 wt. % H_2SO_4 at a reaction temperature of 95°C . In another study, 99% yield of biodiesel was obtained after 4 h by reacting WCO (6% FFA) with methanol in a molar ratio of 245:1 with respect to oil at 70°C (Zheng *et al.*, 2006). Another problem associated with the use of acid catalysts is the fact that, since the most commonly employed homogeneous acid catalysts are strong acids such as sulphuric acid, hydrochloric acid and sulphonic acid (Atadashi *et al.*, 2013) one faces serious environmental and corrosion related problem.

2.4.1.1.3. TWO STEPS HOMOGENEOUS CATALYSED TRANSESTERIFICATION

In order to overcome some of the limitations associated with acid and base homogeneous catalysts while benefitting from their advantages, some studies have explored the use of a combination of both catalysts to produce biodiesel from low quality feedstock. Initially, acid catalyst is used to convert FFA to ester through esterification, and once the FFA content in the oil drops below the required level, transesterification of the oil can be achieved using an alkali catalyst (Zhang *et al.*, 2003a; Marchetti *et al.*, 2008).

A study by Patil *et al.* (2010) showed the reduction of the FFA content of waste cooking oil from 8.7 to $\leq 1\%$ by esterification using 2% ferric sulphate catalyst at a temperature of 100°C after 1h. The treated oil was then transesterified using KOH alkali catalyst also at 100°C and 1h. The methanol to oil ratios used were reported to be 9:1 and 7.5:1 for the acidic and base-catalysed reactions respectively. 96% ester yield was ultimately achieved.

In spite of the benefits associated with the two steps approach, homogeneous catalysed transesterification is still characterised by high cost of biodiesel production. The calculated production cost of biodiesel from several studies (West *et al.*, 2008; Zhang *et al.*, 2003b; Marchetti *et al.*, 2008; Sakai *et al.*, 2009), ranged from \$439/ton to \$858/ton. Furthermore, a huge amount of wastewater (0.2 to 3 litres per litre of biodiesel produced) is generated from

washing out the salts of neutralisation from the products (Veljković *et al.*, 2014) and the catalyst is not reusable (Madras *et al.*, 2004).

Even though homogeneous catalysts are to date the most commonly used types of catalysts for biodiesel production, they are associated with the so many technical and environmental challenges aforementioned, among which: unsuitability to low cost feedstock, difficult separation from product mixture, non-reusability of catalyst and generation of large amount of wastewater. For these reasons, alternative approaches are attracting increasing attention.

2.4.1.2. HETEROGENEOUS CATALYST

Heterogeneous catalysts are defined as catalysts that act in a different phase from the reaction mixture. In biodiesel production, these solid catalysts have proven to alleviate most of the problems associated with the application of homogeneous catalyst. Heterogeneous catalysts can easily be removed from the product mixture through simple processes such as filtration, making the purification steps easier (Semwal *et al.*, 2011). Since no neutralisation step is required, there is no need to wash out the salts of neutralisation, thus reducing the number of process steps and minimising the production of wastewater as well as the need for wastewater treatment. Furthermore, due to the absence of salts of neutralisation, the process provides higher purity esters (> 99%) and glycerol (98% vs. 80% for homogeneous catalysts) which can be more easily separated, obviating expensive refining operations (Kondamudi *et al.*, 2011; Chouhan & Sarma, 2011; Atadashi *et al.*, 2013). Heterogeneous catalysts can also be tuned easily to include desired catalyst properties that make it less sensitive to FFAs and water content in the oil (Aransiola *et al.*, 2014). Besides, they can be reused several times before they need replacement. (Lam *et al.*, 2010; Atadashi *et al.*, 2013). This results in a lower consumption of catalyst for heterogeneous catalytic process when compared to homogeneous process (Romero *et al.*, 2011). Heterogeneous catalysts can be easily used in continuous biodiesel production processes (Sheikh *et al.*, 2013; Sani *et al.*, 2014).

Heterogeneous catalysts for biodiesel production can be classified into three categories: alkali, acid and bi-functional catalysts.

2.4.1.2.1. SOLID ALKALI CATALYST

To date, many solid base catalysts have been investigated and developed for biodiesel production such as calcium oxide, magnesium oxide, sodium silicate, dolomite, etc. (Borges & Dias, 2012). Among others, CaO has attracted much attention due to its relatively high basic strength, low solubility in methanol, long catalyst life and because it requires only moderate reaction conditions (Math *et al.*, 2010; Borges & Díaz, 2012). Besides, CaO can be synthesised

from calcination of cheap calcium sources such as egg shells, mollusc shells, fly ash or wood ash at low cost (Kotwal *et al.*, 2009; Viriya-Empikul *et al.*, 2010; Cho & Seo, 2010; Sharma *et al.*, 2012; Buasri *et al.*, 2013). It can also simply be obtained from thermal decomposition of commercially available calcium salts such as calcium carbonate, calcium acetate, calcium oxalate and calcium nitrate (Yoosuk *et al.*, 2010; López-Grenados *et al.*, 2010).

The use of solid alkali catalyst such as CaO is reported by many to provide for high yield of biodiesel from the transesterification of virgin oil. Table 2-3 shows few of the many studies that reported the performance of CaO catalyst in the transesterification of high quality feedstock.

There has been little publishing on the performance of solid basic catalyst when it comes to the transesterification of low quality feedstock. Of the few studies reviewed, some contradictions have been noted. In the one hand, Kondamudi *et al.* (2011) asserted that the presence of FFA does not affect solid base-catalysed transesterification reaction. This assertion is supported by Lim *et al.* (2009) study in which waste palm oil (6.6-6.8% FFA) was transesterified under the following conditions: 6 wt. % CaO, 65°C, 2.5 h and 0.5: 1 methanol to oil mass ratio.

Table 2-3: CaO solid catalyst for the transesterification reaction of high quality feedstock oil

Authors	Feedstock oil	CaO wt. %	Reaction time	Temperature	MeOH/Oil molar ratio	FAME Yield
Granados <i>et al.</i>, 2007	Sunflower oil	3	100 min	60°C	13:1	94%
Liu <i>et al.</i>, 2008	Soybean oil	8	3h	65°C	12:1	95%
Veljkoci <i>et al.</i>, 2009	Sunflower oil	1	2h	60°C	6:1	98%
Jazie <i>et al.</i>, 2013	Rapeseed oil	3	3h	60°C	9:1	96%

The FAME yield was quantified as 90.4% as opposed 45% and 61% for NaOH and KOH homogeneous catalyst respectively; proving the tolerance of CaO catalyst toward high FFA content feedstock. These results are in contradiction with those reported by Kouzou *et al.* (2008a) who used CaO obtained from calcinations of pulverised limestone CaCO₃ to transesterify refined soybean oil. The catalyst showed good performance with a yield of FAME of 93%, achieved at 60° C after 1 h and for a methanol to oil molar ratio of 12:1. However, the

yield of FAME dropped to 66% when CaO catalysed waste cooking oil with 2.6% FFA and 0.05 wt. % moisture, under the very same reaction conditions. The authors attributed the poor performance of CaO toward the transesterification of WCO to the fact that basic sites of CaO were poisoned by strong absorption of FFA's on its surface. Consequently, part of the catalyst reacted with the absorbed FFA and converted to calcium soap and only 22% of the catalyst could be recovered. Despite the lack of sufficient studies on the topic, several authors asserted that solid base catalysts have low tolerance toward feedstock oil with high FFA content (Leug *et al.*, 2010; Borges & Díaz, 2012). Free fatty acid can react with the basic catalyst, accelerating the basic catalyst deactivation (Borges & Díaz, 2012).

2.4.1.2.2. SOLID ACID CATALYST

Solid acid catalysts have been established as benign alternatives to the heterogeneous alkaline catalysts and the unrecyclable-homogeneous acid and base catalysts, since they combine the benefits of heterogeneous base and liquid acid catalysts (Loterio *et al.*, 2005). Solid acid catalysts present the following peculiar advantages: They are insensitive to FFA contents, which ensures the use of cheaper and readily available feedstock without the need for pre-treatment; and they are able to carry esterification and transesterification simultaneously, while minimising corrosion problem (Issariyakul and Dalai, 2014). The hydrophobic surface of the solid acid catalyst prevents the polar by-products (water and glycerol) from deactivating the active sites which enhances selective adsorption of oily hydrophobic molecules to the catalyst surface (Sani *et al.*, 2014). Solid acid catalysts also have the advantage of being tunable, selective, easily regenerated and recycled.

Borges and Díaz (2012) reviewed the activity of some solid acid catalysts investigated in the simultaneous esterification and transesterification reaction of feedstock with high FFA content. The type of feedstock oil varied largely (Palm oil, Jatropha, Cottonseed, Sunflower, etc.) together with the FFA content ranging from 0.0011 wt. % to 93 wt. %. For most solid catalysts considered, very good performances (up to 98% yield) were reported for optimum reaction temperatures ranging from 150 to 250° C.

It can be suggested from the aforementioned that despite their ability to carry esterification and transesterification of high FFA content oil, simultaneously with very good performances, solid acid catalysts remain unsuitable for industrial large-scale production due to severe reaction conditions requirement.

2.4.1.2.3. BI-FUNCTIONAL SOLID CATALYST

In order to overcome the challenges posed by the basic and acidic solid catalysts discussed in the previous sections, studies have explored the potential of bi-functional solid catalysts that would be able to carry out esterification and transesterification simultaneously, under mild reaction conditions. Bi-functional solid catalysts possess both acidic and basic sites. Two of the few successful bi-functional heterogeneous catalysts developed recently are reviewed in the foregoing.

Kondamudi *et al.* (2011) studied the catalytic activity of synthetic Quintinite-3T for the simultaneous esterification and transesterification of FFA and triglycerides. Three types of oil of variable quality were selected. It was found that irrespective of the FFA content (0 to 30 wt. %); more than 96% yield was obtained. The catalyst successfully converted both FFA and triglycerides in a single step at an optimum temperature of 75°C and a methanol to oil ratio of 12:1.

Borges *et al.* (2011) investigated natural porous silica material pumice as heterogeneous catalyst for biodiesel production from sunflower and waste oil. The natural porous pumice was subjected to ion exchange with an aqueous solution of KOH in order to enhance its activity. The pumice natural material loaded with potassium demonstrated to be an efficient solid catalyst for the simultaneous esterification and transesterification at low temperature (55°C) and a methanol to oil ratio of 21:1. A yield of biodiesel of 90.9 % was obtained with waste oil.

Based on these studies, it can be concluded that bi-functional solids catalysts have the potential to produce biodiesel from low quality feedstock under acceptable reaction conditions.

2.4.1.3. ENZYMES

Transesterification can also be catalysed with environmentally-friendly biocatalysts (enzymes), which have shown great potential to minimise and even eliminate the challenges faced when conventional chemical catalysts are employed: feedstock pre-treatment, catalyst removal, waste water treatment and high-energy requirement (Christopher *et al.*, 2014; Aransiola *et al.*, 2014). Biocatalysts employed in transesterification are naturally occurring lipases which are produced from microorganisms, animals and plants (Gog *et al.*, 2012). Enzymatic transesterification is possible using both extracellular and intracellular lipases. In both cases the enzyme is immobilised. This eliminates downstream operations like separation and recycling (Ranganathan *et al.*, 2008).

Enzyme catalysed transesterification requires low operating temperature in the range 20-50°C (Gog *et al.*, 2012). It is applicable within broader oil range (FFA content up to 80 wt. %) due

to its ability to convert both FFA and triglycerides in a single step (Gog *et al.*, 2012; Lee *et al.*, 2011). Enzyme catalysed transesterification is also tolerant to water content in oil (0.1- 20 wt. %), since water is necessary to activate enzymes (Kaieda *et al.*, 2001; Nourredini *et al.*, 2005; Talebian-Kiakalaieh *et al.*, 2013). Furthermore, the absence of chemical catalysts eliminates the treatment costs associated with catalyst recovery and allows the production of high-grade glycerol, side stream with minimal impurities and water content (Christopher *et al.*, 2014). Enzyme catalysts are biodegradable and environmentally acceptable (Gog *et al.*, 2012).

In spite of the advantages associated with enzyme catalysed production of biodiesel, its application is still associated with certain demerits, especially when implemented on industrial scale. These include: high cost of enzymes, relatively lower rate of reaction when compared to the alkali and acid chemical catalytic process, limited regeneration and reuse of biocatalysts limited due to long operating time (Aransiola *et al.*, 2014; Gog *et al.*, 2012; Abbaszaadeh *et al.*, 2012).

2.4.1.4. SUPERCRITICAL TRANSESTERIFICATION

Supercritical transesterification is a non-catalytic method for biodiesel production in which high pressure and temperature are used to enhance the transesterification reaction (Abbaszaadeh *et al.*, 2012). The process' peculiarity is that it provides for high yield in a very short reaction time in comparison to catalytic processes. In a previous study, Kusdiana and Saka (2001) compared the performance of a conventional alkali catalytic production of biodiesel with that of the supercritical alcohol process. They reported that a time as short as 7 to 15 min was required to achieve a methyl ester yield of 98% for the supercritical alcohol process, while 60 to 360 min was required to obtain 96% yield of methyl ester for the conventional alkali process. Another advantage of the supercritical process is the absence of any catalyst recovery step, resulting in a purer product (Abbaszaadeh *et al.*, 2012). Furthermore, the supercritical transesterification method is more tolerant to the presence of water and FFA, hence can be applied to a wide variety of feedstock. Four samples of both refined and waste lard oils with different amount of FFA and moisture content (0.02 to 1.62 wt. % FFA and 0 to 0.12 g H₂O/100g oil) were supercritically transesterified in a study by Shin *et al.* (2012). For all four samples, high yields (87-90%) were achieved in 15 min at 335°C, 45:1 methanol to oil molar ratio, and 20 MPa. In another study, Samniang *et al.* (2014) produced biodiesel from crude Krating oil (14.5% FFA) and *Jatropha* oil (3.5%) via supercritical transesterification. 90.4% yield of FAME was obtained for Krating oil at 260°C, 16 MPa, and 10 min. Similarly at 320°C, 15 MPa and 5 min, using the same molar ratio of methanol to oil 40:1, transesterification of *Jatropha* resulted in a yield of

84.6. These results show that the presence of FFA and moisture has negligible effect in the production of biodiesel via supercritical transesterification.

The challenge with the supercritical transesterification is its high pressure and temperature requirement (> 8 MPa and $> 239^{\circ}$ C) (Kusdiana & Saka, 2001) as well as its characteristic high methanol to oil ratio (40:1-42:1) that renders the production expensive (Balat & Balat, 2008).

2.4.2. TECHNICAL COMPARISON OF THE DIFFERENT TYPES OF CATALYSED PROCESSES

In the following sections the different catalysed processes for biodiesel production previously discussed in the foregoing are compared in terms of process steps. This is illustrated using process block diagrams (Figure 2-7 to Figure 2-10). Subsequently, these processes are compared on the basis of operating conditions as summarised in Table 2-4 to Table 2-7.

Among the four processes, the supercritical process has the fewer number of steps and the fastest reaction time (Figure 2-10 and Table 2-7). Its main disadvantages are the requirement for relatively high operating temperature ($340-385^{\circ}$ C) which suggests very expensive process. The enzyme catalysed process which has the second fewer number of process steps has the advantage of requiring mild operating conditions. Further, the presence of FFA and water has positive influence on biodiesel production (Table 2-7). The main drawback to this process is the relatively high cost of enzymes.

A comparison of the homogeneous and heterogeneous catalysed processes shows that the two processes differ particularly at the catalyst removal step (Figure 2-7 and Figure 2-8). For the homogeneous process, the catalyst removal occurs through the neutralisation and washing step (as salts in waste water), while for the heterogeneous process, this step is eliminated and the catalyst is removed in its solid state through simple centrifugation or filtration (Table 2-4 and Table 2-5).

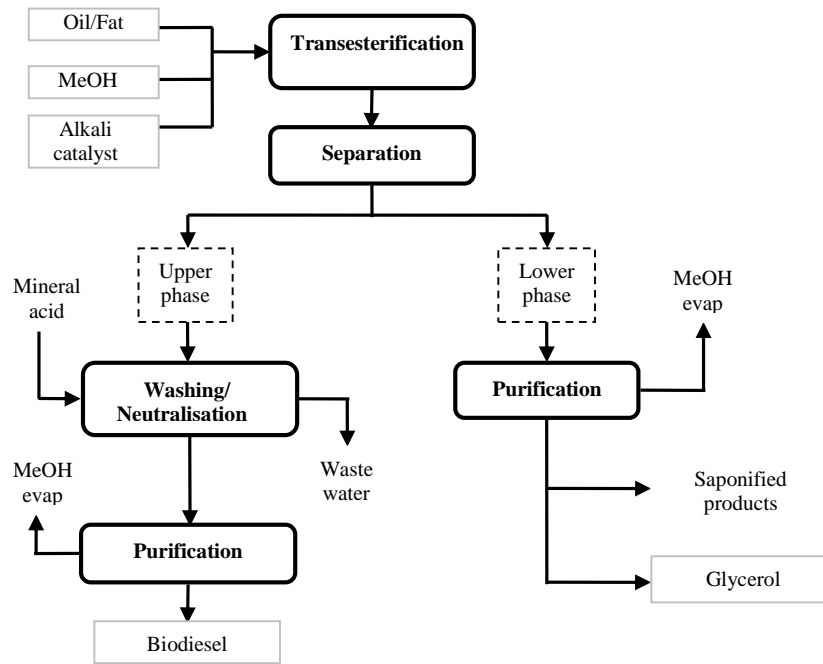


Figure 2-7: Homogeneous alkali-catalysed transesterification process

Table 2-4: Homogeneous catalysed process conditions

	Homogeneous base	Homogeneous acid
Reaction temperature	40-60°C	60-100°C
FFA in feedstock	Saponification	FAME production
Presence of water	Intolerant	Tolerant enough
FAME yield	Normal (> 95° C)	Higher (> 97°C)
Glycerol recovery	Difficult	Difficult
Catalyst removal	Difficult (Neutralisation +Water washing)	
Catalyst cost	Cheap	
Rate of reaction	Fast (1- 6h)	4000 times slower than alkali process

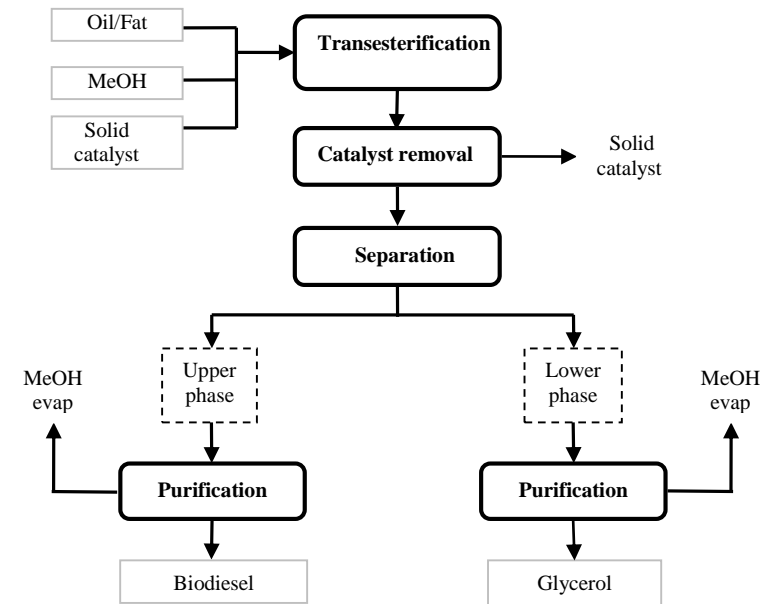


Figure 2-8: Heterogeneous-catalysed transesterification process

Table 2-5: Heterogeneous catalysed process conditions

	Solid base	Solid acid	Bi-functional
Reaction	60-80°C	150-250°C ^a	55-180°C ^a
FFA in feedstock	Saponification	FAME production	FAME production
Presence of water	Leaching	Leaching	Leaching
FAME yield	Normal (> 95° C)	Higher (> 97°C)	Higher (> 97°C)
Glycerol recovery	Comparatively easy		
Catalyst removal	Simple (Centrifugation or filtration)		
Catalyst cost	Cheap		
Rate of reaction	Slower than homogeneous base	Slower than homogeneous acid	Slower than homogeneous catalyst

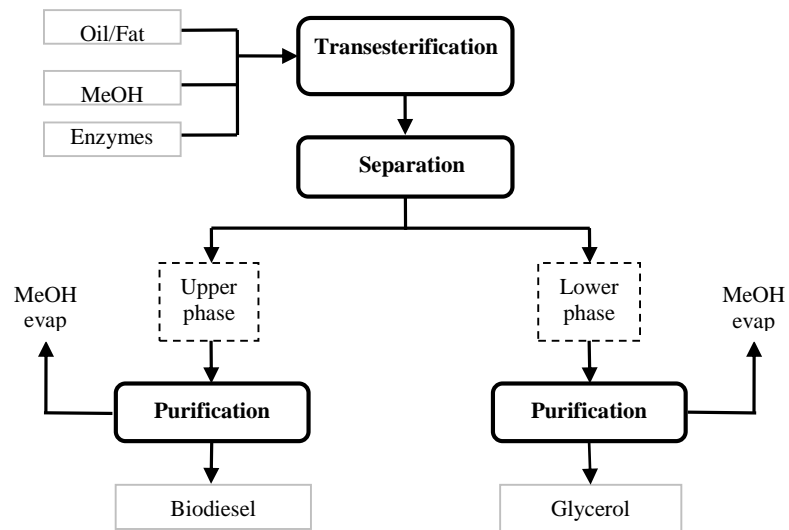


Figure 2-9: Enzyme catalysed transesterification process

Table 2-6: Enzymes-catalysed process conditions

	Enzyme catalysed process
Reaction temperature	20-50°C
FFA in feedstock	FAME production
Presence of water	Enzyme activation (0.1 to 20% water content)
FAME yield	Higher
Glycerol recovery	Easy
Catalyst removal	None (Generally immobilised)
Catalyst cost	Relatively expensive
Rate of reaction	Slower than homogeneous process

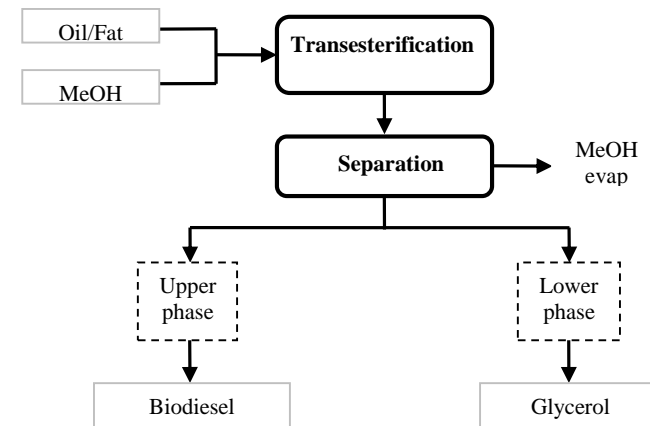


Figure 2-10: Supercritical transesterification process

Table 2-7: Supercritical transesterification process conditions

	Supercritical process
Reaction temperature	340-385°C
FFA in feedstock	FAME production
Presence of water	No influence
FAME yield	Very high (>98)
Glycerol recovery	Very easy
Catalyst removal	None
Catalyst cost	None
Rate of reaction	Very fast (7-15 min)

2.5. ECONOMIC COMPARISON OF THE DIFFERENT TYPES OF CATALYSED PROCESSES

2.5.1. REVIEW OF PREVIOUS STUDIES

Very few studies have been published regarding the economic assessment of heterogeneous catalysed processes for biodiesel production. These studies are reviewed in the foregoing and summarised in Table 2-8.

West *et al.* (2008) performed an economic comparison of four continuous processes to produce biodiesel from WVO at a rate of 8 000 ton/y. Among these four different processes ((i) homogeneous alkali-catalysed, (ii) homogeneous acid-catalysed, (iii) heterogeneous acid-catalysed and (iv) supercritical alcohol process), the heterogeneous acid-catalysed process (iii) was found to be the most economically attractive process as it had the only positive after tax rate of return and the lowest capital investment (Table 2-8).

In a similar study, Marchetti *et al.* (2008) compared three different continuous processes namely (i) homogeneous acid-catalysed, (ii) homogeneous alkali-catalysed process with acid pre-esterification and (iii) heterogeneous solid catalysed process. The plant capacity was 36 000 ton/year using WVO as the the feedstock. At an interest rate of 7%, the net present values for the different processes were evaluated to be \approx \$2, \$1 and \$8 million for process (i), (ii) and (iii) respectively (Table 2-8). This is in agreement with the study of West *et al.* (2008) demonstrating that the heterogeneous acid scenario proved to be the most economically feasible process, with the highest net positive value at the lowest interest rate.

However, these two studies only took into consideration continuous processes, and there was no evidence of whether the mode of process would influence the economics of the process as regards heterogeneous catalyst. In another study, Sakai *et al.* (2009) performed an economic comparison of four different batch processes: two homogeneous KOH catalysed process; one with hot water purification process (of the upper layer of biodiesel) and the other with vacuum FAME distillation, and two heterogeneous CaO catalyst processes with the purification processes employed in the homogeneous catalysis.

Table 2-8: Review of previous studies on the economic comparison of homogeneous and heterogeneous processes for biodiesel production

Oil feedstock	Plant capacity (ton/year)	Process type	Catalytic process	Economic criteria evaluated			Most economical process	References
				Total capital investment*	Total manufacturing cost*	After tax rate of return*		
Waste vegetable oil	8,000	Continuous	(i) Homogeneous alkali	1.59	5.2	-22.2	Heterogeneous acid-catalysed process	West <i>et al.</i> , 2008
			(ii) Homogeneous acid	1.99	4.76	-8.71		
			(iii) Heterogeneous acid	0.63	3.88	58.76		
			(iv) Supercritical alcohol	2.15	4.59	-0.9		
Waste vegetable oil	36,000	Continuous	(i) Homogeneous acid	Net present value (at 7% IRR)			Heterogeneous acid-catalysed process	Marchetti <i>et al.</i> , 2009
			(ii) Homogeneous alkali with acid pre-esterification	\$1 797 000				
			(iii) Heterogeneous acid	\$1 275 000				
Waste cooking oil	1,452-14,520	Batch	(i) Homogeneous alkali (KOH-W)	Manufacturing cost (\$ /ton)			Heterogeneous alkali CaO-W	Sakai <i>et al.</i> , 2009
			(ii) Homogeneous alkali (KOH-D)	598				
			(iii) Heterogeneous alkali (CaO-W)	641				
			(iv) Heterogeneous alkali (KOH-D)	584				
Refined vegetable oil	100,000	Continuous	(i) Homogeneous	Operating costs			Heterogeneous process	Kiss <i>et al.</i> , 2010
			(ii) Heterogeneous	Not specified				
				Not specified				

*Cost reported as \$ million

The study was performed for a plant capacity ranging of 1 452 to 14 520 ton/year using WVO as feedstock. The heterogeneous catalyst batch process with hot water purification process was found to have the lowest manufacturing cost, despite its fixed cost being higher than that of the homogeneous alkali batch process due to equipment costs. These observations show that irrespective of the process mode (batch/continuous), heterogeneous catalysed process is still more viable than homogeneous process.

No record of study was found in the open literature that assessed process economics on the basis of verifying heterogeneous catalyst type (acid, base/bi-functional). However, comparing the study of West *et al.* (2008) and Marchetti *et al.* (2008) which evaluated heterogeneous acid catalyst with that of Sakai *et al.* (2009) which evaluated heterogeneous base catalyst, it can be assumed that irrespective of the type of catalyst (acid, base or acid-base) the heterogeneous catalysed process is still more economically attractive than homogeneous catalyst.

Knowing that all the economic comparisons of the previously reviewed studies were based on separate simulations of designed process models, there is a need to investigate whether an industrial plant using homogeneous catalysed transesterification would benefit from converting to heterogeneous process.

This potential benefit was investigated by Kiss *et al.* (2010) in a more recent study. The anticipated economic and ecological impact of changing from an existing homogeneous process of capacity 100 000 metric tons biodiesel to a heterogeneous process was evaluated. The study revealed the advantages of the heterogeneous process in terms of lower cost of catalyst and maintenance, with an estimated cumulative impact on the reduction of the operating cost of US\$ 59/ton of biodiesel relative to homogeneous process. Nevertheless, the energy consumption and associated costs were found to be higher in the case of heterogeneous catalysed process. The main limitation to the study of Kiss *et al.* (2010) is the fact that all assessments of the impact were made on mere estimations, making the findings arguable.

These economic analyses were all based on international prices and economic cost factors relevant to developed world such as USA, Canada, Russia and Japan. There is no record of studies that have been applied to the African economic environment.

This current study uses actual data to investigate the economic cost benefit of converting a biodiesel plant from homogeneous to heterogeneous catalysed process in South Africa.

2.5.2. MAJOR COST FACTORS FOR BIODIESEL PRODUCTION

In this section, a review of West *et al.* (2008), Marchetti *et al.* (2008) and Sakai *et al.* (2009) economic analyses will be performed with the purpose of determining the major cost factors for biodiesel production, that are a very close function of the type of technology applied (homogeneous and heterogeneous). A breakdown of the unit manufacturing cost (\$/ton of biodiesel produced) for the most economically attractive homogeneous and heterogeneous processes investigated by the authors is presented in Table 2-9. The calculated percentage differences of the heterogeneous process costs relative to the homogeneous process costs are also demonstrated. For comparison purpose, all the breakdown costs were summarised as variable and fixed costs (Figure 2-11). It can be seen that variable costs have the most significant impact on the total manufacturing costs. Hence, particular interest is given to breakdown costs of the total variable costs (Figure 2-12). Raw materials are demonstrated to be the most important variable cost factor, followed by utilities cost, then waste treatment cost and finally, operating supplies costs (Figure 2-12).

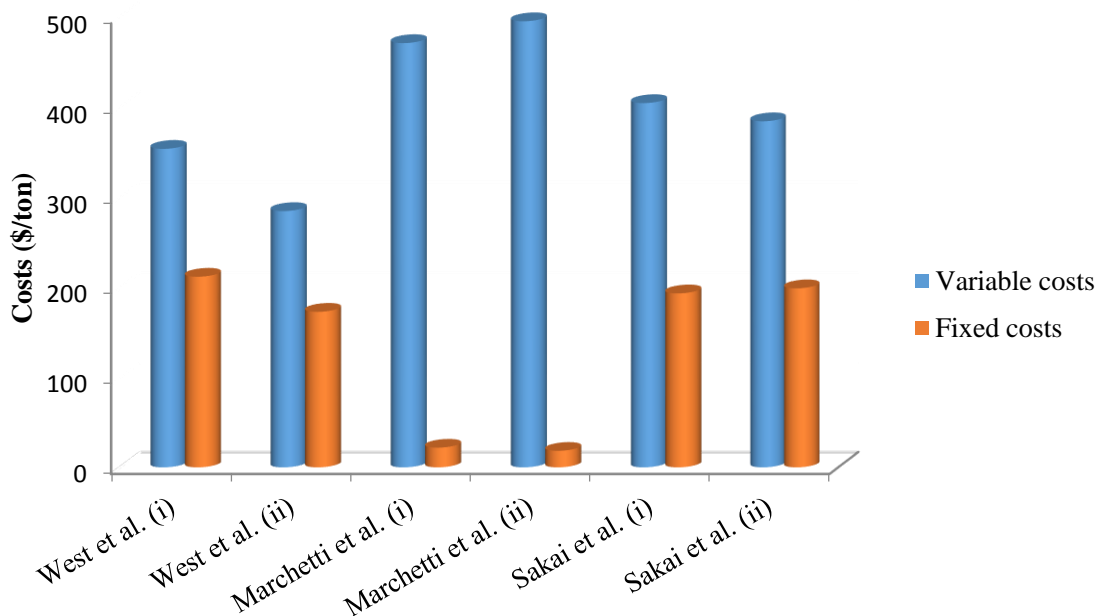


Figure 2-11: Variable and fixed costs trend for West *et al.* (2008), Marchetti *et al.* (2008) and Sakai *et al.* (2009)'s homogeneous (i) and heterogeneous (ii) processes

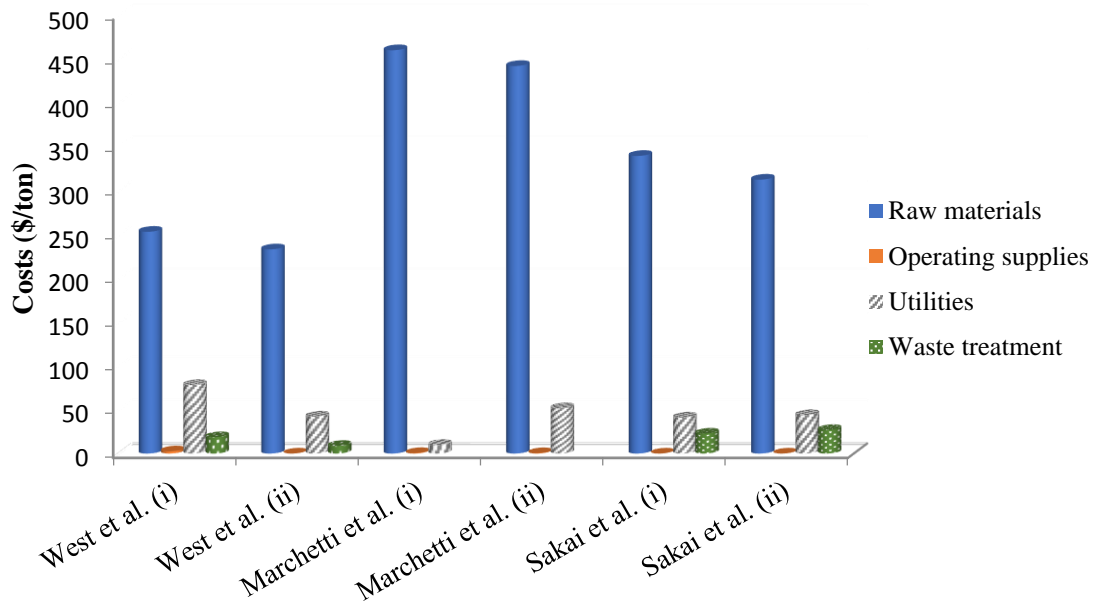


Figure 2-12: Breakdown costs of the unit variable costs for West *et al.* (2008), Marchetti *et al.* (2008) and Sakai *et al.* (2009)'s homogeneous (i) and heterogeneous (ii) processes

Table 2-9: Major cost factors for biodiesel production

Authors	West <i>et al.</i> (2008)			Marchetti <i>et al.</i> (2008)			Sakai <i>et al.</i> (2009)		
Types of processes	Homogeneous acid-catalysed process with WVO (continuous)	Heterogeneous acid-catalysed process with WVO (continuous)	% change	Homogeneous alkali-catalysed process with WVO (continuous)	Heterogeneous acid-catalysed process with WVO (continuous)	% change	KOH-W process (batch)	CaO-W process (batch)	% change
Costs	Costs (\$/ton)	Costs (\$/ton)		Costs (\$/ton)	Costs (\$/ton)		Costs (\$/ton)	Costs (\$/ton)	
Variable costs (A)									
Raw materials	253.8	233.8	-8%	460.1	442.2	-4%	340.0	313.0	-8%
Operating supplies	2.5	0.0	-100%	0.6	0.4	-20%	Not specified	Not specified	–
Utilities	78.8	42.5	-46%	9.9	52.1	+425%	41.4	44.2	+7%
Waste treatment	18.8	8.8	-53%	Not specified	Not specified	–	22.9	27	+18%
Sub-total (A)	353.8	285.0	-19%	470.6	494.7	+5%	404	384	-5%
Fixed costs (B)									
Maintenance & repairs	13.8	3.8	-73%	Not specified	Not specified	–	26.8	27.9	+4%
Operating labour	72.5	72.5	0%	10.1	10.1	0%	60.1	60.1	0%
Lab costs	11.3	11.3	0%	1.9	1.9	0%	Not specified	Not specified	–
Supervision	11.3	11.3	0%	1.1	0.9	-20%	Not specified	Not specified	–
Overheads	57.5	52.5	-9%	7.4	4.6	-37%	Not specified	Not specified	–
Capital charges (Depreciation)	22.5	6.3	-72%	Not specified	Not specified	–	80.4	83.8	+4%
Insurance, taxes & royalties	23.8	16.3	-32%	1.5	0.9	-37%	26.8	27.9	+4%
Sub-total (B)	212.5	173.8	-18%	22.0	18.5	-16%	194	200	+3%
General expenses/other costs (C)	105.0	85.0	-19%	Not specified	Not specified	–	Not specified	Not specified	–
Unit production cost (A)+(B)+(C)	671.3	543.8	-19%	510.0	524.9	+3%	598.4	583.9	-2%
Glycerine credit (C)	76.3	71.3	-7%	70.8	99.3	+29%	0.0	0.0	0%
Unit manufacturing cost (A)+(B)-(C)	595.0	472.5	-21%	439.2	425.6	-3%	598.0	584.0	-2%

2.5.2.1. RAW MATERIALS

By analysing the proportion of each cost relative to the total manufacturing cost, it can be seen from Figure 2-11 and Figure 2-12 that raw material cost is the major cost factor that affects the total production costs of biodiesel production. However, from the homogeneous vs. heterogeneous processes comparison viewpoint, the raw material cost is of minor impact because the feedstock oil remains the same. West *et al.* (2008) and Sakai *et al.* (2009) both estimated a raw material cost of 8% lower in the case of heterogeneous process, while Marchetti *et al.* (2008) estimated the reduction to be of 4%.

2.5.2.2. UTILITIES COSTS

As regards the utilities costs, they were estimated in the three studies (Marchetti *et al.*, 2008; West *et al.*, 2008; Sakai *et al.*, 2009) to have the second highest impact on the total production cost after raw materials cost (Figure 2-12). According to West *et al.* (2008), the application of the heterogeneous process reduces the utilities cost, by 46% as compared to the homogeneous process (Table 2-9). On the contrary, studies by Marchetti *et al.* (2008) and Sakai *et al.* (2009) showed a higher utilities cost in the case of heterogeneous process. Study by Kiss *et al.* (2010) is in agreement with the aforementioned in terms of energy consumption. However, it will be difficult to make an estimation based on their results, as there is a significant difference in the magnitude of the increase (425% vs. 7%). This factor will therefore be of particular interest in this study.

2.5.2.3. WASTE TREATMENT COSTS

According to West *et al.* (2008) and Sakai *et al.* (2009), the costs of waste treatment have minor impact on the total operating cost (Figure 2-12). However the two studies disagree on their impacts as regards whether homogeneous or heterogeneous process is applied. West *et al.* (2008) reported that the waste treatment costs would be reduced by 53% in the case of heterogeneous process while Sakai *et al.* (2009) demonstrated an increase in the magnitude of 18%. This factor will also be of particular interest in the current study.

2.5.2.4. FIXED COSTS

Considering the total fixed cost, West *et al.* (2008) and Marchetti *et al.* (2008) reported a reduction of 16 and 18% consecutively for the heterogeneous process relative to the homogeneous process. On the contrary, Sakai *et al.* (2009) demonstrated an increase of 4% as compared to the homogeneous process.

From the review of the major cost factors for biodiesel production, it is evident that there are numerous discrepancies as regards the economic impact resulting from the technological

difference between homogeneous and heterogeneous catalytic processes in large-scale industrial plants. Hence, the current study aims at quantifying the economic difference resulting from the conversion of a homogeneous to a heterogeneous catalysed biodiesel plant using actual data, as opposed to the previous investigation by Kiss *et al.* (2010), which was solely based on assumptions and anticipated impacts.

2.6. CHAPTER OUTCOMES

- Feedstock oil type and catalyst type are the most important factors affecting the production of biodiesel.
- The use of high FFA feedstock which has the potential to reduce the total processing cost of biodiesel has proved to be incompatible with conventional alkali catalyst.
- Among other catalyst type, heterogeneous catalysts proved to be convenient for the production of biodiesel at a relatively low cost with its ability to simplify the separation of catalyst from crude biodiesel mixture.
- Previous economic analysis showed the economic superiority of heterogeneous catalysed biodiesel production. However, no previous studies have quantified the economic difference resulting from converting a homogeneous to heterogeneous catalysed process for biodiesel production.

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NOMENCLATURE

<u>Abbreviation</u>	<u>Definition</u>
ASTM	American Society For Testing And Materials
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
IRR	Internal Rate Of Return
MeOH	Methanol
WCO	Waste Cooking Oil
WVO	Waste Vegetable Oil

CHAPTER 3: PROCESS SIMULATION

Highlights

- A process model of a batch homogeneous plant for biodiesel production was converted to a heterogeneous one.
- Process performances were compared.
- Reduction of total batch time and increase in annual throughput for the heterogeneous process.
- Lower raw materials requirement and higher energy consumption per unit of biodiesel produced for the heterogeneous process.

3.1. INTRODUCTION

Chapter 3 presents the development of the process models of the homogeneous and modified heterogeneous processes that will be compared on the basis of economics. In a first part, the description of the homogeneous process taken as the base case for this study will be given, followed by the methodology and procedures applied for the process simulation. The modification of the homogeneous process to the heterogeneous one will then be described, and finally both process performances will be assessed.

3.2. BASE CASE OVERVIEW

In this study, a country specific economic data for South Africa that can shed light on the cost benefit of converting a biodiesel plant from homogeneous to heterogeneous catalysed process was considered.

The base case homogeneous process was considered with a production capacity of 1618 kg/batch. The choice was supported by Mbohwa and Mudiwakure (2013) review of a South African biodiesel industry, from which it was concluded that biodiesel industry in South Africa is still in its infancy stage with an average production rate being as low as 1000 litres/day. It was also found out that batch processes are favoured in South Africa because of low acquisition cost, simple design and ease of operation.

3.2.1. BASE CASE PROCESS SPECIFICATIONS

This section discusses the choice for some of the base case process specifications taken into consideration.

3.2.1.1. RAW MATERIALS

Since the South African biodiesel industry mostly uses waste vegetable oil collected from food outlet as feedstock (Mbohwa and Mudiwakure, 2013), the base case process was considered to use waste cooking oil with a FFA content of 5% as reported in other studies (West *et al.*, 2008; Marchetti *et al.*, 2008). Methanol was chosen as the reactant alcohol because it is synthesised at the Sasol plant in SASOLBERG (South Africa) and is therefore relatively abundant and affordable in South Africa. As for the catalyst type, potassium hydroxide was chosen as it has been shown to have a better catalytic activity compared to other homogeneous catalyst such as NaOH and potassium methoxide (Tomasevic & Siler-Marinkovic, 2003; Rashid & Anwar, 2008). It was also the catalyst of choice by a local manufacture, due to the high hygroscopicity of NaOH.

3.2.1.2. TRANSESTERIFICATION REACTION

The transesterification reaction conditions considered for the homogeneous process with 5% FFA content were chosen based on a study reported by Babajide (2011), in which 90% conversion of waste cooking oil (1.37 mgKOH/g) was achieved at the following optimum conditions: 6:1 methanol to oil ratio, 60° C, 90 min and 1.5% wt./wt. KOH. In an attempt to account for the higher FFA content chosen for the current study, 2% KOH loading were assumed instead of the 1.5% reported by Babajide (2011). According to Gerpen (2005), the transesterification of oil containing up to 5% FFA can be catalysed with an alkali catalyst at a higher concentration to compensate for that lost during saponification.

3.2.1.3. SEPARATION STAGE

Following the transesterification reaction, the glycerol separation from biodiesel phase can be achieved by the means of settling or centrifugation. Mbohwa and Mudiwakure (2013) reported that most systems in South Africa are not fitted with centrifuge resulting in longer process settling time (almost 8 hours) but more clearly defined separation giving better yields relative to established producers. Settling was therefore chosen as the base case separation technique. However, a study of the effect of replacing settling with centrifugation on the performance and economy of the process is discussed in Chapter 6.

3.2.1.4. PURIFICATION STAGES

The purification steps of the biodiesel phase include methanol removal, neutralisation and washing as well as biodiesel drying. Only the biodiesel purification stage was considered. Methanol removal and biodiesel drying are both achieved in evaporation units with the drying occurring under vacuum to avoid thermal decomposition of biodiesel (Zhang *et al.*, 2003b). Biodiesel washing is a two-step process. The first step involves washing with a water solution containing sufficient hydrochloric acid required to neutralise potassium hydroxide, while the second step involves water alone. After each washing steps, the mixture is let to settle before the aqueous solution containing salts of neutralisation, methanol, soap and the remaining glycerol is drained off.

The detailed operations conditions for the different process steps are presented in subsequent sections.

3.3. PROCESS SIMULATION OF THE BASE CASE HOMOGENEOUS PROCESS

In order to develop the process models of the biodiesel processes investigated in this study, the commercial simulation software Aspen Batch Process Developer[®] V8.0 developed by Aspen

Technology INC., Cambridge, Massachusetts, USA was used. Aspen Batch Process Developer® (ABPD®) is a recipe driven software package, which allows the user to develop model by creating a text recipe. ABPD® has been specifically designed for the simulation of pharmaceutical, biotech and agricultural chemical processes and was therefore found suitable to model biodiesel processes. The choice of this software was based on its large variety of chemical components and unit operations which enables the user to model batch processes in greater detail.

3.3.1. SIMULATION APPROACH USING ASPEN BATCH PROCESS DEVELOPER®

The procedures used for modelling a chemical process using ABPD® software mainly involve:

- registering the various chemical components and utilities used in the process;
- defining the different chemical reactions;
- setting up the project by selecting the facility in which the process is to be carried (conceptual, generic laboratory or generic plant) and specifying the key raw material and final product;
- selecting the various equipment items;
- developing the process recipe by identifying the different unit procedures, selecting the required equipment items, defining the different unit operations that constitute the process, and specifying the operating conditions and performance parameters for the operations.

Dialog boxes for some of the procedure listed above are presented in APPENDIX A.

3.3.1.1. CHEMICAL COMPONENTS AND UTILITIES SELECTION

Information on most components involved in biodiesel production such as methanol, glycerol, potassium hydroxide, hydrochloric acid, water is available in the default ABPD® component database.

Waste vegetable oil (WVO) is a mixture of triglycerides, diglycerides, monoglycerides, FFA, phospholipids and it may also contain some impurities such as food remains. However, in order to simplify the simulation only triglycerides and FFA were taken into consideration since they are the main fatty acid in vegetable oil (Zhang *et al.*, 2003a). WVO was specified as a predefined mixture of triolein ($C_{57}H_{104}O_6$) and oleic acid ($C_{18}H_{36}O_2$) which were both available in ABPD® component database. Methyl-oleate ($C_{19}H_{36}O_2$), also available in the component

database was taken as the methyl ester product of the transesterification reaction (See Appendix A-1 for an example of the dialog box for selecting chemical component in ABPD®).

Table 3-1 summarises the definition of all chemical components used in the process simulation.

As for the utilities, low pressure steam, cooling water and electricity were selected (See dialog box example in Appendix A-2). The utilities specifications are shown in Table 3-2.

Table 3-1: Definition of components in the simulation software Aspen Batch Process Developer®

Components		Definitions
Waste vegetable oil	WVO	Defined as a predefined mixture with 5% FFA and 95% TG
Triglycerides	TG	Defined as triolein, which is available in ABPD® components database
Free fatty acid	FFA	Defined as oleic acid, which is available in ABPD® components database
Methanol	MeOH	Available in ABPD® components database
Potassium hydroxide	KOH	Available in ABPD® components database
Hydrochloric acid	HCl	Available in ABPD® components database
Potassium chloride	KCl	Available in ABPD® components database
Water	H ₂ O	Available in ABPD® components database
Glycerol	GLY	Available in ABPD® components database
Biodiesel	FAME	Defined as methyl-oleate, which is available in ABPD® components database

Table 3-2: Specifications of utilities selected in the simulation software Aspen Batch Process Developer®

Utilities	Available temperature (°C)	Available pressure (bar)
Steam (high pressure)	275.6	60
Steam (low pressure)	151.8	5
Cooling water	20	1
Electricity	N/A	N/A

3.3.1.2. CHEMICAL REACTIONS DEFINITIONS

Transesterification and neutralisation were the two chemical reactions involved in the homogeneous process under investigation.

Triolein was selected as the limiting reagent for the transesterification reaction with a 90% conversion to methyl-oleate, while total conversion of potassium hydroxide was assumed for the neutralisation reaction (See dialog box example in Appendix A-3).

3.3.1.3. PROJECT SETUP

The generic plant facility which contains sample pilot-scale and full-scale units from each different equipment class was selected. This facility contains more than 150 equipment units in total.

Triolein and methyl-oleate were respectively chosen as the key input and key output of the process step.

3.3.1.4. PROCESS RECIPE DEVELOPMENT

3.3.1.4.1. SELECTION OF UNIT PROCEDURES

In order to develop the process recipe, the first step is to select a unit procedure by entering the name of the unit procedure and selecting the appropriate equipment. (See dialog box example in Appendix A-5 and Appendix A-6)

3.3.1.4.2. EQUIPMENT ITEMS SELECTION

All equipment involved in the simulation of the base case homogeneous process was chosen under the generic plant facility option. The different equipment classes selected from ABPD® equipment catalogue included tanks (mixing tanks, settling tanks and holding tanks), reactor vessels, evaporation unit, pumps and heat exchangers.

3.3.1.4.3. SELECTION OF UNIT OPERATIONS

ABPD® contains four types of unit operations classes (batch, continuous, biotechnology, and chromatography), each containing several units operations as shown in the menu for selection of unit operations in Appendix A-6. For each operation selected is to be initialised with the appropriate engineering data such as charge quantities, scheduling relations, temperature, pressures, percent separation, etc. (See dialog box example in Appendix A-7).

The different unit operations selected for this process include: *Charge*, *Transfer*, *React*, *Decant*, *Distill continuously* and *Adjust pH*.

The *Charge* operation required the input of the charge quantity of a particular chemical component as well as the selection of the destination equipment unit. For the *Transfer* operation, the shortcut transfer model was selected and only required to specify the source and destination units. As for both the *React* and *Adjust pH* operations, the shortcut react model was selected. This operation model considers the reactors as conversion reactors and requires to select the

appropriate reaction data sets and also input the reaction time and final reaction temperature. *Decant* operations were used to simulate the gravity separations processes. Decanting time and percent separations were to be specified. As for the *Distill continuously* operations they were used to simulate the evaporation units. Percent separations were specified.

All process conditions and equipment units specified in the simulation software for the base case homogeneous process are presented in Table 3-3. As for the sequence of unit operations, it is shown in the process recipe presented in Table 3-4 and Table 3-5.

3.3.1.4.4. PLANT CAPACITY DEFINITION

In the early stage of the simulation, the recipe was specified for a WVO charge quantity of 1500 kg/batch. Once all the input for the process recipe were complete, the simulation algorithm conducted mass and energy balance calculations and provided information on occupancy time and required equipment capacity. Appropriate equipment capacity was edited and then the scale up algorithm of the process simulator was used to scale up the recipe to the maximum batch size in the size limiting equipment unit.

Table 3-3: Process conditions for the KOH process input in the simulation software Aspen Batch Process Developer®

Operation	Equipment type	Unit ID	T°C	Pressure	Conditions	References
Oil heating	Double pipe heat exchanger	E-101	60	1 atm	-	-
Methoxide preparation	Tank	V-101	25	1 atm	• 6:1 MeOH to TG molar ratio • 2% w/w. of KOH (with respect to oil)	Babajide (2011) ^a
Transesterification reaction	Stirred tank reactor	R-101	60	1 atm	• 90 min reaction • 90% TG conversion	Babajide (2011)
Biodiesel/ glycerol separation	Cone bottomed vessel	V-102 V-103 ^b	-	1 atm	• 8 h settling time • 99.99% FAME and 0.01% glycerol in oil phase • 70% MeOH and 80% unspecified component to glycerol phase	Mbohwa and Mudiwakure (2013) ^c
Methanol removal (FAME phase)	Evaporator unit	K-101 V-104 ^b	HP steam ^d	1 atm	Methanol evaporation: 98.5%	-
Neutralisation and washing	Cone bottomed vessel	V-105 V-106 V-107 ^b	-	1 atm	• 2h neutralisation • 2 steps washing • 28% v/v of water (to FAME) per step • 1:1 HCl to KOH molar ratio for the 1st step • 8h settling time after each wash ^c	Dermibas (2009)
FAME drying	Evaporator unit	K-102	HP steam ^d	Vacuum (0.2 bar)	Water and MeOH evaporation 99%	-

a: Values of the catalyst loading modified from 1.5% to 2% to account for the higher FFA content of the oil considered in this study
b: Intermediate holding tanks
c: Relative to the settling time reported by Mbohwa and Mudiwakure (2013).
d: High pressure steam was selected by the process simulation

Table 3-4: Recipe of a KOH catalysed batch biodiesel process of capacity 1618 kg/batch

Unit operations	Unit ID	Operations
1. Oil heating	E-101	1.1 Charge Reactor vessel R-101 with 1797.27 kg of WASTE COOKING OIL. Material is charged from WVO storage using Pump P-101. Transfer the feed through Oil preheater E-101. The outlet temperature of the heat exchanger is 60 C.
2. Methoxide preparation	V-101	2.1 Charge Mixing tank V-101 with 6 kmole of METHANOL per 1 kmole of TRIOLEIN in unit Reactor vessel R-101. Material is charged from Fresh MeOH storage.
		2.2 Charge Mixing tank V-101 with 0.02 kg of POTASSIUM-HYDROXIDE per 1 kg of TRIOLEIN in unit Reactor vessel R-101. Material is charged from Storage. Dissolve 100% of all solids.
3. Transesterification reaction	R-101	3.1 Transfer contents of unit Mixing tank V-101 to Reactor vessel R-101. Transfer using Pump P-102.
		3.2 React in unit Reactor vessel R-101 via KOH transesterification. Reaction occurs over 90 min. The final temperature of the batch is 60 C.
		3.3 Transfer contents of unit Reactor vessel R-101 to Settling tank V-102. Transfer using Pump P-103.
4. Biodiesel- glycerol separation	V-102	4.1 Decant in unit Settling tank V-102 over 8 h. Separation is: 99.99% of METHYL-OLEATE goes to Top, 99.99% of GLYCEROL goes to Bottom, 70% of METHANOL goes to Bottom, 80% of OLEIC-ACID goes to Top and 80% of POTASSIUM-HYDROXIDE goes to Bottom. Unspecified materials go to Bottom. Upper Layer Transfer Stream: The stream is sent to Holding tank V-103.
		4.2 Transfer contents of unit Settling tank V-102 to Crude glycerol storage. The transfer stream belongs to category: Hazardous Waste. Transfer using Pump P-104.
5. Methanol removal (FAME phase)	K-101	5.1 Distill continuously the mixture from unit Holding tank V-103 in unit Methanol evaporator K-101. The mixture feed rate is 500 kg/h. Separation is: 98.5% of METHANOL goes to Overhead. Unspecified materials go to Bottoms. Distillate Stream: The distillate is sent to Unreacted MeOH storage. Bottoms Stream: bottom stream is sent to Holding tank V-104.
		5.2 Transfer contents of unit Holding tank V-104 to Washing vessel V-105. Transfer using Pump P-105.

Table 3-5: Recipe of a KOH catalysed batch biodiesel process of capacity 1618 kg/batch (continued)

Unit operations	Unit ID	Operations
6. Neutralisation and washing	V-105 V-106	6.1 Charge Washing vessel V-105 with 0.28 litre of WATER per 1 litre of METHYL-OLEATE in unit Washing vessel V-105. Material is charged from Tap water.
		6.2 Charge Washing vessel V-105 with 1 kmole of HYDROGEN-CHLORIDE per 1 kmole of POTASSIUM-HYDROXIDE in unit Washing vessel V-105.
		6.3 Adjust pH in unit Washing vessel V-105. The final pH is 7. pH adjust via reaction Neutralisation. Reaction time is 2 h.
		6.4 Decant in unit Washing vessel V-105 over 8 h. Separation is: 90% of WATER goes to Bottom, 95% of POTASSIUM-CHLORIDE goes to Bottom, 100% of METHYL-OLEATE goes to Top and 85% of OLEIC-ACID goes to Bottom. Unspecified materials go to Bottom. Upper Layer Transfer Stream: The stream is sent to Washing vessel V-106.
		6.5 Transfer contents of unit Washing vessel V-105 to Waste water storage. The transfer stream belongs to category: High BOD Waste. Transfer using Pump P-106.
		6.6 Charge Washing vessel V-106 with 0.28 litre of WATER per 1 litre of METHYL-OLEATE in unit Washing vessel V-106. Material is charged from Tap water.
		6.7 Decant in unit Washing vessel V-106 over 8 h. Separation is: 85% of WATER goes to Bottom and 100% of METHYL-OLEATE goes to Top. Unspecified materials go to Bottom. Upper Layer Transfer Stream: The stream is sent to Holding tank V-107.
		6.8 Transfer contents of unit Washing vessel V-106 to Waste water storage. The transfer stream belongs to category: High BOD Waste. Transfer using Pump P-107.
7. FAME drying	K-102	7.1 Distill continuously the mixture from unit Holding tank V-107 in unit FAME dryer K-102. Separation is: 99% of WATER goes to Overhead and 99% of METHANOL goes to Overhead. Unspecified materials go to Bottoms. The bottoms pressure is 0.2 bar. Distillate Stream: The distillate is sent to Atmosphere. Bottoms Stream: The bottom stream is sent to Biodiesel storage. Transfer using Pump P-108.

3.4. MODIFICATION OF THE BASE CASE MODEL FROM HOMOGENEOUS TO HETEROGENEOUS CATALYSIS PROCESS

This section discusses the changes made to the base case homogeneous process model in order to convert it to a heterogeneous process in the simulator ABPD®.

Since the purpose is to evaluate the economic impact of converting an existing homogeneous process to heterogeneous, no changes were made in the capacity of process equipment that are similar to the ones used for the KOH process.

Calcium oxide was selected as the heterogeneous catalyst for the modified process because of its relatively high basic strength, low solubility in methanol, long catalyst life and its requirement for moderate reaction conditions as discussed in section 2.4.1.2.1 of the previous chapter.

The modification of the type of catalyst used, necessitated the modification of process conditions for the transesterification reaction. The new process conditions applied were based on Akhiero (2014) study who reported a 97.75% yield of biodiesel from the transesterification of *Jatropha* seed oil under the following conditions: 1 wt. % CaO, 65°C, 60 min and 10:1 methanol to oil molar ratio. Since the percentage conversion of oil was not reported, a 90% conversion of TG to FAME and a 70 % conversion of FFA to FAME were assumed under these conditions.

With the use of CaO solid catalyst, the downstream purification steps were also to be modified. The neutralisation, water washing and drying steps required for the KOH catalyst removal were eliminated. Centrifugation and filtration have been reported as appropriate methods for solid catalyst removal (Semwal *et al.*, 2011). For this process, filtration has been selected. However, the effect of using centrifugation instead of filtration as the catalyst removal method for the heterogeneous process is reported in Chapter 6 of this thesis.

3.4.1. PROCESS SIMULATION OF THE MODIFIED HETEROGENEOUS PROCESS

The heterogeneous process was simulated similarly to the homogeneous process using ABPD®, with the replacement of potassium hydroxide by calcium oxide which was also available in the software component database. For the heterogeneous process, both the transesterification and esterification reaction were considered. The process conditions and process recipe for the heterogeneous catalysed process are presented in Table 3-6 and Table 3-7.

Table 3-6: Process conditions for the modified CaO process input in the simulation software Aspen Batch Process Developer®

Operation	Equipment type	Equipment ID	T°C	Conditions	References
Oil heating	Double pipe heat exchanger	E-201	65	-	-
Methanol/ CaO mixing	Tank	V-201	25	<ul style="list-style-type: none"> • 10:1 MeOH to TG molar ratio • 1% w/w. of CaO (with respect to oil) 	Akhihiero (2014)
Transesterification reaction	Stirred tank reactor	R-201	65	<ul style="list-style-type: none"> • 60 min reaction • 90% TG conversion ^a • 70% FFA conversion ^a 	Akhihiero (2014)
Catalyst removal	Filter	Fr-201 V-202 _b	-	• Separation of 99.99% of solid FAME	-
Methanol removal (FAME phase)	Evaporator unit	K-201 V-203 ^b	Use HP steam	Methanol evaporation: 98.5%	-
Biodiesel/glycerol separation	Cone bottomed vessel	V-204	-	<ul style="list-style-type: none"> • 8 h settling time • 99.99% FAME and 0.01% glycerol in oil phase • 80% unspecified component to glycerol phase 	-
<p>a : Percentage conversion assumed in order to meet the 97.75% yield of biodiesel based on Akhihiero (2014) study</p> <p>b : Intermediate holding tanks</p> <p>All operations performed at atmospheric pressure</p>					

Table 3-7: Recipe of the modified CaO catalysed batch biodiesel process of capacity 1433 kg/batch

Unit operation	Unit ID	Operation
1. Oil heating	E-201	1.1 Charge Reactor vessel R-201 with 1583.71 kg of WASTE COOKING OIL. Material is charged from WVO storage using Pump P-201. Transfer the feed through Oil preheater E-201. The outlet temperature of the heat exchanger is 65 C.
2. Methanol/ CaO mixing	V-201	2.1 Charge Mixing tank V-201 with 10 kmole of METHANOL per 1 kmole of TRIOLEIN in unit Reactor vessel R-201. Material is charged from Fresh MeOH storage.
		2.2 Charge Mixing tank V-201 with 0.01 kg of CALCIUM-OXIDE per 1 kg of TRIOLEIN in unit Reactor vessel R-201. Material is charged from Storage.
3. Transesterification reaction	R-201	3.1 Transfer contents of unit Mixing tank V-201 to Reactor vessel R-101. Transfer using Pump P-202.
		3.2 React in unit Reactor vessel R-201 via CaO transesterification. Reaction occurs over 60 min. The final temperature of the batch is 65 C.
4. Catalyst removal	Fr-201	4.1 Filter the batch from unit Reactor vessel R-201 in filter Fr-201. The mother liquor is sent to Holding tank V-202 using Pump P-203. The filter separates 99.99% of all solids.
5. Methanol removal (FAME phase)	K-201	5.1 Distill continuously the mixture from unit Holding tank V-202 in unit Methanol evaporator K-201. Separation is: 99.98% of METHANOL goes to Overhead. Unspecified materials go to Bottoms. Distillate Stream: The distillate is sent to Unreacted MeOH storage. Bottoms Stream: The bottom stream is sent to Holding tank V-203.
		5.2 Transfer contents of unit Holding tank V-203 to Settling tank V-204. Transfer using Pump P-204.
6. Biodiesel/ glycerol separation	V-204	6.1 Decant in unit Settling tank V-204 over 8 h. Separation is: 99.99% of GLYCEROL goes to Bottom, 99.99% of METHYL-OLEATE goes to Top, 80% of OLEIC-ACID goes to Bottom and 80% of METHANOL goes to Bottom. Unspecified materials go to Bottom. Upper Layer Transfer Stream: The stream is sent to Biodiesel storage. Transfer using Pump P-205.

3.5. PROCESS SIMULATION RESULTS

After simulation of both processes, simulation reports were generated from the ABPD® simulator. Output reports considered included executive summary, equipment capacities, utilities and material balance reports.

Henceforth, the terms KOH process and CaO process will be employed to refer to the homogeneous KOH and heterogeneous CaO catalysed process for biodiesel production respectively.

3.5.1. PROCESS SIMULATION RESULTS FOR THE KOH PROCESS

Figure 3-1 shows the process flow sheet for the KOH process. The composition of all inlet and outlet streams is presented in Table 3-8. Stream numbers from the process flow diagram are associated to the relevant operation number as presented in Table 3-4 and Table 3-5.

Table 3-9 displays the characteristics of the main equipment involved in the KOH process. The capacity of all process vessels suggested by the simulator were harmonised to standard sizes (3m^3 and 1m^3) for ease of costing.

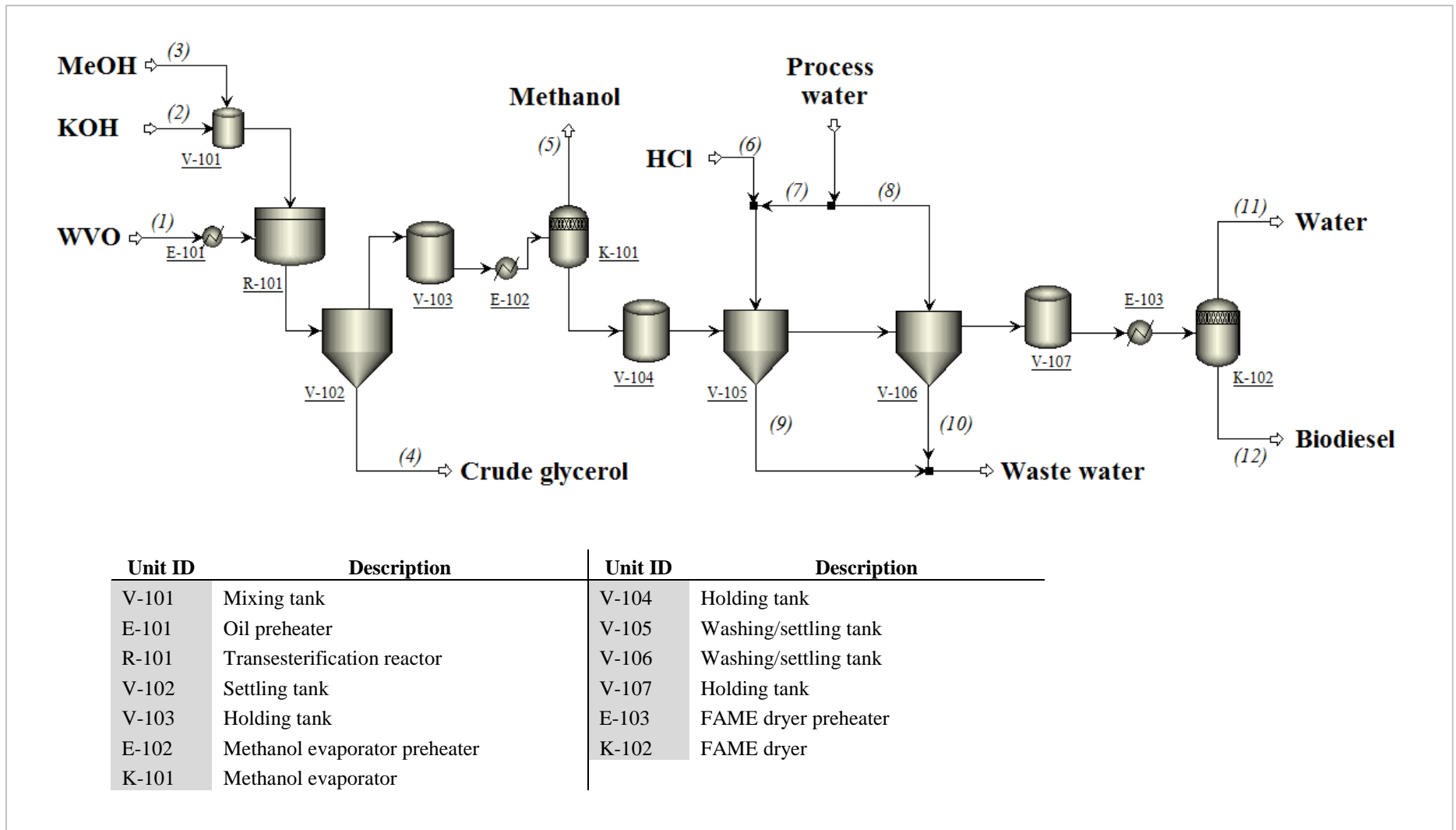


Figure 3-1: Process flow diagram of the KOH catalysed process for biodiesel production

Table 3-8: Stream table of the KOH catalysed process for biodiesel production (1618 kg/batch)

a. Feed streams (KOH process)						
Stream number	1	3	2	7	6	8
Operation number	1.1	2.1	2.2	6.1	6.2	6.5
From unit	WVO storage	MeOH storage	KOH storage unit	Tap water	HCl storage unit	Tap water
To unit	Oil preheater E-101	Mixing tank V-101	Mixing tank V-101	Washing vessel V-104	Washing vessel V-104	Washing vessel V-106
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0
Pressure (kPa)	101.3	101.3	101.3	101.3	101.3	101.3
Total volume (L/batch)	1964.4	492.9	17.5	554.3	3.9	525.2
Total mass (kg/batch)	1797.3	388.3	35.8	554.3	4.6	525.2
<i>Component mass fraction</i>						
Triolein	0.995	-	-	-	-	-
Oleic acid	0.005	-	-	-	-	-
Methanol	-	1.000	-	-	-	-
Potassium hydroxide	-	-	1.000	-	-	-
Water	-	-	-	1.000	-	1.000
Hydrochloric acid	-	-	-	-	1.000	-

b. Product streams (KOH process)						
Stream number	4	5	9	10	11	12
Operation number	4.2	5.1	6.5	6.8	7.1	7.1
From unit	Settling tank V-102	MeOH evaporator K-101	Washing vessel V-105	Washing vessel V-106	FAME dryer K-102	FAME dryer K-102
To unit	Crude glycerol storage	Unreacted MeOH storage	Waste water storage	Waste water storage	Atmosphere	Biodiesel storage
Temperature (°C)	59.9	64.7	36.7	27.7	60.1	77.4
Pressure (kPa)	101.3	101.3	101.3	101.3	20.0	20.0
Total volume (L/batch)	542.8	84.3	513.6	495.2	86.3	1938.8
Total mass (kg/batch)	526.3	63.1	517.0	495.2	86.2	1617.5
<i>Component mass fraction</i>						
Triolein	0.3398	0.0000	0.0000	0.0000	0.0000	0.0000
Oleic acid	0.0034	0.0000	0.0118	0.0022	0.0000	0.0000
Methanol	0.2841	1.0000	0.0019	0.0000	0.0000	0.0000
Potassium hydroxide	0.0544	0.0000	0.0000	0.0000	0.0000	0.0000
Potassium chloride	0.0000	0.0000	0.0000	0.0010	0.0000	0.0000
Water	0.0000	0.0000	0.9688	0.9969	1.0000	0.0005
Hydrochloric acid	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Methyl-oleate	0.0003	0.0000	0.0000	0.0000	0.0000	0.9995
Glycerol	0.3181	0.0000	0.0000	0.0000	0.0000	0.0000

Table 3-9: Specifications of the main equipment units involved in the KOH process for biodiesel production

Equipment unit	ID	Required capacity ^a	Actual capacity ^b	Material of construction
Reactor vessel	R-101	3.00 m ³	3.00 m ³	CS
Mixing tank	V-101	0.60 m ³	1.00 m ³	CS
Settling tank	V-102	3.00 m ³	3.00 m ³	CS
Holding tank	V-103	2.36 m ³	3.00 m ³	CS
Holding tank	V-104	2.34 m ³	3.00 m ³	CS
Washing vessel	V-105	2.88 m ³	3.00 m ³	SS304
Washing vessel	V-106	2.88 m ³	3.00 m ³	CS
Holding tank	V-107	2.93 m ³	3.00 m ³	CS
Methanol evaporator	K-101	-	3.00 m ³	CS
FAME dryer	K-102	-	3.00 m ³	CS
Oil preheater	E-101	-	1.22 m ²	CS
Methanol evaporator preheater	E-102	-	0.10 m ²	CS
FAME dryer preheater	E-103	-	0.17 m ²	CS
Pumps	P-101 to 8		1 kW	Cast iron
a: Required capacity suggested by the process simulator (accounts for 85% fill capacity) b: Harmonised capacity for ease of costing				

3.5.2. PROCESS SIMULATION RESULTS OF THE CaO PROCESS

Figure 3-2 shows the process flowsheet for the CaO process. The composition of all inlet and outlet streams is presented in Table 3-10. Stream numbers from the process flow diagram are associated to the relevant operation number as presented in Table 3-7.

Table 3-11 displays the characteristics of the main equipment units involved in the CaO process. All equipment units employed for the CaO process that are similar to the ones involved in the KOH process had their sizes kept unchanged.

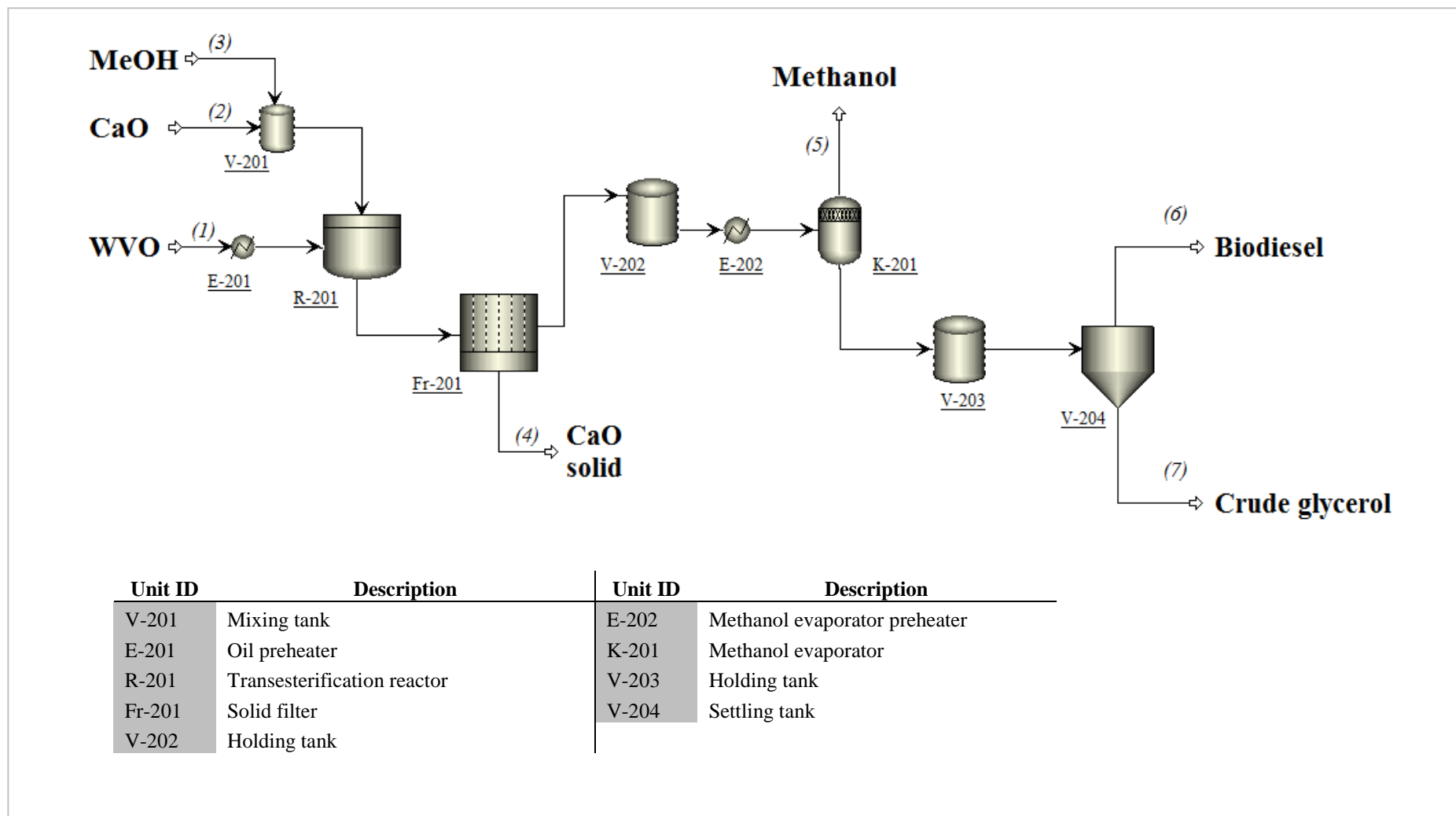


Figure 3-2: Process flow diagram of the modified CaO catalysed process for biodiesel production

Table 3-10: Material stream table for the modified CaO process for biodiesel production (1433 kg/batch)

a. Feed streams			
Stream number	1	3	2
Operation number	1.1	2.1	2.2
From unit	WVO storage	MeOH storage	CaO storage unit
To unit	Oil preheater E-201	Mixing tank V-201	Mixing tank V-201
Temperature (°C)	25.0	25.0	25.0
Pressure (kPa)	101.3	101.3	101.3
Total volume (L/batch)	1731.02	723.90	4.70
Total mass (kg/batch)	1583.71	570.24	15.76
<i>Component mass fraction</i>			
Triolein	0.995	-	-
Oleic acid	0.005	-	-
Methanol	-	1.000	-
Potassium hydroxide	-	-	1.000
Water	-	-	-
Hydrochloric acid	-	-	-

b. Product streams				
Stream number	4	5	6	7
Operation number	4.1	5.1	6.1	6.2
From unit	Filter	MeOH evaporator K-201	Settling tank V-204	Settling tank V-204
To unit	Filter pot	Unreacted MeOH storage	Biodiesel storage	Crude glycerol storage
Temperature (°C)	65.0	64.7	75.3	75.3
Pressure (kPa)	101.3	101.3	101.3	101.3
Total volume (L/batch)	0.00	552.32	1714.40	284.75
Total mass (kg/batch)	15.76	413.58	1433	300.94
<i>Component mass fraction</i>				
Triolein	0.0000	0.0000	0.0000	0.5011
Oleic acid	0.0000	0.0000	0.0003	0.0063
Methanol	0.0000	1.0000	0.0000	0.0002
CaO	1.0000	0.0000	0.0000	0.0000
Water	0.0000	0.0000	0.0000	0.0012
Methyl-oleate	0.0000	0.0000	0.9996	0.0005
Glycerol	0.0000	0.0000	0.0000	0.4907

Table 3-11: Specifications of the main equipment involved in the CaO process for biodiesel production

Equipment unit	ID	Required capacity ^a	Actual capacity ^b	Material of construction
Reactor vessel	R-201	3.00 m ³	3.00 m ³	CS
Mixing tank	V-201	0.86 m ³	1.00 m ³	CS
Holding tank	V-202	2.98 m ³	3.00 m ³	CS
Holding tank	V-203	2.36 m ³	3.00 m ³	CS
Settling tank	V-204	2.36 m ³	3.00 m ³	CS
Methanol evaporator	K-201	-	3.00 m ³	CS
Oil preheater	E-201	-	1.22 m ²	CS
Methanol evaporator preheater	E-202	-	0.10 m ²	CS
Solid filter	Fr-201	-	-	CS
Pumps	P-101 to 6		1 kW	Cast iron
a: Required capacity suggested by the process simulator (accounts for 85% fill capacity) b: Harmonised capacity for ease of costing				

3.6. PROCESSES PERFORMANCE COMPARISON

In this section, the performance of the KOH and modified CaO processes will be compared in terms of scheduling, process productivity (product and by-product) and process consumption (raw materials and energy).

3.6.1. PROCESS SCHEDULING

Figure 3-3 shows that the duration of one batch for the KOH process was 37.51 hours, which is about 2.5 times longer than that of the CaO process with 15.20 hours (Figure 3-4). This is mainly due to the neutralisation and washing steps, which are the longest operations that happen over 20.44 hours considering the settling times, charge times and holding times (Figure 3-3). This indicates that the washing and neutralisation operations are the bottleneck of the entire process. A modification of the process to reduce the duration of the separation procedures is addressed in Chapter 6 of this thesis.

In this study, an operating year of 330 days (7 920 hours) was specified. In order to increase the number of batches that can be processed per year, hence the production capacity, the overlapping sequencing of batches was assumed. This occurs when the time limiting operation repeats itself without waiting time between batches.

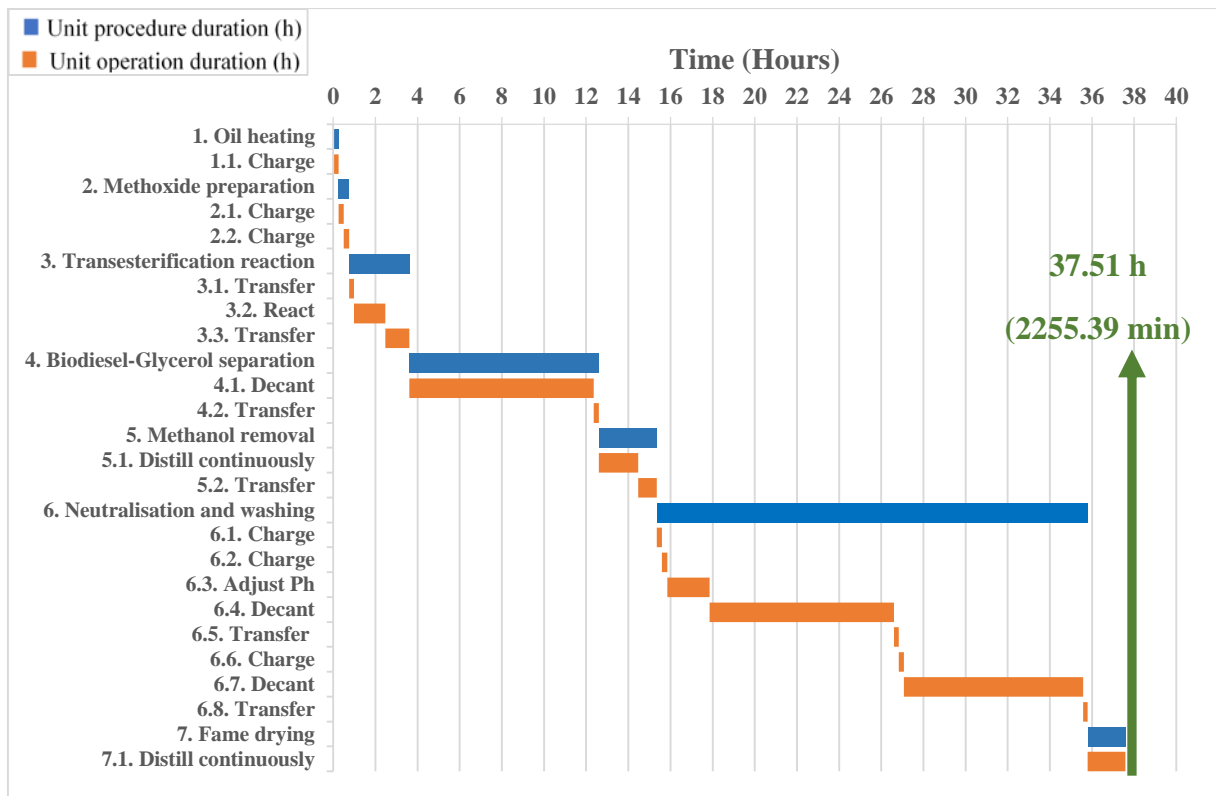


Figure 3-3: Process scheduling of the KOH process for biodiesel production

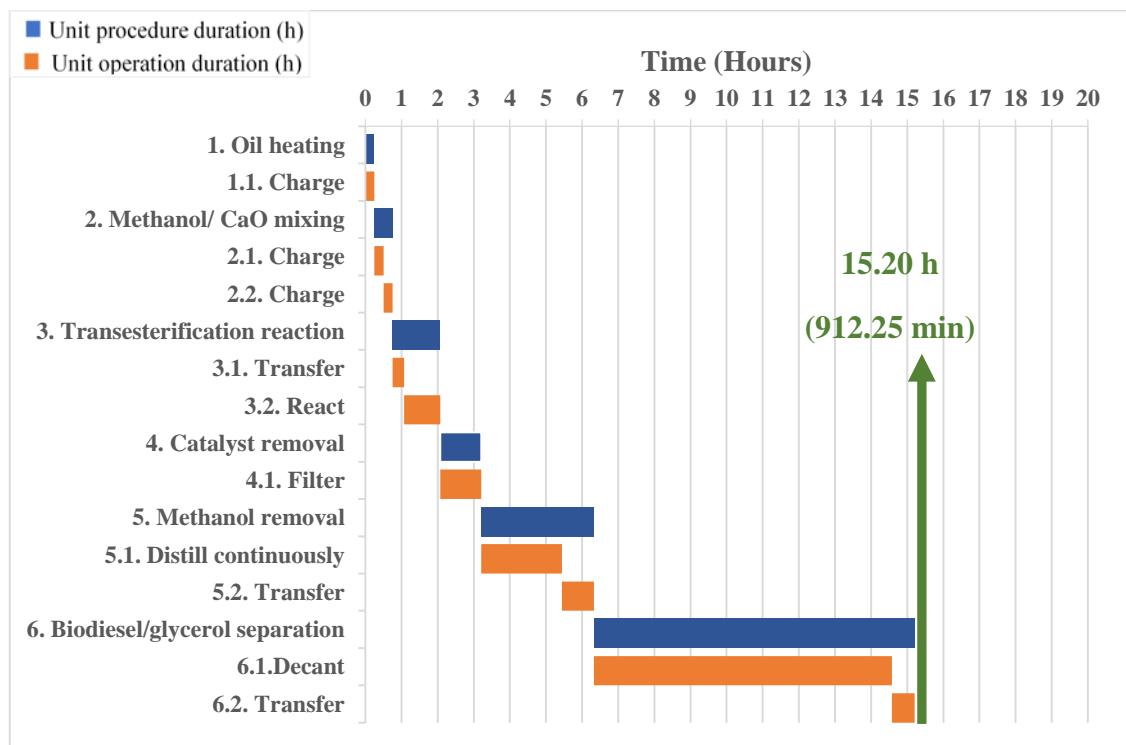


Figure 3-4: Process scheduling of the CaO process for biodiesel production

The process simulator estimated a maximum number of batches of 639 and 810 for the KOH and CaO processes respectively. The fewer number of batches for the KOH process is expected due to the longer batch time.

3.6.2. PROCESS PRODUCTIVITY

Biodiesel and glycerol productions (in a batch and annual basis) for the KOH and CaO processes are presented in Table 3-12.

Table 3-12: Biodiesel and glycerol production in a batch and annual basis for the KOH and CaO processes

	Biodiesel production		Glycerol production	
	KOH process	CaO process	KOH process	CaO process
kg/batch	1618	1433	526	301
ton/year	1033.6	1160.5	335.8	243.8

Figure 3-5 shows a 11.4% reduction in the biodiesel production per batch for the CaO process in comparison to the KOH process. This is due to the increase in the methanol to oil ratio for the CaO process (10:1 vs 6:1 for KOH process). Indeed, this increase in the amount of methanol would require an increase in the reactor volume in order to achieve the same production output as the KOH process. However, since the size of similar equipment between the KOH and CaO processes was kept the same, it resulted in a reduction in the reactor volume efficiency.

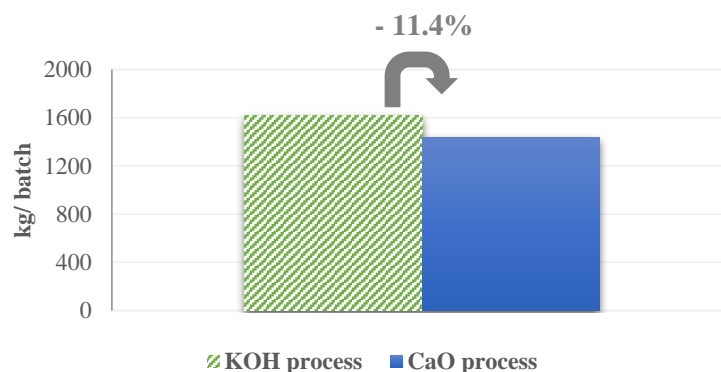


Figure 3-5: Comparison of biodiesel production in a batch basis for the KOH and CaO processes

Because of the higher number of batches for the CaO process, resulting from the reduction in the total batch time, the annual production of biodiesel for the CaO process is found to be 12.3% higher than that of the KOH process (Figure 3-6). The CaO process is therefore expected to have a higher revenue from sales when compared to the KOH process.

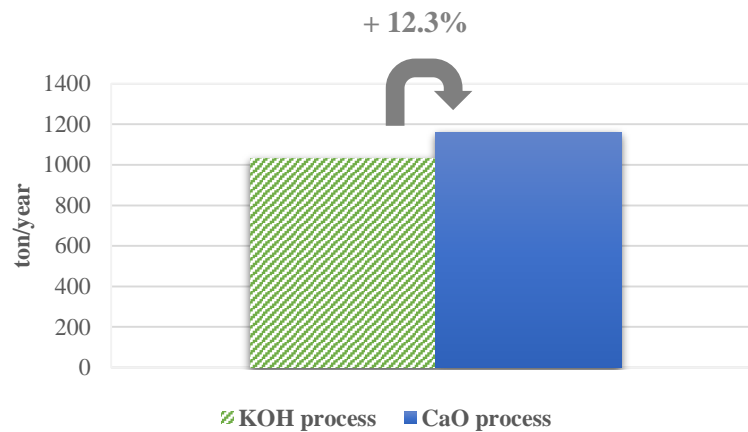


Figure 3-6: Comparison of the annual biodiesel production for the KOH and CaO processes

As regards the glycerol production, the conversion of this batch biodiesel production process from KOH to CaO catalysis reduces the annual glycerol production by 27.4 % (Figure 3-6). This implies that the profit that the industrial plant can obtain from glycerol, if any, is much lower when the plant operates on the CaO process.

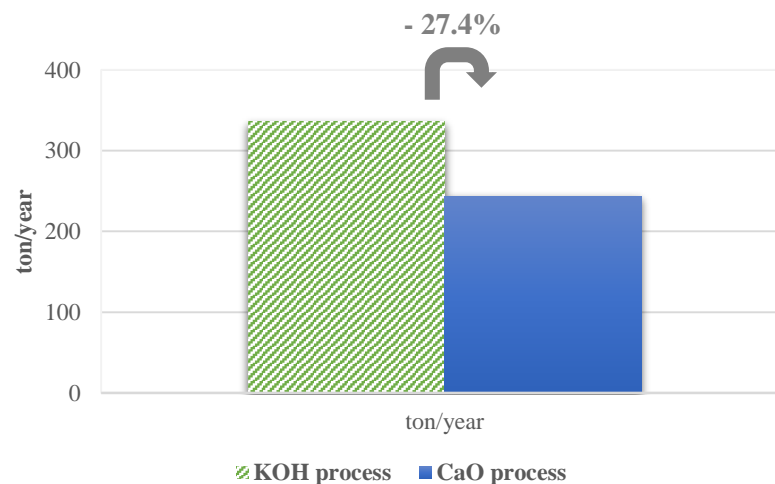


Figure 3-7: Comparison of the annual glycerol production from the KOH and CaO processes

3.6.3. COMPARISON OF THE PROCESS CONSUMPTION FOR THE KOH AND CaO PROCESSES

3.6.3.1. RAW MATERIAL CONSUMPTION

Table 3-13 shows the different raw materials consumption for the KOH and CaO processes. It can be noted that converting the KOH to CaO process by fixing the size of equipment used, led to a reduction in the WVO initial charge amount per batch of about 12%. However with respect

to the amount of biodiesel produced through each process, this difference is marginal (Figure 3-8).

Table 3-13: Raw materials consumption for the KOH and CaO processes

Raw materials	KOH process		CaO process	
	kg/ batch	kg/kg biodiesel produced	kg/ batch	kg/kg biodiesel produced
WVO	1797.3	1.111	1583.7	1.105
MeOH	388.3	0.240	570.2	0.398
KOH	35.8	0.022	-	-
CaO	-	-	15.8	0.011
Water	1079.4	0.667	-	-
HCl	4.6	0.003	-	-
Total	3305.4	2.043	2169.7	1.514

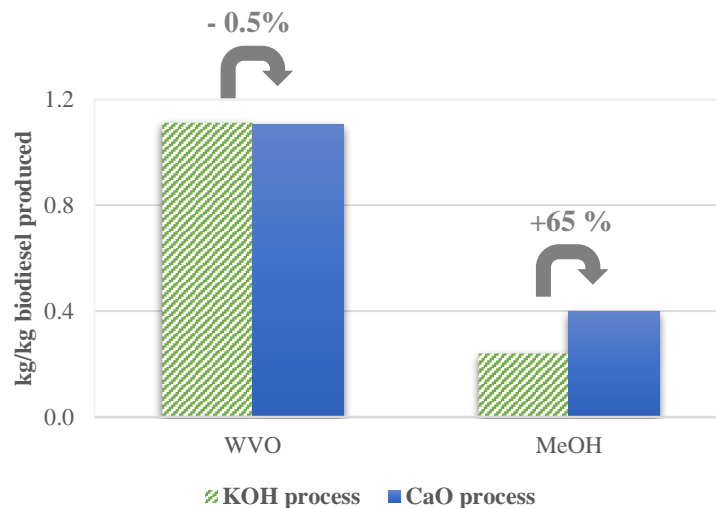


Figure 3-8: Comparison of the WVO and MeOH consumption for the KOH and CaO processes

Regarding the methanol consumption, an increase of about 47% is observed when changing from KOH to CaO process on a batch basis (Table 3-13). This correspond to an even higher amount of methanol required per kg of biodiesel produced (+65%) for the CaO process, relative to the KOH process (Figure 3-8). As regards the total raw material consumption, the CaO process requires 26% less raw materials per unit of biodiesel produced with 1.51 kg/kg as opposed to 2.04 kg/kg for the KOH process (Table 3-13). Since the raw materials account for the major part of the total manufacturing as demonstrated in Section 2.5.2, it can be assumed that the CaO process would have a lower unit manufacturing cost than the KOH process.

3.6.3.2. ENERGY CONSUMPTION

This section compares the energy consumed during the production of biodiesel from the KOH and CaO catalysed process. The energy consumed during both processes is provided by steam, cooling water and electricity.

3.6.3.2.1. STEAM AND COOLING WATER CONSUMPTION

Steam and cooling water consumptions for KOH and CaO processes are summarised in Table 3-14 and Table 3-15. The utility reports from the process simulator are shown in Appendix A-9 and Appendix A-10.

Table 3-14: Steam and cooling water consumption for the KOH process

Equipment ID	Unit operation	kg/batch	ton/year	kg/kg biodiesel produced	MJ/batch
a. Steam (High pressure)					
E-101	Oil heating	82.01	52.40	0.05	128.25
R-101	Transesterification	146.57	93.66	0.09	309.86
K-101 (E-102)	Methanol removal	57.21	36.56	0.04	89.48
K-102 (E-103)	FAME drying	152.59	97.51	0.09	238.64
TOTAL		438.38	280.13	0.27	766.23
b. Cooling water					
K-101 (E-102)	Methanol removal	5 775.40	3 690.48	3.57	64.67
K-102 (E-103)	FAME drying	5 813.08	3 714.56	3.59	200.12
TOTAL		11 588.48	7 405.04	7.16	264.79

Table 3-15: Steam and cooling water consumption for the CaO process

Equipment ID	Unit operation	kg/batch	ton/year	kg/kg biodiesel produced	MJ/batch
a. Steam (High pressure)					
E-201	Oil heating	82.79	67.06	0.06	129.47
R-201	Transesterification	183.39	148.55	0.13	286.80
K-201 (E-202)	Methanol removal	302.45	244.98	0.21	473.01
TOTAL		568.63	460.59	0.40	889.28
b. Cooling water					
K-201 (E-102)	Methanol removal	7 243.32	5 867.09	5.06	453.80
TOTAL		7 243.32	5 867.09	5.06	453.80

The steam consumption per batch for the CaO process (568.63 kg/batch) is higher than that of the KOH process (438.38 kg/batch) (Table 3-14a and Table 3-15a). The higher steam consumption for the CaO process can be attributed to the methanol removal operation which alone accounts for 53.2% of the total consumption. Comparatively, the methanol removal operation of the CaO process consumes 5.3 fold more steam than the KOH process. This is due

to the higher amount of methanol in the inlet stream of the evaporator K-201, which requires a higher energy input in order to evaporate most of the methanol present.

Overall there is a 48.1% increase in the steam consumption per kg of biodiesel when converting from the KOH and CaO (Figure 3-9).

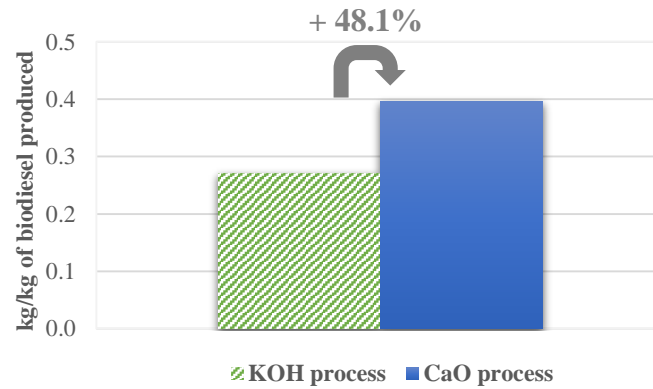


Figure 3-9: Comparison of the steam consumption per kg of biodiesel produced for the KOH and CaO processes

Cooling water was selected for the condensing steps of the evaporation operations. The total cooling water consumption per kg of biodiesel produced for the CaO process is found to be 29.3% lower than that of the KOH process (Figure 3-10). This is due to the fact that cooling water is only used in one unit operation in the CaO process, whereas in the KOH process it is used in two unit operations. However, considering the methanol removal operation alone, there is a 41.7% increase in the cooling water consumption when converting from KOH to CaO process, due to the higher amount of methanol used in the CaO process.

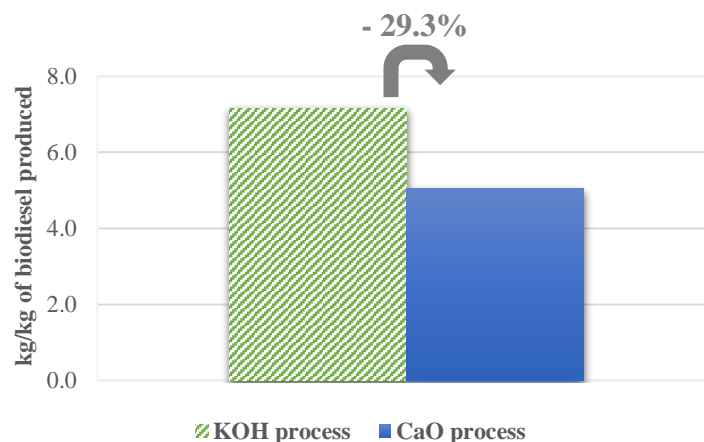


Figure 3-10: Comparison of the cooling water consumption per kg of biodiesel produced for the KOH and CaO processes

3.6.3.2.2. POWER CONSUMPTION

Since the cost of heating was accounted for in the cost of steam, the power consumption for each process was evaluated by considering only pumping and agitation. Regarding pumping, a pump power requirement of 1 kW was estimated for each pump since it is the minimum pump power allowed by the CAPCOST software that was used for equipment costing. The total power consumption from pumping was estimated by multiplying the power requirement for all pumps with the total pumping time calculated from the stream table report generated by the process simulator (Appendix A-11 and Appendix A-12).

Regarding agitation, the power consumed was calculated using McCabe *et al.* (1993) suggestion that power supply in the range of 0.1 to 0.2 kW/m³ provide mild mixing and 0.4 to 0.6 kW/m³ provide vigorous mixing. Vigorous mixing was assumed for the entire duration of the transesterification reactions (units R-101 and R-201), for mixing catalyst and methanol (units V-101 and V-201) and in the case of KOH process, it was assumed for the duration of the pH adjustment operation (unit V-105). Mild mixing was assumed for the charge time of process water in the second washing step (unit V-106). See Figure 3-1 and Figure 3-2 for the reference of equipment ID and Figure 3-3 and Figure 3-4 for the duration of process operations. The power consumption for the KOH and CaO processes is presented in Table 3-16 and Table 3-17.

The power consumption per ton of biodiesel produced for the CaO process is 22.5% lower than that of the KOH process (Figure 3-11). The difference can be attributed to the elimination of the washing steps in the CaO process as well as the fewer number of pumps.

Table 3-16: Power consumption for the KOH process

Equipment ID	Unit procedure	kWh/batch	kWh/ton biodiesel produced	MJ/batch
R-101	React	2.30	1.42	0.64
V-101	Charge	0.08	0.16	0.02
V-105	Adjust pH (React)	3.06	1.89	0.85
V-106	Charge (mixing)	0.12	0.08	0.03
P-101 to P-108	Transfer + charge	41.49	25.65	11.52
TOTAL		47.04	29.19	13.07

Table 3-17: Power consumption for the CaO process

Equipment ID	Unit procedure	kWh/batch	kWh/ton biodiesel produced	MJ/batch
R-201	React	1.53	1.07	0.43
V-201	Charge	0.11	0.08	0.03
P-201 to P-207	Transfer + charge	30.77	21.47	8.55
TOTAL		32.41	22.62	9.00

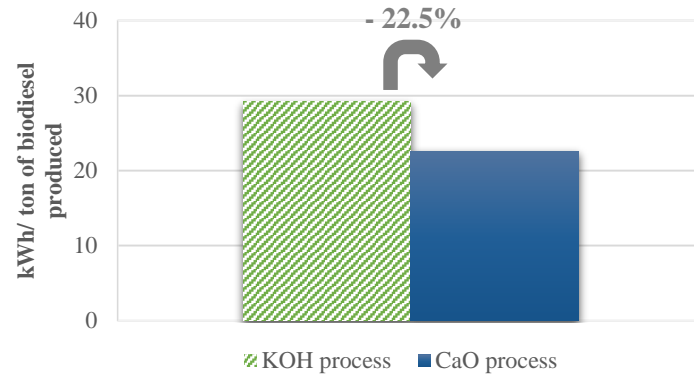


Figure 3-11: Comparison of the power consumption per ton of biodiesel produced for the KOH and CaO processes

3.6.3.2.3. TOTAL ENERGY CONSUMPTION

The overall energy consumption per kg of biodiesel produced for the CaO process was found to be almost 45% higher when converting from KOH to heterogeneous process (Figure 3-12).

Table 3-18: Total energy consumed for the KOH and CaO processes

	MJ/batch	MJ/kg biodiesel produced
KOH process	1,044.14	0.65
CaO process	1,352.09	0.94

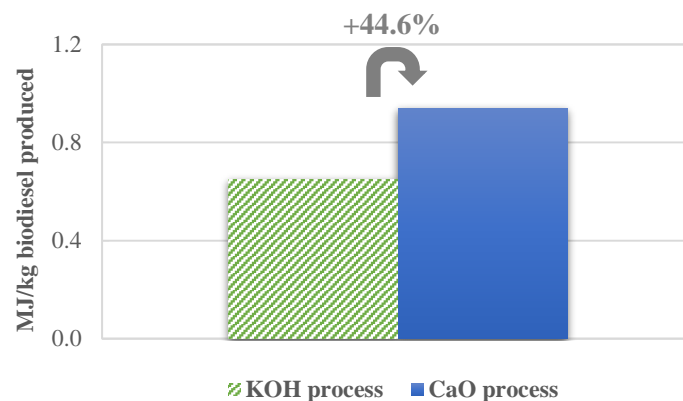


Figure 3-12: Comparison of the total energy consumption per kg of biodiesel produced for the KOH and CaO processes

3.7. CHAPTER OUTCOMES

In this chapter, the process model of a homogeneous catalysed process for biodiesel production and its modified heterogeneous process was developed using the Aspen Batch Process Developed® software. Details on material and energy balances as well as information on scheduling were obtained. A technological comparison of both processes was carried out. The findings are summarised below:

- Both processes proved to be technically feasible since they were both able to produce high quality biodiesel under reasonable operating conditions.
- The heterogeneous process was the simplest process with the lowest number of process equipment. This was due to the absence of the neutralisation and washing steps for the heterogeneous process.
- Converting from homogeneous to heterogeneous process reduced the batch time from 37.51 to 15.20 hours with as a result, an increase of 12.3% in the total annual throughput of biodiesel.
- Converting from homogeneous to heterogeneous process also resulted in a lower raw material requirement and higher energy consumption per unit of biodiesel produced.
- The process performances for both processes are summarised in Table 3-19.

Table 3-19: Process performances summary

	KOH process	CaO process
Batch size (kg)	1 618	1 431
Number of batches (per year)	639	818
Batch time (h)	37.51	15.20
Raw material consumption (kg/kg biodiesel)	2.04	1.51
Glycerol production rate (kg/kg biodiesel)	0.33	0.21
Energy consumption (MJ/kg biodiesel)	0.65	0.94

Simulation results derived from this chapter provide a basis for the economic analysis and sensitivity analysis discussed in subsequent chapters.

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NOMENCLATURE

<u>Abbreviation</u>	<u>Definition</u>
ABPD®	ASPEN BATCH PROCESS DEVELOPER®
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GLY	Glycerol
MeOH	Methanol
SS304	Type 304 Stainless Steel
TG	Triglyceride
WVO	Waste Vegetable Oil

CHAPTER 4: ECONOMIC ANALYSIS

Highlights

- Economic analysis of the homogeneous and heterogeneous processes was performed.
- Cost factors relative to two different economic environments were used.
- Heterogeneous process had a lower fixed capital cost and a higher manufacturing cost.
- It is profitable to convert from homogeneous to heterogeneous catalysed process for biodiesel production.
- The choice of cost factors has a significant impact on the process economics.

4.1. INTRODUCTION

This chapter focusses on the economic analysis that was conducted on the process models of the batch homogeneously and heterogeneously catalysed for biodiesel production discussed in the previous chapter. The economic evaluation performed includes the estimation of capital and manufacturing costs, which are further combined into economic criteria to evaluate and compare the profitability of both processes.

4.2. THEORY AND METHOD

The first steps required to perform an economic analysis are to determine the total capital investment and total manufacturing costs associated with the construction and the day-to-day operations of the plant. Once these costs are estimated, a discounted cash flow analysis is conducted with the purpose of assessing the profitability of the plant. This section describes the theory involved, as well as the method and assumptions that were required to assess the economics of the KOH and CaO processes.

4.2.1. CAPITAL COSTS ESTIMATION

Capital costs refer to the one-time costs associated with the construction of the plant. According to the definition of capital cost provided by Turton *et al.* (2013), the economic analysis performed in this study is classified as a “study estimate” with an expected accuracy ranging from -20% to +30%. The present cost estimation is based on limited cost data and rough sizing of equipment. Information such as layout plot of the plant or piping and instrumentation was not considered. Although the results from this study are only an estimate of the actual final cost of constructing the process plants under investigation, the technique is sufficient for comparison between different process alternatives. The total capital investment (TCI) of a plant is the sum of the fixed capital cost and working capital cost which are discussed in the following sub-sections.

4.2.1.1. ESTIMATION OF THE FIXED CAPITAL COST

Fixed capital cost (FCC) represents the total cost of the plant ready for start-up, while the working capital cost (WCC), is the additional investment required over the FCC for starting and operating the plant to the point when income is earned (Sinnot, 1999). In this study, the WCC was assumed to represent 15% of the FCC (Zhang *et al.*, 2003; West *et al.*, 2008).

The total fixed capital cost is generally estimated by taking into consideration three types of costs: the total installed costs of equipment, contingencies and fees, and auxiliary facility costs.

The total installed costs of equipment include the direct project expenses (purchase costs of equipment, materials required for installation and labour associated) and the indirect project expenses (freight, insurance, taxes, construction overhead and contractor engineering expenses). The best generally accepted approach for the preliminary estimation of the total installed costs of equipment is the module costing technique introduced by Guthrie (1970). This method which was applied in this study is further discussed in the subsequent sub-sections.

Contingencies and fees costs represent a fraction of the total installed costs of equipment to account and cover for oversight and faulty information. A value of 18% was assumed in this study as suggested by Turton *et al.* (2013). As regards the auxiliary and facilities costs, they include costs of items such as site development, auxiliary building, utilities and off-sites. For the present study, the auxiliary and facilities costs were not included because it was assumed that the process plant would be built in an already existing facility, with all utilities being purchased from public utilities suppliers and wastewater being treated by a third party at a fixed price per unit volume.

4.2.1.1.1. MODULE COSTING TECHNIQUE

This technique explained in detail by Turton *et al.* (2013) relates all costs back to the purchase cost of equipment evaluated for some base case conditions (material of construction: carbon steel; unit operating at near ambient pressure). The sum of direct and indirect costs of each equipment is called the bare module equipment cost (C_{BM}). It is calculated using Equation (4-1)

$$C_{BM} = C_p^0 F_{BM} \quad (4-1)$$

Where C_{BM} = bare module equipment cost

F_{BM} = bare module cost factor accounting for specific equipment conditions

C_p^0 = purchased cost of equipment at base case conditions.

The bare module cost factor (F_{BM}) and the purchase cost of equipment at base case conditions (C_p^0) are calculated using Equation (4-2) and Equation (4-3) respectively.

$$\log_{10} C_p^0 = K_1 + K_2 \log_{10}(A) + K_3 [\log_{10}(A)]^2 \quad (4-2)$$

$$F_{BM} = B_1 + B_2 F_M F_P \quad (4-3)$$

Where K_i = constant specific to the type of unit

A = Capacity or size parameter of the unit

F_M = Factor for specific material of construction

F_P = Factor for specific equipment pressure

B_i = Constant specific to the type of unit

The constants K_i , B_i as well as F_M and F_P are all obtained from a series of cost equations and curves presented in Turton *et al.* (2013).

In order to avoid tedious hand calculations, a computer program developed by Turton *et al.* (2013) that applied the module costing technique was used in this study for estimation of the total bare module cost of the plants under investigation. The software called CAPCOST is programmed in a Microsoft Excel spreadsheet within which all the cost equations and curves mentioned above are encoded. The program requires the user to select the specific type of equipment and input information such as its capacity, operating pressure and material of construction. Since all data for the purchased cost of equipment were obtained in 2001, the program allows the user to adjust cost data for inflation by specifying the actual value of CEPCI (Chemical Engineering Plant Cost Index). For the present study, a CEPCI value of 576.2 for June 2014 was used (Bailey, 2014).

4.2.1.1.2. TOTAL MODULE COST

Once the total bare module cost for the plant was estimated using CAPCOST, the total module cost also referred as total plant cost was calculated using Equation (4-4).

$$C_{TM} = 1.18 \sum_{i=1}^n C_{BM,i} \quad (4-4)$$

4.2.2. MANUFACTURING COSTS ESTIMATION

The total manufacturing costs (TMC) are the costs associated with the day-to-day operation of the plant. Following the evaluation of the capital investment, an estimate of these costs is essential to evaluate the profitability of the plant and to make choices between alternative processes.

The total manufacturing cost of a chemical can be divided into three categories: direct manufacturing costs, fixed manufacturing costs and general expenses (Turton *et al.*, 2013).

4.2.2.1. DIRECT MANUFACTURING COSTS

They represent the operating expenses that are dependent on the production rate. These expenses include the costs of the items listed below:

- **Raw materials**
- **Utilities**
- **Waste treatment**
- **Operating labour** (salaries of personnel required for plant operation)
- **Maintenance and repairs** (cost of labour and material associated with maintenance)
- **Laboratory charges** (cost of laboratory analysis required for quality control and process monitoring)
- **Direct supervisory labour** (cost of administrative, engineering and support personnel)
- **Operating supply** (cost of all miscellaneous materials -not raw materials or maintenance materials- required to operate the plant)
- **Patent and royalties** (cost of patented or licensed technology)

4.2.2.2. FIXED MANUFACTURING COSTS

Fixed manufacturing are costs that are not affected by the level of production. They include:

- **Depreciation** (fraction of the capital investment recovered as operating charges for tax purpose)
- **Local taxes and insurance** (costs associated with site and plant insurance)
- **Plant overhead** (costs associated with operations of auxiliary facilities supporting the manufacturing process)

4.2.2.3. GENERAL EXPENSES

They refer to the costs associated with management level and administrative activities. They are not directly related to the production process. These costs include:

- **Administration costs** (include salaries, buildings and other related activities)
- **Distribution and selling costs** (costs of sales and marketing, salaries and other related miscellaneous costs)
- **Research and development** (include salaries, and funds for research-related equipment and supply)

4.2.2.4. COST FACTOR FOR ESTIMATION OF MANUFACTURING COST

The total manufacturing cost of a plant can be determined once the raw materials, utilities, operating labour, waste treatment and fixed capital cost are known. All other costs can be estimated from equations involving at least one of these costs with a particular multiplication factor (Turton *et al.*, 2013).

A lot of manufacturing costs for biodiesel production that are reported in literature were estimated using the multiplication factors reported by Turton *et al.* (2013) (You *et al.*, 2008; West *et al.*, 2008; Zhang *et al.*, 2003). Those cost factors are the mid values of ranges obtained from an analysis of operation records of several different chemical plants. However, Peters & Timmerhaus (1990) mentioned that these values can vary depending on many factors, such as plant location, type of process and complexity of instrumentation. Since the ranges of value were all encountered in typical chemical plants located in developed countries such as the United States, the accuracy of the cost estimation for a chemical plant located in a developing country such as South Africa is questionable.

With the purpose of improving the reliability of cost estimation for African countries, Amigun (2008) adjusted the costs factors reported by Turton *et al.* (2003) to the economic conditions of Africa. The author did so by collecting cost data from an operating rural African biofuel industry before using the multiplication or factored approach to correlate these costs in a similar way to that reported elsewhere (Peters & Timmerhaus, 1990; Ulrich, 1984). Table 4-1 shows the cost factors for estimating the manufacturing cost reported by Turton *et al.* (2013), and the corresponding factors determined by Amigun (2008) for the African biofuel industry.

With the exception of the direct supervisory labour (1.e) and laboratory charges (1.h) (Table 4-1), all the other cost factors reported by Amigun (2008) are lower or equal to the corresponding ones from Turton *et al.* (2013). The author attributed the remarkable difference in the supervisory labour cost factor (0.18 for Turton *et al.* against 0.63 for Amigun) (Table 4-1), to the presence of an annexed plant with which the actual plant shares utilities and support systems. It can be assumed that in the absence of the annexed plant, the supervisory labour cost factor would decrease and have a value closer to 0.18.

Table 4-1: Cost factors for estimating manufacturing costs from Turton *et al.* (2013) and Amigun (2008)

Cost items	Values of cost factors (Turton <i>et al.</i> , 2013)	Values of cost factors (Amigun, 2008)
1. Direct Manufacturing Costs		
a. Raw materials	C_{RM}	C_{RM}
b. Utilities	C_{UT}	C_{UT}
c. Waste treatment	C_{WT}	C_{WT}
d. Operating labour	C_{OL}	C_{OL}
e. Direct supervisory labour	$0.18 C_{OL}$	$0.63 C_{OL}$
f. Maintenance and repairs	$0.06 FCC$	$0.01 FCC$
g. Operating supplies	$0.009 FCC$	$0.009 FCC$
h. Laboratory charges	$0.15 C_{OL}$	$0.20 C_{OL}$
i. Patents and royalties	$0.03 TMC$	0
2. Fixed Manufacturing Costs		
a. Depreciation	$0.1 FCC$	$0.04 FCC$
b. Local taxes and insurance	$0.032 FCC$	$0.002 FCC$
c. Plant overhead	$0.6 (1.d + 1.e + 1.f)$	$0.03 (1.d + 1.e + 1.f)$
3. General Manufacturing Expenses		
a. Administration costs	$0.15 (1.d + 1.e + 1.f)$	$0.11 (1.d + 1.e + 1.f)$
b. Distribution and selling costs	$0.11 TMC$	$0.014 TMC$
c. Research and development	$0.05 TMC$	0
✓ TMC (Turton <i>et al.</i>) = $1.23 (C_{RM} + C_{UT} + C_{WT}) + 2.73 C_{OL} + 0.180 FCC + DEPC$		
✓ TMC (Amigun) = $1.014 (C_{RM} + C_{UT} + C_{WT}) + 2.09 C_{OL} + 0.023 FCC + DEPC$		

For this present study, both types of cost factors were used for manufacturing costs estimation. The purpose was to test the cost factors developed by Amigun (2008) and evaluate the impact of using cost factors appropriate to the relevant economic environment.

4.2.2.5. COST DATA FOR MANUFACTURING COSTS ESTIMATION

The manufacturing costs can only be obtained once certain costs are known or can be estimated. The amount of raw material and utilities required for calculating their costs were determined as shown in Chapter 3. For the KOH process, a credit was given to wastewater because of the presence of potassium chloride salts which makes it attractive for fertilisers' producers. The operating labour costs was based on the estimation that the plant will operate three shifts per day for 330 days a year. Three operators per shift including one skilled and two unskilled operators were assumed to be required because of the small plant capacity and the lower level

of process complexity. Indeed with a plant capacity of 8000ton/year, Zhang et al. (2003b) and West *et al.* (2008) both reported 12 operators per day (4 operators per shift).

Table 4-2 lists all the costs necessary to perform the economic analysis of the two processes under investigation. Because the profitability analysis performed in this study seeks to be relevant to the South African economic environment, most cost data presented are local costs converted to \$US (Exchange rate: \$1= R10.70, average from 01 January to 30 June 2014).

Table 4-2: Unitary cost data for economic analysis

	R/unit	\$/unit	Source
Raw materials			
Waste cooking oil	R 4.00 /l	\$408/ton	Green-Diesel (2014)
Methanol	R 6750 /ton	\$630/ton	SASOL SA (2014)
Potassium hydroxide	R 16.40 /kg	\$1531/ton	Crest Chemicals (2014)
Hydrochloric acid	R 3.20 /kg	\$299/ton	Crest Chemicals (2014)
Calcium oxide		\$250/ton	Alibaba.com (2014)
Process water	R 10.51 /kl	\$1/ton	City of Cape Town (2014)
Product			
Biodiesel	R 12.59 /l	\$1337/ton	Green-Diesel (2014)
By-product			
Glycerol	R 0.5 /l	\$37/ton	
Waste water	R 0.15 /l	\$14.4/ton	
Utilities			
Electricity	R 1.1152/kWh	\$0.104/kWh	City of Cape Town (2014)
Cooling water	-	\$0.0148/ton	Turton <i>et al.</i> (2013)
Low pressure steam	-	\$29.29/ton	Turton <i>et al.</i> (2013)
High pressure steam	-	\$29.97/ton	Turton <i>et al.</i> (2013)
Disposal services			
Liquid waste	R 1.45/kg	\$135/ton	City of Cape Town (2014)
Solid waste	R 333.20/ton	\$31/ton	City of Cape Town (2014)
Labour			
Unskilled operator salary	R4000/month	\$372	www.jobcrystal.co.za
Skilled operator salary	R7000/month	\$652	

4.2.3. PROFITABILITY ANALYSIS

After evaluating the capital investment and the total manufacturing cost of a project, the profit anticipated from an investment must be assessed based on certain profitability criteria.

4.2.3.1. PROFITABILITY CRITERIA FOR PROJECT EVALUATION

The methods to evaluate the profitability of a project can be divided into two categories: the non-discounted cash flow methods and the discounted cash flow methods. The non-discounted cash flow methods such as payback period and return on investment have the disadvantage of not considering the time value of money which makes them unsuitable for final project evaluation. The discounted cash flow methods are more rigorous method since they take into consideration the time value of money and estimate the cash flow throughout the entire project life (Turton *et al.*, 2013). The discounted cash flow methods that have been used in the present study to evaluate the profitability of the economic models under investigation are the discounted payback period (DPBP), the net present value (NPV) and the discounted cash flow rate of return.

- **Discounted payback period**

The discounted payback period is defined as the time required after start-up to recover the fixed capital cost necessary for the project, with all cash flow discounted back to time 0. It correspond to the time when the cumulative present value crosses over from negative to positive hitting 0. When options are compared, the project with the lowest discounted payback period is the most profitable. The disadvantage of evaluating the profitability of a project solely based on the payback period is the fact that it does not take into consideration the performance of the project after the payback period. Therefore supplement information are required to make sound decision (Turton *et al.*, 2013).

- **Net present value**

The net present value also called the cumulative discounted cash position is defined as the worth of the project at the end of the project life. It is the sum of all inflows and outflows cash flow discounted to the present value by the given interest rate. A positive NPV indicates a project that is acceptable and the higher the NPV the more profitable the project (Sinnot, 1999).

- **Discounted cash flow rate of return**

It is defined as the maximum interest rate at which all cash flow could be discounted with the project still able to break even by the end of the project life ($NPV=0$). A project with a DCFROR higher than the internal interest rate is regarded as profitable and the higher the DCFROR, the more profitable the project (Sinnot, 1999).

The evaluation of the above criteria was done using a Microsoft Excel spreadsheet.

4.2.3.2. INVESTMENT PARAMETERS

The investment parameters that were specified in order to evaluate the profitability of the two processes under investigation included the project life, the start-up period, the capital investment distribution during construction period, the salvage value, the depreciation method, the taxation rate and the desired discount rate.

The project life refers to the period of time over which the profitability of the project is evaluated. According to Turton *et al.* (2013), typical periods of 10, 12 and 15 are used for this purpose. In this current study, a 12 years project life was assumed; and for the purpose of simplicity all equipment were assumed to equally have 12 years of useful lives. The salvage value which is an estimated fraction of the fixed capital investment recovered at the end of the project life was conservatively specified to be zero. Prior to the project start-up, a period of two years was assumed to complete the construction of the plant. The total fixed capital investment which does not include the cost of land, was assumed to be spread over the first and second year of construction by 60% and 40% respectively. The working capital which was set as 15% of the fixed capital investment, was invested at the end of year two. As for depreciation, the straight line method was used over the first five year after project start-up. Regarding taxation rate, the corporate income tax in South Africa is payable at the rate of 28% (SARS). This value was assumed for this study. Finally, a 10% desired discount rate was assumed as suggested by Turton *et al.* (2013).

4.3. RESULTS AND DISCUSSION

This section presents and discusses the cost differences resulting from the conversion of a homogeneous process to heterogeneous. According to Turton *et al.* (2013), the study estimate, which is the one performed in this study can present up to 30% error. In an attempt to limit the error during comparison, only differences above 5% will be considered significant.

4.3.1. TOTAL CAPITAL INVESTMENT EVALUATION

The total capital investments for the KOH and CaO processes were evaluated from the total bare module cost estimated using the CAPCOST software. The software results which are presented in Appendix B-1 and Appendix B-2 are summarised in Table 4-3 and Table 4-4.

The total purchased costs of the listed equipment for the KOH and CaO processes were estimated to be \$226 110 and \$187 910 respectively, thus a reduction of about 17% when converting from homogeneous to heterogeneous catalysed process. This was expected due to

the fewer number of process units involved in the CaO process in comparison to the KOH process.

Table 4-3: Total capital investment for the KOH process for biodiesel production (1 618 kg/batch)

Equipment class	Unit ID	Purchase cost (\$)	Bare module cost (\$)
Reactor	Reactor vessel R-101	33 200	133 000
Tank	Mixing tank V-101	5 490	22 300
	Settling tank V-102	7 890	32 100
	Holding tank V-103	7 890	32 100
	Holding tank V-104	7 890	32 100
	Washing vessel V-105	7 890	62 400
	Washing vessel V-106	7 890	32 100
	Holding tank V-107	7 890	32 100
Heat exchanger	Oil preheater E-101	3 380	11 100
	Evaporator preheater E-102	3 210	10 600
	Evaporator preheater E-103	3 210	10 600
Evaporators	Methanol evaporator K-101	20 200	61 300
	FAME dryer K-102	20 200	61 300
Pumps (8)	Centrifugal pumps	28 480	92 000
Storage vessels	WVO storage T-101	17 400	70 900
	Methanol storage T-102	7 490	30 500
	Crude glycerol tank T-102	7 910	32 200
	Biodiesel storage T-103	17 200	70 200
	Waste water tank T-104	11 400	46 300
Total purchased cost (listed equipment), C_p		<u>226 110</u>	
Total bare module cost (listed equipment), $C_{BM-list}$		-	875 200
Total installation cost, $C_{BM} = 1.25 C_{BM-list}$			<u>1 094 000</u>
Contingency and fee cost, $C_{FC} = 0.18 C_{BM}$			196 920
Fixed capital cost, $FCC = C_{BM} + C_{FC}$			<u>1 290 920</u>
Working capital, $WCC = 0.15 FCC$			193 638
Total capital investment, $TCI = FCC + WCC$			1 484 558

In the calculation of the fixed capital cost, an extra 25% of the total bare module cost of all listed equipment was assumed in order to account for all unlisted equipment. The fixed capital cost for the KOH process was estimated to be \$1 290 920, as opposed to \$962 585 for the CaO process. These results suggest a 25.4% saving when building a CaO catalysed batch process plant rather than a KOH process plant. This trend agrees with Marchetti *et al.* (2008) and West *et al.* (2008) who reported capital investments showing cost savings of 31.6% and 68.8% respectively for the heterogeneous process. These results however contradict Sakai *et al.* (2009), who reported a 4.3% increase in the capital investment for the heterogeneous process relative to the homogeneous process. This contradiction is attributed to the fact that the author

still included equipment relative to water purification steps in the capital cost estimation, while the heterogeneous catalysed reactor was also accounted for.

Table 4-4: Total capital investment for the CaO process for biodiesel production (1 034 kg/batch)

Equipment class	Unit ID	Purchase cost (\$)	Bare module cost (\$)
Reactor	Reactor vessel R-201	33 200	133 000
Tank	Mixing tank V-201	5 490	22 300
	Holding tank V-202	7 890	32 100
	Holding tank V-203	7 890	32 100
	Settling tank V-204	7 890	32 100
Heat exchanger	Oil preheater E-201	3 380	11 100
	Evaporator preheater E-202	3 210	10 600
Evaporator	Methanol evaporator K-201	20 200	61 300
Filter	Filter Fr-201	27 400	45 200
Pumps (6)		21 360	69 000
Storage vessels	WVO storage T-201	17 400	70 900
	Methanol storage T-202	7 490	30 500
	Crude glycerol tank T-203	7 910	32 200
	Biodiesel storage T-204	17 200	70 200
Total purchased cost (listed equipment), C_P		<u>187 910</u>	
Total bare module cost (listed equipment), $C_{BM-list}$			652 600
Total installation cost, $C_{BM} = 1.25 C_{BM-list}$			<u>815 750</u>
Contingency and fee cost, $C_{FC} = 0.18 C_{BM}$			146 835
Fixed capital cost, $FCC = C_{BM} + C_{FC}$			<u>962 585</u>
Working capital, $WCC = 0.15 FCC$			144 388
Total capital investment, $TCI = FCC + WCC$			1 106 973

The equipment items involved in the biodiesel processes investigated in this study can be divided into four sub-processes:

- Storage process equipment: storage vessels for input and output materials, pumps
- Transesterification process equipment: mixing tank, reactor, pump, preheater
- Separation process equipment: Settling tank, holding tanks, pump
- Purification process equipment: Evaporators, heat exchangers, holding tanks washing vessels, filter.

These four sub-processes contribute to the total equipment cost. Figure 4-1 and Figure 4-2 show the percentage contribution of each of these process areas on the total bare module cost of listed equipment. The charts show that the biggest contribution to the total bare module cost for the KOH process is attributed to the purification process equipment with a contribution of 36%.

The purification process equipment contribution is reduced to 29% for the CaO process as shown in Figure 4-2. This is attributed to the elimination of equipment unit such as the washing vessels. In both cases, the storage process equipment shows to have a considerable contribution to the total cost, while the separation equipment shows to require the lowest investment of all.

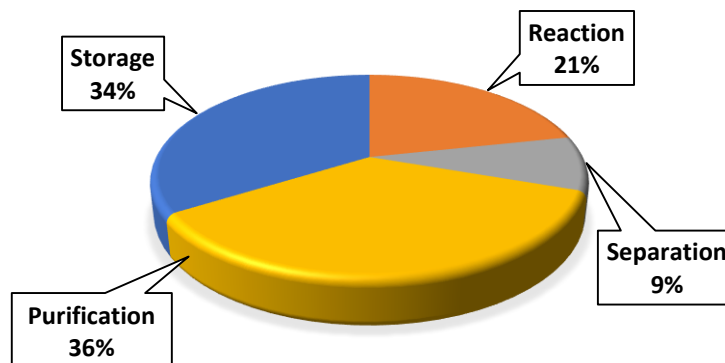


Figure 4-1: Process areas contribution to the total bare module cost for the KOH process

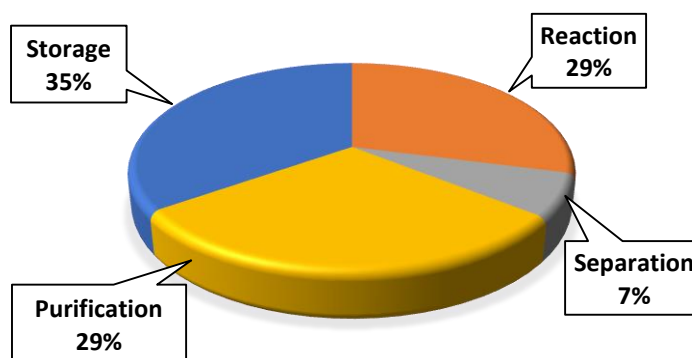


Figure 4-2: Process areas contribution to the total bare module cost for the CaO process

4.3.2. TOTAL MANUFACTURING

The total manufacturing costs of biodiesel for the KOH and CaO processes were evaluated using the cost factors reported by Turton *et al.* (2013) (USA cost factors) and Amigun (2009) (SA cost factors).

Henceforth, the terms KOH-USA, CaO-USA, KOH-SA and CaO-SA will be employed to refer to the costs of one of the two processes, estimated using the two authors' derived cost factors.

Table 4-5 shows the results for the total manufacturing costs of the KOH and CaO processes estimated using the USA and SA cost factors. Details of the Microsoft Excel spreadsheet for each cost are presented in Appendix B-3 and Appendix B-4.

Table 4-5: Total manufacturing costs for KOH and CaO processes

Cost items	USA cost factors		SA cost factors	
	KOH process	CaO process	KOH process	CaO process
1. Direct Manufacturing Costs				
a. Raw materials	661 448	817 568	661 448	817 568
b. Utilities	11 643	16 621	11 643	16 621
c. Waste treatment	0	0	0	0
d. Operating labour	50 256	50 256	50 256	50 256
e. Direct supervisory labour	9 046	9 046	31 661	31 661
f. Maintenance and repairs	77 455	57 755	12 909	9 626
g. Operating supplies	8 663	8 663	8 663	8 663
h. Laboratory charges	7 538	7 538	10 051	10 051
i. Patents and royalties	35 388	41 729	0	0
2. Depreciation	129 092	96 259	51 637	38 503
3. Fixed Manufacturing Costs				
a. Local taxes and insurance	41 309	30 803	2 582	1 925
b. Plant overhead	82 054	70 234	2 845	2 746
4. General Manufacturing Expenses				
a. Administration costs	20 514	17 559	10 431	10 070
b. Distribution and selling costs	129 755	153 005	11 135	13 597
c. Research and development	58 980	69 548	0	0
5. Total production cost	1 308 683	1 390 956	865 262	1 011 289
6. By-products credit				
a. Glycerine credit	12 443	9 019	12 443	9 019
b. Waste water credit	9 056	0	9 056	0
Total Manufacturing Cost	1 287 185	1 381 937	843 763	1 002 269

The total manufacturing cost for the CaO process is found to be higher for the two types of cost factors used. This is mainly due to the higher amount of raw materials required for the CaO process relative to the KOH process (\$817 560 vs. \$661 448). It can be observed from Figure 4-3 and Figure 4-4 that the cost of raw materials is the highest contributor to the total manufacturing cost, with proportion of 56%, 57%, 79% and 84% for the KOH-Turton, CaO-USA, KOH-SA and CaO-SA processes respectively. The estimation of the total manufacturing cost using the SA cost factors shows that the direct costs constitute almost the entire proportion of the total manufacturing cost (> 90%). Regarding the fixed costs and the general expenses estimated using the SA cost factors, they were found to be about 20 times and 10 times lower respectively than when estimated using the USA cost factors. This may reveal a low industry

development in Africa that puts little focus on marketing, factory development, research and development, and administration. However since the SA cost factors were developed based on the biofuel industry that is known to still be in its infancy, they may not actually reflect and be applicable to other types of industry.

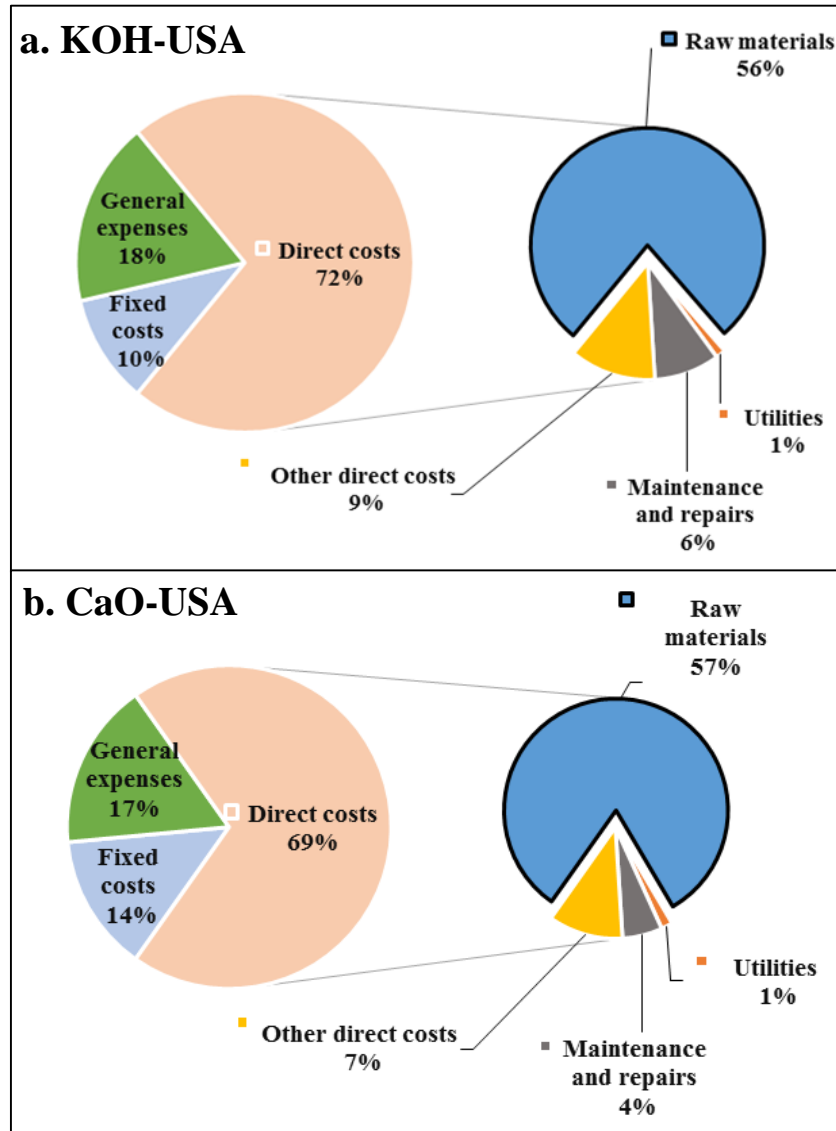


Figure 4-3: Breakdown costs of the total manufacturing costs for the KOH-USA and CaO-USA processes

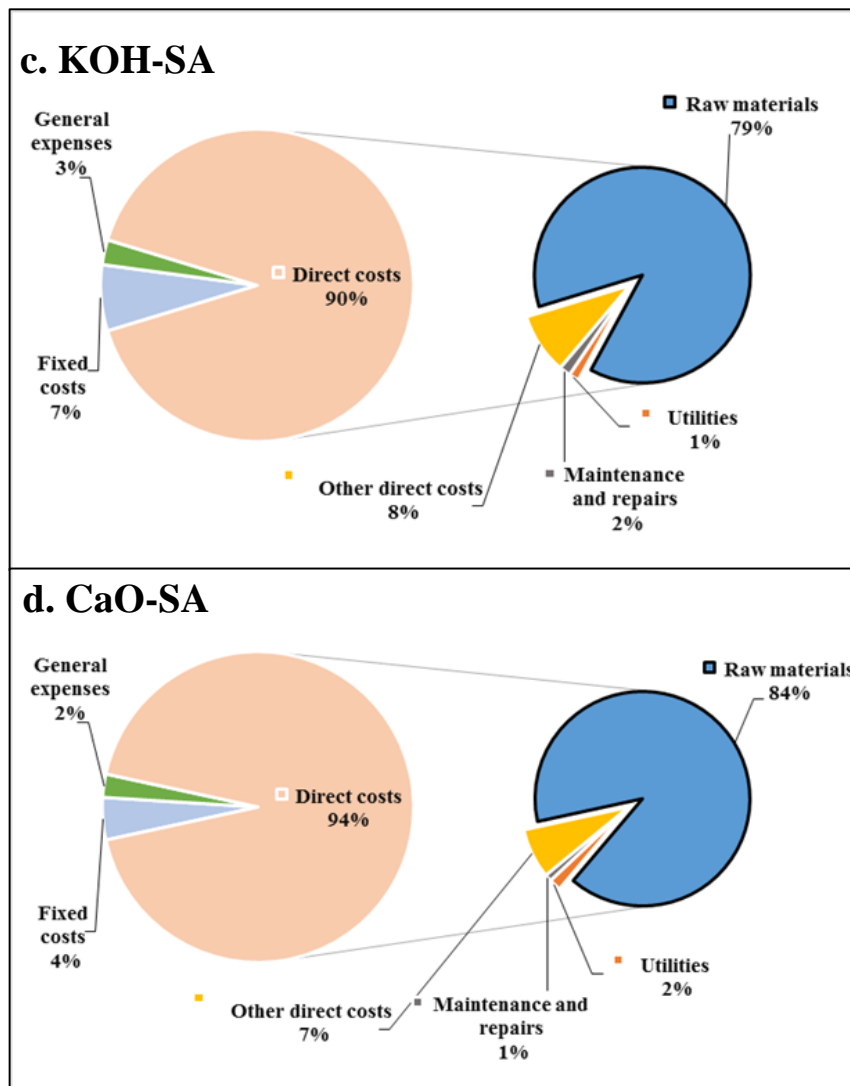


Figure 4-4: Breakdown costs of the total manufacturing costs for the KOH-SA and CaO-SA processes

The use of USA and SA cost factors suggests an increase of 7.4% and 18.7% respectively in the total manufacturing cost per year when converting a batch biodiesel plant from KOH to CaO process. The trend disagree with previous work who estimated a lower manufacturing cost for the CaO process (West *et al.*, 2008; Marchetti *et al.*, 2008; Sakai *et al.*, 2009). However, considering the higher annual production rate for the CaO process resulting from the higher number of batches per year, an increase in the total manufacturing cost was expected. A comparison based on the unitary production cost of biodiesel as done by Sakai *et al.* (2009) who also evaluated batch processes, is more appropriate.

Figure 4-5 shows that when changing from KOH to CaO process, the unitary cost of manufacture of biodiesel estimated using the USA cost factors decreases from \$1.245/kg to \$1.191/kg (- 4.3%), while it is shown to increase from to \$0.816/kg to \$0.864/kg (+5.8%) when using the SA cost factors. Based on the 5% threshold, converting from homogeneous to

heterogeneous process does not affect the unitary cost of manufacture when estimated using USA cost factors. As for the increase in the unit manufacturing cost when estimated using SA cost factors, this can be attributed to the higher energy requirement for the CaO process.

Regarding individual processes, it is also observed that the use of the SA cost factors reduces by 34.4% (KOH process: \$1.245/kg vs. \$0.817/kg) and by 27.5% (CaO process: \$1.191/kg vs. \$0.864/kg) the estimation of the unitary production cost of biodiesel using the USA cost factors. These costs are all lower than the actual market price of biodiesel which is \$1.337/kg, showing a potential for profitability.

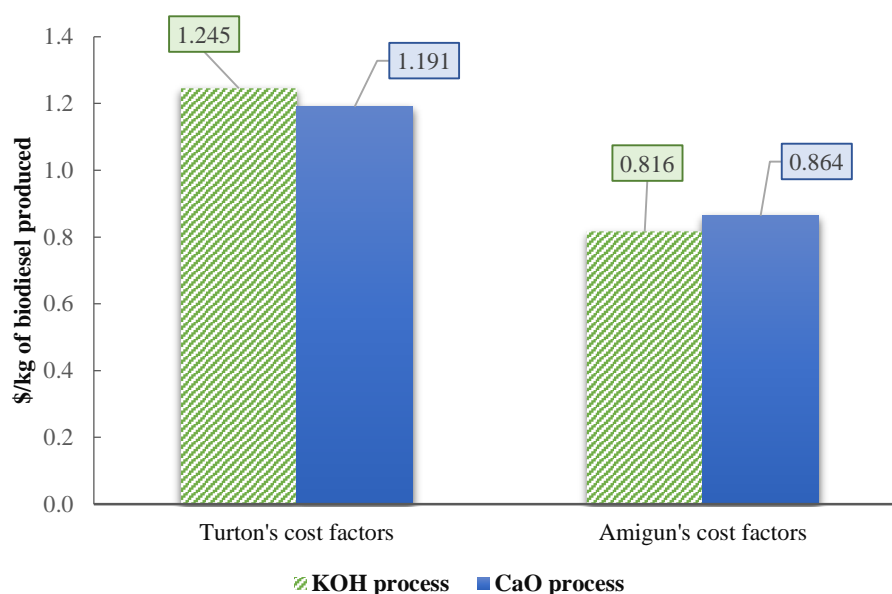


Figure 4-5: Comparison of the unit production costs of biodiesel for the KOH and CaO processes

The contradictory estimations given by the use of cost factors from Turton *et al.* (2013) and Amigun (2008) show the importance of the type of factors used while evaluating and comparing process economics. Since the cost factors developed by Amigun (2009) are supposed to reflect the African economic environment while the ones reported by Turton *et al.* (2013) were developed based on the developed countries economy, we can conclude that the use of cost factors irrelevant to the particular economic environment of the process under analysis can lead to wrong estimations.

4.3.3. PROFITABILITY ANALYSIS

Figure 4-6 and Figure 4-7 show the discounted cash flow diagrams for the four different economic models under investigation. The discounted cash flow table and profitability parameters for each process are presented in Appendix B-5 to Appendix B-8.

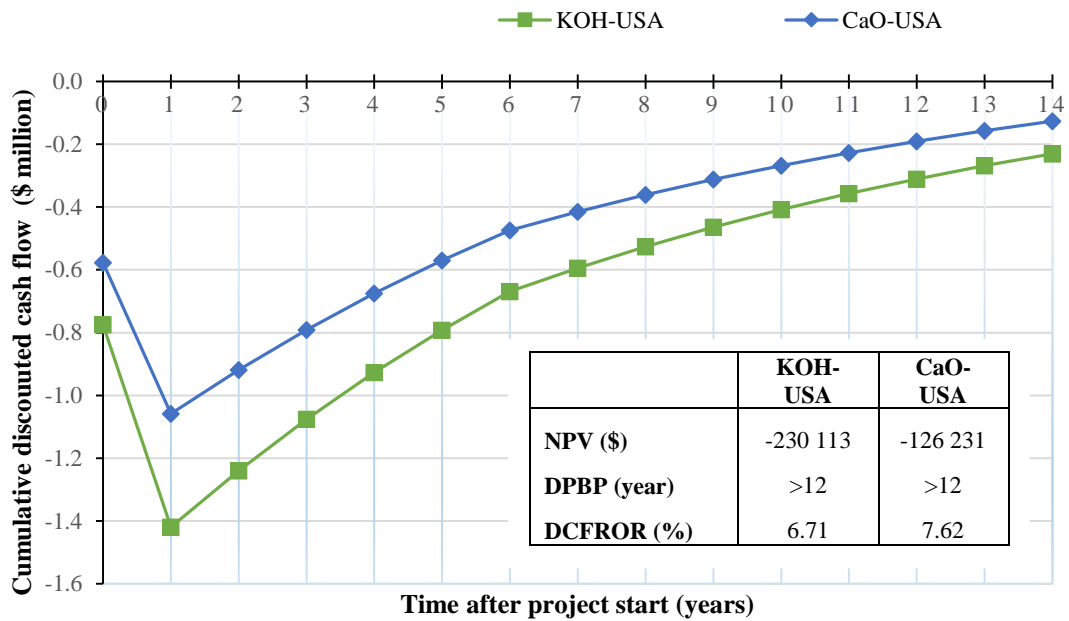


Figure 4-6: Discounted cash flow diagram for the KOH-USA and CaO-USA processes

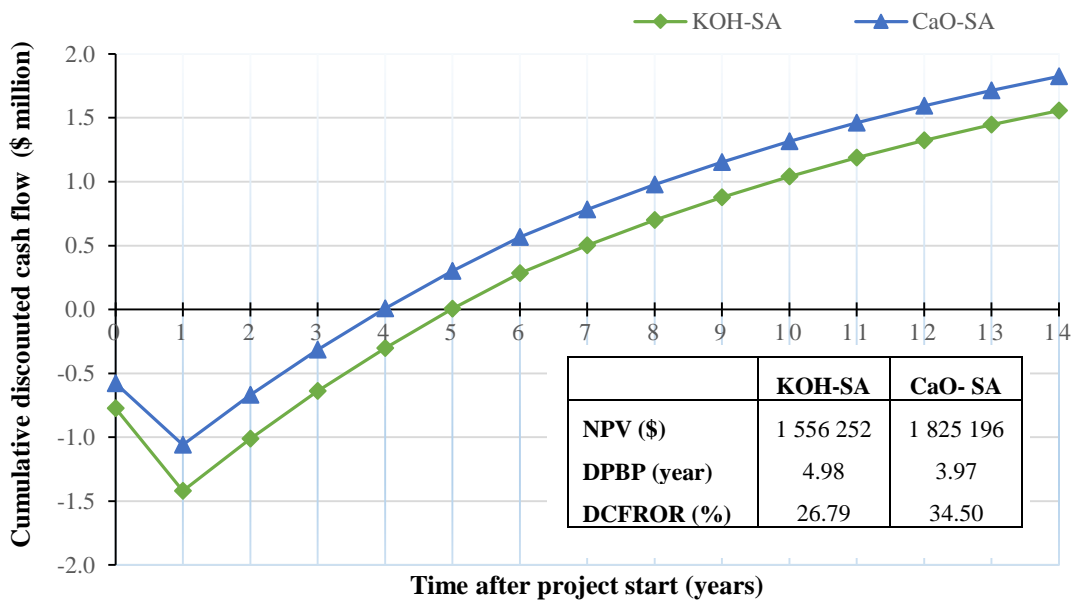


Figure 4-7: Discounted cash flow diagram for the KOH-SA and CaO-SA processes

From Figure 4-6 and Figure 4-7, it can be observed that the cumulative discounted cash flows for the KOH-USA and CaO-USA do not cross over from negative to positive, suggesting that the discounted payback period is longer than the 12 years project life which starts at year 2 after construction. The negative NPVs for both models show that they are not profitable. However, the NPV for the KOH-USA model is lower than the one for CaO-USA. The DCFROR for both models are 6.71% and 7.62% for the KOH-USA and CaO-USA models respectively. The fact

that the DCFROR are lower than the desired discount rate assumed at 10%, confirms the unprofitability of the projects within 12 years.

The DCFROR for the KOH-SA and CaO-SA economic models are 26.79% and 34.50% respectively (Figure 4-7). Since these values are higher than the desired discount rate and the NPVs are greater than zero, the two process models are considered economically profitable. With the shortest DPBP (3.97 years from beginning of construction) and the higher NPV and DCFROR, the CaO process proves to be the more favourable.

Although the profitability of the KOH and CaO processes is dependent on the type of cost factors used for economic evaluation, the CaO process proved in all cases to be more attractive than the KOH process. This confirms previous similar economic comparisons from Marchetti *et al.* (2008), West *et al.* (2008) and Sakai *et al.* (2009).

The question that is raised from the above is to know which of the two types of cost factors used in this study better reflects the actual economic of the processes under investigation. In order to provide a sound answer to this question, practical data would need to be obtained. It can be assumed that since homogeneous biodiesel plants operating in South Africa in the range of the plant capacity investigated in this study are profitable, then the cost factors developed by Amigun (2008) which renders the processes profitable is the more appropriate.

Considering the results obtained when using the SA cost factors, it can be noted that while the higher unitary manufacturing cost for the heterogeneous process (+5.8%) let us assume that it would be less profitable than the homogeneous process, it is the opposite that is observed. The heterogeneous process is more profitable than the homogeneous process over the prescribed project life of 12 years. This fact can be attributed to the significantly lower capital cost of the heterogeneous process relative to the homogeneous process. We can therefore expect that over a much longer project life, the heterogeneous process would be less profitable than the homogeneous process.

4.4. CHAPTER OUTCOMES

In this chapter, an economic comparison of the KOH and CaO processes developed in Chapter 3 was carried out with the purpose of evaluating the economic impact of converting from KOH to CaO process for biodiesel production. The two processes were compared in terms of capital cost, manufacturing cost and profitability indicators. Two types of cost factors were used in the

evaluation: USA cost factors relevant to developed economy and SA cost factors relevant to South African economic environment. The findings listed below are summarised in Table 4-6.

- It was found a 25.4% savings in the total capital cost for the CaO process relative to the KOH process, owing to the fewer number of process equipment.
- For economic analysis performed based on USA cost factors, converting from KOH to CaO process resulted in the following:
 - A 7.4% higher total manufacturing cost for the CaO process
 - A 4.3% lower unit manufacturing cost for the CaO process (insignificant)
 - A higher DCFROR for the CaO process although both value are below the acceptable 10%
 - A higher NPV for the CaO process (despite both values being negative)
 - Payback period still longer than the 12 years project life

It can be concluded that although both process are unprofitable when using USA cost factors for economic analysis, the CaO process is more acceptable than the KOH process.

- For economic analysis performed based on SA cost factors, converting from KOH to CaO process resulted in the following:
 - A 18.7% higher total manufacturing cost for the CaO process
 - A 5.8% higher unit manufacturing cost for the CaO
 - A higher DCFROR for the CaO process (both values > 10%)
 - A higher NPV for the CaO process (both positive values)
 - A shorter payback period for the CaO process (3.97 vs. 4.98 years for the KOH process)

It can be concluded that converting from KOH to CaO process results in a more profitable process when economics is evaluated using SA cost factors.

- The difference obtained when evaluating economics using the USA and SA costs factors revealed the significant importance of choosing cost factors relevant to the particular economic environment in process economics.
- The SA cost factors were assumed appropriate for the economic evaluation performed in this study. Findings obtained using this type of cost factors can be supported by previous study from Marchetti *et al.* (2008), West *et al.* (2008) and Sakai *et al.* (2009).

Table 4-6: Economic evaluation summary

	USA cost factors		SA cost factors	
	KOH process	CaO process	KOH process	CaO process
Total capital investment (\$)	1 484 558	1 106 973	1 484 558	1 106 973
Production rate (ton/year)	1 034	1 160	1 034	1 160
Total production cost (\$)	1 308 683	1 390 956	865 262	1 011 289
Discounted cash flow rate of return	6.71%	7.62%	26.79%	34.50%
Discounted payback period (year)	>12	>12	4.98	3.97
NPV at 10% interest (\$)	-230 113	-126 231	1 556 252	1 825 196

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NOMENCLATURE

<u>Abbreviation</u>	<u>Definition</u>	
CEPCI	Chemical Engineering Plant Cost Index	
DCFROR	Discounted Cash Flow Rate of Return	
FAME	Fatty Acid Methyl Ester	
FCC	Fixed Capital Cost	
NPV	Net Present Value	
DPBP	Discounted Payback Period	
TCI	Total Capital Investment	
<u>Symbol</u>	<u>Definition</u>	<u>Units</u>
C_{BM}	Bare module equipment cost	\$
F_{BM}	Bare module cost factor	-
F_M	Factor for specific material of construction	-
F_P	Factor for specific equipment pressure	-
B_i	Constant specific to the type of unit equipment	-
K_i	Constant specific to the type of unit equipment	-

A	Capacity or size parameters of unit equipment	m^3 or m^2
C_{TM}	Total module cost	\$
C_{UT}	Utilities cost	\$
C_{WT}	Waste treatment cost	\$
C_{OL}	Operating labor cost	\$
C_{RM}	Raw materials cost	\$
C_P⁰	Purchased cost of equipment	\$

CHAPTER 5: ECONOMIC SENSITIVITY ANALYSIS

Highlights

- Economic feasibility of biodiesel production with uncertainties was assessed.
- Feedstock oil price and biodiesel selling price have the highest impact on the profitability of the processes.
- The maximum price of oil feedstock to achieve 90% probability of profitability was determined.

5.1. INTRODUCTION

When evaluating project economics, decisions are rarely taken in conditions of absolute certainty. The uncertainties of some parameters can lead to risks, which can affect the viability of the project. The sensitivity analysis is the approach used in this chapter for assessing the uncertainty of the projects under evaluation. The uncertain or variable parameters evaluated in this study are the plant capacity and the price of raw materials and products.

5.2. SENSITIVITY ANALYSIS TO THE PLANT CAPACITY

In order to ease the sensitivity analysis to the change in plant capacities, plant capacities ratio of 0.5, 1, 2 and 5 fold the plant capacity used in the previous chapters were considered (1618 and 1433 kg/batch for the KOH and CaO processes respectively).

The total capital costs, manufacturing costs and net present values for the different plant capacities were evaluated as shown in Chapter 4. The details of the total capital costs, total manufacturing costs and discounted cash flow diagrams for the different plant capacities are presented in Appendix C-1 to Appendix C-12. The graphs of total capital cost, manufacturing cost and net present value vs. the different plant capacities ratio are shown in Figure 5-1, Figure 5-2 and Figure 5-3.

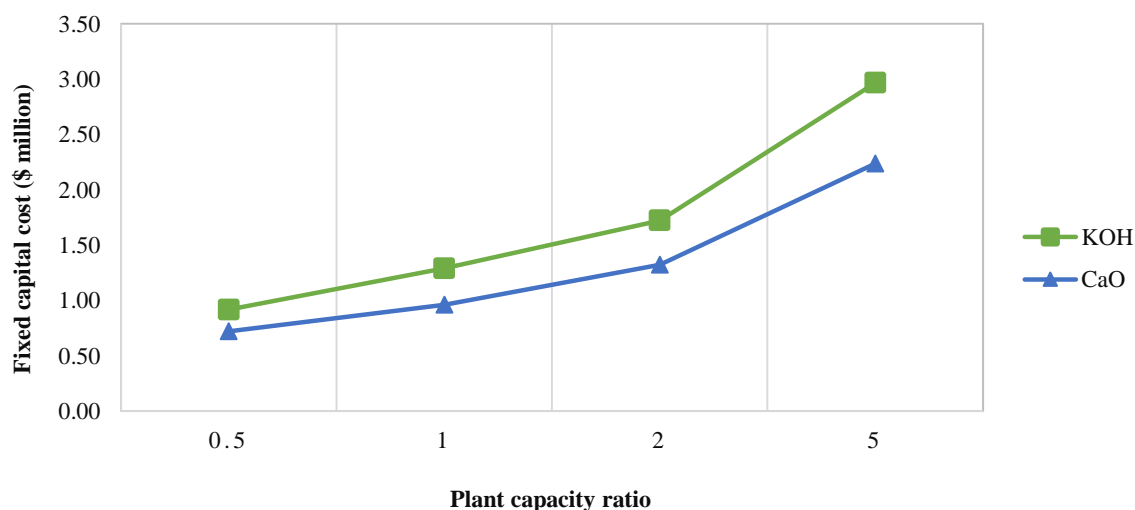


Figure 5-1: Fixed capital cost vs. plant capacity ratio (“1” = 1618 kg/batch for the KOH process)

From Figure 5-1 it can be seen that the fixed capital costs for the KOH and CaO processes increase with the increase in the plant capacity. With regards to the difference between the KOH and CaO processes, it can be observed that as the plant capacity increases, there is a deeper

difference in the fixed capital costs between both processes, with the KOH process having the highest fixed capital cost. This can be attributed to the higher number of process steps for the KOH process when compared to the CaO process.

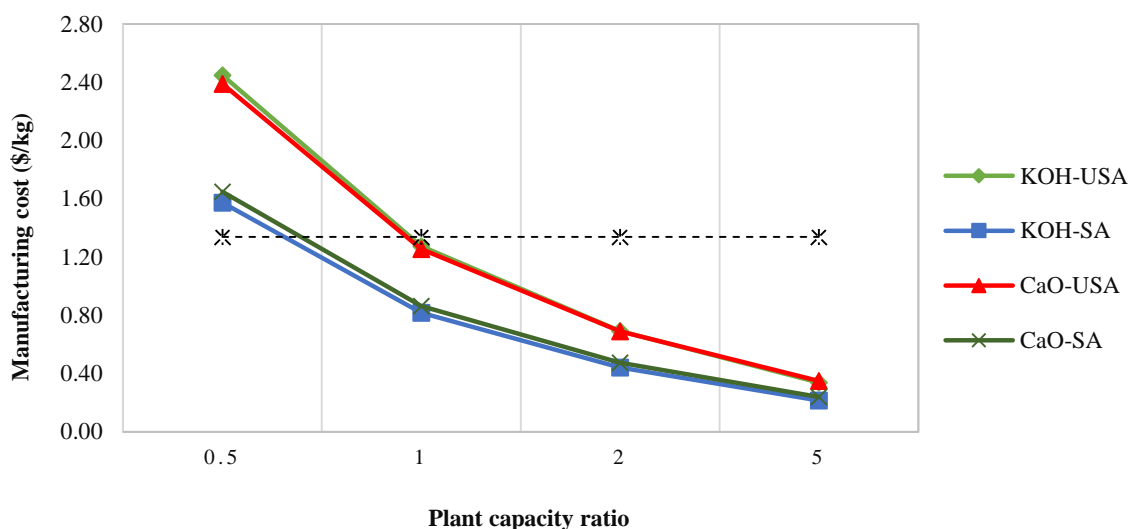


Figure 5-2: Unit manufacturing cost vs. plant capacity ratio (“1” = 1618 kg/batch for the KOH process)

Figure 5-2 shows a decrease in the total manufacturing cost per kg of biodiesel produced for each process. From 0.5 to 5 fold the base case plant capacity, the total manufacturing cost per kg of biodiesel produced is reduced by about 85%. It is also observed that the unitary manufacturing costs for the KOH and CaO processes at plant capacity ratio of 0.5 are higher than the current selling price of biodiesel (\$ 1.337/kg). This indicates that at this plant capacity, the processes have a higher level of risk of being unprofitable since it is not able to break even. The intersections between the manufacturing costs curves and the line representing the price of biodiesel, suggest that the processes reach the break-even point at a plant capacity ratio of about 0.7 if estimated using the SA cost factors whereas the process is only able to break even at plant capacity ratio of 1 if estimated using the USA cost factors. It is also interesting to observe that as the plant capacity increases, the unit manufacturing cost values estimated using both types of cost factors get closer.

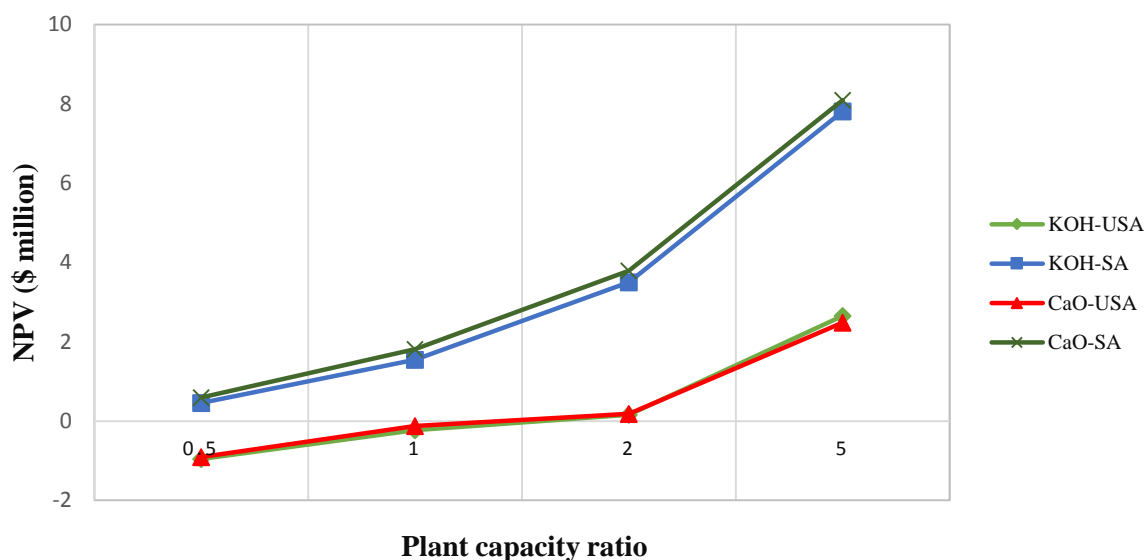


Figure 5-3: Net present value vs. plant capacity ratio (“1” = 1618 kg/batch for the KOH process)

From Figure 5-3, it can be noticed that the NPV estimated using the SA cost factors is positive all over the range of plant capacity investigated, indicating that the processes are profitable. However, regarding the NPV estimated using the USA cost factors; it only becomes positive value at a plant capacity ratio of about 1.5. Therefore, assuming that the USA cost factors reflect the economics of the processes under investigation, 1.5 should be the minimum acceptable plant capacity ratio to be considered in order for the processes to be profitable. We can also notice that for a plant capacity ratio of 5, the KOH-USA process has a higher NPV than the CaO-USA process, suggesting that at a bigger plant capacity, the heterogeneous catalysed process is less profitable than the homogeneous process, when using the USA cost factors. This fact contradicts previous economic studies in which the homogeneous and heterogeneous catalysed processes were compared at much larger plant capacities using the USA cost factors (Marchetti *et al.*, 2008; West *et al.*, 2008; Sakai *et al.*, 2009). This may be attributed to the irrelevance of the USA cost factors in the evaluation of projects based in the African economic environment.

5.3. COST SENSITIVITY ANALYSIS

In this section, the sensitivity analysis for the four economic models under investigation was conducted to evaluate the sensitivity of the net present values to changes in different parameters. The parameters investigated in this study were the raw materials prices (feedstock oil, methanol and catalysts) and the selling prices of products and by-products (biodiesel and glycerol).

The price of feedstock oil was varied from -80% to +200% of the current trading price of WVO (\$408/ton). The choice of the minimum value of -80% was based on the assumption that waste

vegetable oil would be obtained at no cost from restaurants but that the costs of collection would add some cost to it. As for the maximum value it was chosen assuming that the plant may have to run on virgin oil which is about 3 times more expensive than waste vegetable oil (Math *et al.*, 2010).

Methanol is one of the major internationally traded chemical commodities. SASOL, which is the main supplier of methanol in South Africa currently sells its methanol in bulk at a price of R6 750/ton (\$630/ton at 1US\$ = R10.71). In 2006 it was sold at a price R3 450/ton (Nolte, 2007), which is half the current selling price of methanol. Based on the former, a twofold increase in the price of methanol (+100%) was also assumed in selecting the maximum value of the range over which to perform the sensitivity analysis. As for the minimum value, a -30% of the current price was considered (Nolte, 2007).

According to the OECD/FAO (2013), the world prices of biodiesel are expected to reach values of about \$170/hl (\$1 954/ ton) in 2022, hence 46% higher than the current value used in this study (See chart in Appendix C-13). In 2002, the price of biodiesel was about \$80/hl (\$920/ ton), which was 31% lower than the current value. Based on the above, the sensitivity over the change of biodiesel prices was studied over the range of -30% to +50% of the current price of biodiesel used in this study (\$ 1 337/ton).

As regards the credit given to glycerine, the sensitivity analysis was performed for values ranging from \$0 to \$111/ ton equivalent to changes of -100% to +200%. The lower bound of \$0/ton was taken into consideration assuming that there will be no market for the crude glycerol produced from this process due to the oversupply of glycerol worldwide. As for the upper bound \$111/ton it assumes a potential discovery of new viable market outlets for glycerol that will increase the market value of crude glycerol.

The sensitivity of the NPV over changes in the price of catalysts was evaluated by varying the current scenario of catalyst prices by $\pm 30\%$.

Table 5-1 summarises the minimum and maximum values considered for the sensitivity analysis of the NPV performed in this study.

Table 5-1: Summary of minimum and maximum values for the uncertain parameters

	Feedstock oil	Methanol	Glycerol	Biodiesel	KOH	CaO
Min (\$/ton)	-80% (82)	-30% (441)	-100% (0)	-30% (936)	-30% (1072)	-30% (175)
Baseline \$/ton	408	630	37	1337	1531	250
Max (\$/ton)	+200% (1224)	+100% (1260)	+200% (111)	+50% (2006)	+30% (1990)	+30% (325)

5.3.1. SINGLE PARAMETER ANALYSIS

The results of the single parameter sensitivity analysis performed in this section, show only the variation of the NPV due to the change in the particular parameter. The remaining variables have been maintained constant.

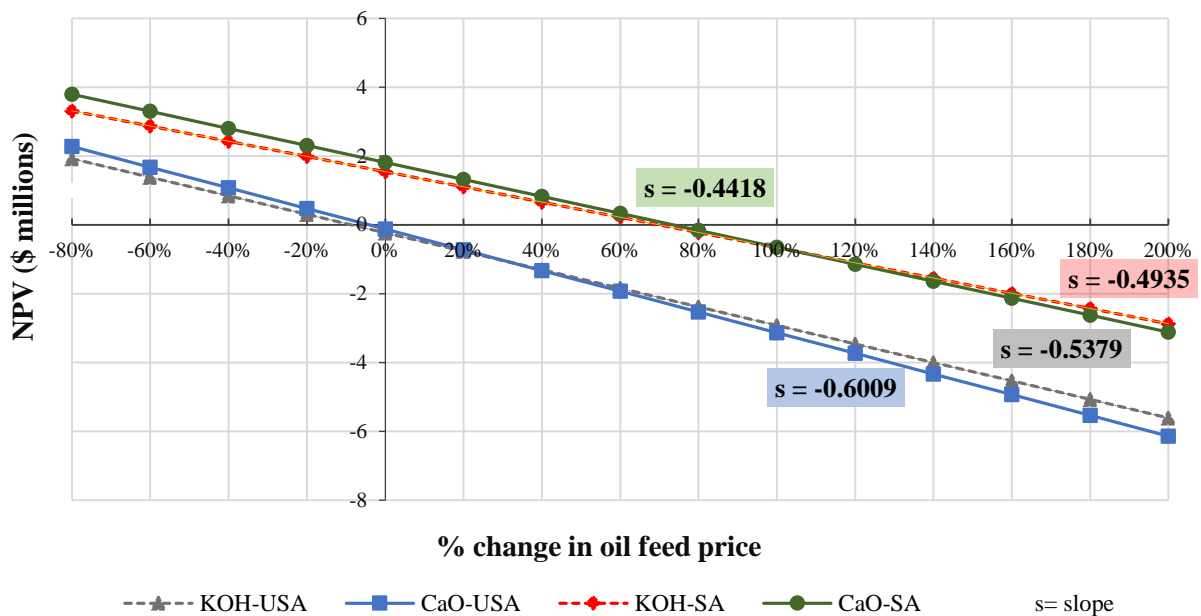


Figure 5-4: Sensitivity of the NPVs of the four economic models to the price of oil feed

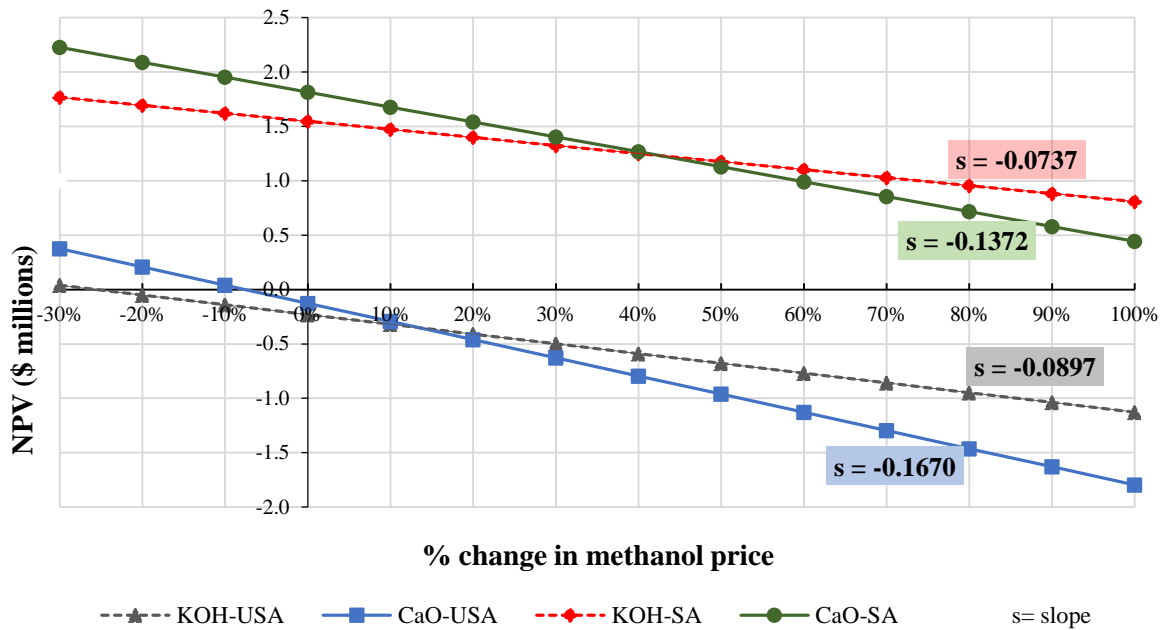


Figure 5-5: Sensitivity of the NPVs of the four economic models to the price of methanol

The sensitivity analysis to the price of oil feedstock for the four economic models is shown in Figure 5-4. The results show that for every $\pm 20\%$ change in the price of oil feed, the NPV changes by approximately \$0.54, \$0.60, \$0.44 and \$0.49 million for the KOH-USA, CaO-USA, KOH-SA and CaO-SA processes respectively. The slopes of the trend lines of each process were evaluated. The steeper the slope, the more sensitive the process is. With the steepest slope of all, the CaO-USA process shows to be the most sensitive to the change in price of oil feed, followed in order by the KOH-USA, KOH-SA and CaO-SA processes.

Figure 5-5 shows the sensitivity of the NPVs to the change in price of methanol. The results indicate that for every $\pm 20\%$ change in the price of oil feed, the NPV changes by approximately \$0.18, \$0.33, \$0.15 and \$0.27 million for the KOH-USA, CaO-USA, KOH-SA and CaO-SA processes respectively. An analysis of the slopes of the trend lines shows that the overall influence of the price of methanol is less than the influence of the price of oil feed on the profitability of the four economic models. The CaO-USA process is the most influenced by the change in price of methanol.

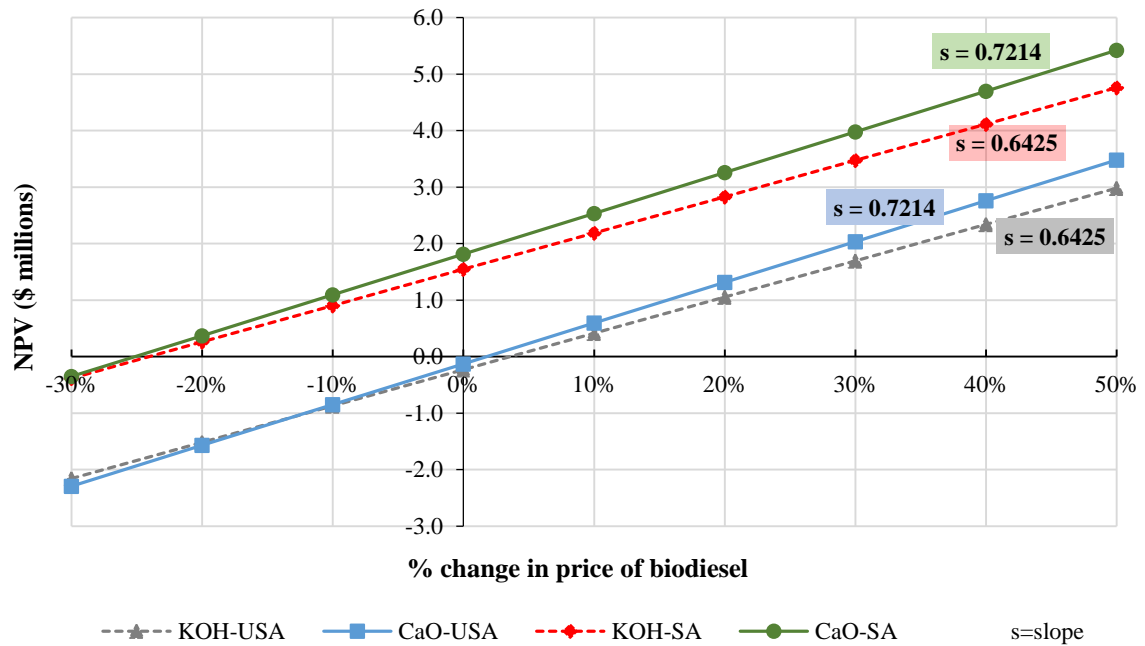


Figure 5-6: Sensitivity of the NPVs of the four economic models to the price of biodiesel product

The sensitivity of the selling price of biodiesel product is shown in Figure 5-6. The results indicate that for every $\pm 20\%$ change in the price of biodiesel, the NPV changes by approximately \$1.29 for the KOH-USA and KOH-SA processes and by \$1.44 for the CaO-USA and CaO-SA processes. A comparison of the slopes of the trend lines shows that the overall influence of the selling price of biodiesel on the profitability of the four economic models is higher than that of the price of oil feed and methanol.

As regards the price of glycerol by-product and catalysts, they have a relatively low impact on the profitability of the four economic models as demonstrated by the relatively flat slopes of the trend lines (Figure 5-7 and Figure 5-8).

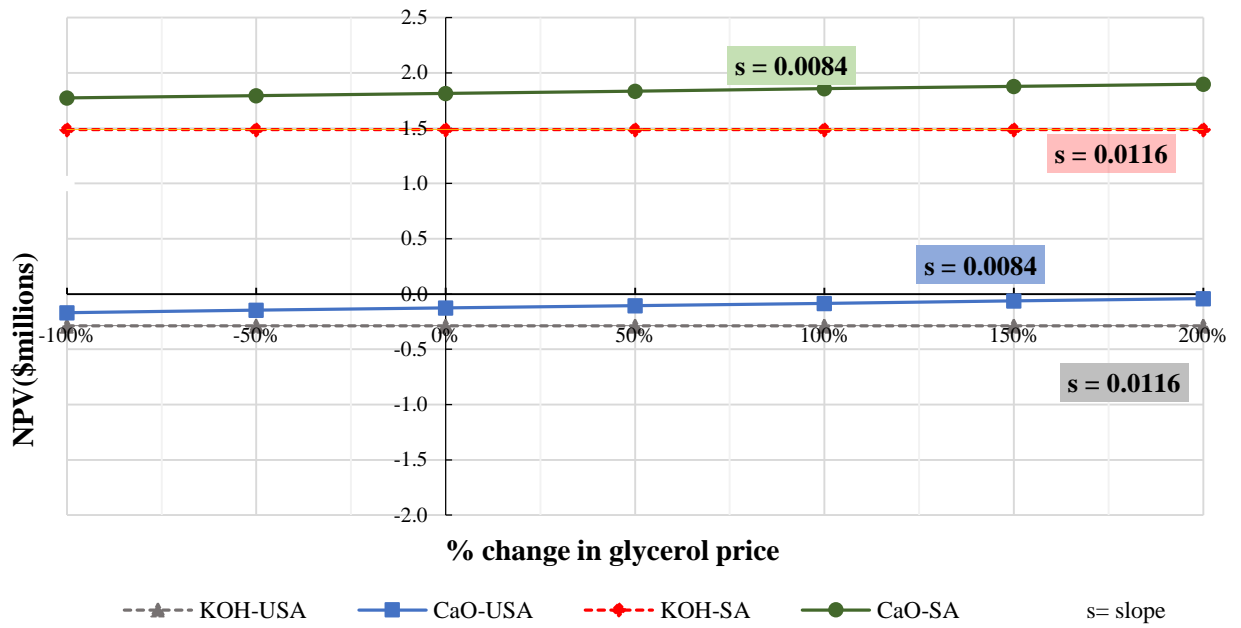


Figure 5-7: Sensitivity of the NPVs of the four economic models to the price of glycerol by-product

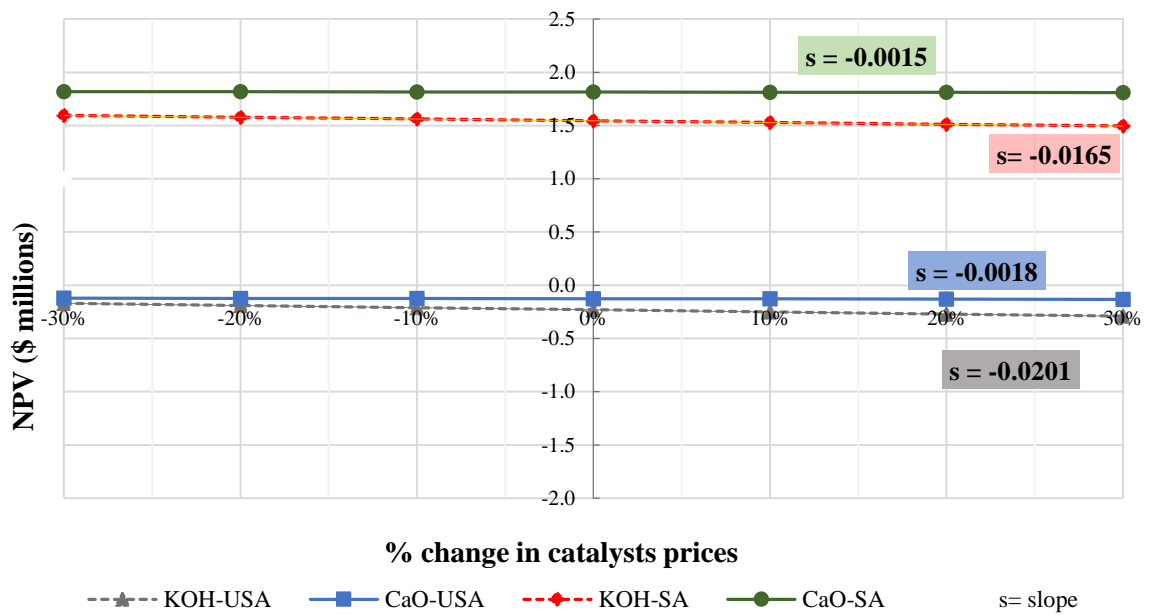


Figure 5-8: Sensitivity of the NPVs of the four economic models to the price of catalysts (KOH and CaO)

From Figure 5-4 to Figure 5-8, it can be noticed that the NPV is more sensitive to the price of feed oil, the price of methanol and the biodiesel selling price. The price of catalyst and the selling price of glycerol have shown not to have a significant impact of the profitability on the processes under investigation.

5.3.2. MULTIPLE PARAMETER ANALYSIS

In the above section, the impact of the prices of raw materials and products were evaluated individually. In reality those parameters are more likely to vary simultaneously. In order to evaluate how the aggregate risks and uncertainties of all those economic parameters influence the profitability of the project, a Monte Carlo simulation was performed.

The Monte Carlo simulation was programmed in the Excel spreadsheets used to perform the previous economic analysis, using the Crystal Ball® simulation software which is an Excel add-in. For the Monte Carlo simulation, the input cells (cells containing the prices of raw material and products in this case), can take different values drawn randomly from a statistical distribution that describe the uncertainty of the data. In this case, all parameters were described by triangle distributions which were defined based on the upper and lower bound considered for the single parameter analysis. The input cells which contain the uncertain parameters are called “Assumptions”. The output cell which is in this case the value of the NPV is called “Forecast”.

When the simulation is run, the software replaces the values in the “Assumptions” cells with a random number, drawn from the specified distribution. This automatically updates the calculation in the whole spreadsheet, hence updating the value in the forecast cell. This process is repeated a predefined number of times, called iteration. The values in the forecast cells are stored for each iteration and can be presented in interactive histograms and descriptive statistics such as mean, standard deviation and correlations. For these simulations, 1000 iterations have been performed.

The Monte Carlo simulation results of the different economic models are presented in the histograms and descriptive statistics presented in Figure 5-9 to Figure 5-12.

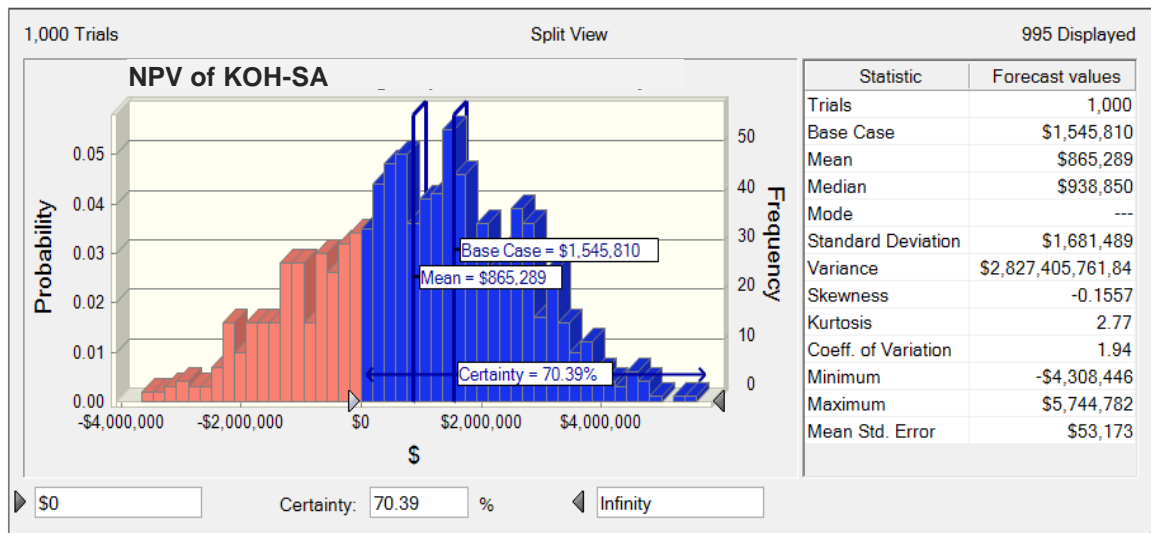


Figure 5-9: Probability certainty chart for NPV>0 for the KOH-SA model

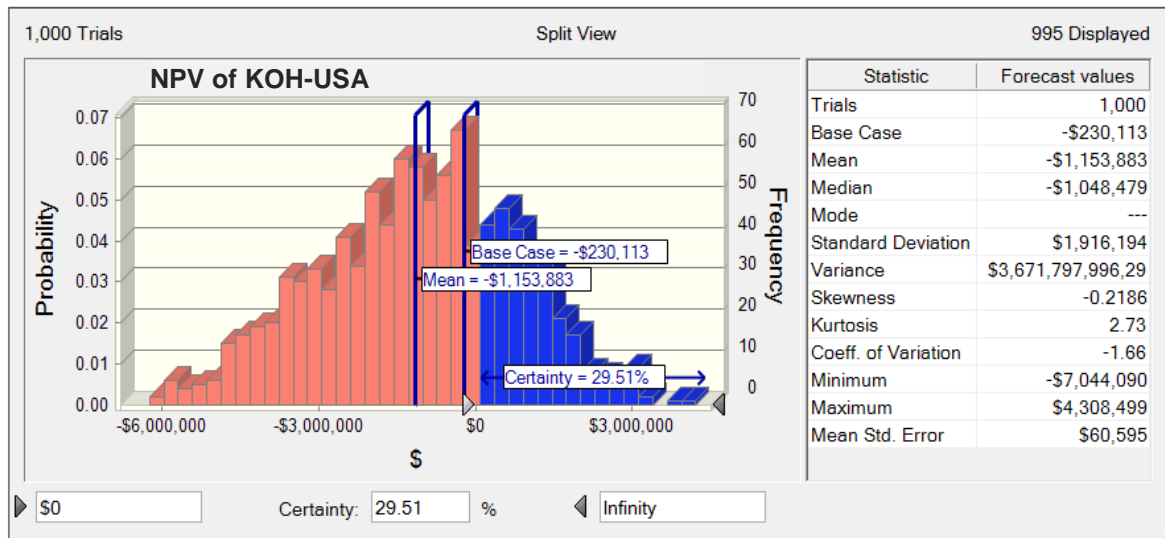


Figure 5-10: Probability certainty chart for NPV>0 for the KOH-USA model

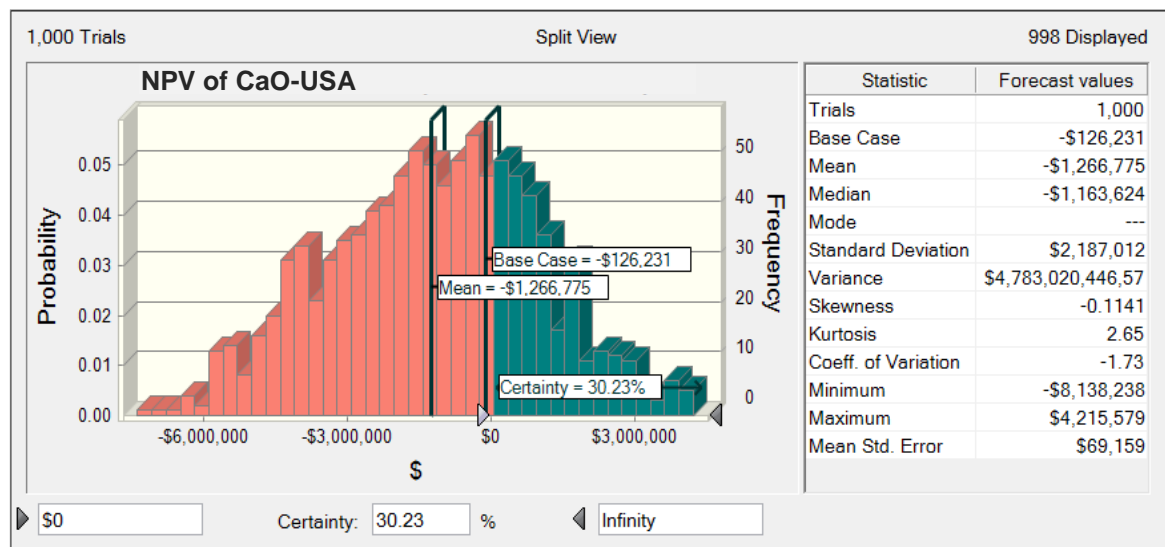


Figure 5-11: Probability certainty chart for NPV>0 for the CaO-USA model

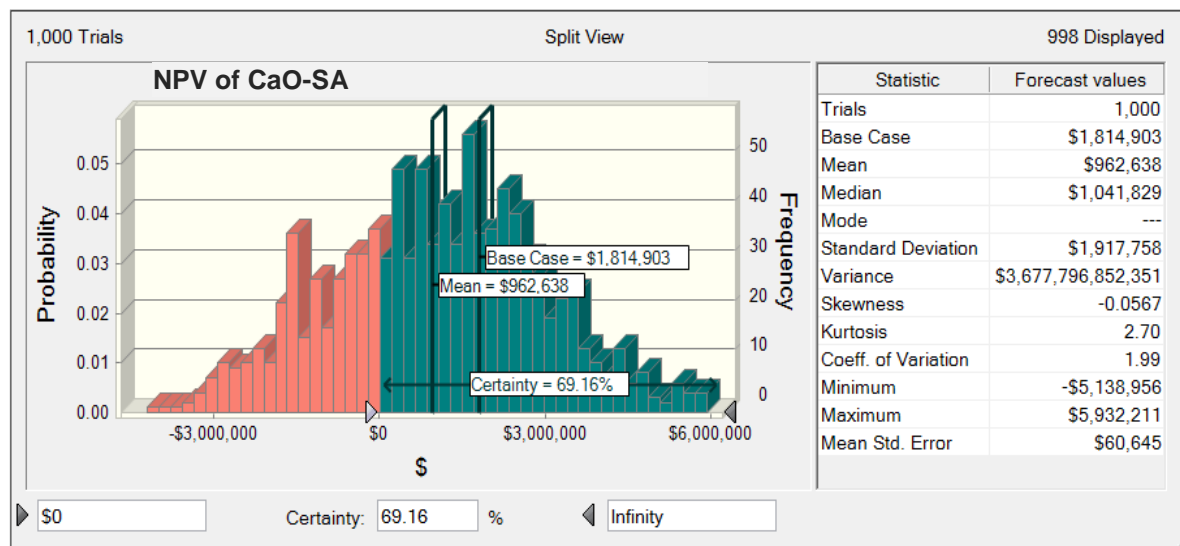


Figure 5-12: Probability certainty chart for NPV>0 for the CaO-SA model

The results indicate a mean NPV of \$0.87 million with a 70.4% probability of positive NPV for the KOH-SA process (Figure 5-9 to Figure 5-12). Although most investors would prefer at least a 90% probability of success to invest in a project (Yeboah *et al.*, 2013), 70.4% probability of success for this project indicates that it is more likely to succeed than to fail. As regards the KOH-USA model, the histogram shows a 29.5% probability of achieving positive project NPV if implemented, hence a 71.5% risk to have a significant loss (Figure 5-10). The CaO-SA and CaO-USA processes indicate a 30.2 and 69.2% probability of success respectively (Figure 5-11 and Figure 5-12).

The models developed based on the USA cost factors present a far higher risk of failure (NPV<0) than the ones developed based on the SA cost factors. However when comparing the probability of profitability over the uncertainty of prices of raw materials and products between the KOH and CaO processes, it is observed that the heterogeneous CaO process presents a higher risk of unprofitability when considering the SA cost factors and a lower risk when considering the USA cost factor.

The sensitivity charts presented in Figure 5-13 to Figure 5-16 allow to determine the influence that each assumption has on the forecast, by the ranking of the different variables to their contribution to risk in the model. Positive percentages indicate that an increase in the assumption is associated with an increase in the forecast, while negative percentages imply the reverse.

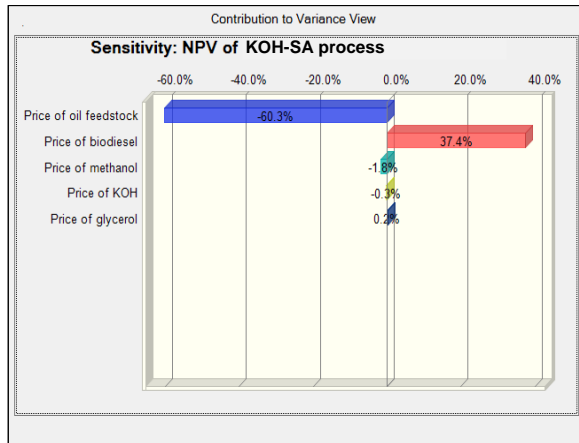


Figure 5-13: Sensitivity chart- KOH-SA process

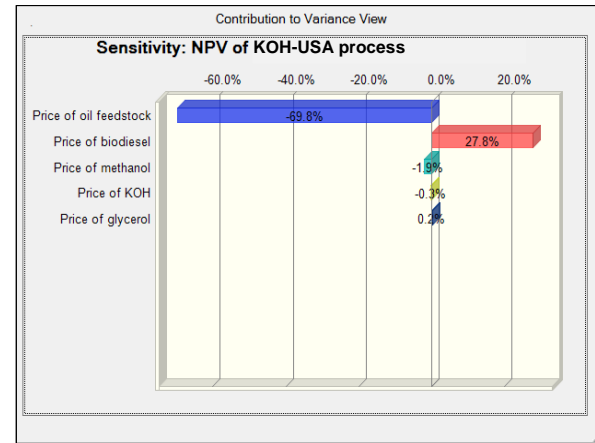


Figure 5-14: Sensitivity chart- KOH-USA process

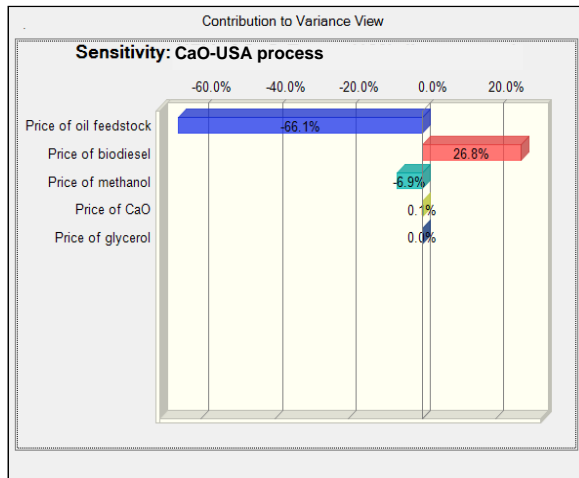


Figure 5-15: Sensitivity chart- CaO-USA process

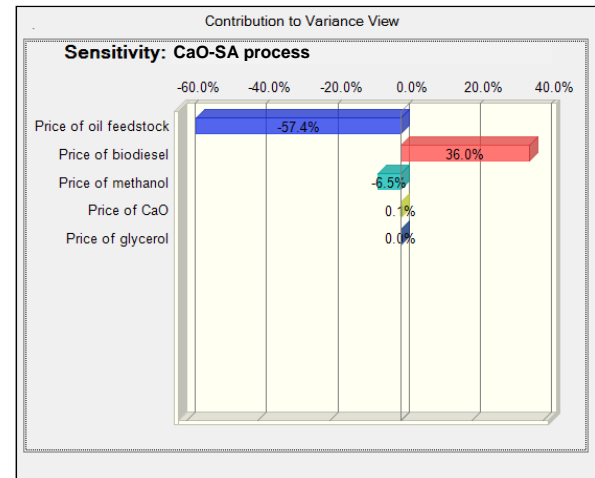


Figure 5-16: Sensitivity chart- CaO-SA process

As concluded from the single parameter risk analysis, the price of feed oil (represented by the blue colour) has the highest impact on the profitability of the different process models. The sensitivity charts show that a decrease in the price of oil feed is required in order to increase the probability of success ($NPV > 0$). Focussing market research on lower cost suppliers for oil feed would be advisable.

In order to give an estimate of the maximum price of oil feed required to guarantee a probability of positive NPV of 90% (minimum certainty level favourable to investors according to Yeboah *et al.*, 2013), the sensitivity of the NPV to the change in price of oil feed was evaluated using the Monte Carlo analysis. The price of oil was varied one value at the time, while keeping the uncertainty of the other prices. The histograms results presented in Appendix C-14 to Appendix C-23 are summarised in Table 5-2 to Table 5-5.

Table 5-2: Sensitivity analysis of the impact of feedstock oil price on the probability of success (NPV>0) for the KOH-USA process. Feedstock oil price (\$/ton)

NPV/Scenario	-80%	-40%	Baseline	+40%	+80%	+120%	+160%	+200%
	(\$82)	(\$245)	(\$408)	(\$571)	(\$734)	(\$898)	(\$1 061)	(\$1 224)
*Mean NPV	2.126	1.043	-0.020	-1.041	-2.149	3.193	-4.273	-5.355
*Min NPV	-0.468	-1.513	-2.729	-3.653	-4.585	-5.726	-6.884	-8.051
*Max NPV	5.172	4.040	2.797	1.666	0.894	-0.040	-1.271	-2.710
Probability (NPV>0)	99.24%	81.48%	46.20%	17.86%	2.00%	0.00%	0.00%	0.00%

* Values in \$ millions, computed from simulation

Table 5-3: Sensitivity analysis of the impact of feedstock oil price on the probability of success (NPV>0) for the KOH-SA process. Feedstock oil price (\$/ton)

NPV/Scenario	-80%	-40%	Baseline	+40%	+80%	+120%	+160%	+200%
	(\$82)	(\$245)	(\$408)	(\$571)	(\$734)	(\$898)	(\$1 061)	(\$1 224)
*Mean NPV	3.558	2.664	1.796	0.966	0.050	-0.804	-1.690	-2.580
*Min NPV	1.047	0.217	-0.826	-1.568	-2.315	-3.217	-4.181	-5.188
*Max NPV	6.534	5.608	4.546	3.632	3.021	2.269	1.248	-0.006
Probability (NPV>0)	100.00%	100.00%	95.78%	79.72%	49.42%	22.59%	7.79%	0.00%

* Values in \$ millions, computed from simulation

Table 5-4: Sensitivity analysis of the impact of feedstock oil price on the probability of success (NPV>0) for the CaO-USA process. Feedstock oil price (\$/ton)

NPV/Scenario	-80%	-40%	Baseline	+40%	+80%	+120%	+160%	+200%
	(\$82)	(\$245)	(\$408)	(\$571)	(\$734)	(\$898)	(\$1 061)	(\$1 224)
*Mean NPV	2.444	1.174	0.008	-1.216	-2.357	-3.555	-4.812	-6.063
*Min NPV	-0.770	-1.920	-2.954	-4.392	-5.997	-6.916	-7.966	-8.965
*Max NPV	5.718	4.788	3.413	2.314	1.207	-0.045	-1.356	-2.597
Probability (NPV>0)	98.00%	82.49%	47.63%	17.26%	4.18%	0.00%	0.00%	2.00%

* Values in \$ millions, computed from simulation

Table 5-5: Sensitivity analysis of the impact of feedstock oil price on the probability of success (NPV>0) for the CaO-SA process. Feedstock oil price (\$/ton)

NPV/Scenario	-80%	-40%	Baseline	+40%	+80%	+120%	+160%	+200%
	(\$82)	(\$245)	(\$408)	(\$571)	(\$734)	(\$898)	(\$1 061)	(\$1 224)
*Mean NPV	4.016	2.966	2.012	1.006	0.079	-0.909	-1.944	-2.977
*Min NPV	0.978	-0.004	-0.840	-1.989	-3.357	-4.117	-4.929	-5.776
*Max NPV	0.718	6.478	5.325	4.422	3.555	2.470	1.430	0.376
Probability (NPV>0)	100.00%	99.89%	96.46%	78.13%	48.88%	25.09%	5.98%	0.78%

* Values in \$ millions, computed from simulation

The results indicate that the probability of positive NPV when considering the baseline price of oil feed (\$408/ton) while keeping the uncertainty of the other prices is 46.20%, 95.78%, 47.63% and 96.46% for the KOH-USA, KOH-SA, CaO-USA and CaO-SA models respectively. In order to guarantee a 90% probability of positive NPV, the maximum price of oil feed needs to be \$160, \$161, \$512 and \$514/ton for the KOH-USA, KOH-SA, CaO-USA and CaO-SA models respectively (interpolation).

5.4. CHAPTER OUTCOMES

In this chapter, the impact of uncertain parameters on the profitability of the KOH and CaO processes under investigation was evaluated. The variable parameters considered are the plant capacity and the price of raw materials and products. Plant capacity ratios of 0.5, 1, 2 and 5 fold the current plant capacities used in the previous chapters were considered. The findings are listed below.

- It was found that an increase in the plant capacity resulted in a decrease in the total manufacturing cost per kg of biodiesel produced and in an increase in the net present value. This suggests that the processes are more profitable at higher plant capacities up to 5 fold the current plant capacities.
- It was also observed that converting from KOH to CaO process is more profitable when the NPV was evaluated based on the SA cost factors as opposed to when evaluated using the USA cost factors.
- As regards the sensitivity analysis over the cost of raw materials and products, the results of the Monte Carlo analysis showed that feedstock oil and biodiesel prices were the factors with the highest impact on the profitability of the processes. In order to guarantee a 90% probability of success ($NPV > 0$), the maximum price of feedstock oil needs to be \$160 and \$512 for the KOH and CaO processes respectively.

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NOMENCLATURE

<u>Abbreviations</u>	<u>Definitions</u>
NPV	Net Present Value
WVO	Waste Vegetable Oil

CHAPTER 6: PROCESS DEBOTTLENECKING: CENTRIFUGE VS. SETTLING

Highlights

- The study is performed to eliminate the time bottlenecks of the process.
- The proposed process scenarios consist of replacing settling with centrifugation.
- Higher investment cost for the new process scenario is observed.
- The process scenarios adopting centrifugation were more profitable.

6.1. INTRODUCTION

In the process simulation performed in this study, settling was chosen as the means of separation. The process scheduling presented in Chapter 3 showed that the operations using settling tanks were the bottlenecks of the process. The debottlenecking performed in this study focuses on eliminating the time bottlenecks associated with settling operations.

6.2. DEBOTTLENECKING METHODOLOGY

The total production capacity of a batch plant within a given period is equivalent to the batch size times the number of batches performed during that period. Therefore, increasing the plant capacity requires increasing either the batch size or the number of batches or both (Petrides *et al.*, 2002). In the current study, it was assumed that the process operates at its maximum batch size, so that the process debottlenecking will focus on increasing the number of batches.

The bottlenecks that limit the number of batches are known as time or scheduling bottlenecks (Petrides *et al.*, 2002). Time bottlenecks' equipment units which are characterised by the longest cycle time, determine the maximum number of batches and the plant cycle time. They can be identified by tracking the occupancy time of the different equipment units. The occupancy time of the equipment items for the KOH and CaO processes is graphically displayed in Figure 6-1 and Figure 6-2.

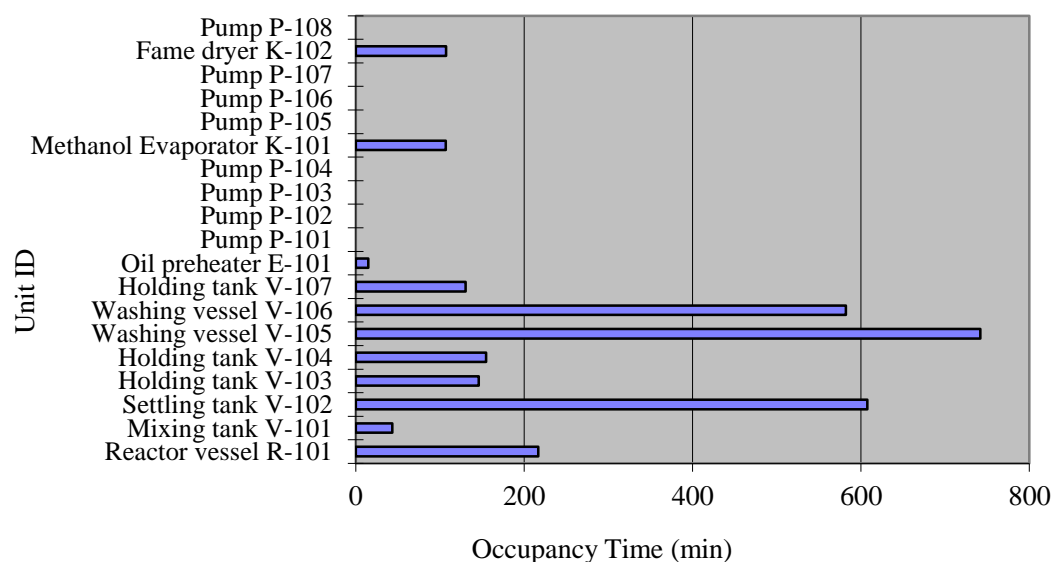


Figure 6-1: Equipment occupancy chart for the KOH process

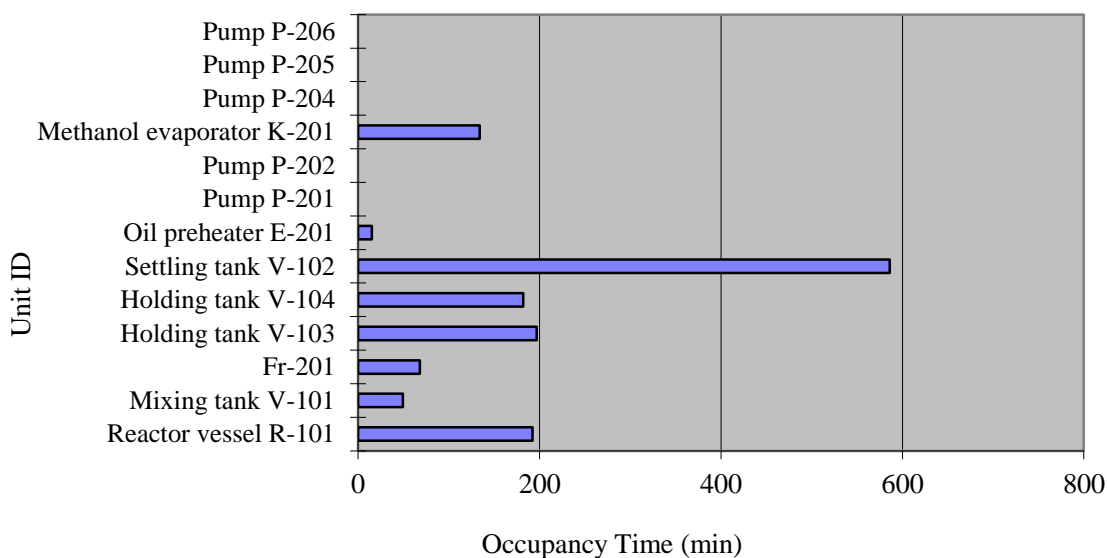


Figure 6-2: Equipment occupancy chart for the CaO process

Time bottlenecks are generally due to sharing of equipment and long process operations. Bottlenecks caused by equipment sharing can be removed by installing additional equipment. If time bottlenecks are caused by long process operation, they can be removed by assigning bottleneck operations to other non-bottleneck equipment unit. Whenever removing the process bottlenecks requires the purchase of new equipment, economic analysis should be performed in order to validate this recommendation. Indeed, the final decision cannot be based on throughput considerations alone (Petrides *et al.*, 2002).

Figure 6-1 and Figure 6-2 show that the washing vessels V-105 and V-106 and the settling tank V-102 are the time bottlenecks for the KOH process while the settling tank V-202 is the bottleneck of the CaO process. Adding a centrifuge after each washing vessel and replacing each settling tank with a centrifuge eliminate the above bottlenecks (See PFD's in Appendix D-1 and Appendix D-2). With each centrifuge assumed to operate for 60 min, the batch time is reduced and the number of batches is increased from 639 to 1804 and from 810 to 2639 for the KOH and CaO processes respectively (See Appendix D-3 and Appendix D-4 for process scheduling charts). The annual production is consequently increased from 1033.6 to 2918 and from 1160.5 to 3780 ton/year.

As mentioned above, the throughput consideration is not sufficient enough to validate the recommendation to include centrifuges. An economic analysis has been performed for this purpose.

6.3. ECONOMIC ANALYSIS

The economic analysis of the KOH and CaO processes with the scenario including the centrifuges was demonstrated in Chapter 4. The fixed capital costs and the total manufacturing costs were first evaluated followed by a profitability analysis in which the net present value, payback period and discounted cash flow rate of return were estimated. The details of the economic analysis are presented in Appendix D-5 to Appendix D-8.

In Figure 6-3 the fixed capital costs for the KOH and CaO processes when using settling and centrifugation as means of separation are compared. The fixed capital cost for the KOH process is 11% higher when implementing centrifugation as compared to only 4% for the CaO process. This was expected due to the higher cost of a centrifuge as compared to a settling tank. The difference between the KOH and CaO processes can be attributed to the fact that the KOH process requires 3 centrifuges as opposed to 1 for the CaO process.

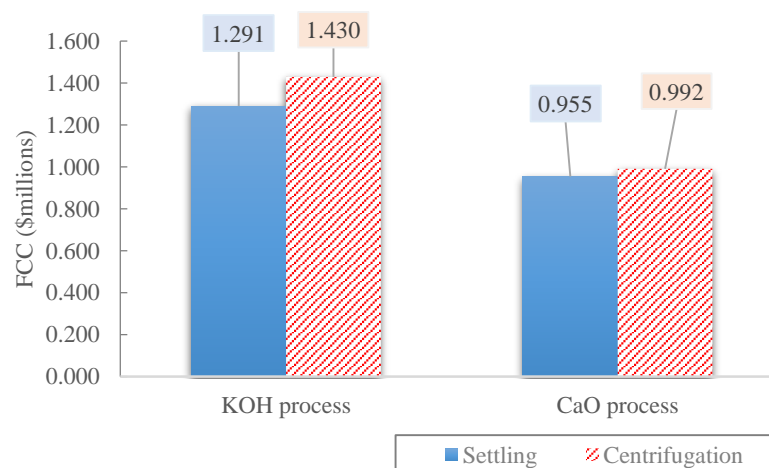


Figure 6-3: Comparison of the fixed capital cost for the KOH and CaO processes when using settling and centrifugation as means of separation

Figure 6-4a compares the total manufacturing costs estimated for the KOH-USA, KOH-SA, CaO-USA and CaO-SA processes when using settling and centrifugation. It can be observed that for all four economic models, the total manufacturing cost is higher when using centrifugation. It is expected due to the higher number of batches which increases the plant throughput for the process using centrifugation.

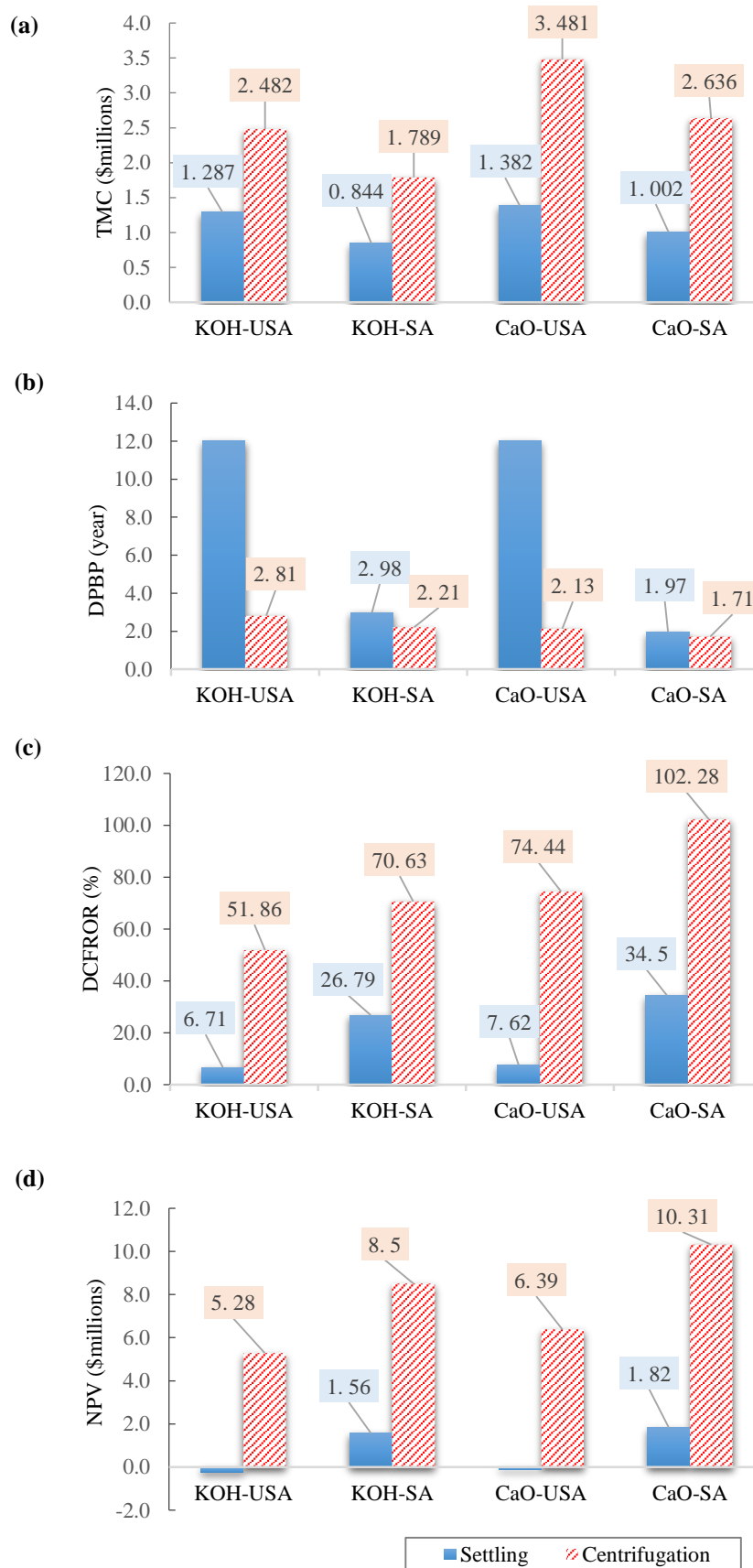


Figure 6-4: Economic comparison for the KOH and CaO processes when using settling and centrifugation as means of separation. (a) Total manufacturing cost, (b) Discounted payback period, (c) Discounted cash flow rate of return, (d) Net present value.

Figure 6-4b to Figure 6-4d compare the four economic models based on discounted payback period, discounted cash flow rate of return and net present value. A shorter payback period is observed for the processes using centrifugation. The KOH-USA and CaO-USA characterised by payback period higher than the project life when using settling, are improved to payback periods of 2.81 and 2.13 years respectively when centrifugation is employed as a means of separation. It shows therefore that the processes using centrifugation are more profitable. This is confirmed by the DCFROR which is higher for the processes using centrifugation (Figure 6-4c).

Higher NPV observed for the processes using centrifugation also corroborate the fact that using centrifugation as a means of separation in biodiesel production renders the process more profitable as compared to settling. The KOH-USA and CaO-USA processes shown to be unprofitable ($NPV < 0$) with settling separation, are characterised with NPV values of \$5.28 and \$6.39 million respectively, when centrifugation is employed as the means of separation.

The new process scenario including centrifuges is recommended since it eliminates the time bottlenecks and improves the process economics.

6.4. CHAPTER OUTCOMES

This chapter focused on eliminating the time bottleneck associated with the use of settling operations in the biodiesel production processes developed in Chapter 3. The proposed scenario was to add a centrifuge after each washing vessel and replace all settling tanks with centrifuges. The economic analysis performed on this process scenario revealed higher cost of investment and annual manufacturing cost. However, the profitability analysis performed based on DCFROR, DPBP and NPV showed that the process scenario using centrifugation was more profitable than the base case using settling over the prescribed period. It can therefore be concluded that despite the higher cost of investment, centrifugation should be applied in batch biodiesel production instead of settling owing to the economic advantages associated its use.

REFERENCE

Petrides, D., Koulouris, A., Siletti, C. 2002. Throughput Analysis and Debottlenecking of Biomanufacturing Facilities - A Job for Process Simulators. *BioPharm*, 15(8): 28-64.

NOMENCLATURE**Abbreviation****Definition****DCFROR**

Discounted Cash Flow Rate of Return

FCC

Fixed Capital Cost

NPV

Net Present Value

DPBP

Discounted Payback Period

TMC

Total Manufacturing Cost

**CHAPTER 7: GENERAL CONCLUSIONS AND
RECOMMENDATIONS**

7.1. INTRODUCTION

The current study explored the economics of biodiesel production processes. From a review of literature presented in Chapter 2, heterogeneous catalyst proved to be a potential alternative to conventional homogeneous catalyst. Economic analyses performed in previous studies have demonstrated the economic superiority of heterogeneous catalysed process. However, no studies have investigated the economic impact of converting an existing homogeneous catalysed process of biodiesel production to an heterogeneous one.

The aim of this thesis was to evaluate the potential economic benefits of converting a batch biodiesel plant from a homogeneous to a heterogeneous catalysed process. A small-scale batch homogeneous catalysed process for biodiesel production located in South Africa was taken as the base case. The process scale and economics were assumed typical in the African context, and perhaps the developing world. The development of the base case process model, its conversion to heterogeneous process and the comparison of both process performances were discussed in Chapter 3. The data obtained from process simulation using Aspen Batch Process Developer[®] for both processes was used to perform an economic analysis. Both processes were compared in terms of capital cost, manufacturing cost and profitability indicators as discussed in Chapter 4. Sensitivity analysis of six parameters (feedstock oil price, methanol price, by-product glycerol price, biodiesel selling price, KOH and CaO catalysts price) was further conducted in order to evaluate the robustness of the processes by examining the effect of positive and negative changes in project parameters on profitability. The analysis was presented in Chapter 5. The study also addressed the debottlenecking of the processes under investigation in Chapter 6.

7.2. SUMMARY OF FINDINGS

The process models of the homogeneous KOH and heterogeneous CaO processes for biodiesel production were found to be technically feasible since they were both able to produce high-grade biodiesel under reasonable operating conditions. Converting from homogeneous to heterogeneous process resulted in a simpler process with a fewer number of process equipment. The batch time was significantly reduced resulting in 12.3% increase in the annual throughput for the heterogeneous process relative to the homogeneous process. The heterogeneous process was also found to require a lower amount of raw materials (-26%) while being more energy intensive (+45%).

The economic comparison conducted on both processes revealed a 25.4% saving in the total capital cost of the heterogeneous process relative to the homogeneous process. As regards the manufacturing costs and profitability analysis, they were estimated using two types of cost factors. The use of USA cost factors as typical of the developed world economic environment revealed unprofitable processes, with the CaO process being more acceptable than the homogeneous process. On the otherhand, the use of SA cost factors as typical of the developing world economic environment, revealed profitable processes, with the CaO process further emerging as more profitable than the KOH process. The SA cost factors were assumed to be the more appropriate for the economic analysis performed in this study. Based on this, a slightly higher unit manufacturing cost was obtained for the CaO process relative to the KOH process, with a higher DCFROR and NPV. The payback period was also reduced from 4.98 to 3.97 years. This shows that over the 12 years of project life prescribed, there is economic benefit when converting from homogeneous to heterogeneous process. However, the higher unit manufacturing cost of biodiesel for the heterogeneous process suggest that heterogeneous process would be less profitable over a much longer project life.

Results from the sensitivity analysis conducted on the KOH and CaO processes revealed that feedstock oil price and biodiesel selling price were the most significant factors contributing to the profitability of the processes. These were further studied through Monte Carlo analysis performed using the Crystal Ball[®] software. In order to guarantee a 90% probability of success ($NPV > 0$), the maximum price of feedstock oil needs to be \$160 and \$512 for the KOH and CaO processes respectively. The heterogeneous process proved to be more tolerable to higher feedstock price. This substantiates the superior profitability of the heterogeneous process and confirms the potential viability of converting from homogeneous catalysed process.

The study also demonstrated that time bottleneck of the KOH and CaO processes under investigation could be removed by implementing centrifugation instead of settling. Economic analysis revealed the higher investment cost and higher annual manufacturing cost for the process scenario adopting centrifugation. However, based on profitability indicators, the scenarios adopting centrifugation were found to be more profitable. These results validate the employment of centrifugation as opposed to settling in biodiesel production.

This study revealed the economic benefits of converting a batch biodiesel plant from homogeneous to heterogeneous catalysed process and the importance of using cost factors relevant to the appropriate economic environment of the project under investigation.

7.3. SIGNIFICANCE OF THE RESEARCH

This study presents the first process simulation for biodiesel production using Aspen Batch Process Developer[®] software available in open literature to the knowledge of the author. It also reports one of the first economic analyses for biodiesel production performed using cost factors based on the African economic environment and confirms the necessity to use cost factors relevant to a particular economic environment when performing economic analysis of a project. It is envisaged that this will open up new studies that would be directed at establishing cost factors relevant to particular economic environments in order to ease the accuracy of future economic analysis.

Previous studies have reported the economic superiority of heterogeneous catalysed process for biodiesel production over the homogeneous one, thus providing preliminary insight for new investors as regards the type of process to develop. This current study has quantified the economic benefit of converting from homogeneous to heterogeneous catalysed process. The outcome provides preliminary insight for owners of existing homogeneous catalysed process plants whereby decisions needs to be made on whether or not to convert to a heterogeneous process.

The decision of implementing settling over centrifugation for small biodiesel plants in South Africa is generally influenced by the investment cost. It is believed that the outcome of the economic and profitability comparison performed for both scenarios, can give a better insight concerning this decision.

7.4. RECOMMENDATIONS FOR FURTHER WORK

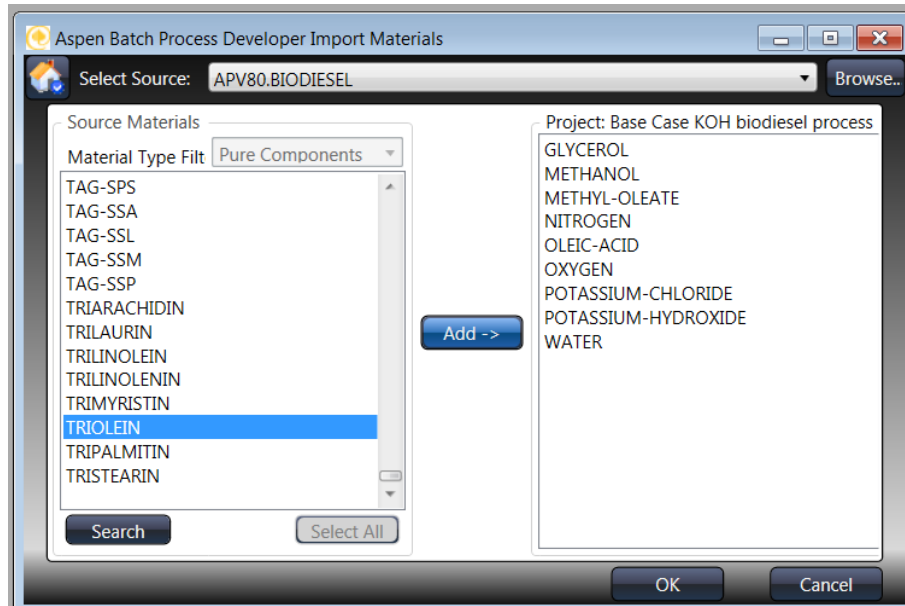
Based on the general findings reported herein, future investigations should consider the following:

- The uncertainty in the purchased cost of equipment in South Africa can be reduced by obtaining the actual data from local vendor.
- It is necessary to further develop cost factors relevant to developing economic environment in order to allow more accurate cost estimations of process plants located in the particular areas.

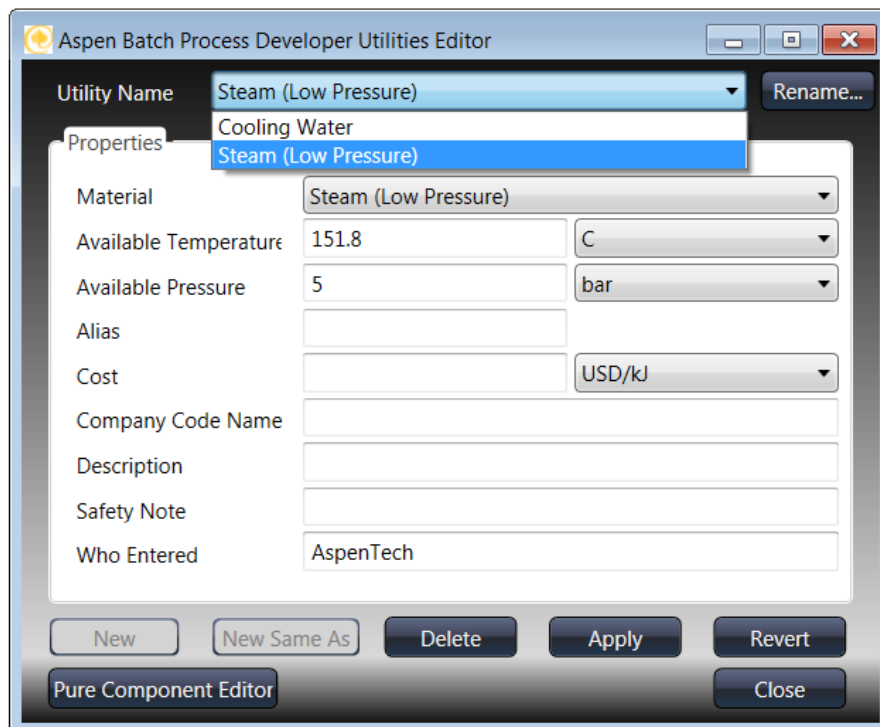
APPENDICES

APPENDIX A. Process simulation

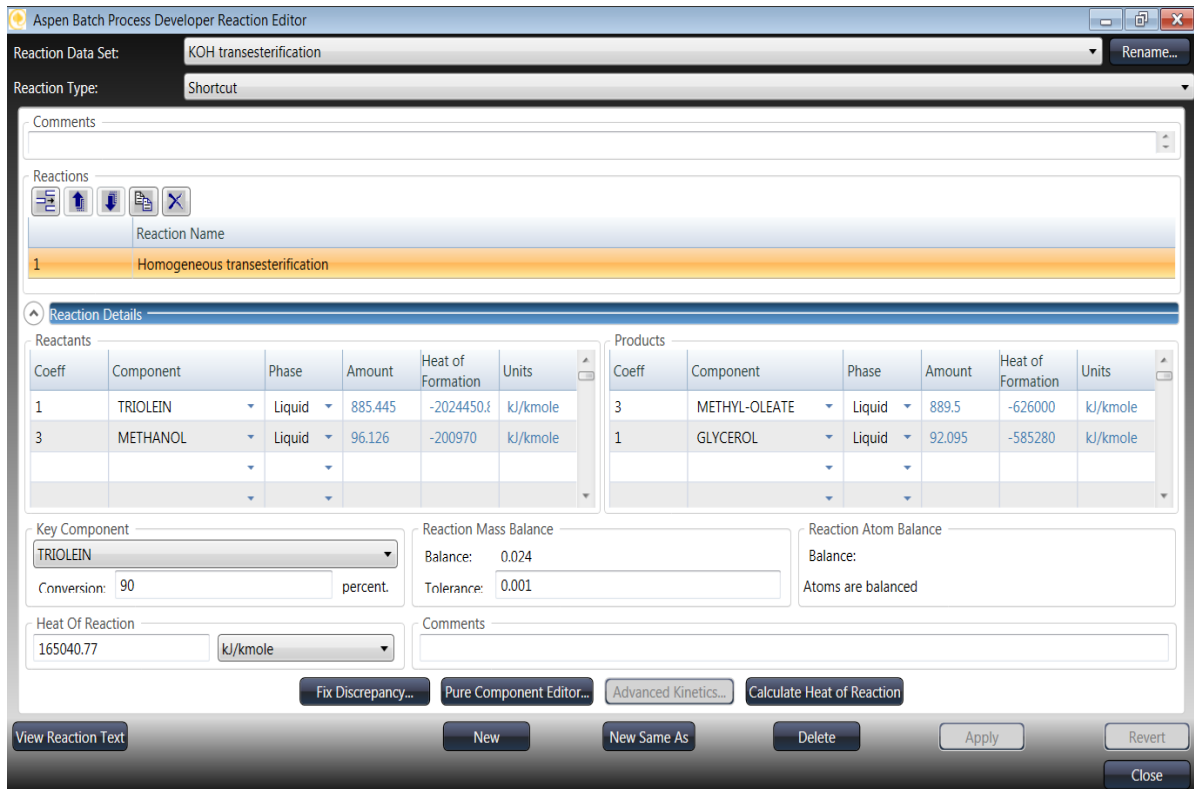
Appendix A-1. Example of dialog box for selection of chemical components



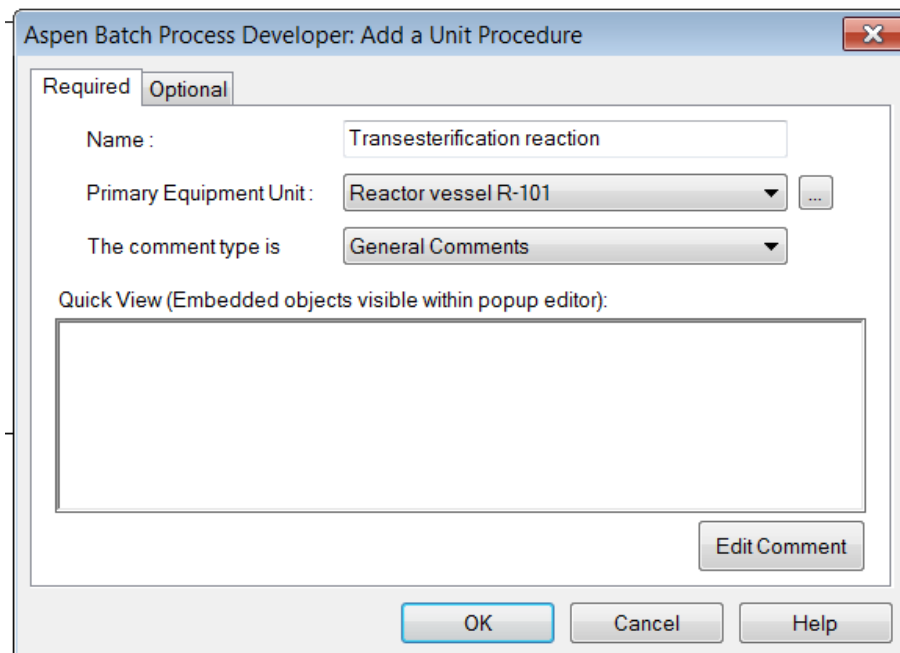
Appendix A-2. Example of dialog box for specifying utilities



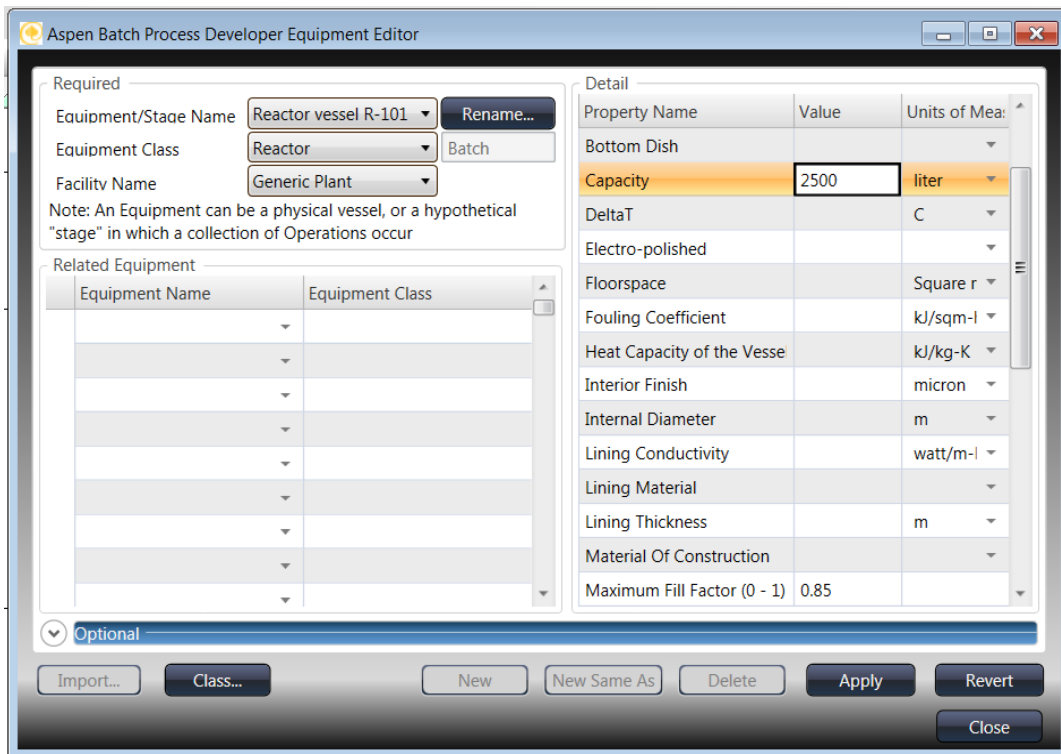
Appendix A-3. Example of dialog box for specifying reaction parameters



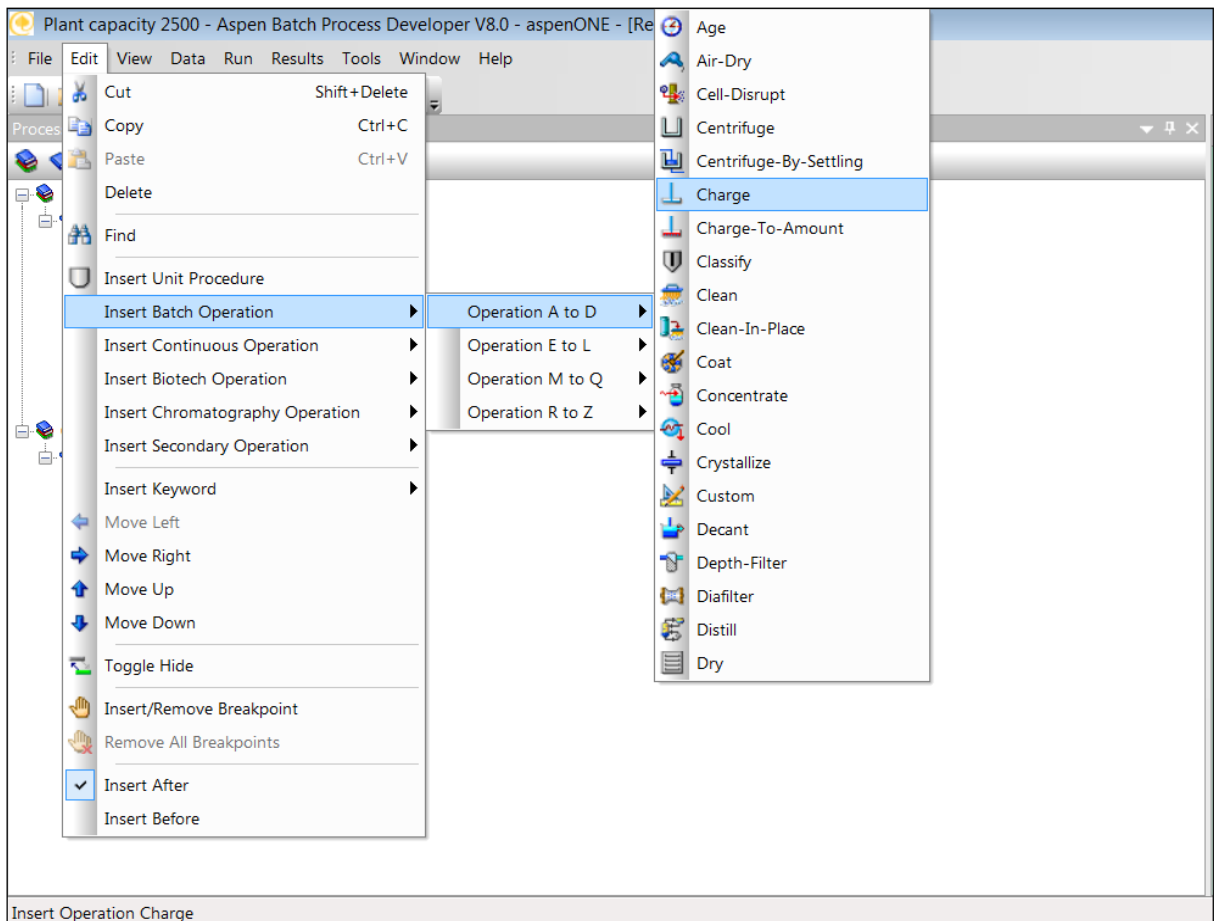
Appendix A-4. Example of dialog box for adding a unit procedure



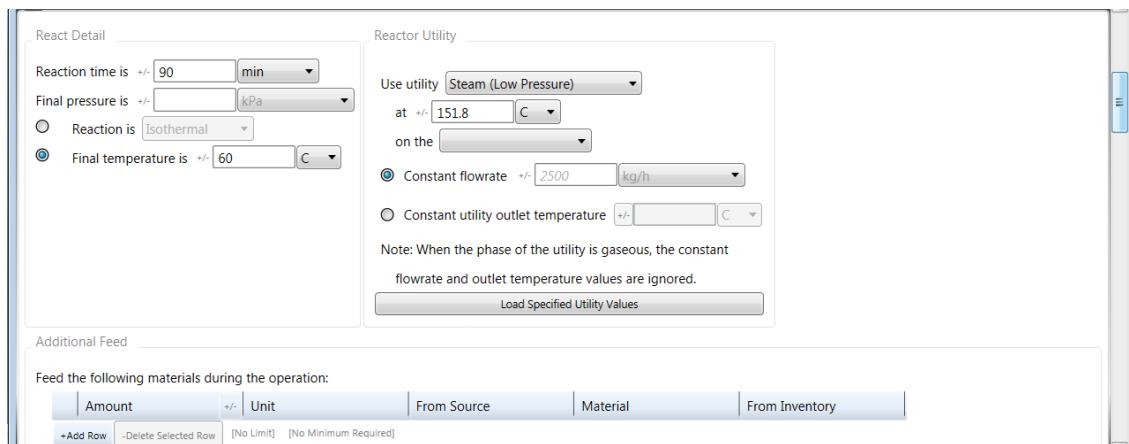
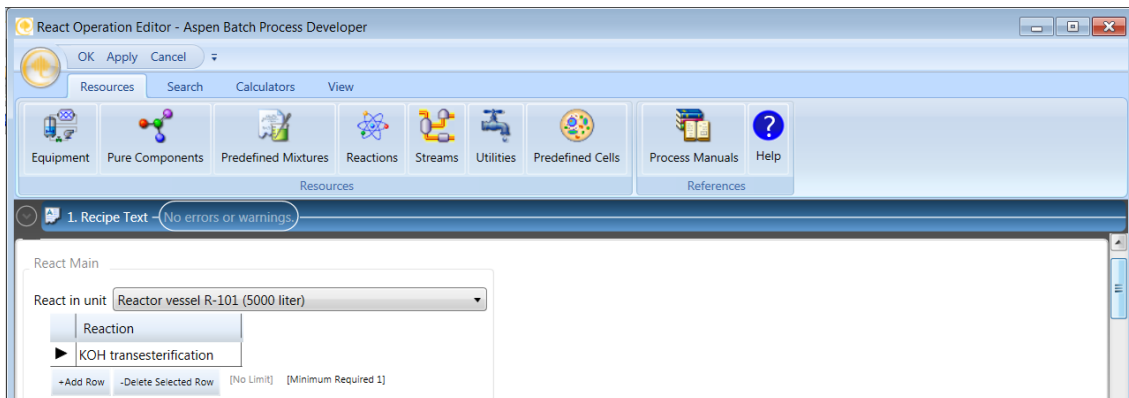
Appendix A-5. Example of dialog box for editing equipment unit specifications



Appendix A-6. Example of dialog box for choosing unit operations



Appendix A-7. Example of dialog box for editing unit operation



Appendix A-8. Example of dialog box for recipe scaling

Recipe Scaling for a Step

Step: KOH catalyst
Version: 1.0
Key Output Intermediate: METHYL-OLEATE
Current Output Batch Size: 904.03 kg
Original Output Batch Size: 482.27 kg
Maximum Output Batch Size: 1123.36 kg
Minimum Output Batch Size: 0 kg
Current Input Batch Size: 1000 kg

Scale the Batch:

To original scale at time of data entry.

To maximum batch size in the size limiting equipment unit.

To maximum batch size in equipment unit

To Key Output Intermediate batch size of
gmole
kg
lb

To Key Input Intermediate batch size of

To times the current batch size.

To minimum batch size (based on the minimum stirred volume in vessels)

To minimum batch size in equipment unit

Save the scaled recipe in Unit of Measure Set

Appendix A-9. Utility stream table for the KOH process

Process	KOH process	Key Input	
(Version):	(1.0)	Intermediate:	TRIOLEIN
	KOH catalyst		METHYL-
Step (Version):	(1.0)	Key Output Intermediate:	OLEATE
		Number of	
		Batches:	1
		Plan Quantity:	1,616.66 kg

BATCH PLUS Stream Label	1.1. Charge-4	3.2. React-13	5.1. Distill-Continuously-28	5.1. Distill-Continuously-29	6.3. pH-Adjust-38	7.1. Distill-Continuously-56	7.1. Distill-Continuously-57
Utility Name	Steam (High Pressure)	Steam (Low Pressure)	Steam (High Pressure)	Cooling Water	Cooling Water	Steam (High Pressure)	Cooling Water
Operation	1.1. Charge	3.2. React	5.1. Distill-Continuously	5.1. Distill-Continuously	6.3. pH-Adjust	7.1. Distill-Continuously	7.1. Distill-Continuously
Unit ID	Oil preheater E-101	Reactor vessel R-101	Methanol evaporator K-101		Washing vessel V-105	FAME dryer K-102	
Start Time (min)	0.00	58.61	756.09	756.09	946.03	2 142.92	2 142.92
End Time (min)	15.00	148.61	862.86	862.86	1 066.03	2 250.39	2 250.39
Total Time (min)	15.00	90.00	106.77	106.77	120.00	107.47	107.47
Inlet Service Temperature (C)	275.60	151.80	275.60	20.00	20.00	275.60	20.00
Outlet Service Temperature (C)	275.60	151.80	275.60	22.67	21.13	275.60	28.22
Mass Flowrate (kg/min)	5.47	1.63	0.54	54.09	54.09	1.42	54.09
Volume Flowrate (litre/h)	13 842.08	38 318.57	1 356.67	3 250.00	3 250.00	3 594.99	3 250.00
Total Heat Duty (kJ)	1.28E+05	3.10E+05	8.95E+04	-6.47E+04	-3.08E+04	2.39E+05	-2.00E+05

Appendix A-10. Utility stream table for the process

Process (Version):	CaO process (1.0)	Key Input Intermediate:	TRIOLEIN
Step (Version):	CaO catalyst (1.0)	Key Output Intermediate:	METHYL-OLEATE
		Number of Batches:	1
		Plan Quantity:	1 432.21 kg

BATCH PLUS Stream Label	1.1. Charge-4	3.2. React-13	5.1. Distill-Continuously-25	5.1. Distill-Continuously-26
Utility Name	Steam (High Pressure)	Steam (High Pressure)	Steam (High Pressure)	Cooling Water
Operation	1.1. Charge	3.2. React	5.1. Distill-Continuously	5.1. Distill-Continuously
Unit ID	Oil preheater E-201	Reactor vessel R-101	Methanol evaporator K-201	
Start Time (min)	0.00	64.43	192.43	192.43
End Time (min)	15.00	124.43	326.34	326.34
Total Time (min)	15.00	60.00	133.91	133.91
Inlet Service Temperature (C)	275.60	275.60	275.60	20.00
Outlet Service Temperature (C)	275.60	275.60	275.60	34.96
Mass Flowrate (kg/min)	5.52	3.06	2.26	54.09
Volume Flowrate (litre/h)	13 973.78	7 738.69	5 718.55	3 250.00
Total Heat Duty (kJ)	1.29E+05	2.87E+05	4.73E+05	-4.54E+05

Appendix A-11. Material stream table for the KOH process

Process (Version): KOH process (1.0)

Step (Version): KOH catalyst (1.0)

Key Input Intermediate:

Key Output Intermediate:

Number of Batches:

Plan Quantity:

TRIOLEIN

METHYL-OLEATE

1

1 616.66 kg

BATCH PLUS Stream Label		1.1. Charge-1	1.1. Charge-2	2.1. Charge-5	2.2. Charge-7	3.1. Transfer-9	3.3. Transfer-14
Operation		1.1. Charge	1.1. Charge	2.1. Charge	2.2. Charge	3.1. Transfer	3.3. Transfer
Start Time	(min)	0.00	0.00	15.00	30.00	45.00	148.61
End Time	(min)	15.00	15.00	30.00	45.00	58.61	216.61
Total Time	(min)	15.00	15.00	15.00	15.00	13.61	68.00
From Unit		WVO storage	Oil preheater E-101	Fresh MeOH storage	Storage	Mixing tank V-101	Reactor vessel R-101
To Unit		Oil preheater E-101	Reactor vessel R-101	Mixing tank V-101	Mixing tank V-101	Reactor vessel R-101	Settling tank V-102
Stream Type		Input	Intermediate	Input	Input	Intermediate	Intermediate
Total (Kg)	Mol (Wt.)	1 797.2700	1 797.2700	388.2806	35.7657	424.0463	2 221.3599
METHANOL	32.04			388.2806		388.2806	213.5543
GLYCEROL	92.10						167.3992
OLEIC-ACID	282.47	8.9864	8.9864				8.9863
METHYL-OLEATE	296.50						1 616.8260
HYDROGEN-CHLORIDE	36.46						
POTASSIUM-HYDROXIDE	56.11				35.7657	35.7657	35.7657
POTASSIUM-CHLORIDE	74.55						
TRIOLEIN	885.45	1 788.2837	1 788.2837				178.8284
WATER	18.02						
Total Mass	(kg)	1 797.27	1 797.27	388.28	35.77	424.05	2 221.36
Total Volume	(litre)	1 964.45	1 964.45	492.91	17.50	510.44	2 550.00
Mass Flowrate	(kg/min)	119.82	119.82	25.89	2.38	31.15	32.67
Volume Flowrate	(litre/h)	7 857.80	7 857.80	1 971.65	69.99	2 250.00	2 250.00
Composite Product Factor		1.11	1.11	0.24	0.02	0.26	1.37
Phase		Liquid1	Liquid1	Liquid1	Solid	Liquid1	Liquid1
Temperature	(C)	25.00	60.00	25.00	25.00	25.00	60.00
Average Density	(kg/Cubic m)	914.90	914.90	787.73	2 043.92	830.74	871.12
Average Viscosity	(cp)	60.79	18.63	0.92	0.00	0.92	2.35
Average Heat Capacity	(kJ/kg-K)	2.00	2.07	2.35	0.00	2.15	0.64
Average Molecular Weight		876.09	876.09	32.04	56.11	33.24	150.02

BATCH PLUS Stream Label		4.1. Decant-17	4.2. Transfer-20	5.1. Distill-Continuously-23	5.1. Distill-Continuously-24	5.1. Distill-Continuously-25	5.2. Transfer-30	
Operation		4.1. Decant	4.2. Transfer	5.1. Distill-Continuously	5.1. Distill-Continuously	5.1. Distill-Continuously	5.2. Transfer	
Start Time	(min)	711.61	741.61	756.09	761.16	761.16	862.86	
End Time	(min)	741.61	756.09	857.79	862.86	862.86	916.03	
Total Time	(min)	30.00	14.48	101.71	101.71	101.71	53.16	
From Unit		Settling tank V-102	Settling tank V-102	Holding tank V-103	Methanol evaporator K-101	Methanol evaporator K-101	Holding tank V-104	
To Unit		Holding tank V-103	Crude glycerol storage	Methanol evaporator K-101	Unreacted MeOH storage	Holding tank V-104	Washing vessel V-105	
Stream Type		Intermediate	Output	Intermediate	Output	Intermediate	Intermediate	
Total (Kg)								
	Mol (Wt.)	1 695.0895	526.2703	1 695.0895	63.1053	1 631.9842	1 631.9842	
METHANOL	32.04	64.0663	149.4880	64.0663	63.1053	0.9610	0.9610	
GLYCEROL	92.10	0.0167	167.3825	0.0167		0.0167	0.0167	
OLEIC-ACID	282.47	7.1891	1.7973	7.1891		7.1891	7.1891	
METHYL-OLEATE	296.50	1 616.6643	0.1617	1 616.6643		1 616.6643	1 616.6643	
HYDROGEN-CHLORIDE	36.46							
POTASSIUM-HYDROXIDE	56.11		7.1531	28.6125	7.1531		7.1531	
POTASSIUM-CHLORIDE	74.55							
TRIOLEIN	885.45		178.8284					
WATER	18.02							
Total Mass		(kg)	1 695.09	526.27	1 695.09	63.11	1 631.98	1 631.98
Total Volume		(litre)	2 006.99	542.84	2 006.63	84.27	1 994.81	1 993.65
Mass Flowrate		(kg/min)	56.50	36.36	16.67	0.62	16.05	30.70
Volume Flowrate		(litre/h)	4 013.99	2 250.00	1 183.79	49.72	1 176.82	2 250.00
Composite Product Factor			1.11	1.05	0.33	1.05	0.04	1.01
Phase			Liquid1	Liquid1	Liquid1	Liquid1	Liquid1	Liquid1
Temperature		(C)	59.91	59.91	59.69	64.70	103.73	103.05
Average Density		(kg/Cubic m)	844.59	969.48	844.74	748.80	818.11	818.59
Average Viscosity		(cp)	0.92	6.98	0.92	0.92	0.92	0.92
Average Heat Capacity		(kJ/kg-K)	2.00	0.33	1.64	0.33	2.35	0.25
Average Molecular Weight			876.09	876.09	32.04	56.11	33.24	150.02

BATCH PLUS Stream Label		6.8. Transfer-49	7.1. Distill-Continuously-52	7.1. Distill-Continuously-53	7.1. Distill-Continuously-54	
Operation		6.8. Transfer	7.1. Distill-Continuously	7.1. Distill-Continuously	7.1. Distill-Continuously	
Start Time	(min)	2 129.72	2 142.92	2 148.17	2 148.17	
End Time	(min)	2 142.92	2 245.15	2 250.39	2 250.39	
Total Time	(min)	13.20	102.23	102.23	102.23	
From Unit		Washing vessel V-106	Holding tank V-107	FAME dryer K-102	FAME dryer K-102	
To Unit		Waste water storage	FAME dryer K-102	Atmosphere	Biodiesel storage	
Stream Type		Output	Intermediate	Output	Output	
Total (Kg)						
	Mol (Wt.)	495.2401	1 703.7854	86.2499	1 617.5355	
METHANOL	32.04					
GLYCEROL	92.10					
OLEIC-ACID	282.47	1.0784				
METHYL-OLEATE	296.50		1 616.6643		1 616.6643	
HYDROGEN-CHLORIDE	36.46					
POTASSIUM-HYDROXIDE	56.11					
POTASSIUM-CHLORIDE	74.55		0.4752			
TRIOLEIN	885.45					
WATER	18.02	493.6865	87.1212	86.2499	0.8712	
Total Mass		(kg)	495.24	1 703.79	86.25	1 617.54
Total Volume		(litre)	495.15	1 949.70	86.25	1 938.84
Mass Flowrate		(kg/min)	37.51	16.67	0.84	15.82
Volume Flowrate		(litre/h)	2 250.00	1 144.34	50.62	1 137.96
Composite Product Factor			1.11	0.31	1.05	0.05
Phase			Liquid1+Solid	Liquid1	Liquid1	Liquid1
Temperature		(C)	27.65	27.64	60.07	77.38
Average Density		(kg/Cubic m)	1 000.18	873.87	999.96	834.28
Average Viscosity		(cp)	0.86	0.92	0.48	0.92
Average Heat Capacity		(kJ/kg-K)	2.00	4.17	0.45	4.17
Average Molecular Weight			876.09	18.07	165.62	18.02

Appendix A-12. Material stream table for the CaO process

Process (Version): CaO process (1.0)

Step (Version): CaO catalyst (1.0)

Key Input

Intermediate:

Key Output Intermediate:

Number of Batches:

Plan Quantity:

TRIOLEIN

METHYL-OLEATE

1

1 432.21 kg

BATCH PLUS Stream Label		1.1. Charge-1	1.1. Charge-2	2.1. Charge-5	2.2. Charge-7	3.1. Transfer-9	4.1. Filter-14
Operation		1.1. Charge	1.1. Charge	2.1. Charge	2.2. Charge	3.1. Transfer	4.1. Filter
Start Time	(min)	0.00	0.00	15.00	30.00	45.00	124.43
End Time	(min)	15.00	15.00	30.00	45.00	64.43	192.43
Total Time	(min)	15.00	15.00	15.00	15.00	19.43	68.00
From Unit		WVO storage	Oil preheater E-201	Fresh MeOH storage	Storage	Mixing tank V-101	Reactor vessel R-101
To Unit		Oil preheater E-201	Reactor vessel R-101	Mixing tank V-101	Mixing tank V-101	Reactor vessel R-101	Fr-201
Stream Type		Input	Intermediate	Input	Input	Intermediate	Intermediate
Total		1 583.7100	1 583.7100	570.2388	15.7579	585.9967	2 169.7455
METHANOL	32.04			570.2388		570.2388	414.9613
GLYCEROL	92.10						148.1636
OLEIC-ACID	282.47	7.9186	7.9186				2.3756
METHYL-OLEATE	296.50						1 436.8576
CALCIUM-OXIDE	56.08				15.7579	15.7579	15.7579
TRIOLEIN	885.45	1 575.7915	1 575.7915				151.2760
WATER	18.02						0.3536
Total Mass	(kg)	1 583.71	1 583.71	570.24	15.76	586.00	2 169.75
Total Volume	(litre)	1 731.02	1 731.02	723.90	4.70	728.61	2 550.00
Mass Flowrate	(kg/min)	105.58	105.58	38.02	1.05	30.16	31.91
Volume Flowrate	(litre/h)	6 924.10	6 924.10	2 895.61	18.82	2 250.00	2 250.00
Composite Product Factor		1.11	1.11	0.40	0.01	0.41	1.51
Phase		Liquid1	Liquid1	Liquid1	Solid	Liquid1+Solid	Liquid1+Solid
Temperature	(C)	25.00	65.00	25.00	25.00	25.00	65.00
Average Density	(kg/Cubic m)	914.90	914.90	787.73	3 350.00	804.27	850.88
Average Viscosity	(cp)	60.79	16.16	0.92	0.00	0.90	1.98
Average Heat Capacity	(kJ/kg-K)	2.00	2.08	2.35	1.34	2.32	0.83
Average Molecular Weight		876.09	876.09	32.04	56.08	32.42	109.11

BATCH PLUS Stream Label		4.1. Filter-15	5.1. Distill-Continuously-20	5.1. Distill-Continuously-21	5.1. Distill-Continuously-22	5.2. Transfer-27	6.1. Decant-30	
Operation		4.1. Filter	5.1. Distill-Continuously	5.1. Distill-Continuously	5.1. Distill-Continuously	5.2. Transfer	6.1. Decant	
Start Time	(min)	124.43	192.43	197.51	197.51	326.34	874.66	
End Time	(min)	192.43	321.26	326.34	326.34	379.66	904.66	
Total Time	(min)	68.00	128.83	128.83	128.83	53.32	30.00	
From Unit		Fr-201	Holding tank V-103	Methanol evaporator K-201	Methanol evaporator K-201	Holding tank V-104	Settling tank V-102	
To Unit		Holding tank V-103	Methanol evaporator K-201	Unreacted MeOH storage	Holding tank V-104	Settling tank V-102	Biodiesel storage	
Stream Type		Intermediate	Intermediate	Output	Intermediate	Intermediate	Output	
Total (kg)		Mol (Wt.)	2 147.2365	2 147.2365	413.5776	1 733.6589	1 733.6589	1 432.7147
METHANOL	32.04	413.6604	413.6604	413.5776	0.0827	0.0827	0.0165	
GLYCEROL	92.10	147.6991	147.6991		147.6991	147.6991	0.0148	
OLEIC-ACID	282.47	2.3681	2.3681		2.3681	2.3681	0.4736	
METHYL-OLEATE	296.50	1 432.3530	1 432.3530		1 432.3530	1 432.3530	1 432.2098	
CALCIUM-OXIDE	56.08	0.0016	0.0016		0.0016	0.0016		
TRIOLEIN	885.45	150.8017	150.8017		150.8017	150.8017		
WATER	18.02	0.3525	0.3525		0.3525	0.3525		
Total Mass		(kg)	2 147.24	2 147.24	413.58	1 733.66	1 733.66	1 432.71
Total Volume		(litre)	2 537.26	2 537.09	552.32	1 999.78	1 999.47	1 714.40
Mass Flowrate		(kg/min)	31.58	16.67	3.21	13.46	32.51	47.76
Volume Flowrate		(litre/h)	2 238.76	1 181.56	257.22	931.33	2 250.00	3 428.79
Composite Product Factor			1.50	1.50	1.50	0.29	1.21	1.21
Phase			Liquid1+Solid	Liquid1+Solid	Liquid1	Liquid1+Solid	Liquid1+Solid	Liquid1
Temperature		(C)	64.97	64.89	64.70	75.70	75.48	75.26
Average Density		(kg/Cubic m)	846.28	846.34	748.80	866.92	867.06	835.70
Average Viscosity		(cp)	2.00	2.00	0.92	1.90	1.91	0.92
Average Heat Capacity		(kJ/kg-K)	0.83	0.83	0.83	2.35	0.46	0.46
Average Molecular Weight			109.87	109.87	109.87	32.04	261.27	261.27

BATCH PLUS Stream Label		6.2. Transfer-32
Operation		6.2. Transfer
Start Time	(min)	904.66
End Time	(min)	912.25
Total Time	(min)	7.59
From Unit		Settling tank V-102
To Unit		Crude glycerol storage
Stream Type		Output
Total (kg)	Mol (Wt.)	300.9441
METHANOL	32.04	0.0662
GLYCEROL	92.10	147.6844
OLEIC-ACID	282.47	1.8945
METHYL-OLEATE	296.50	0.1432
CALCIUM-OXIDE	56.08	0.0016
TRIOLEIN	885.45	150.8017
WATER	18.02	0.3525
Total Mass	(kg)	300.94
Total Volume	(litre)	284.75
Mass Flowrate	(kg/min)	39.63
Volume Flowrate	(litre/h)	2 250.00
Composite Product Factor		1.50
Phase		Liquid1+Solid
Temperature	(C)	75.26
Average Density	(kg/Cubic m)	1 056.87
Average Viscosity	(cp)	6.65
Average Heat Capacity	(kJ/kg-K)	0.83
Average Molecular Weight		109.87

APPENDIX B.

Economic analysis

Appendix B-1. Results from CAPCOST2011 for the KOH process

Unit Number		100						
CEPCI		576.2						
User Added Equipment								
Evaporators		Area (square meters)	Pressure (barg)	MOC	Volume (cubic meters)	Purchased Equipment Cost	Bare Module Cost	
K-101	Jacketed Vessel with Coil		0	Carbon Steel	3	\$ 20,200	\$ 61,300	
K-102	Jacketed Vessel with Coil		0	Carbon Steel	3	\$ 20,200	\$ 61,300	
Exchangers		Shell Pressure (barg)	Tube Pressure (barg)	MOC	Area (square meters)	Purchased Equipment Cost	Bare Module Cost	
E-101	Double Pipe		0	Carbon Steel / Carbon Steel	1.22	\$ 3,380	\$ 11,100	
E-102	Double Pipe		0	Carbon Steel / Carbon Steel	0.07	\$ 3,210	\$ 10,600	
E-103	Double Pipe		0	Carbon Steel / Carbon Steel	0.17	\$ 3,210	\$ 10,600	
Pumps (with drives)		Power (kilowatts)	# Spares	MOC	Discharge Pressure (barg)	Purchased Equipment Cost	Bare Module Cost	
P-101	Centrifugal	1	0	Cast Iron	0	\$ 3,560	\$ 11,500	
P-102	Centrifugal	1	0	Cast Iron	0	\$ 3,560	\$ 11,500	
P-103	Centrifugal	1	0	Cast Iron	0	\$ 3,560	\$ 11,500	
P-104	Centrifugal	1	0	Cast Iron	0	\$ 3,560	\$ 11,500	
P-105	Centrifugal	1	0	Cast Iron	0	\$ 3,560	\$ 11,500	
P-106	Centrifugal	1	0	Cast Iron	0	\$ 3,560	\$ 11,500	
P-107	Centrifugal	1	0	Cast Iron	0	\$ 3,560	\$ 11,500	
P-108	Centrifugal	1	0	Cast Iron	0	\$ 3,560	\$ 11,500	
Reactors		Volume (cubic meters)			Purchased Equipment Cost	Bare Module Cost		
R-101	Jacketed Agitated	3			\$ 33,200	\$ 133,000		
Vessels		Length/Height (meters)	Diameter (meters)	MOC	Demister MOC	Pressure (barg)	Purchased Equipment Cost	Bare Module Cost
V-101	Vertical	1.97	0.98	Carbon Steel		0	\$ 5,490	\$ 22,300
V-102	Vertical	2.48	1.24	Carbon Steel		0	\$ 7,890	\$ 32,100
V-103	Vertical	2.48	1.24	Carbon Steel		0	\$ 7,890	\$ 32,100
V-104	Vertical	2.48	1.24	Carbon Steel		0	\$ 7,890	\$ 32,100
V-105	Vertical	2.48	1.24	Stainles Steel		0	\$ 7,890	\$ 62,400
V-106	Vertical	2.48	1.24	Carbon Steel		0	\$ 7,890	\$ 32,100
V-107	Vertical	2.48	1.24	Carbon Steel		0	\$ 7,890	\$ 32,100
V-108	Vertical	3.82	1.91	Carbon Steel		0	\$ 17,400	\$ 70,900
V-109	Vertical	2.41	1.2	Carbon Steel		0	\$ 7,490	\$ 30,500
V-110	Vertical	2.49	1.24	Carbon Steel		0	\$ 7,910	\$ 32,200
V-111	Vertical	3.8	1.9	Carbon Steel		0	\$ 17,200	\$ 70,200
V-112	Vertical	3.06	1.53	Carbon Steel		0	\$ 11,400	\$ 46,300
Total Bare Module Cost							\$	875,200

Appendix B-2. Results from CAPCOST2011 for the CaO process

Unit Number 200

CEPCI 576.2

User Added Equipment

Evaporators	Type	Area (square meters)	Pressure (barg)	MOC	Volume (cubic meters)	Purchased Equipment Cost	Bare Module Cost
K-201	Jacketed Vessel with Coil		0	Carbon Steel	3	\$ 20,200	\$ 61,300

Exchangers	Exchanger Type	Shell Pressure (barg)	Tube Pressure (barg)	MOC	Area (square meters)	Purchased Equipment Cost	Bare Module Cost
E-201	Double Pipe		0	Carbon Steel / Carbon Steel	1.22	\$ 3,380	\$ 11,100
E-202	Double Pipe		0	Carbon Steel / Carbon Steel	0.07	\$ 3,210	\$ 10,600

Filters	Type	Area (square meters)	Purchased Equipment Cost	Bare Module Cost
Fr-201	Gravity	1	\$ 27,400	\$ 45,200

Pumps (with drives)	Pump Type	Power (kilowatts)	# Spares	MOC	Discharge Pressure (barg)	Purchased Equipment Cost	Bare Module Cost
P-201	Centrifugal	1	0	Cast Iron	0	\$ 3,560	\$ 11,500
P-202	Centrifugal	1	0	Cast Iron	0	\$ 3,560	\$ 11,500
P-203	Centrifugal	1	0	Cast Iron	0	\$ 3,560	\$ 11,500
P-204	Centrifugal	1	0	Cast Iron	0	\$ 3,560	\$ 11,500
P-205	Centrifugal	1	0	Cast Iron	0	\$ 3,560	\$ 11,500
P-206	Centrifugal	1	0	Cast Iron	0	\$ 3,560	\$ 11,500

Reactors	Type	Volume (cubic meters)	Purchased Equipment Cost	Bare Module Cost
R-201	Jacketed Agitated	3	\$ 33,200	\$ 133,000

Vessels	Orientation	Length/Height (meters)	Diameter (meters)	MOC	Demister MOC	Pressure (barg)	Purchased Equipment Cost	Bare Module Cost
V-201	Vertical	1.97	0.98	Carbon Steel		0	\$ 5,490	\$ 22,300
V-202	Vertical	2.48	1.24	Carbon Steel		0	\$ 7,890	\$ 32,100
V-203	Vertical	2.48	1.24	Carbon Steel		0	\$ 7,890	\$ 32,100
V-204	Vertical	2.48	1.24	Carbon Steel		0	\$ 7,890	\$ 32,100
V-205	Vertical	3.82	1.91	Carbon Steel		0	\$ 17,400	\$ 70,900
V-206	Vertical	2.41	1.2	Carbon Steel		0	\$ 7,490	\$ 30,500
V-207	Vertical	2.49	1.24	Carbon Steel		0	\$ 7,910	\$ 32,200
V-208	Vertical	3.8	1.9	Carbon Steel		0	\$ 17,200	\$ 70,200
Total Bare Module Cost								\$ 652,600

Appendix B-3. **Batch and annual operating costs for the KOH process**

	Amount per batch		Cost per batch (\$)	Annual amount		Annual cost (\$/year)
Raw materials						
Waste cooking oil	1.797	ton	\$733.29	1148.5	ton	\$468 570
Methanol	0.388	ton	\$244.62	248.1	ton	\$156 310
Potassium hydroxide	0.036	ton	\$54.76	22.9	ton	\$34 990
Hydrochloric acid	0.005	ton	\$1.39	3.0	ton	\$888
Calcium oxide	0.000	ton	\$0.00	0.0	ton	\$0
Tap water	1.079	ton	\$1.08	689.7	ton	\$690
Product						
Biodiesel	1.618	ton	\$2 162.64	1033.6	ton	\$1 381 930
By-product (To be sold)						
Waste water	1.012	ton	\$14.17	646.8	ton	\$9 056
Glycerol	0.526	ton	\$19.47	336.3	ton	\$12 443
Utilities						
Electricity	47.222	kwh	\$4.91	30175	kwh	\$3 138
Cooling water	11.588	ton	\$0.17	7405	ton	\$110
Low pressure steam	0.000	ton	\$0.00	0	ton	\$0
High pressure steam	0.438	ton	\$13.14	280.1	ton	\$8 395
Disposal services						
Liquid waste	0.0	ton	\$0.00	0.0	ton	\$0
Solid waste	0	ton	\$0.00	0	ton	\$0
Labour						
3 operators/shift 3shifts/day			\$78.65	12	months	\$50 256

Appendix B-4. **Batch and annual operating costs for the CaO process**

	Amount per batch		Cost per batch (\$)	Annual amount		Annual cost (\$/year)
Raw materials						
Waste cooking oil	1.584	ton	\$646.15	1282.8	ton	\$523 384
Methanol	0.570	ton	\$359.25	461.9	ton	\$290 993
Potassium hydroxide	0.000	ton	\$0.00	0.0	ton	\$0
Hydrochloric acid	0.000	ton	\$0.00	0.0	ton	\$0
Calcium oxide	0.016	ton	\$3.94	12.8	ton	\$3 191
Tap water	0.000	ton	\$0.00	0.0	ton	\$0
Product						
Biodiesel	1.433	ton	\$1 915.54	1160.5	ton	\$1 551 587
By-product (To be sold)						
Waste water	0.0	ton	\$0.00	0.0	ton	\$0
Glycerol	0.3	ton	\$11.13	243.8	ton	\$9 019
Utilities						
Electricity	32.406	kwh	\$3.37	26249	kwh	\$2 730
Cooling water	7.243	ton	\$0.11	5867.1	ton	\$87
Low pressure steam	0.000	ton	\$0.00	0	ton	\$0
High pressure steam	0.569	ton	\$17.04	460.59	ton	\$13 804
Disposal services						
Liquid waste	0.0	ton	\$0.00	0.0	ton	\$0
Solid waste	0	ton	\$0.00	0	ton	\$0
Labour						
3 operators/shift, 3shifts/day			\$62.04	12	months	\$50 256

Appendix B-5. **Cash flow analysis for the KOH-USA process**

Cost of land	\$0
Total fixed capital investment	\$1 290 920
FCI, year 1	\$774 552
FCI, year 2	\$516 368
Working capital at start-up	\$193 638
Plant start-up at end of year	2
Cost of manufacturing (without depreciation)	\$1 179 591
Revenue from sales	\$1 381 930
Taxation rate	0.28
Depreciation method	Straight line
Internal rate of return	0.1
Project life for profitability assessment	12

End of year	Capital investment	DEPC	Operating costs without depreciation	Sales revenues	Taxed income	Net cash flow	Cash Flow (discounted)	Cumulative Cash Flow (discounted)
0	-774 552	0	0	0	0	- 774 552	- 774 552	- 774 552
1	-710 006	0	0	0	0	- 710 006	- 645 460	-1 420 012
2	0	258 184	1 179 591	1 381 930	217 976	217 976	180 145	-1 239 867
3	0	258 184	1 179 591	1 381 930	217 976	217 976	163 768	-1 076 098
4	0	258 184	1 179 591	1 381 930	217 976	217 976	148 880	- 927 218
5	0	258 184	1 179 591	1 381 930	217 976	217 976	135 346	- 791 872
6	0	258 184	1 179 591	1 381 930	217 976	217 976	123 042	- 668 831
7	0	0	1 179 591	1 381 930	145 684	145 684	74 759	- 594 072
8	0	0	1 179 591	1 381 930	145 684	145 684	67 963	- 526 109
9	0	0	1 179 591	1 381 930	145 684	145 684	61 784	- 464 325
10	0	0	1 179 591	1 381 930	145 684	145 684	56 168	- 408 157
11	0	0	1 179 591	1 381 930	145 684	145 684	51 061	- 357 096
12	0	0	1 179 591	1 381 930	145 684	145 684	46 419	- 310 676
13	0	0	1 179 591	1 381 930	145 684	145 684	42 200	- 268 477
14	0	0	1 179 591	1 381 930	145 684	145 684	38 363	- 230 113

Appendix B-6. **Cash flow analysis for the CaO-USA process**

Cost of land	\$0
Total fixed capital investment	\$962,585
FCI, year 1	\$577,551
FCI, year 2	\$385,034
Working capital at start-up	\$144,388
Plant start-up at end of year	2
Cost of manufacturing (without depreciation)	\$1,390,956
Revenue from sales	\$1,551,587
Taxation rate	0.28
Depreciation method	Straight line
Internal rate of return	0.1
Project life for profitability assessment	12

End of year	Capital investment	DEPC	Operating costs without depreciation	Sales revenues	Taxed income	Net cash flow	Cash Flow (discounted)	Cumulative Cash Flow (discounted)
0	- 577 551	0	0	0	0	- 577 551	- 577 551	- 577 551
1	- 529 422	0	0	0	0	- 529 422	- 481 293	-1 058 844
2	0	192 517	1 390 956	1 551 587	169 559	169 559	140 131	- 918 712
3	0	192 517	1 390 956	1 551 587	169 559	169 559	127 392	- 791 320
4	0	192 517	1 390 956	1 551 587	169 559	169 559	115 811	- 675 509
5	0	192 517	1 390 956	1 551 587	169 559	169 559	105 283	- 570 226
6	0	192 517	1 390 956	1 551 587	169 559	169 559	95 712	- 474 515
7	0	0	1 390 956	1 551 587	115 654	115 654	59 349	- 415 166
8	0	0	1 390 956	1 551 587	115 654	115 654	53 954	- 361 212
9	0	0	1 390 956	1 551 587	115 654	115 654	49 049	- 312 164
10	0	0	1 390 956	1 551 587	115 654	115 654	44 590	- 267 574
11	0	0	1 390 956	1 551 587	115 654	115 654	40 536	- 227 038
12	0	0	1 390 956	1 551 587	115 654	115 654	36 851	- 190 187
13	0	0	1 390 956	1 551 587	115 654	115 654	33 501	- 156 686
14	0	1	1 390 956	1 551 587	115 654	115 654	30 455	- 126 231

Appendix B-7. **Cash flow analysis for the KOH-SA process**

Cost of land	\$0
Total fixed capital investment	\$962,585
FCI, year 1	\$577,551
FCI, year 2	\$385,034
Working capital at start-up	\$144,388
Plant start-up at end of year	2
Cost of manufacturing (without depreciation)	\$971,247
Revenue from sales	\$1,551,587
Taxation rate	0.28
Depreciation method	Straight line
Internal rate of return	0.1
Project life for profitability assessment	12

End of year	Capital investment	DEPC	Operating costs without depreciation	Sales revenues	Taxed income	Net cash flow	Cash Flow (discounted)	Cumulative Cash Flow (discounted)
0	- 577 551	0	0	0	0	- 577 551	- 577 551	- 577 551
1	- 529 422	0	0	0	0	- 529 422	- 481 293	-1 058 844
2	0	192 517	971 247	1 551 587	471 750	471 750	389 876	- 668 968
3	0	192 517	971 247	1 551 587	471 750	471 750	354 433	- 314 535
4	0	192 517	971 247	1 551 587	471 750	471 750	322 211	7 676
5	0	192 517	971 247	1 551 587	471 750	471 750	292 919	300 596
6	0	192 517	971 247	1 551 587	471 750	471 750	266 290	566 886
7	0	0	971 247	1 551 587	417 845	417 845	214 421	781 307
8	0	0	971 247	1 551 587	417 845	417 845	194 928	976 234
9	0	0	971 247	1 551 587	417 845	417 845	177 207	1 153 442
10	0	0	971 247	1 551 587	417 845	417 845	161 097	1 314 539
11	0	0	971 247	1 551 587	417 845	417 845	146 452	1 460 991
12	0	0	971 247	1 551 587	417 845	417 845	133 138	1 594 129
13	0	0	971 247	1 551 587	417 845	417 845	121 035	1 715 164
14	0	0	971 247	1 551 587	417 845	417 845	110 032	1 825 196

Appendix B-9. **Cash flow analysis for the CaO-SA process**

Cost of land	\$0
Total fixed capital investment	\$962,585
FCI, year 1	\$577,551
FCI, year 2	\$385,034
Working capital at start-up	\$144,388
Plant start-up at end of year	2
Cost of manufacturing (without depreciation)	\$971,247
Revenue from sales	\$1,551,587
Taxation rate	0.28
Depreciation method	Straight line
Internal rate of return	0.1
Project life for profitability assessment	12

End of year	Capital investment	DEPC	Operating costs without depreciation	Sales revenues	Taxed income	Net cash flow	Cash Flow (discounted)	Cumulative Cash Flow (discounted)
0	- 577 551	0	0	0	0	- 577 551	- 577 551	- 577 551
1	- 529 422	0	0	0	0	- 529 422	- 481 293	-1 058 844
2	0	192 517	973 461	1 551 587	470 156	470 156	388 559	- 670 285
3	0	192 517	973 461	1 551 587	470 156	470 156	353 235	- 317 050
4	0	192 517	973 461	1 551 587	470 156	470 156	321 123	4 073
5	0	192 517	973 461	1 551 587	470 156	470 156	291 930	296 003
6	0	192 517	973 461	1 551 587	470 156	470 156	265 391	561 393
7	0	0	973 461	1 551 587	416 251	416 251	213 603	774 996
8	0	0	973 461	1 551 587	416 251	416 251	194 184	969 180
9	0	0	973 461	1 551 587	416 251	416 251	176 531	1 145 711
10	0	0	973 461	1 551 587	416 251	416 251	160 483	1 306 194
11	0	0	973 461	1 551 587	416 251	416 251	145 893	1 452 087
12	0	0	973 461	1 551 587	416 251	416 251	132 630	1 584 718
13	0	0	973 461	1 551 587	416 251	416 251	120 573	1 705 291
14	0	0	973 461	1 551 587	416 251	416 251	109 612	1 814 903

APPENDIX C.

Economic sensitivity analysis

Appendix C-1. Estimation of the Fixed Capital Cost for the KOH process at a plant capacity ratio of 0.5.

Equipment class	Unit ID	Purchase cost (\$)	Bare module cost (\$)
Reactor	Reactor vessel R-101	22 900	91 800
Tank	Mixing tank V-101	2 860	11 600
	Settling tank V-102	5 490	22 300
	Holding tank V-103	5 160	21 000
	Holding tank V-104	5 160	21 000
	Washing vessel V-105	5 490	22 300
	Washing vessel V-106	5 490	22 300
	Holding tank V-107	5 160	21 000
Heat exchanger	Oil preheater E-101	3 210	10 600
	Evaporator preheater E-102	3 210	10 600
	Evaporator preheater E-103	3 210	10 600
Evaporators	Methanol evaporator K-101	16 400	49 600
	FAME dryer K-102	16 400	49 600
Pumps (8)		28 480	92 000
Storage vessels	WVO storage T-101	11 100	45 300
	Methanol storage T-102	5 250	21 400
	Crude glycerol tank T-102	5 540	22 600
	Biodiesel storage T-103	11 100	45 300
	Waste water tank T-104	7 580	30 800
Total purchased cost (listed equipment), C_P		<u>169 190</u>	
Total bare module cost (listed equipment), $C_{BM-list}$		-	621 700
Total installation cost, $C_{BM} = 1.25 C_{BM-list}$			<u>777 125</u>
Contingency and fee cost, $C_{FC} = 0.18 C_{BM}$			139 883
Fixed capital cost, $C_{FC} = C_{BM} + C_{FC}$			<u>917 008</u>
Working capital, $C_{WC} = 0.15 C_{FC}$			137 551
Total capital investment, $C_{TCI} = C_{FC} + C_{WC}$			1 054 559

Appendix C-2. **Estimation of the Fixed Capital Cost for the CaO process at a plant capacity ratio of 0.5**

Equipment class	Unit ID	Purchase cost (\$)	Bare module cost (\$)
Reactor	Reactor vessel R-201	22,900	91,800
Tank	Mixing tank V-201	2 860	11 600
	Holding tank V-202	5 160	21 000
	Holding tank V-203	5 160	21 000
	Settling tank V-204	5 490	22 300
Heat exchanger	Oil preheater E-201	3 210	10 600
	Evaporator preheater E-202	3 210	10 600
Evaporator	Methanol evaporator K-201	16 800	50 800
Filter	Filter Fr-201	27 400	45 200
Pumps (6)		21 360	69 000
Storage vessels	WVO storage T-201	11 100	45 300
	Methanol storage T-202	5 250	21 400
	Crude glycerol tank T-203	5 540	22 600
	Biodiesel storage T-204	11 100	45 300
Total purchased cost (listed equipment), C_P		<u>146 540</u>	
Total bare module cost (listed equipment), $C_{BM-list}$		-	488 500
Total installation cost, $C_{BM} = 1.25 C_{BM-list}$			<u>610 625</u>
Contingency and fee cost, $C_{FC} = 0.18 C_{BM}$			109 913
Fixed capital cost, $C_{FC} = C_{BM} + C_{FC} + C_{AC}$			<u>720 538</u>
Working capital, $C_{WC} = 0.15 C_{FC}$			108 081
Total capital investment, $C_{TCI} = C_{FC} + C_{WC}$			828 618

Appendix C-3. **Estimation of the Fixed Capital Cost for the KOH process at a plant capacity ratio of 2**

Equipment class	Unit ID	Purchase cost (\$)	Bare module cost (\$)
Reactor	Reactor vessel R-101	47 900	192 000
Tank	Mixing tank V-101	5 490	22 300
	Settling tank V-102	11 800	48 100
	Holding tank V-103	10 600	43 100
	Holding tank V-104	10 600	43 100
	Washing vessel V-105	11 800	48 100
	Washing vessel V-106	11 800	48 100
	Holding tank V-107	10 600	43 100
Heat exchanger	Oil preheater E-101	4 040	13 300
	Evaporator preheater E-102	3 210	10 600
	Evaporator preheater E-103	3 210	10 600
Evaporators	Methanol evaporator K-101	25 100	75 900
	FAME dryer K-102	25 100	75 900
Pumps (8)		30 480	98 400
Storage vessels	WVO storage T-101	28 300	115 000
	Methanol storage T-102	11 200	45 700
	Crude glycerol tank T-102	11 900	48 500
	Biodiesel storage T-103	28 000	114 000
	Waste water tank T-104	17 800	72 300
Total purchased cost (listed equipment), C_P		<u>308 930</u>	
Total bare module cost (listed equipment), $C_{BM-list}$		-	1 168 100
Total installation cost, $C_{BM} = 1.25 C_{BM-list}$			<u>1 460 125</u>
Contingency and fee cost, $C_{FC} = 0.18 C_{BM}$			262 823
Fixed capital cost, $C_{FC} = C_{BM} + C_{FC}$			<u>1 722 948</u>
Working capital, $C_{WC} = 0.15 C_{FC}$			258 442
Total capital investment, $C_{TCI} = C_{FC} + C_{WC}$			1 981 390

Appendix C-4. **Estimation of the Fixed Capital Cost for the CaO process at a plant capacity ratio of 2**

Equipment class	Unit ID	Purchase cost (\$)	Bare module cost (\$)
Reactor	Reactor vessel R-201	47 900	192 000
Tank	Mixing tank V-201	5 490	22 300
	Holding tank V-202	10 600	43 100
	Holding tank V-203	10 600	43 100
	Settling tank V-204	11 800	48 100
Heat exchanger	Oil preheater E-201	4 040	13 300
	Evaporator preheater E-202	3 210	10 600
Evaporator	Methanol evaporator K-201	25 100	75 900
Filter	Filter Fr-201	31 700	52 400
Pumps (6)		22 860	73 800
Storage vessels	WVO storage T-201	28 300	115 000
	Methanol storage T-202	11 200	45 700
	Crude glycerol tank T-203	11 900	48 500
	Biodiesel storage T-204	28 000	114 000
Total purchased cost (listed equipment), C_P		<u>252 700</u>	
Total bare module cost (listed equipment), $C_{BM-list}$		-	897 800
Total installation cost, $C_{BM} = 1.25 C_{BM-list}$			<u>1 122 250</u>
Contingency and fee cost, $C_{FC} = 0.18 C_{BM}$			202 005
Fixed capital cost, $C_{FC} = C_{BM} + C_{FC} + C_{AC}$			<u>1 324 255</u>
Working capital, $C_{WC} = 0.15 C_{FC}$			198 638
Total capital investment, $C_{TCI} = C_{FC} + C_{WC}$			1 522 893

Appendix C-5. **Estimation of the Fixed Capital Cost for the KOH process at a plant capacity ratio of 5**

Equipment class	Unit ID	Purchase cost (\$)	Bare module cost (\$)
Reactor	Reactor vessel R-101	78 000	312 000
Tank	Mixing tank V-101	8 630	35 100
	Settling tank V-102	21 600	87 900
	Holding tank V-103	18 600	75 500
	Holding tank V-104	18 600	75 500
	Washing vessel V-105	21 600	87 900
	Washing vessel V-106	21 600	87 900
	Holding tank V-107	18 600	75 500
Heat exchanger	Oil preheater E-101	4 930	16 200
	Evaporator preheater E-102	3 210	10 600
	Evaporator preheater E-103	3 210	10 600
Evaporators	Methanol evaporator K-101	41 700	126 000
	FAME dryer K-102	41 700	126 000
Pumps (8)		32 720	105 600
Storage vessels	WVO storage T-101	57 800	235 000
	Methanol storage T-102	20 300	82 800
	Crude glycerol tank T-102	21 800	88 600
	Biodiesel storage T-103	57 300	233 000
	Waste water tank T-104	34 100	139 000
Total purchased cost (listed equipment), C_P		<u>526 000</u>	
Total bare module cost (listed equipment), $C_{BM-list}$		-	2 010 700
Total installation cost, $C_{BM} = 1.25 C_{BM-list}$			<u>2 513 375</u>
Contingency and fee cost, $C_{FC} = 0.18 C_{BM}$			452 408
Fixed capital cost, $C_{FC} = C_{BM} + C_{FC}$			<u>2 965 783</u>
Working capital, $C_{WC} = 0.15 C_{FC}$			444 867
Total capital investment, $C_{TCI} = C_{FC} + C_{WC}$			3 410 650

Appendix C-6. **Estimation of the Fixed Capital Cost for the CaO process at a plant capacity ratio of 5**

Equipment class	Unit ID	Purchase cost (\$)	Bare module cost (\$)
Reactor	Reactor vessel R-201	78 000	312 000
Tank	Mixing tank V-201	8 630	35 100
	Holding tank V-202	18 600	75 500
	Holding tank V-203	18 600	75 500
	Settling tank V-204	21 600	87 900
Heat exchanger	Oil preheater E-201	4 930	16 200
	Evaporator preheater E-202	3 210	10 600
Evaporator	Methanol evaporator K-201	41 700	126 000
Filter	Filter Fr-201	35 500	58 500
Pumps (6)		24 540	79 200
Storage vessels	WVO storage T-201	57 800	235 000
	Methanol storage T-202	20 300	82 800
	Crude glycerol tank T-203	21 800	88 600
	Biodiesel storage T-204	57 300	233 000
Total purchased cost (listed equipment), C_P		<u>412 510</u>	
Total bare module cost (listed equipment), $C_{BM-list}$		-	1 515 900
Total installation cost, $C_{BM} = 1.25 C_{BM-list}$			<u>1 894 875</u>
Contingency and fee cost, $C_{FC} = 0.18 C_{BM}$			341 078
Fixed capital cost, $C_{FC} = C_{BM} + C_{FC} + C_{AC}$			<u>2 235 953</u>
Working capital, $C_{WC} = 0.15 C_{FC}$			335 393
Total capital investment, $C_{TCI} = C_{FC} + C_{WC}$			2 571 345

Appendix C-7. Total manufacturing costs estimation for the KOH and CaO processes at a plant capacity ratio of 0.5

Cost items	USA cost factors		SA cost factors	
	KOH process	CaO process	KOH process	CaO process
1. Direct Manufacturing Costs				
a. Raw materials	345 949	430 482	345 949	430 482
b. Utilities	6 719	16 554	6 719	16 554
c. Waste treatment	0	0	0	0
d. Operating labour	36 864	36 864	36 864	36 864
e. Direct supervisory labour	6 636	6 636	23 224	23 224
f. Maintenance and repairs	55 020	43 232	9 170	7 205
g. Operating supplies	6 485	6 485	6 485	6 485
h. Laboratory charges	5 530	5 530	7 373	7 373
i. Patents and royalties	22 480	26 157	0	0
2. Fixed Manufacturing Costs				
a. Depreciation	91 701	72 054	36 680	28 822
b. Local taxes and insurance	29 344	23 057	1 834	1 441
c. Plant overhead	59 112	52 039	2 078	2 019
3. General Manufacturing Expenses				
a. Administration costs	14 778	13 010	36 680	28 822
b. Distribution and selling costs	82 428	95 911	1 834	1 441
c. Research and development	37 467	43 596	2 078	2 019
5. By-products credit				
a. Glycerine credit	6 508	4 749	6 508	4 749
b. Waste water credit	4 737	0	4 737	0
Total Manufacturing Cost	749 349	871 917	445 872	548 056

Cost in \$

Appendix C-8. **Total manufacturing costs estimation for the KOH and CaO processes at a plant capacity ratio of 2**

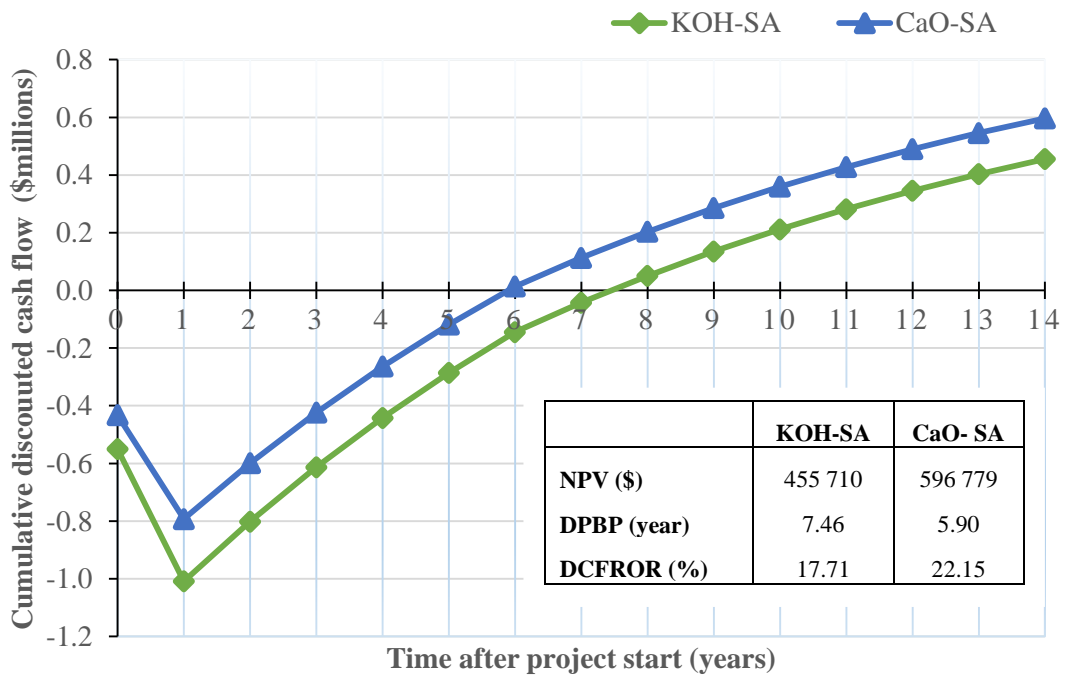
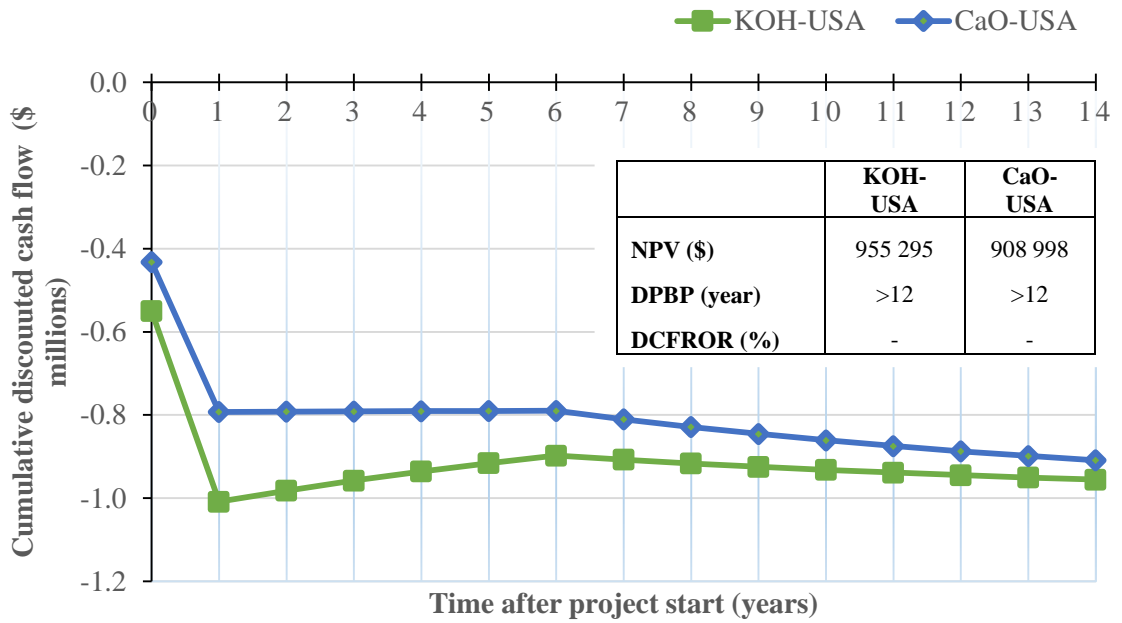
Cost items	USA cost factors		SA cost factors	
	KOH process	CaO process	KOH process	CaO process
1. Direct Manufacturing Costs				
a. Raw materials	1 211 101	1 481 716	1 211 101	1 481 716
b. Utilities	20 218	16 695	20 218	16 695
c. Waste treatment	0	0	0	0
d. Operating labour	90 432	90 432	90 432	90 432
e. Direct supervisory labour	16 278	16 278	56 972	56 972
f. Maintenance and repairs	103 377	79 455	17 229	13 243
g. Operating supplies	11 918	11 918	11 918	11 918
h. Laboratory charges	13 565	13 565	18 086	18 086
i. Patents and royalties	64 808	75 434	0	0
2. Fixed Manufacturing Costs				
a. Depreciation	172 295	132 426	68 918	52 970
b. Local taxes and insurance	55 134	42 376	3 446	2 649
c. Plant overhead	126 052	111 699	4 939	4 819
3. General Manufacturing Expenses				
a. Administration costs	31 513	27 925	18 110	17 671
b. Distribution and selling costs	237 631	276 593	20 174	24 325
c. Research and development	108 014	125 724	0	0
5. By-products credit				
a. Glycerine credit	22 782	13 690	22 782	13 690
b. Waste water credit	16 582	0	16 582	0
Total Manufacturing Cost	2 160 281	2 514 477	1 441 025	1 737 530

Cost in \$

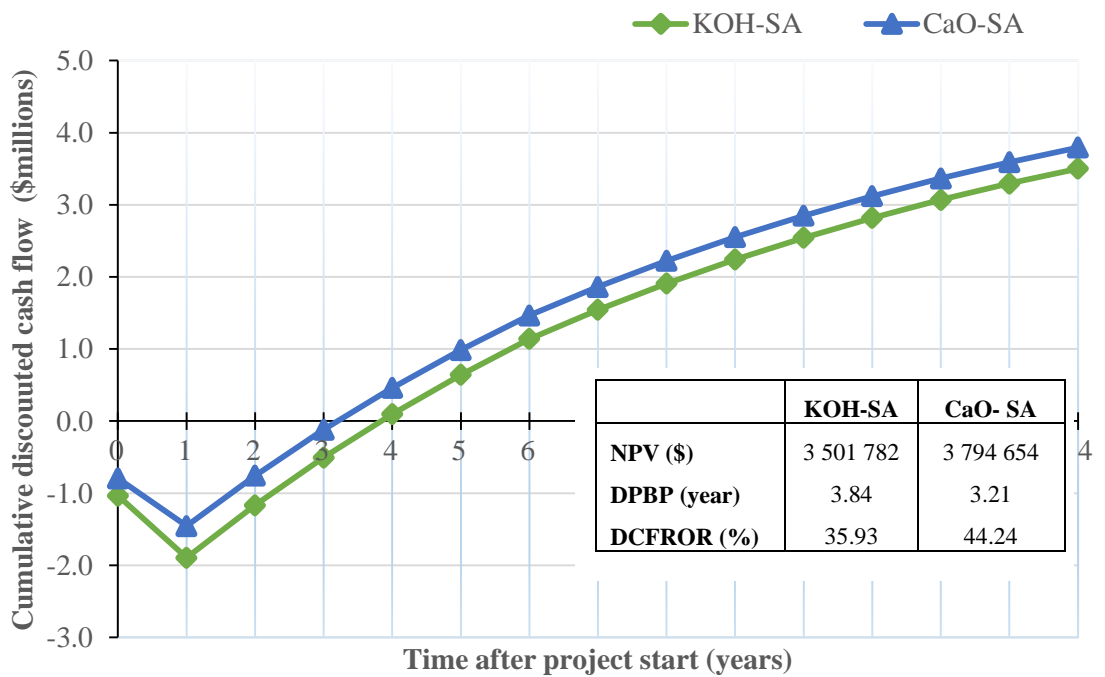
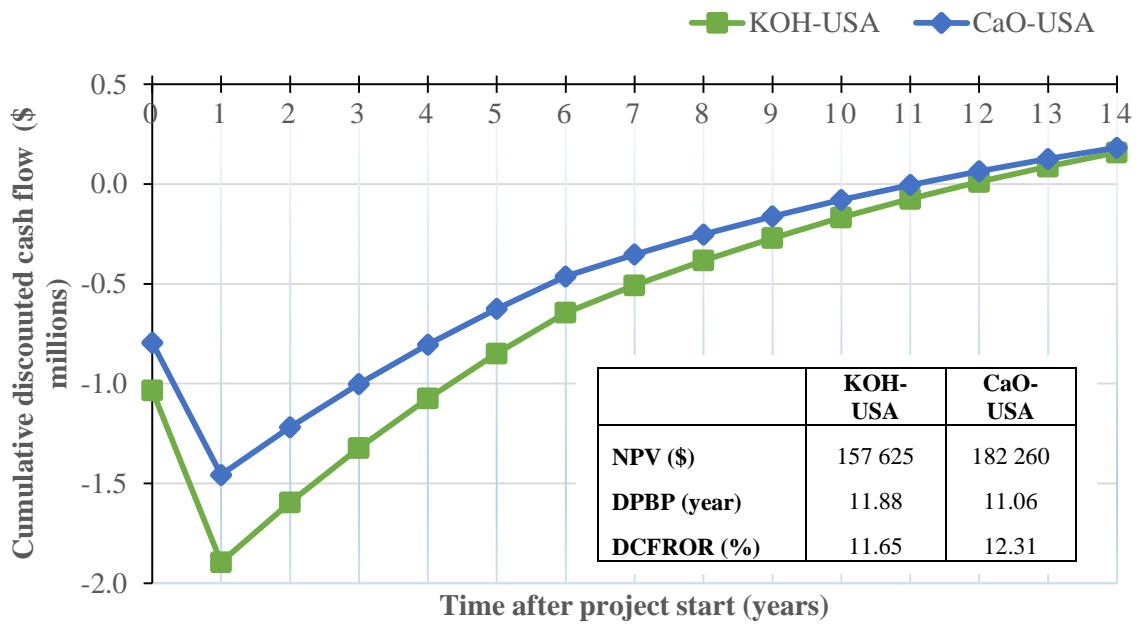
Appendix C-9. **Total manufacturing costs estimation for the KOH and CaO processes at a plant capacity ratio of 0.5**

Cost items	USA cost factors		SA cost factors	
	KOH process	CaO process	KOH process	CaO process
1. Direct Manufacturing Costs				
a. Raw materials	345 949	430 482	345 949	430 482
b. Utilities	6 719	16 554	6 719	16 554
c. Waste treatment	0	0	0	0
d. Operating labour	36 864	36 864	36 864	36 864
e. Direct supervisory labour	6 636	6 636	23 224	23 224
f. Maintenance and repairs	55 020	43 232	9 170	7 205
g. Operating supplies	6 485	6 485	6 485	6 485
h. Laboratory charges	5 530	5 530	7 373	7 373
i. Patents and royalties	22 480	26 157	0	0
2. Fixed Manufacturing Costs				
a. Depreciation	91 701	72 054	36 680	28 822
b. Local taxes and insurance	29 344	23 057	1 834	1 441
c. Plant overhead	59 112	52 039	2 078	2 019
3. General Manufacturing Expenses				
a. Administration costs	14 778	13 010	36 680	28 822
b. Distribution and selling costs	82 428	95 911	1 834	1 441
c. Research and development	37 467	43 596	2 078	2 019
5. By-products credit				
a. Glycerine credit	6 508	4 749	6 508	4 749
b. Waste water credit	4 737	0	4 737	0
Total Manufacturing Cost	749 349	871 917	445 872	548 056

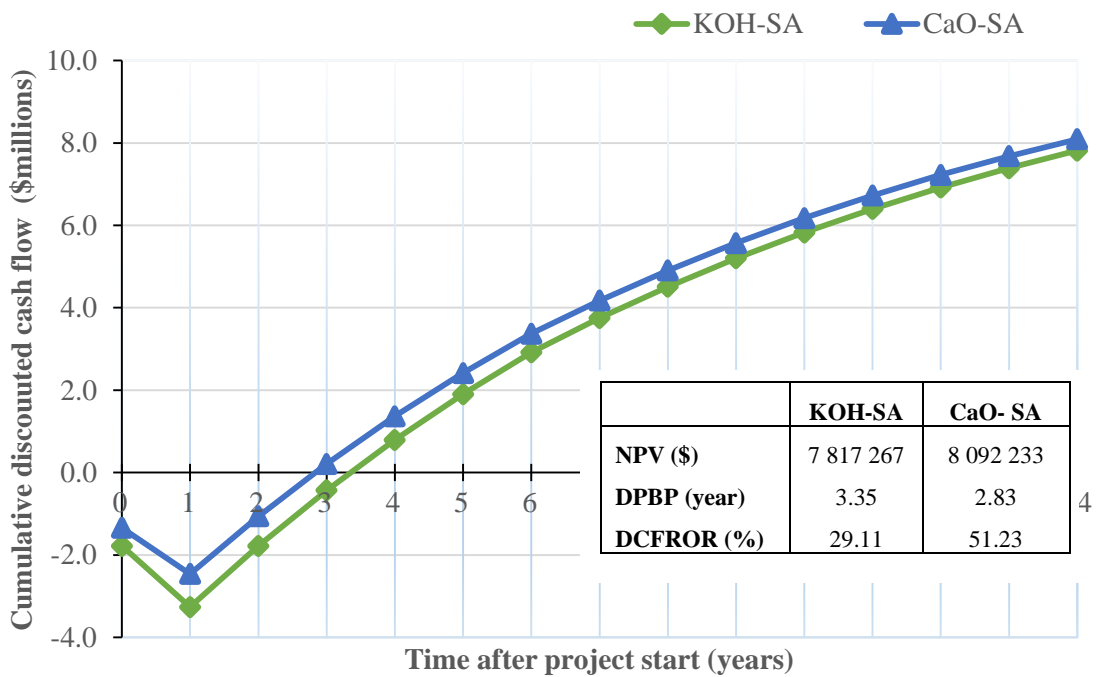
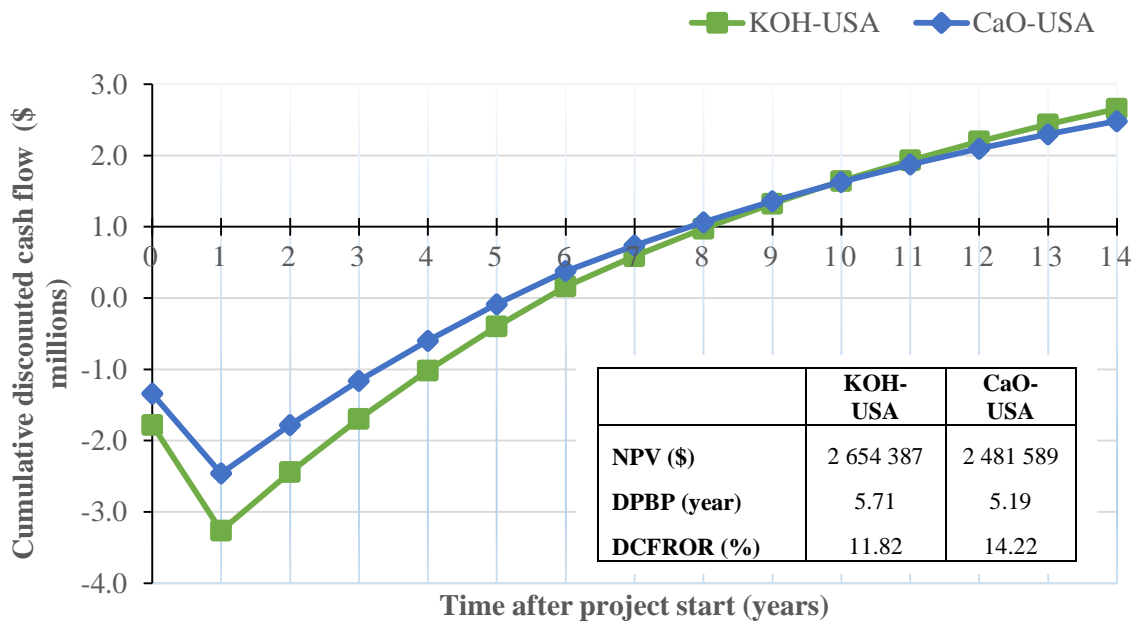
Appendix C-10. Discounted cash flow diagrams for the KOH and CaO processes at plant capacity ratio of 0.5



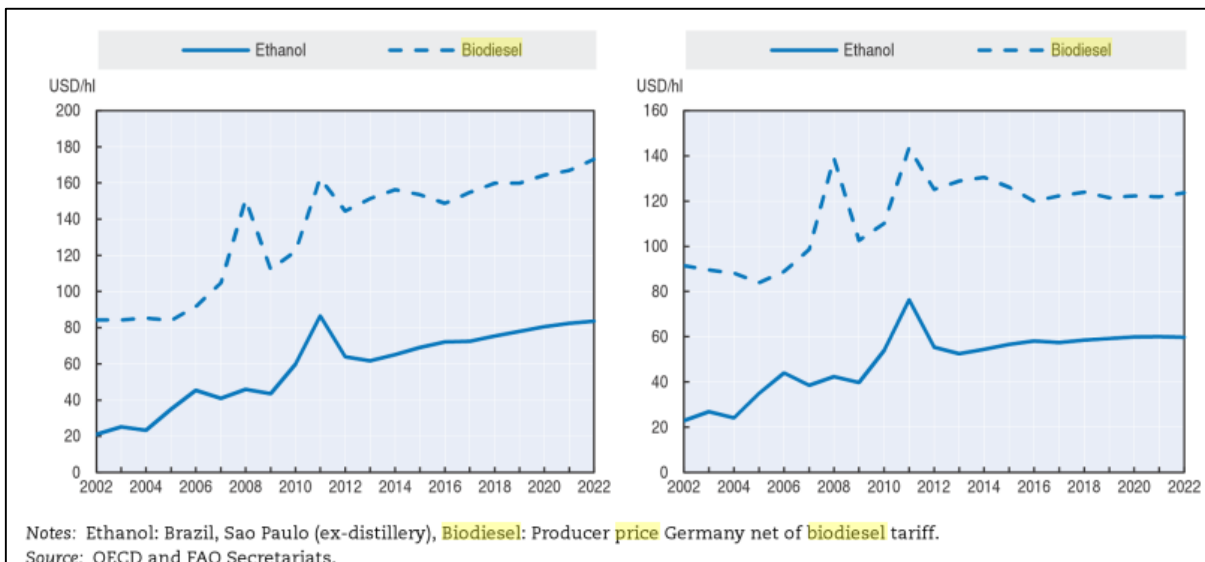
Appendix C-11. Discounted cash flow diagrams for the KOH and CaO processes at plant capacity ratio of 2



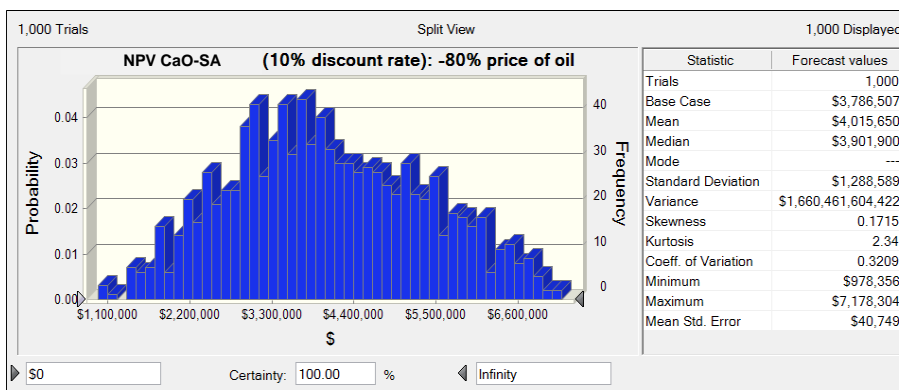
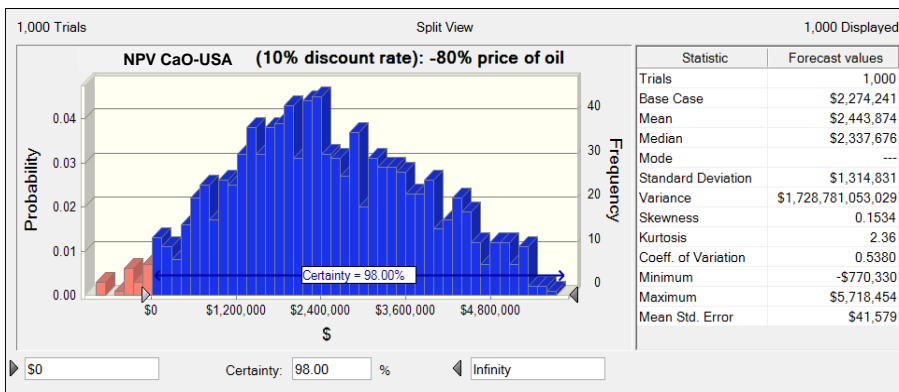
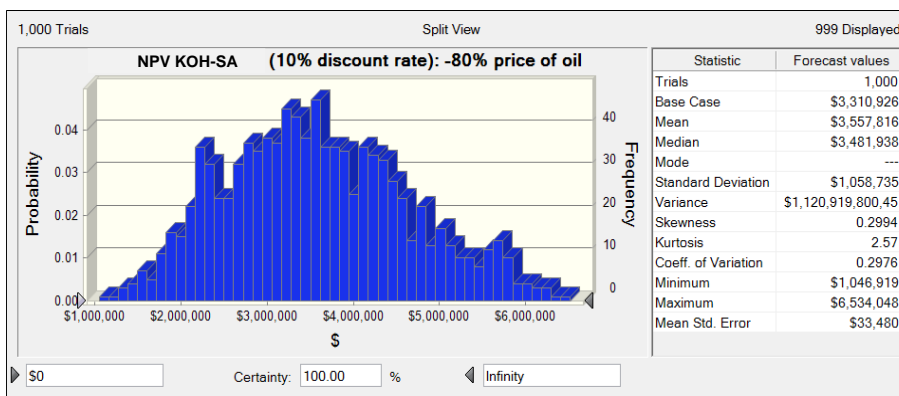
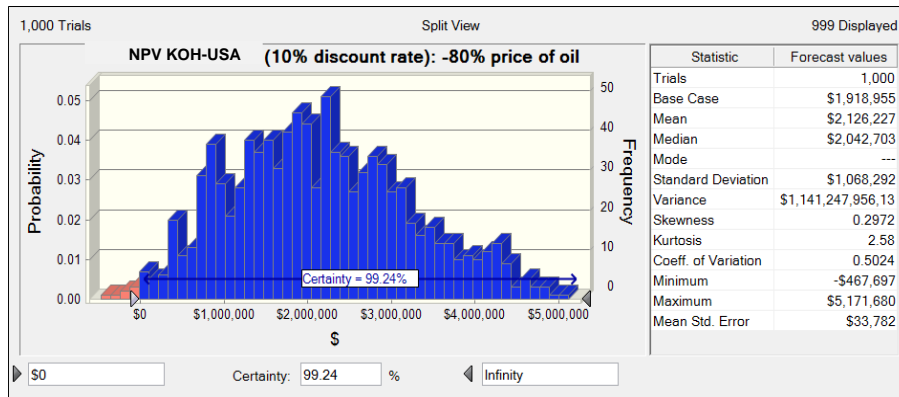
Appendix C-12. Discounted cash flow diagrams for the KOH and CaO processes at plant capacity ratio of 5



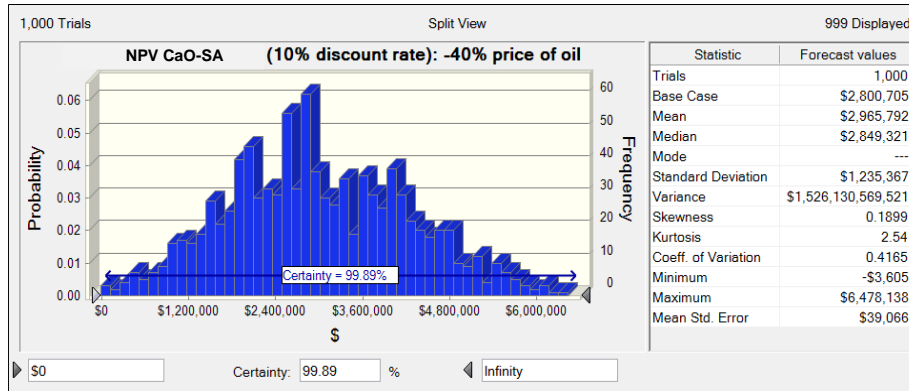
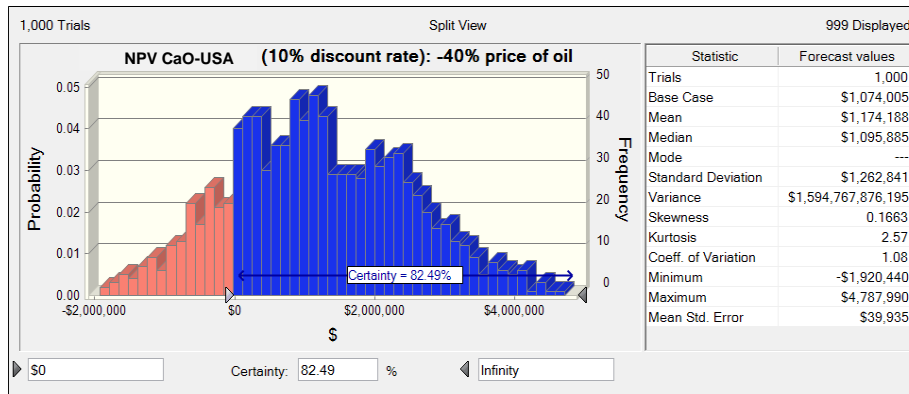
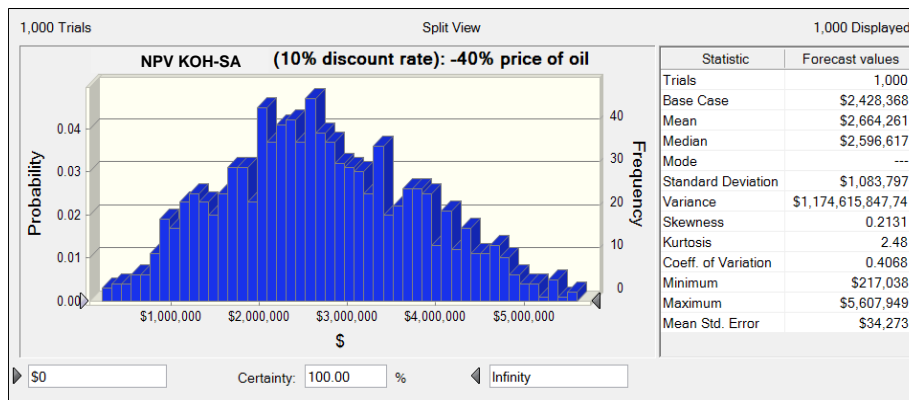
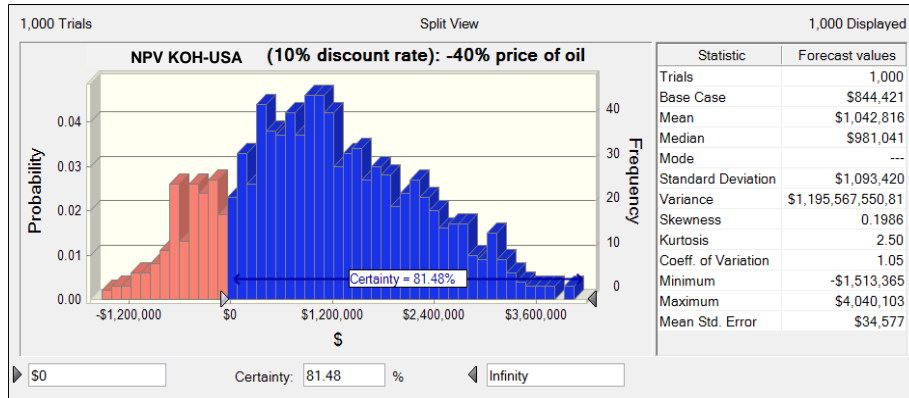
Appendix C-13. **Projection of biodiesel and ethanol prices over the outlook period (2013-2022). Evolution of prices expressed in nominal terms (left) and in real terms (right)**



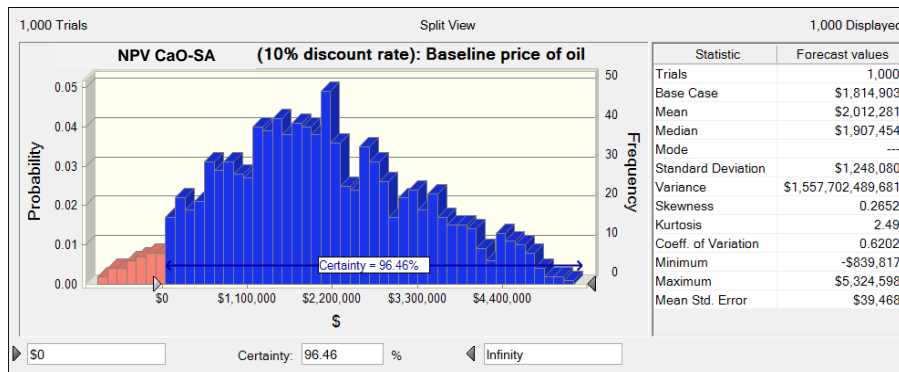
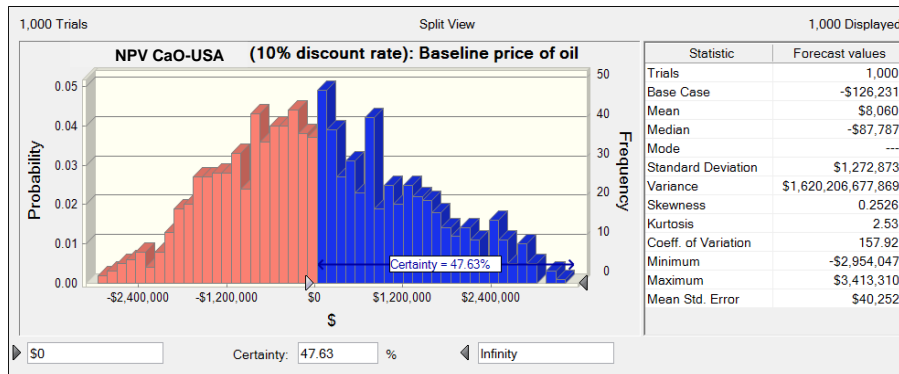
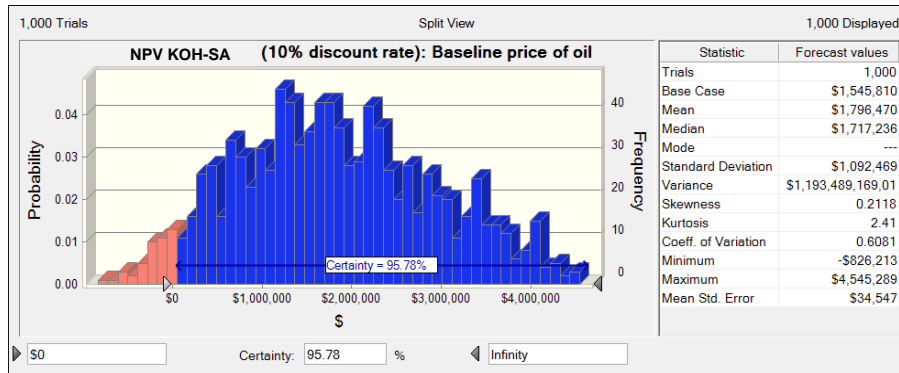
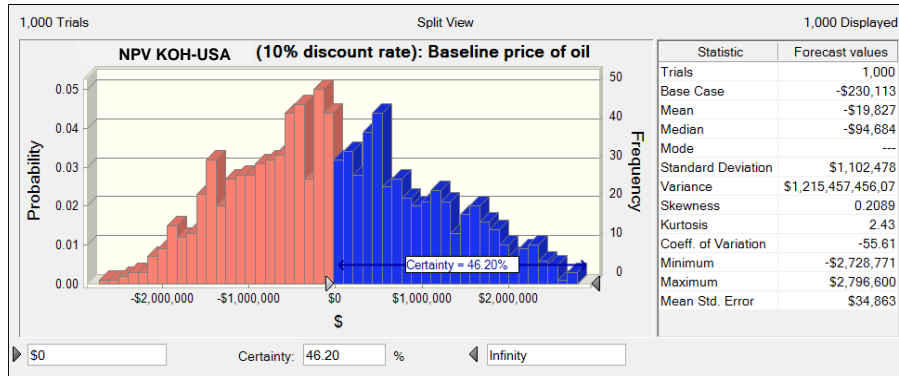
Appendix C-14. Sensitivity analysis of NPV to 80% decrease in the price of oil (Probability NPV > 0) for the KOH-USA, KOH-SA, CaO-USA and CaO-SA processes



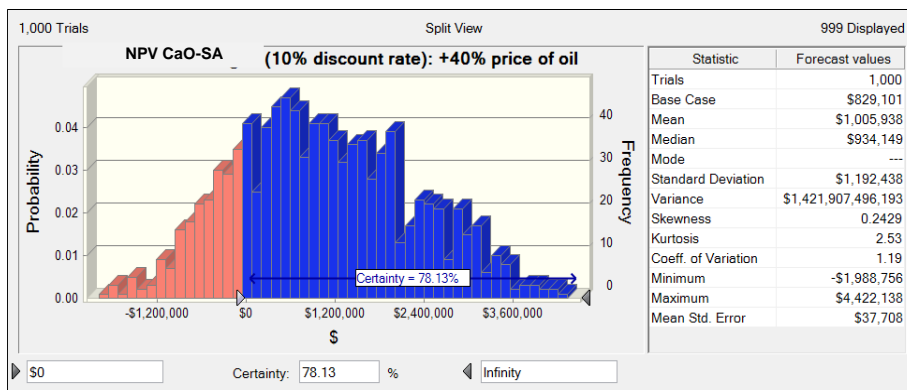
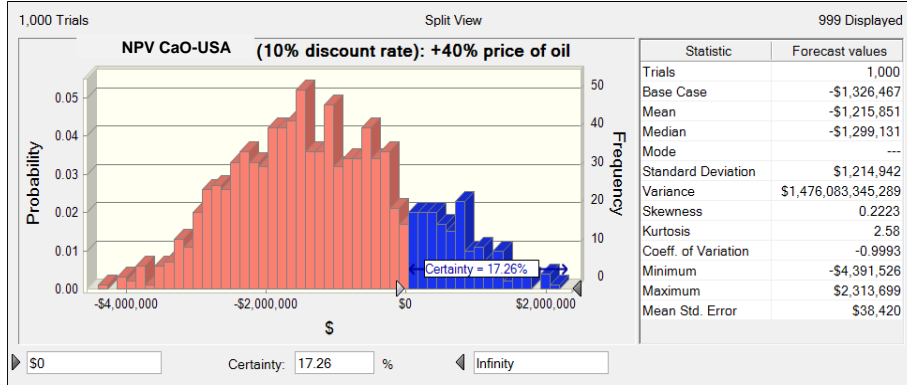
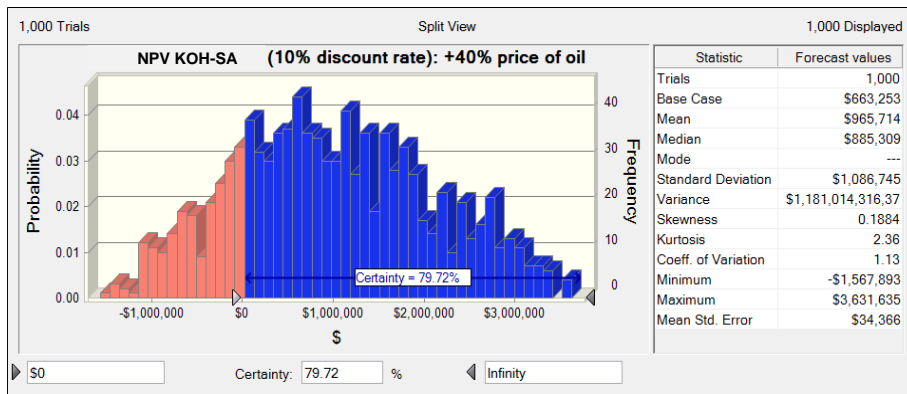
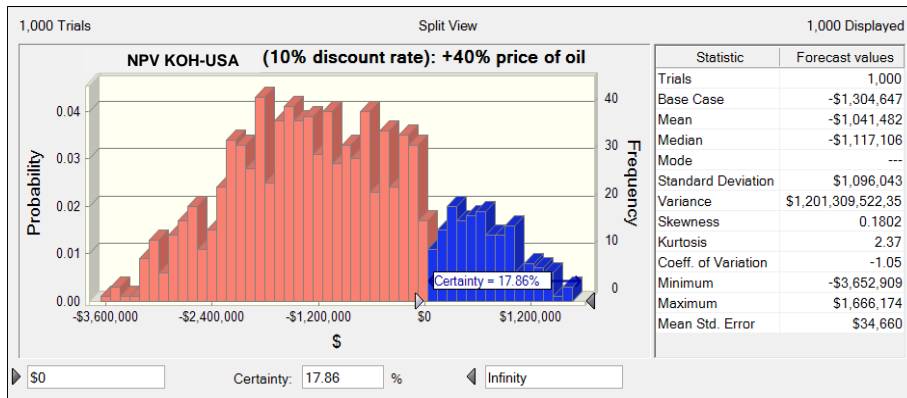
Appendix C-15. Sensitivity analysis of NPV to 40% decrease in the price of oil (Probability NPV > 0) for the KOH-USA, KOH-SA, CaO-USA and CaO-SA processes



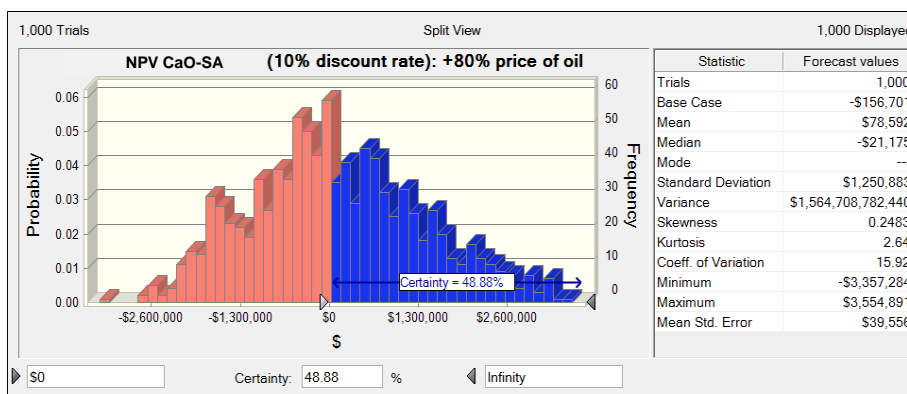
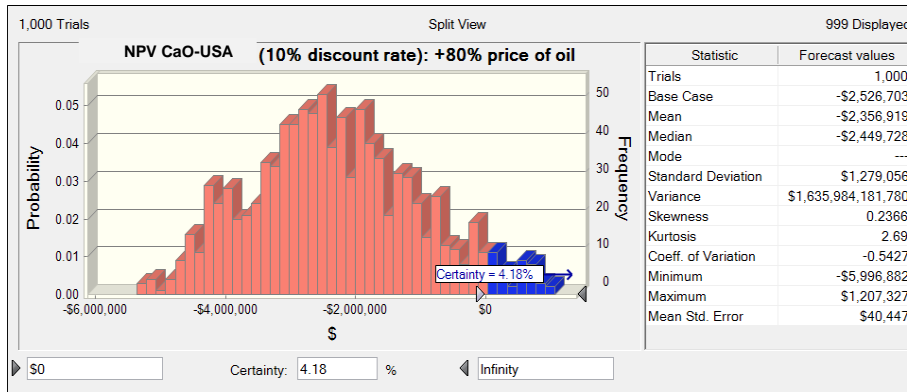
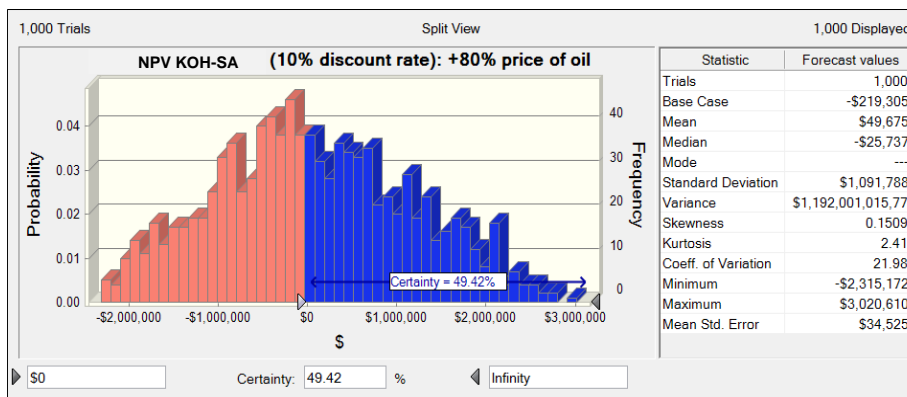
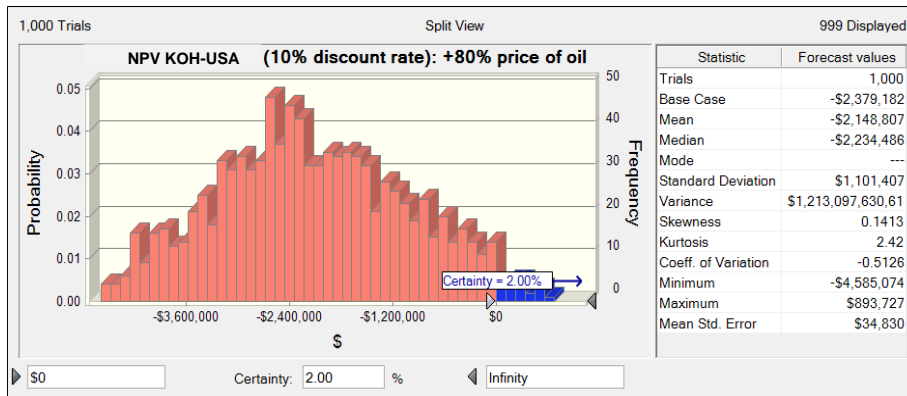
Appendix C-17. Sensitivity analysis of NPV to baseline price of oil (Probability NPV > 0) for the KOH-USA, KOH-SA, CaO-USA and CaO-SA processes



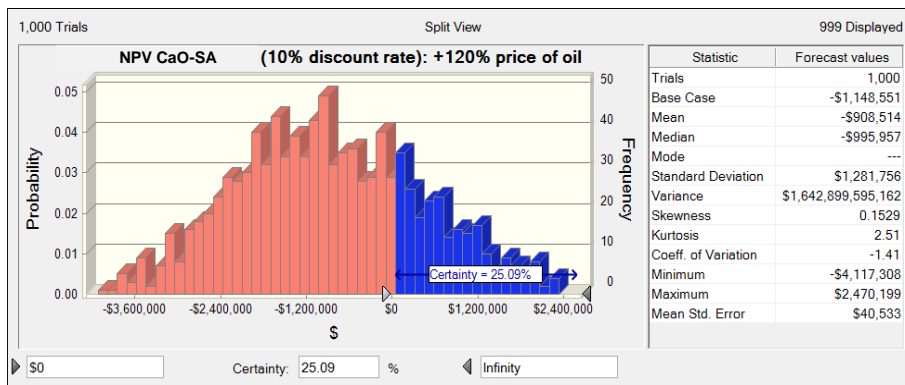
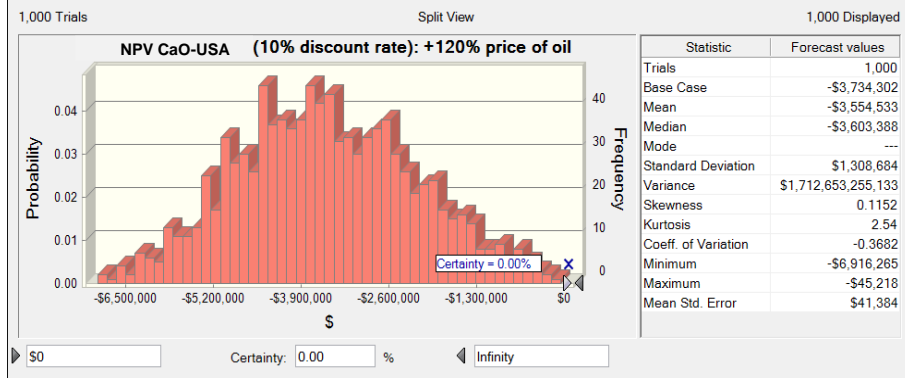
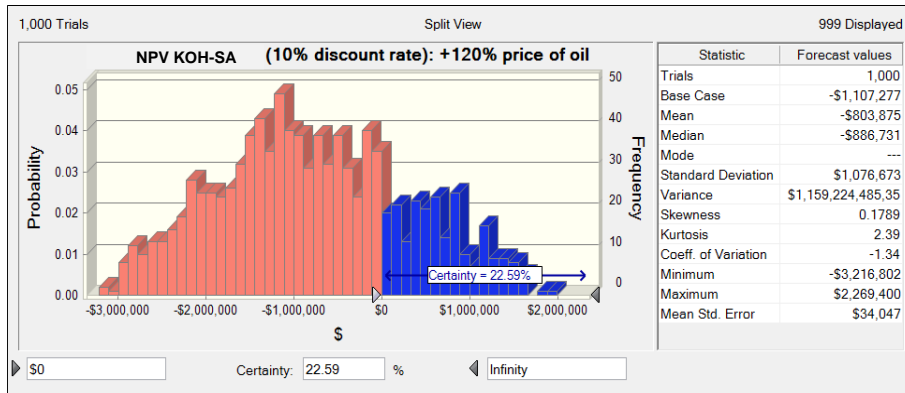
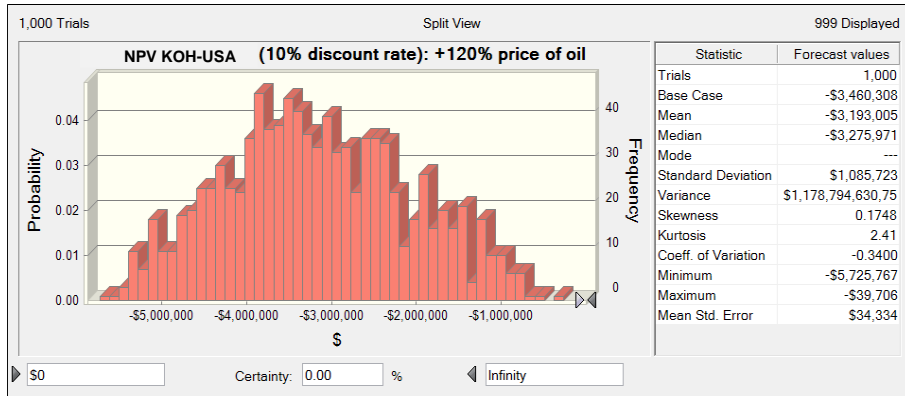
Appendix C-19. Sensitivity analysis of NPV to 40% increase in the price of oil (Probability NPV > 0) for the KOH-USA, KOH-SA, CaO-USA and CaO-SA processes



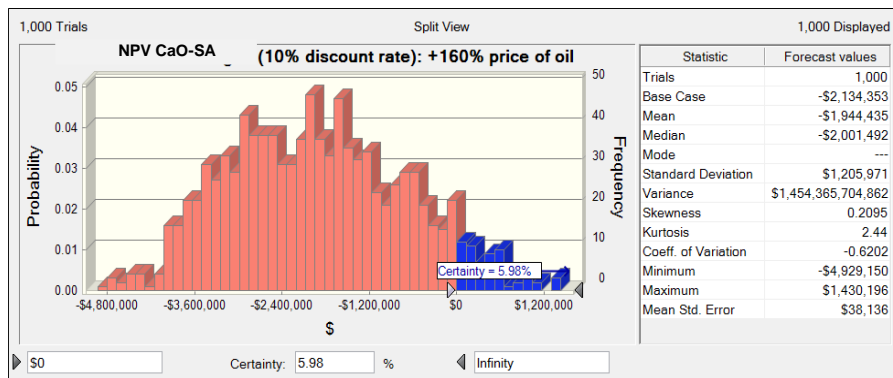
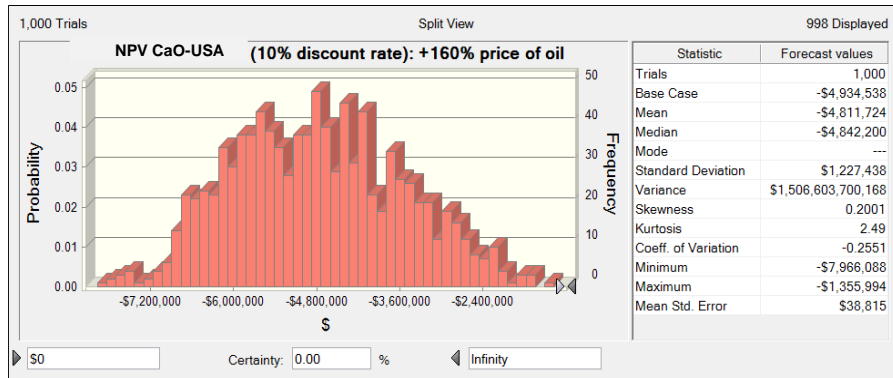
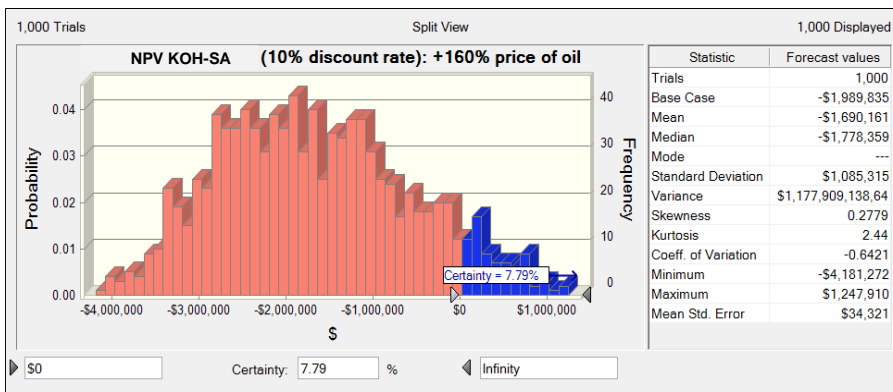
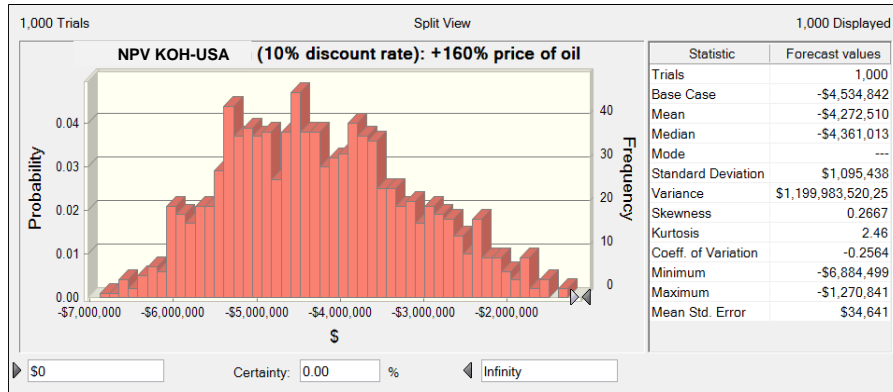
Appendix C-20. Sensitivity analysis of NPV to 80% increase in the price of oil (Probability NPV > 0) for the KOH-USA, KOH-SA, CaO-USA and CaO-SA processes



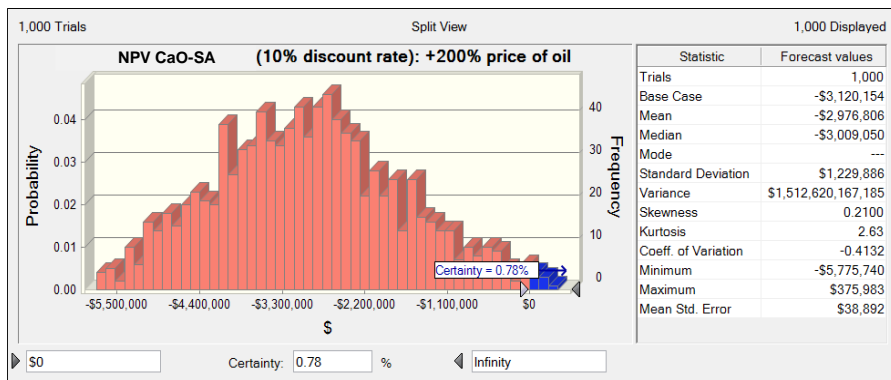
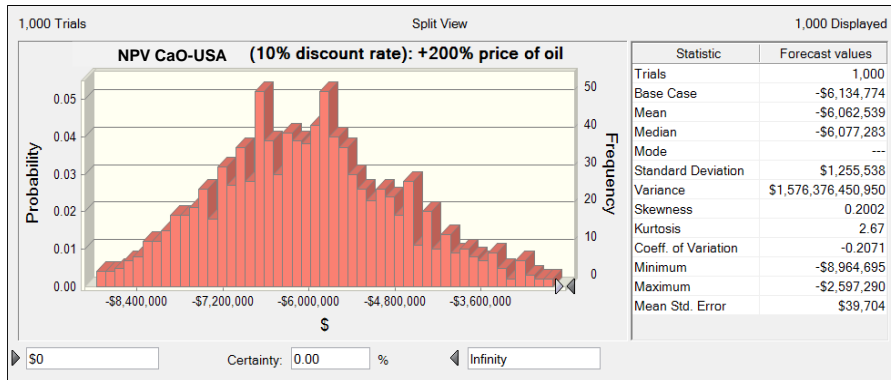
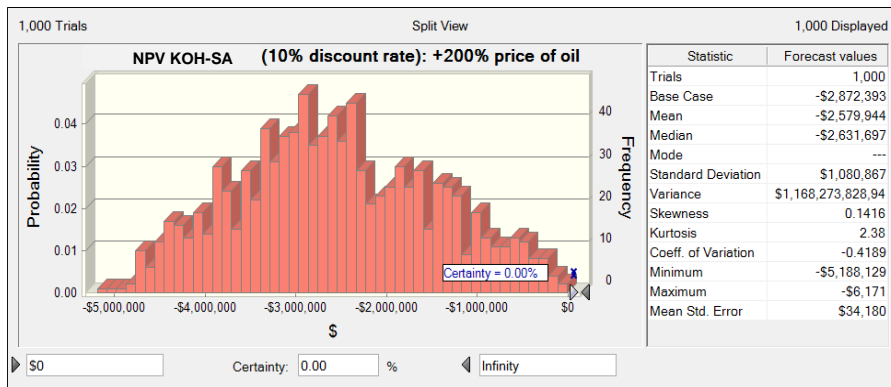
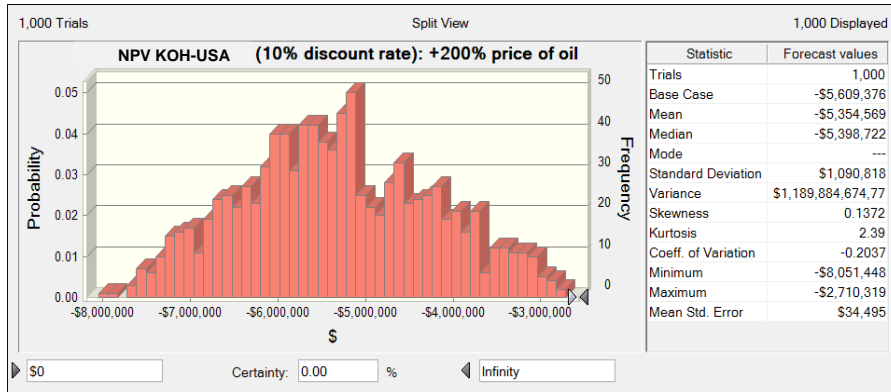
Appendix C-21. Sensitivity analysis of NPV to 120% increase in the price of oil (Probability NPV > 0) for the KOH-USA, KOH-SA, CaO-USA and CaO-SA processes



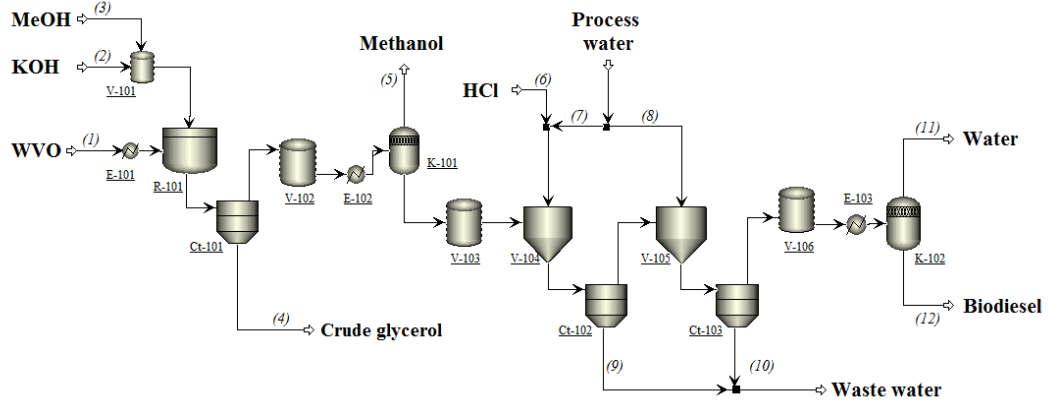
Appendix C-22. Sensitivity analysis of NPV to 160% increase in the price of oil (Probability NPV > 0) for the KOH-USA, KOH-SA, CaO-USA and CaO-SA processes



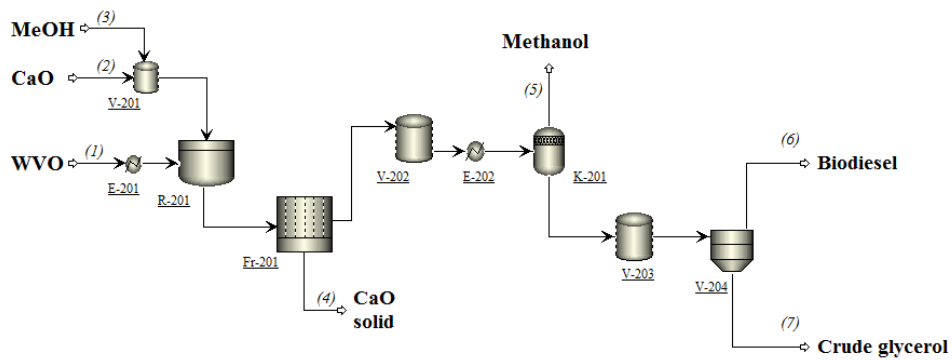
Appendix C-23. Sensitivity analysis of NPV to 200% increase in the price of oil (Probability NPV > 0) for the KOH-USA, KOH-SA, CaO-USA and CaO-SA processes



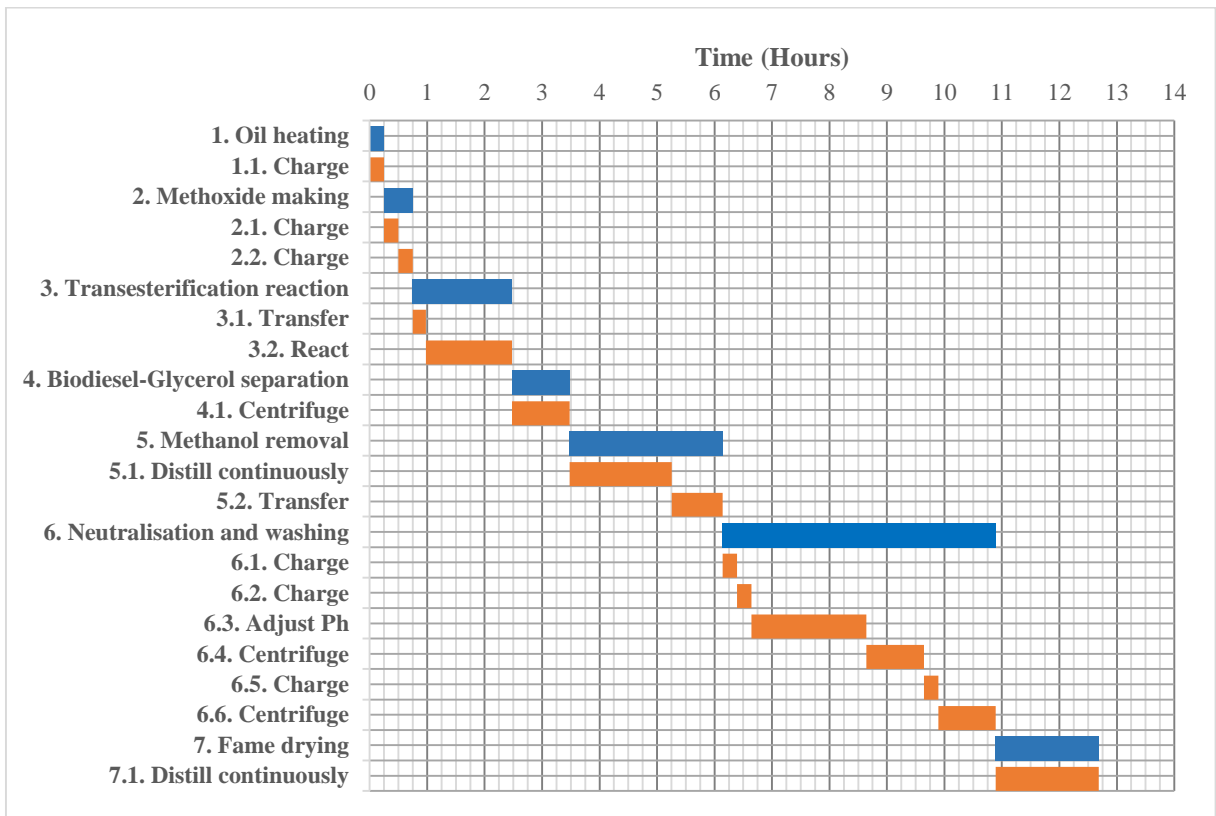
Appendix D-1. **Process flow diagram of the KOH catalysed process for biodiesel production with the presence of centrifuges**



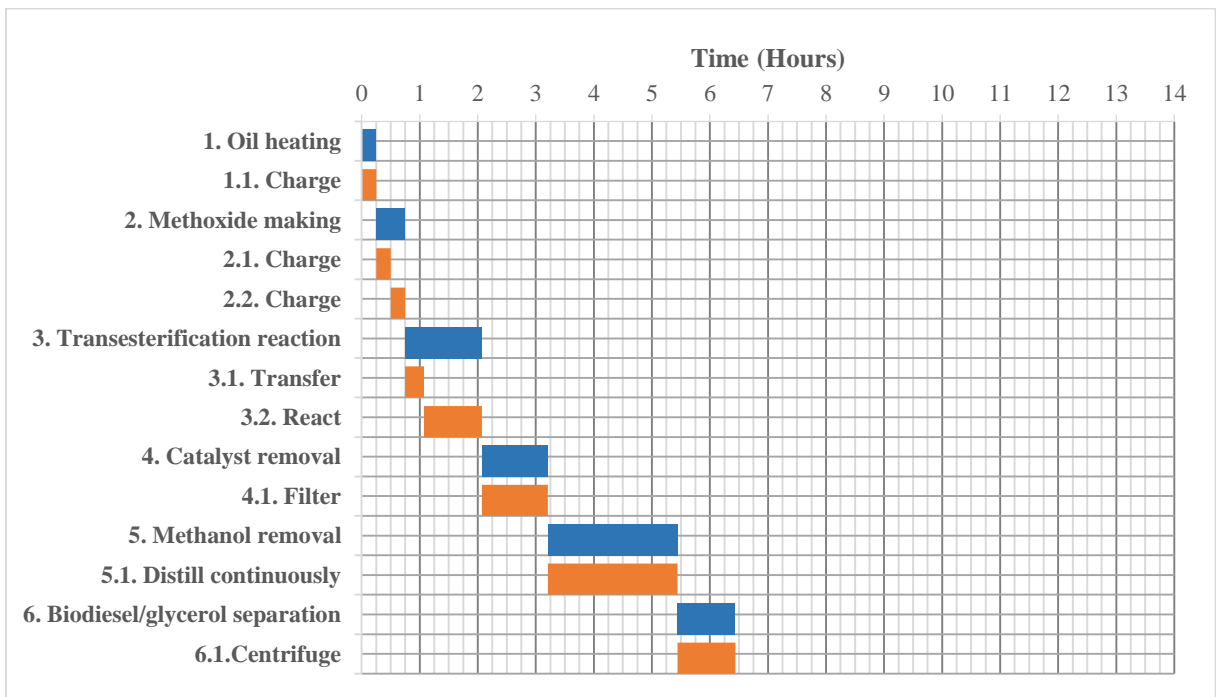
Appendix D-2. **Process flow diagram of the CaO catalysed process for biodiesel production with the presence of centrifuges**



Appendix D-3. **Process scheduling for the KOH process with the centrifuges scenario**



Appendix D-4. **Process scheduling for the CaO process with centrifuges scenario**



Appendix D-5. Fixed Capital Cost estimation for the KOH process in the centrifuges scenario

Equipment class	Unit ID		Purchase cost (10³ USD)	Bare module cost (10³ USD)
Reactor	Reactor vessel	R-101	33 200	133 000
Tank	Mixing tank	V-101	5 490	22 300
	Holding tank	V-103	7 890	32 100
	Holding tank	V-104	7 890	32 100
	Washing vessel	V-105	7 890	32 100
	Washing vessel	V-106	7 890	32 100
	Holding tank	V-107	7 890	32 100
Heat exchanger	Oil preheater	E-101	3 380	11 100
	Evaporator preheater	E-102	3 210	10 600
	Evaporator preheater	E-103	3 210	10 600
Evaporators	Methanol evaporator	K-101	20 200	61 300
	FAME dryer	K-102	20 200	61 300
Centrifuges	Centrifuge	Ct-101	33 300	52 300
	Centrifuge	Ct-102	33 300	52 300
	Centrifuge	Ct-103	33 300	52 300
Pumps (8)			28 480	92 000
Storage vessels	WVO storage	T-101	17 400	70 900
	Methanol storage	T-102	7 490	30 500
	Crude glycerol tank	T-102	7 890	32 100
	Biodiesel storage	T-103	17 200	70 200
	Waste water tank	T-104	11 400	46 300
Total purchased cost (listed equipment), C_P			<u>318 100</u>	
Total bare module cost (listed equipment), $C_{BM-list}$			-	969 600
Total installation cost, $C_{BM} = 1.25 C_{BM-list}$				<u>1 212 000</u>
Contingency and fee cost, $C_{FC} = 0.18 C_{BM}$				218 160
Fixed capital cost, $C_{FC} = C_{BM} + C_{FC}$				<u>1 430 160</u>
Working capital, $C_{WC} = 0.15 C_{FC}$				214 524
Total capital investment, $C_{TCI} = C_{FC} + C_{WC}$				1 644 684

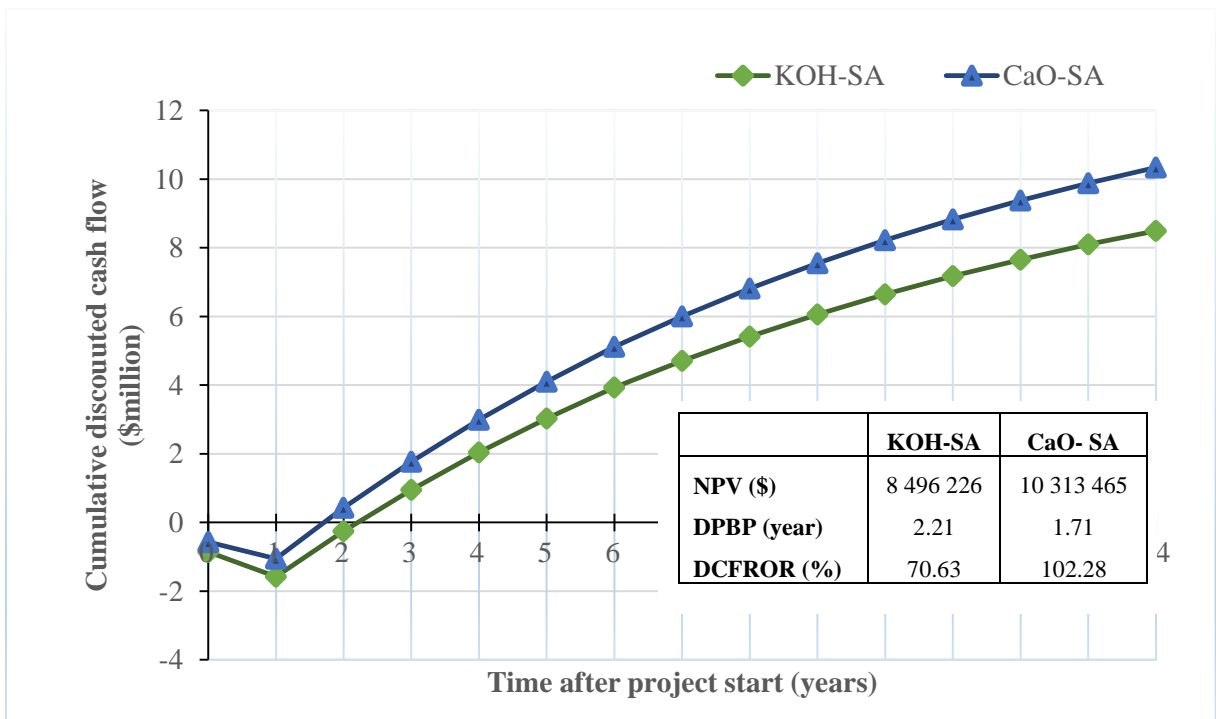
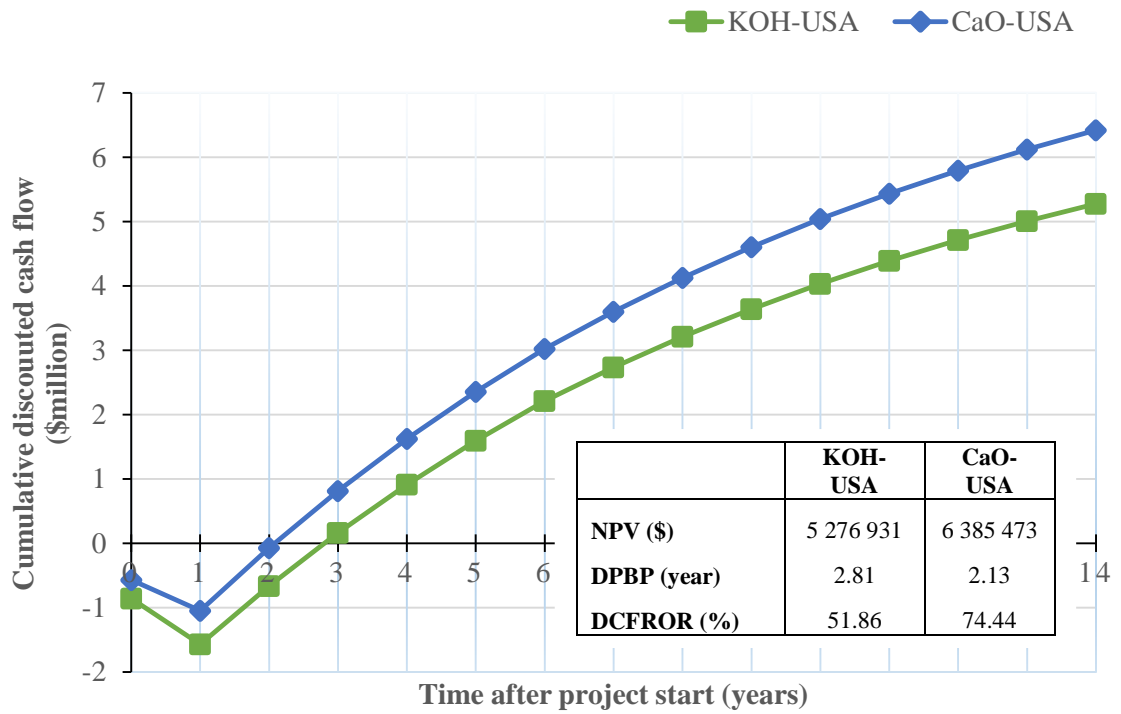
Appendix D-6. **Fixed Capital Cost estimation for the CaO process in the centrifuges scenario**

Equipment class	Unit ID		Purchase cost (10 ³ USD)	Bare module cost (10 ³ USD)
Reactor	Reactor vessel	R-201	33 200	133 000
Tank	Mixing tank	V-201	5 490	22 300
	Holding tank	V-202	7 890	32 100
	Holding tank	V-203	7 890	32 100
Heat exchanger	Oil preheater	E-201	3 380	11 100
	Evaporator preheater	E-202	3 210	10 600
Evaporator	Methanol evaporator	K-201	20 200	61 300
Filter	Filter	Fr-201	27 400	45 200
Centrifuge	Centrifuge	Ct-201	33 300	52 300
Pumps (6)			21 360	69 000
Storage vessels	WVO storage	T-201	17 400	70 900
	Methanol storage	T-202	7 890	30 500
	Crude glycerol tank	T-203	7 890	32 200
	Biodiesel storage	T-204	17 400	70 200
Total purchased cost (listed equipment), C_P			<u>213 900</u>	
Total bare module cost (listed equipment), $C_{BM-list}$			-	672 800
Total installation cost, $C_{BM} = 1.25 C_{BM-list}$				<u>841 000</u>
Contingency and fee cost, $C_{FC} = 0.18 C_{BM}$				151 380
Fixed capital cost, $C_{FC} = C_{BM} + C_{FC} + C_{AC}$				<u>992 380</u>
Working capital, $C_{WC} = 0.15 C_{FC}$				148 857
Total capital investment, $C_{TCI} = C_{FC} + C_{WC}$				1 141 237

Appendix D-7. Total manufacturing cost estimation for the KOH and CaO processes with the centrifuges scenario

Cost items	USA cost factors		SA cost factors	
	KOH process	CaO process	KOH process	CaO process
1. Direct Manufacturing Costs				
a. Raw materials	1 711 218	2 488 636	1 711 218	2,488,636
b. Utilities	25 161	34 485	25 161	34,485
c. Waste treatment	0	0	0	0
d. Operating labour	26 784	26 784	26 784	26,784
e. Direct supervisory and clerical labour	4 821	4 821	16 874	16,874
f. Maintenance and repairs	85 810	59,543	14 302	9,924
g. Operating supplies	8 596	8,931	8 596	8,931
h. Laboratory charges	4 018	4 018	5 357	5,357
i. Patents and royalties	74 449	104 419	0	0
2. Fixed Manufacturing Costs				
a. Depreciation	143 016	99,238	57 206	39,695
b. Local taxes and insurance	45 765	31,756	2 860	1,985
c. Plant overhead	70 449	54,689	1 739	1,607
3. General Manufacturing Expenses				
a. Administration costs	17 612	13,672	6 376	5,894
b. Distribution and selling costs	272 979	382,869	25 049	36,901
c. Research and development	124 081	174,032	0	0
4. Glycerine credit	35 126	29 384	35 126	29 384
5. Waste water credit	25 566	0	25 566	0
Total Manufacturing Cost without depreciation	2 481 628	3 480 631	1 789 228	2 635 805

Appendix D-8. Discounted cash flow diagrams for the KOH and CaO processes for the centrifuges scenarios



APPENDIX E.

Data files included in CD-ROM

<u>Name</u>	<u>Type</u>	<u>Size</u>
CHAPTER 3_Process simulation	File folder	13.1 MB
CHAPTER 4 and 5_ Economic and sensitivity analysis	File folder	66.1 MB
CHAPTER 6_ Debottlenecking study	File folder	20.0 MB