

**PROCESS INTENSIFICATION ON BIODIESEL PRODUCTION FROM
JATROPHACURCAS SEED OIL**

BY

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BY

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JULY, 2015

DECLARATION

I hereby declare that the work in this dissertation titled “Process Intensification on Biodiesel Production from *Jatropha curcas* seed oil” was performed by me in the Department of Chemical Engineering under the supervision of Prof. A. S. Ahmed, Prof. I. M. Bugaje and Dr. I. A. Muhammed-Dabo.

The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this work has been submitted for another degree or diploma at any institution.

Ibrahim, Haruna

Date

CERTIFICATION

This dissertation titled “Process Intensification on Biodiesel Production from *Jatropha curcas* seed oil” meets the regulation governing the award of the degree of Doctor of Philosophy of the Ahmadu Bello University, and is approved for its contribution of knowledge and literary presentation.

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DEDICATION

Verily in the face of truth, all falsehood will varnish and disappear, however much the patrons of falsehood may be averse.

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I thank almighty Allah for giving me everything I required to carry out this work. I thank my family for their patience, support and prayers I enjoyed during this research. I wish to thank my mentor, Prof. Idris Muhammed Bugaje for his moral, financial and academic supports that saw me through this work. I pray to almighty Allah to reward him abundantly. I thank the Chairman of my supervisory committee, Prof Abdulkarim. Salau.Ahmed and members, Prof Idris Muhammed Bugaje and Dr. Ibrahim Ali Mohammed-Dabo for their inputs into this work which success would have not been possible without their guidance. I also wish to thank Prof. Baba Jibril El-Yakub for his unquantifiable contribution to this work. I thank Engr. Yusuf Buba for his financial contribution to the success of this work. I must not forget to thank all the academic and non-academic staff of the Department of Chemical Engineering of Ahmadu Bello University, Zaria for their contributions in one way or the other for the success of this work.

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ABSTRACT

The challenges of continual depletion, economic crisis and environmental issues of the petroleum fuels have attracted the scientists' interest to seek for alternatives to fossil fuels. Biodiesel is the alternative to petrol diesel because; it has similar physicochemical properties to petrol diesel. However, biodiesel has not been competing favourably well economically with petrol diesel due to high cost of production. A process intensification technology was introduced in this work to produce safer, neater and cheaper biodiesel with fewer unit operations. A process intensify pilot plant was simulated, designed and constructed to produce biodiesel from *Jatropha curcas* seed oil and methanol in a molar ratio of 1:3 oil to methanol using five synthesized solid base catalysts. The pilot plant was made up of a stainless steel continuous stirred tank reactor, a stainless steel tank containing the oil and mixer for methanol/catalyst, a control panel, and solid-liquid separator. The process intensification excluded the following unit operations; neutralizer, washer, dryer, condenser and distillation column which are in the conventional process. Five solid base catalysts; bulk calcium oxide (CaO), super base calcium oxide (CaO/(NH₄)₂CO₃), bulk magnesium oxide (MgO), calcium oxide/magnesium oxide (CaO/MgO) and 10% potassium impregnated calcium oxide/magnesium oxide (10%K-CaO/MgO) were synthesized. These catalysts were first tested for their efficacy for production of biodiesel. Studies of the yields of biodiesel, glycerol and other impurities were carried out with transesterification reactions catalyzed by these catalysts, except bulk magnesium oxide at 60⁰C with time. They all performed very well with CaO/MgO catalyzed reactions producing no glycerol for all the reaction conditions. Complete conversion of feedstocks to biodiesel without glycerol and other impurities were recorded in some of the reactions runs using CaO/MgO and 10%K-CaO/MgO catalysts. The methyl esters yields of 97.952%, 96.94%, 95.76%, 99.99% and 98.25% were obtained with bulk calcium oxide, super base calcium oxide, bulk magnesium oxide, calcium oxide/magnesium oxide and 10%K impregnated calcium oxide/magnesium oxide catalysts respectively. The biodiesel produced was characterized and its physicochemical properties were compared to the ASTM and EN standards. They had 53, 54, 48, 48 and 55 cetane numbers respectively. They all had energy value greater than the minimum required for biodiesel standard of 47 MJ/kg. Transesterification with 3:1 methanol/oil molar ratio had complete reaction. Commercial viability of the pilot plant was evaluated. The total investment cost and income generated per annum were N5 458 305.26 and N5 912 633.30. The return on investment was found to be 7.75% and the payback period was found to be 13 years. These analyses indicated that the pilot plant was commercially viable as compared with conventional technology.

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LISTS OF ABBREVIATIONS/SYMBOLS

| | |
|----------|--|
| ASTM | America Standard Testing Method |
| CHCT | Continuous Heterogeneous Catalytic Transesterification |
| CSTR | Continuous Stirred Tank Reactor |
| EN | European Nations |
| F_A | Reactant molar flow rate out of reactor |
| F_{AO} | Reactant molar flow rate into reactor |
| R | Universal gas constant |
| A | Frequency factor |
| E | Activation energy |
| T | Temperature |
| k_A | Rate constant |
| r_A | Rate of reaction |
| X_A | Conversion |
| V | volume of reactor |
| Φ | Volume flow rate |
| τ | residence time |
| FFA | Free Fatty Acid |
| ISO | International Standard Organization |
| MF | Molecular formula |
| SEM | Scanning Electron Microscope |

| | |
|------|-----------------------------|
| FTIR | Fourier Transform Infra-Red |
| BET | Brunauer-Emmett-Teller |
| IRR | Internal Rate of Return |
| ROI | Rate on Investment |
| NPV | Net Present Value |

CHAPTER ONE

1.0 INTRODUCTION

Process Intensification is the strategy of making dramatic reduction of the size of unit operations within chemical plants, in order to achieve given production objectives. Process Intensification (PI) leads to a substantially smaller, cleaner and cheaper and safer and more energy efficient processes (Reay *et al.*, 2008). As a future prospective fuel, biodiesel has to compete economically with petroleum diesel fuels; therefore, the only way of reducing the biodiesel cost is to use less expensive process and yet optimizes the production output.

The depletion of world petroleum and coal reserves and the increased environmental concerns have stimulated the search for alternative sources of petroleum based fuels, including diesel fuels. Biodiesel has drawn more attention in recent years because it is renewable, biodegradable and has less detrimental effects on the environment as compared to conventional diesel from petro-diesel (Deng *et al.*, 2011).

Biodiesel, a biodegradable energy, is defined as mono alkyl esters of fatty acids derived from renewable sources such as vegetable oils and animal fats via transesterification processes. Biodiesel has similar and sometimes better physical and chemical properties than petro-diesel, such as flash point, ultra-lower sulphur concentration, better lubricating efficiency, high cetane number and few pollutants (Deng *et al.*, 2011). Biodiesel has many advantages which include the following: its sustainability, safe for use in all conventional diesel engines, offers the same performance and engine durability as petro-diesel fuel, nonflammable and nontoxic, reduces tailpipe emissions, visible smoke and noxious fumes and odours (Akbar *et al.*, 2009). Presently,

biodiesel from fatty acid methyl ester (FAME) and fatty acid ethyl ester (FAEE) derived from plant and animal has been accepted worldwide as the potential to replace petro-diesel. Above all, the use of biodiesel from renewable oil sources have the benefits of lower sulphur content, lower aromatic content, higher heat content, biodegradability, readily availability and liquid nature portability (Fei and Teong, 2008).

1.1 PROBLEM STATEMENT

A lot of work has been carried out in recent years on biodiesel production. Many of these need further refining to develop economically viable plant. This research is therefore, designed to address the following problems:

1. The high cost of biodiesel production.
2. The use of too many unit operations in biodiesel processing.
3. Application of excess methanol in biodiesel processing.

1.2 AIM AND OBJECTIVES

The aim of this research is to develop an intensified biodiesel pilot plant that is smaller, safer and of cleaner and cheaper product.

The specific objectives are:

- i. To model, design and fabricate a process intensified pilot plant that would use among other unit operations continuous stirred tank reactor (CSTR).
- ii. To synthesize five solid base catalysts suitable for transesterification.
- iii. To characterize the synthesized catalysts

- iv. To operate the pilot plant to produce biodiesel from local non-edible vegetable oil sources with solid the catalysts.
- v. To analyze the biodiesel oil produced and compares its properties with those of international standards.
- vi. To evaluate economic implication of the pilot plant.

1.3 JUSTIFICATION

- i. This technology uses less unit operations compared to current available technologies, hence saves space.
- ii. The product of this process is of higher purity than the conventional ones.
- iii. Operation of this technology is environmentally and labours friendly.
- iv. The technology has advantage of less methanol consumption, therefore lowering the production cost.

1.4 SCOPE OF THE RESEARCH

The scope of this work is limited to:

- i. Simulation, design and fabrication of a process intensified pilot plant.
- ii. Synthesis of five solid base catalysts suitable for transesterification.
- iii. Operation of the pilot plant to produce biodiesel using *Jatropha curcas* seedoil, methanol and the solid base catalysts.
- iv. Characterization of the biodiesel produced and catalysts synthesized.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 DEFINITION OF BIODIESEL

Biodiesel refers to a vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, ethyl or propyl) esters. It is meant to be used in standard diesel engines and is thus distinct from the vegetable and waste oils used to fuel converted diesel engines (NBB, 2009). It can be used alone, or blended with petro diesel and can also be used as a low carbon alternative to heating oil. It can be made from new or used vegetable oils and animal fats, which are nontoxic, biodegradable, and renewable. It is always produced by means of transesterification of vegetable oil or animal fat (Yun *et al.*, 2013) with monohydric alcohol into fatty acid methyl esters (FAME). Glycerin (used in pharmaceuticals and cosmetics, among other markets) is produced as a co-product.

Biodiesel can be produced using a variety of transesterification technologies. The oils and fats are filtered and preprocessed to remove water and contaminants. If free fatty acids are present, they can be removed or transformed into biodiesel using special pretreatment technologies (esterification). The pretreated oils and fats are then mixed with an alcohol (usually methanol) and a catalyst. The oil molecules (triglycerides) are broken apart and reformed into alkyl esters and glycerin, which are then separated from each other and purified.

2.1.1 Basics of Biodiesel Production

The reaction is catalyzed mostly by base (such as sodium hydroxide, potassium hydroxide or sodium methoxide) and in some cases strong acid such as sulphuric acid. Presently, a lot of heterogeneous catalysts have been formulated that are more effective than the homogeneous catalysts (Ibrahim, 2013).

2.1.1.1 Animal fats

Animal fats are a by-product of meat production, its use for producing biodiesel adds value to the livestock industry. However, producing biodiesel with animal fat that would have otherwise been discarded as waste and possibly polluting the environment replace some percentage of petroleum diesel usage(Christopher, 2007). Currently a 5-million dollar plant is built in the USA, with the intent of producing 11.4 million litres biodiesel from some of the estimated 1 billion kg of chicken fat produced annually at local Tyson poultry plant (Christopher, 2007). Today, multi-feedstock biodiesel facilities are producing high quality animal-fat based biodiesel.

2.1.1.2 Waste vegetable oil (WVO)

If waste vegetable oil (WVO) is used, it is first filtered to remove dirt, charred food, and other non-oil materials often found. Waste oils contain much free fatty acid. The longer and the hotter the oil has been cooked the more FFAs it contains (Journey to forever, 2011). It is essential to titrate the oil to find out how much free fatty acid it contains so that one can calculate how much methanol and sulphuric acid will be required to esterify it. Water is removed because its presence causes the triglycerides to hydrolyze, giving salts of the fatty acids (soaps) instead of undergoing transesterification to give biodiesel (Gerpen *et al.*, 2004).

A sample of the cleaned feedstock oil is titrated with a standardized base solution in order to determine the concentration of free fatty acids (carboxylic acids) present in it. These acids are then either esterified into biodiesel, or removed, typically through neutralization. Many advocates suggest that waste oil is the best source of oil to produce biodiesel, but since the available supply is drastically less than the amount of petroleum based diesel that is burned for transportation and home heating in the world, hence the suggestion does not scale well rather, *Jatropha* oil that is non-edible should be the best.

2.1.2.3 Virgin vegetable oil (VVO)

Unlike biodiesel, virgin vegetable oil (VVO) cannot be used without modifying the engine, because its viscosity is higher than that of petro-diesel and biodiesel (Journey to forever, 2011). There have to be two-tank virgin vegetable oil or otherwise known as straight vegetable oil (SVO) systems which pre-heat the oil to make it thinner. One has to start the engine on ordinary petro-diesel (or biodiesel) in one tank and then switch to SVO in the other tank when the vegetable oil is hot enough (i.e. thin enough), and switch back again to the petro-diesel tank before stopping the engine, or else the injectors will coke up (Journey to forever, 2011).

The published engineering literature strongly indicates that the use of straight vegetable oil will lead to reduced engine life (NREL, 2010). This reduced engine life is caused by the buildup of carbon deposits inside the engine.

2.1.1.4 Alcohols

Simple straight chained mono-alcohol such as methanol, ethanol and propanol are used in producing biodiesel. Methanol is most commonly used in the commercial production, since it is generally less expensive than other alcohols, but ethanol prevails in regions such as Brazil where it is less expensive than methanol (Moser, 2009). Methanol is more reactive and the fatty-acid methyl esters (FAME) produced are more volatile than fatty-acid ethyl esters (FAEE) (Yusuf, *et al.*, 2011). In the presence of acid or base catalyst, triglycerides (TG) in oil or fats reacts with commonly used alcohol, methanol, to produce biodiesel, which is also known as fatty acid methyl ester (FAME), and release glycerol (Ohet *al.*, 2013)..

2.1.1.5 Catalysis

Either base or acid can be used to catalyze the alcohol oil reaction to biodiesel. Most of the biodiesel produced today is done with the homogeneous base catalyzed reaction for several reasons itemized here (NBB, 2007):

1. It requires low temperature and pressure,
2. It yields high conversion (98%) with minimal side reactions and reaction time,
3. It is a direct conversion to biodiesel with no intermediate compounds, and
4. No exotic materials of construction are needed.

The most commonly used base catalysts are sodium hydroxide (NaOH), potassium hydroxide (KOH) and, sodium and potassium methoxide (MeONa, MeOK) which are collectively called lye. Strong acid (e.g. H₂SO₄, HCl or H₃PO₄) catalysts show tolerance to free fatty acids (FFAs) but they catalyze the transesterification reaction very slowly (Chak-Tong and Hongxing, 2008).

However, the use of homogeneous base catalyzed reaction for the production of biodiesel has the following drawbacks (Wayne, 2008):

1. The catalysts are hazardous and difficult to handle,
2. Process requires difficult pH control to maintain quality,
3. The need for intensive biodiesel separation and purification protocols,
4. The catalysts are used only once and must be neutralized to remove the final products,
5. Water washing is extensively used to process products, and
6. Waste water is usually produced which requires treatment to avoid pollution.

The above listed shortcomings of homogeneous production process of biodiesel necessitate the search for alternate process which is ongoing with the trials of heterogeneous process. Reports have shown that, several solidbasic and acid catalysts, such as CaO, ZrO₂, ZnO, SO₄⁻²/SnO₂, SO₄⁻²/ZrO₂, KNO₃/KL zeolite and KNO₃/ZrO₂ produced high yield of biodiesel.

2.2 PLANT RAW MATERIALS FOR PROCESSING ESTERS TO BIODIESEL

There are several plants that provide oils for the production of biodiesel. The major components of vegetable oils are *triglycerides*. *Triglycerides* are *esters with* long-chain acids, commonly called *fatty acids* (Gerpen, n.d).According to Jason (2004), it has been estimated that in Germany, palm oil biodiesel has less than one third of the production costs of rapeseed biodiesel. First generation biodiesel production from palm oil is in demand globally. Biodiesel, produced from USA soybean oil alone accounted for about 90% of all fuel stock (NBB, 2008).Rapeseed (*Brassica napus L.*) or Field Mustard (*Brassica campestris L.* or *Brassica Rapa var.*) also refers to as Canola (Dupont, *et al.*, 1989; Zeratsky, 2009). The oil is also suitable for use as biodiesel.

Atadashi (2007) produced biodiesel with cotton seed oil using homogenous batch process and obtained 98% methyl esters content.

The above mentioned feedstocks are the first generation biodiesel feedstocks, their use for energy is currently the source of a heated debate on the threat that energy security poses to food security. Therefore, in this study second generation biodiesel feedstock *Jatropha curcas* seed oil was used.

2.2.1 *Jatropha curcas* oil

Jatropha curcas was first classified by Karl Von Linnr in 1753 and he named it botanically as *Jatropha curcas* (Becker and Makkar, 2008). *Jatropha Curcasis* a plant belonging to *Euphorbiaceae* family, which is a nonedible oil-bearing plant widespread in arid, semi-arid and tropical regions of the world (Fan and Burton, 2009). *Jatrophacurcas* oil is non-nutritional oil because, it contains toxicants, phorbol esters (Ahmed and Salimon, 2009) and this makes it very attractive for energy and fuel source. Though the plant exists in two genotypes; toxic and nontoxic. The nontoxic type is only found in Mexico (Becker and Makkar, 2008). *Jatrophacurcas* oil was used as mineral diesel substitute during the Second World War in Madagascar, Cape Verde and Benin (Akbar *et al.*, 2009). *Jatrophacurcas* seed oil contains about 42% methyl oleate (triolein) whose molecular formula is $C_{57}H_{104}O_6$ and a molecular weight of 885.4 as depicted by its structural formulain Figure 1. *Jatropha*oil could be used as fuel in diesel engines directly and by blending it with methanol (Fan and Burton, 2009). Crops like *Jatropha*, used for biodiesel, can thrive on marginal agricultural land. *Jatropha* cultivation can provide benefits for local communities(Fan and Burton, 2009). It is well-suited to semi-arid lands and can contribute to slow down desertification, according to its advocates.

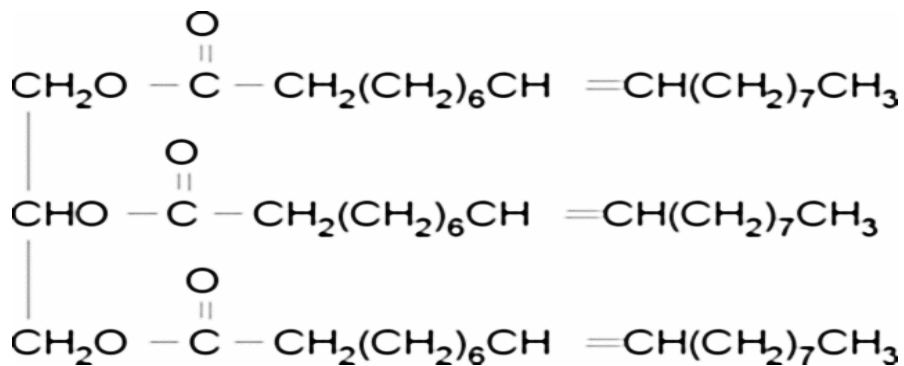


Figure 2.1: Structural formula of triolein in *Jatropha curcas* oil (Sigma-Aldrich, 2011)

Jatropha is a valuable multi-purpose crop to alleviate soil degradation, desertification and deforestation, which can be used for bio-energy to replace petro-diesel, for soap production and climatic protection, and hence deserves specific attention (CJP, 2011). Table 2.1 presents the triglycerides in *Jatropha curcas* oil.

Table 2.1: Triglycerides and their composition in *Jatropha curcas* oil

| S/N | Saturated triglycerides | Unsaturated triglycerides |
|-----|---|---|
| 1 | $ \begin{array}{c} \text{H}_2 - \text{C} - \text{OOC}(\text{CH}_2)_{12}\text{CH}_3 \\ \\ \text{H} - \text{C} - \text{OOC}(\text{CH}_2)_{12}\text{CH}_3 \\ \\ \text{H}_2 - \text{C} - \text{OOC}(\text{CH}_2)_{12}\text{CH}_3 \end{array} $ <p>Glyceryl trimyristate (Tritetradecanoate)</p> | $ \begin{array}{c} \text{H}_2 - \text{C} - \text{OOC}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_5\text{CH}_3 \\ \\ \text{H} - \text{C} - \text{OOC}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_5\text{CH}_3 \\ \\ \text{H}_2 - \text{C} - \text{OOC}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_5\text{CH}_3 \end{array} $ <p>Glyceryl tripalmitoleate (tri-9-hexadecenoate)</p> |
| 2 | $ \begin{array}{c} \text{H}_2 - \text{C} - \text{OOC}(\text{CH}_2)_{14}\text{CH}_3 \\ \\ \text{H} - \text{C} - \text{OOC}(\text{CH}_2)_{14}\text{CH}_3 \\ \\ \text{H}_2 - \text{C} - \text{OOC}(\text{CH}_2)_{14}\text{CH}_3 \end{array} $ <p>Glyceryl tripalmitin (Trihexadecanoate)</p> | $ \begin{array}{c} \text{H}_2 - \text{C} - \text{OOC}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3 \\ \\ \text{H} - \text{C} - \text{OOC}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3 \\ \\ \text{H}_2 - \text{C} - \text{OOC}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3 \end{array} $ <p>Glyceryl trioleate (cis-tri-9-octadecenoate)</p> |

| | | |
|---|---|---|
| 3 | $\begin{array}{c} \text{H}_2-\text{C}-\text{OOC}(\text{CH}_2)_{15}\text{CH}_3 \\ \\ \text{H}-\text{C}-\text{OOC}(\text{CH}_2)_{15}\text{CH}_3 \\ \\ \text{H}_2-\text{C}-\text{OOC}(\text{CH}_2)_{15}\text{CH}_3 \end{array}$ <p>Glyceryl triheptadecanoate</p> | $\begin{array}{c} \text{H}_2-\text{C}-\text{OOC}(\text{CH}_2)_7\text{CH}=\text{CH}\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_4\text{CH}_3 \\ \\ \text{H}-\text{C}-\text{OOC}(\text{CH}_2)_7\text{CH}=\text{CH}\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_4\text{CH}_3 \\ \\ \text{H}_2-\text{C}-\text{OOC}(\text{CH}_2)_7\text{CH}=\text{CH}\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_4\text{CH}_3 \end{array}$ <p>Glyceryl linoleate (cis-tri-9,12-octadecadienoate)</p> |
| 4 | $\begin{array}{c} \text{H}_2-\text{C}-\text{OOC}(\text{CH}_2)_{16}\text{CH}_3 \\ \\ \text{H}-\text{C}-\text{OOC}(\text{CH}_2)_{16}\text{CH}_3 \\ \\ \text{H}_2-\text{C}-\text{OOC}(\text{CH}_2)_{16}\text{CH}_3 \end{array}$ <p>Glyceryl tristearitate (Trioctadecanoate)</p> | $\begin{array}{c} \text{H}_2-\text{C}-\text{OOCCH}_2\text{CH}=\text{CH}(\text{CH}_2)_{15}\text{CH}_3 \\ \\ \text{H}-\text{C}-\text{OOCCH}_2\text{CH}=\text{CH}(\text{CH}_2)_{15}\text{CH}_3 \\ \\ \text{H}_2-\text{C}-\text{OOCCH}_2\text{CH}=\text{CH}(\text{CH}_2)_{15}\text{CH}_3 \end{array}$ <p>Glyceryl cis-tri-3-eicosenoate</p> |
| 5 | $\begin{array}{c} \text{H}_2-\text{C}-\text{OOC}(\text{CH}_2)_{18}\text{CH}_3 \\ \\ \text{H}-\text{C}-\text{OOC}(\text{CH}_2)_{18}\text{CH}_3 \\ \\ \text{H}_2-\text{C}-\text{OOC}(\text{CH}_2)_{18}\text{CH}_3 \end{array}$ <p>Glyceryl tricicosanoate</p> | $\begin{array}{c} \text{H}_2-\text{C}-\text{OOC}(\text{CH}_2)_7\text{CH}=\text{CH}\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{CH}_3 \\ \\ \text{H}-\text{C}-\text{OOC}(\text{CH}_2)_7\text{CH}=\text{CH}\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{CH}_3 \\ \\ \text{H}_2-\text{C}-\text{OOC}(\text{CH}_2)_7\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{CH}_3 \end{array}$ <p>Glyceryl tri-α-linoleate (-tri- 9,12,15-octadecatrienoate)</p> |
| 6 | $\begin{array}{c} \text{H}_2-\text{C}-\text{OOC}(\text{CH}_2)_{20}\text{CH}_3 \\ \\ \text{H}-\text{C}-\text{OOC}(\text{CH}_2)_{20}\text{CH}_3 \\ \\ \text{H}_2-\text{C}-\text{OOC}(\text{CH}_2)_{20}\text{CH}_3 \end{array}$ <p>Glyceryl tridocosanoate</p> | |
| 7 | $\begin{array}{c} \text{H}_2-\text{C}-\text{OOC}(\text{CH}_2)_{22}\text{CH}_3 \\ \\ \text{H}-\text{C}-\text{OOC}(\text{CH}_2)_{22}\text{CH}_3 \\ \\ \text{H}_2-\text{C}-\text{OOC}(\text{CH}_2)_{22}\text{CH}_3 \end{array}$ <p>Glyceryl tritetraicosanoate</p> | |

Source; Becker and Makkar, 2011; Sigma-Aldrich, 2011

Jatropha can help to increase rural incomes, self-sustainability and alleviate poverty for tribal communities, small farmers, women, elderly, children and men. It can as well help to increase income from plantations and agro-industries. Moreover, villagers often find that they can grow other crops in the shade of the trees. With average oil yield of 5MT/hectare/annum, *Jatropha* seems to be most promising resource and being outside food menu, its use will not affect the food price as in the case of other food crops (Bugaje and Mohammed, 2007). Their communities will avoid importing expensive diesel and there will be some for export too. The percentage

composition of the triglycerides varies with source location. When the triglycerides in Table 2.1 oxidized the fatty acids in Table 2.2 are formed (Becker and Makker, 2008).

Table 2.2: Fatty acid composition of non-toxic and toxic *Jatropha curcas* oil

| Molecular Formula | Scientific Name | Systematic Name | % In non-Toxic | % In Toxic |
|------------------------------|--------------------------|------------------------|-----------------------|-------------------|
| 14:00 | Tetradecanoic | Myristic | 0.2 | 0.1 |
| 16:00 | Hexadecanoic | Palmitic | 13.4 | 15.3 |
| 17:00 | Heptadecanoic | Heptadecanoic | 0.1 | 0.1 |
| 18:00 | Octadecanoic | Stearic | 6.4 | 6.6 |
| 20:00 | Eicosanoic | Arachidic | 0.2 | 0.2 |
| 22:00 | Docosanoic | Behenic | Tr | Tr |
| 24:00:00 | Tetracosanoic | Lignoceric | Tr | 0.1 |
| Total saturated | | | 20.3 | 22.4 |
| 16:1n-7 | 9-Hexadecenoic | Palmitoleic | 0.8 | 0.9 |
| 18:1n-9 | cis-9-Octadecenoic | Oleic | 36.5 | 41 |
| 20:1n-3 | cis-11Eicosenoic | Eicosenic | 0.1 | 0.1 |
| Total monounsaturated | | | 37.4 | 42 |
| 18:2n-6 | cis-9,12-Octadecadienoic | Linoleic | 42.18 | 35.3 |
| 18:3n-3 | 9,12,15-Octadecatrienoic | Linolenic | 0.2 | 0.3 |
| Total polyunsaturated | | | 42.3 | 35.6 |
| Total acid | | | 100.0 | 100.0 |

Source; Becker and Makkar, 2011

It can be cultivated on marginal, nonagricultural land; hence its cultivation does not affect food crops cultivation (Biozio, 2011). Therefore, unlike the common biofuel crops of today (corn and sugar), they are very easy to cultivate even on poor land in Africa providing great social and economic benefits for that region. It is fast growing and it begins producing seeds within 12 months, but the effective yield is obtained after 2-3 years (Biozio, 2011).

2.3 TRANSESTERIFICATION REACTION

Transesterification is the process of exchanging the alkyl groups of an ester with the alkyl group of an alcohol. These reactions are often catalyzed by the addition of an acid or base catalyst. The

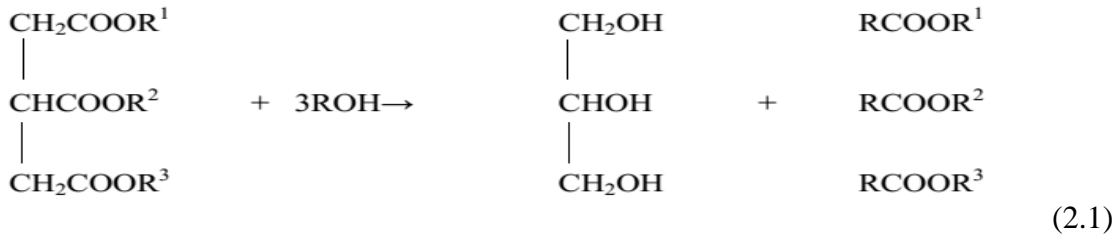
reaction can be accomplished with the help of enzymes (biocatalyst) particularly lipases (E.C.3.1.1.3) (Yucel *et al.*, 2013). Strong acids catalyze the reaction by donating a proton to the carbonyl group, thus making it a more potent electrophile, while bases catalyze the reaction by removing a proton from the alcohol thus making it more nucleophile (Gerpen *et al.*, 2004).

Fats and oils are primarily water insoluble, hydrophobic substances in the animals and plants that are made up of one glycerol and three fatty acids and are commonly called triglycerides. In the transesterification process, the alcohol is deprotonated with a base to make it a stronger nucleophile (Absolute astronomy, 2011). Commonly, ethanol and methanol are used. Normally, this reaction will proceed either exceedingly slowly or not at all. Heat, as well as an acid or base catalyst is used to help the reaction proceed more quickly. It is important to note that the acid or base is not consumed by the transesterification reaction, thus they are not reactants but catalysts.

Almost all biodiesel is produced from virgin vegetable oils using the base-catalyzed technique as it is the most economical process for treating virgin vegetable oils, requiring only low temperatures and pressures and producing over 98% conversion yield (NBB, n.d) (provided the starting oil is low in moisture and free fatty acids). Since natural oils are typically used in this process, the alkyl groups of the triglyceride are not necessarily the same. Therefore, distinguishing these different alkyl groups, we have a more accurate depiction of the reaction:

R^1, R^2, R^3 : Alkyl groups

During the transesterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkali (NaOH, KOH, or Alkoxides) as depicted in Equation (2.1), a mixture of methyl esters and glycerol are produced.



Triglyceride Alcohol Glycerol Biodiesel

The main reason for doing a titration to produce biodiesel, is to find out how much alkaline is needed to completely neutralize any free fatty acids present, thus ensuring a complete transesterification. The alcohol reacts with the fatty acids to form the mono-alkyl ester (or biodiesel) and crude glycerol. The reaction between the bio-lipid (fat or oil) and the alcohol is a reversible reaction (Fan Burton, 2009) so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion as claimed by some researchers. According to Gerpen *et al.*, (2004) 60% to 100% excess methanol is usually added to ensure that the reaction goes to completion.

Once the alcohol/catalyst mixture is made, it is added to the triglyceride (preferably heated to about 60⁰C) the reaction that follows produces fatty acid alkyl esters and glycerol. This reaction requires heat and agitation to bring the reactants into intimate contact as they are miscible.

2.3.1 Base catalyzed transesterification

According to Gerpen, (n.d) the simplest method for producing alcohol esters is to use a batch, stirred tank reactor. Alcohol to triglyceride ratios from 4:1 to 20:1 (mole: mole) have been

reported, with a 6:1 ratio most common. The reactor may be sealed or equipped with a reflux condenser. The operating temperature is usually about 65°C, although temperatures from 25°C to 85°C have been reported. Any strong base capable of deprotonating the alcohol will do (e.g. NaOH, KOH, Sodium methoxide, etc.). The most commonly used catalyst is sodium hydroxide, with potassium hydroxide also used. Typical catalyst loadings range from 0.3 % to about 1.5%. Commonly the base (KOH, NaOH) is dissolved in the alcohol to make a convenient method of dispersing the otherwise solid catalyst into the oil. The stoichiometric reaction requires 1 mole of a triglyceride and 3 moles of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed (Schuchardt *et al.*, 1998).

According to Gerpen *et al.* (2004) thorough mixing is necessary at the beginning of the reaction to bring the oil, catalyst and alcohol into intimate contact. Towards the end of the reaction, less mixing can help increase the extent of reaction by allowing the inhibitory product, glycerol, to phase separate from the ester/oil phase. Completions of 85% to 94 % are reported. Figure 2.1 shows a process flow diagram for a typical batch system.

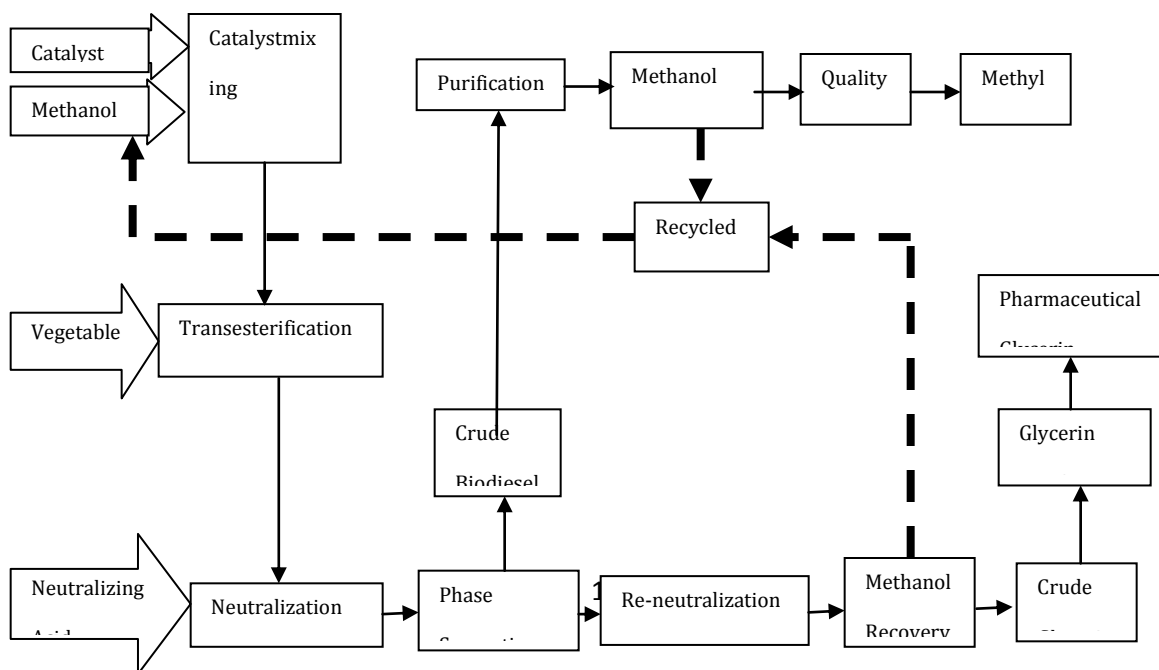


Figure 2.2: Base Catalyzed Batch Reaction Process (source, NBB 2007)

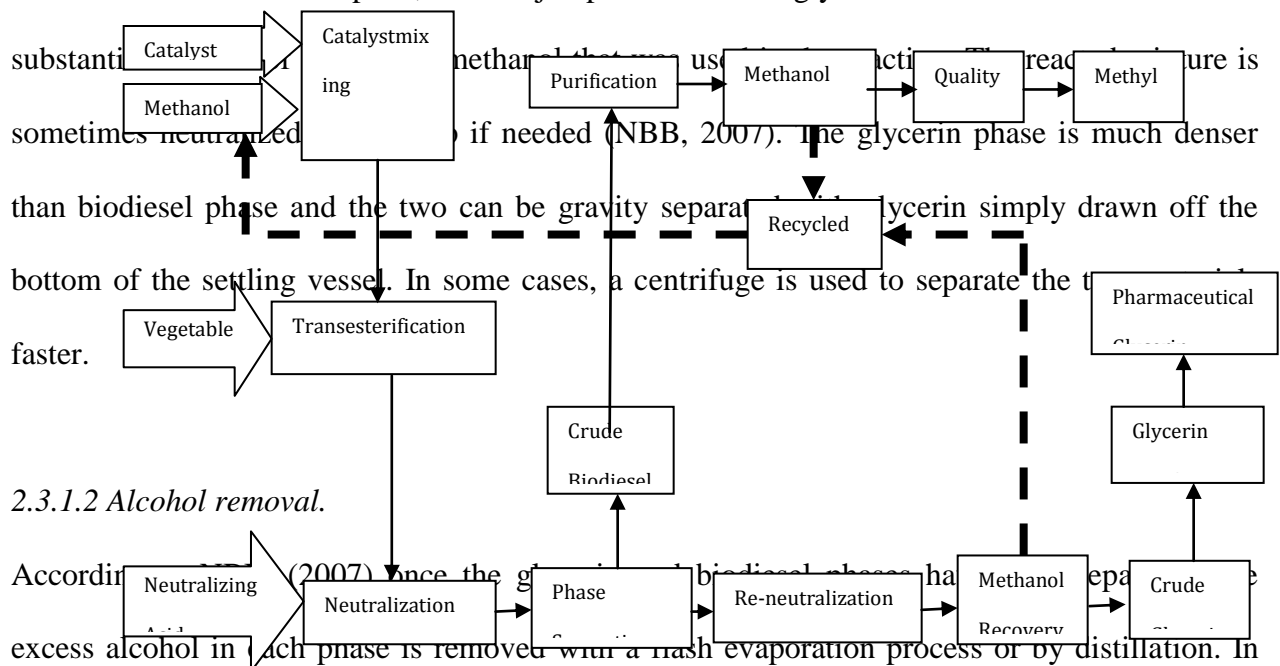
Some groups use a two-step reaction, with glycerol removal between steps, to increase the final reaction extent to 95+ percent (Gerpen, n.d). Higher temperatures and higher alcohol: oil ratios also can enhance the percent completion. Typical reaction times range from 20 minutes to more than one hour. The oil is first charged to the system, followed by the mixture of catalyst and methanol. The catalyst is typically sodium hydroxide (caustic soda) or potassium hydroxide (potash). It is dissolved in the alcohol using a standard agitator or mixer.

2.3.1.1 Separation.

Once the reaction is complete, two major products exist: glycerin and biodiesel. Each has a substantial amount of methanol dissolved in it. The glycerol phase is much denser than the biodiesel phase and the two can be gravity separated. The glycerol simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two phases faster.

2.3.1.2 Alcohol removal.

According to Gerpen (2007) once the glycerol phase has been removed, the biodiesel phase has excess alcohol in it. Each phase is removed with a flash evaporation process or by distillation. In



other systems, the alcohol is removed and the mixture neutralized before the glycerin and esters have been separated. In either case, the alcohol is recovered using distillation equipment and is re-used.

2.3.1.3 Glycerin neutralization

The glycerin by-product contains residual catalyst and soaps that are neutralized with an acid and sent to storage as crude glycerin. In some cases the salt formed during this phase is recovered for use as fertilizer (NBB, 2007). In most cases the salt is left in the glycerin. Water and alcohol are removed to produce 80-88% pure glycerin that is ready to be sold as crude glycerin. In more sophisticated operations, the glycerin is distilled to 99% or higher purity and sold into the cosmetic and pharmaceutical companies.

2.3.1.4 Methyl ester washes

Once separated from the glycerin, the biodiesel is sometimes purified by washing gently with warm water to remove residual catalyst or soaps, dried, and sent to storage. In some processes this step is unnecessary. This is normally the end of the production process resulting in a clear amber-yellow liquid with a viscosity similar to petroleum diesel (NBB, 2007). In some systems the biodiesel is distilled in an additional step to remove small amounts of color bodies to produce a colourless biodiesel.

2.3.2 Direct Acid Transesterification

High free fatty acid feedstocks will react with the catalyst and form soaps if they are fed to a base catalyzed system. The maximum amount of free fatty acids acceptable in a base catalyzed

system is less than 2 percent, and preferably less than 1 percent (Au and Dai, 2008; Gerpen *et al.*, 2004). Some approaches to using high free fatty acid feedstocks use this concept to “refine” the free fatty acids out of the feed for disposal or separate treatment in an acid esterification unit (Gerpen *et al.*, 2004). The caustic is added to the feedstock and the resulting soaps are stripped out using a centrifuge. This is called caustic stripping.

According to Gerpen *et al.* (2004) some triglycerides are lost with the soaps during caustic stripping. The soap mixture can be acidulated to recover the fatty acids and lost oils in a separate reaction tank. The refined oils are dried and sent to the transesterification unit for further processing. Rather than waste the free fatty acids removed in this manner, they can be transformed into methyl esters using an acid esterification process. Acid catalyzed processes can be used for the direct esterification of free fatty acids in a high FFA feedstock. Less expensive feedstocks, such as tallow or yellow grease, are characteristically high in free fatty acids (FFA).

Direct acid esterification of a high free fatty acid feed requires water removal during the reaction, or the reaction will be quenched prematurely. Also, a high alcohol to FFA ratio required, usually between 20:1 and 40:1. The esterification reaction of FFAs with methanol produces byproduct water that must be removed together with acid catalyst, but the resulting mixture of esters and triglyceride, can be used directly in a conventional base catalyzed system. The water can be removed by settling, or centrifugation as an acid-water mixture. Counter-current continuous-flow systems will wash out the water with the exiting stream of acidic methanol (Gerpen *et al.*, 2004).

One approach to the acid catalyst system has been to use phosphoric acid as the initial catalyst, neutralize with an excess of KOH for the base step, and then neutralize with phosphoric acid

upon completion (Gerpen *et al.*, 2004). The insoluble potassium phosphate is recovered, washed, and dried for use as a fertilizer. Figure 2.2 shows a typical acid catalyzed, direct esterification process. According to Gerpen *et al.* (2004) an alternative approach to utilization of high FFA feedstocks is to use a base catalyst to deliberately form soap from the FFAs. The soap is recovered, the oil dried, and then used in a conventional base catalyzed system.

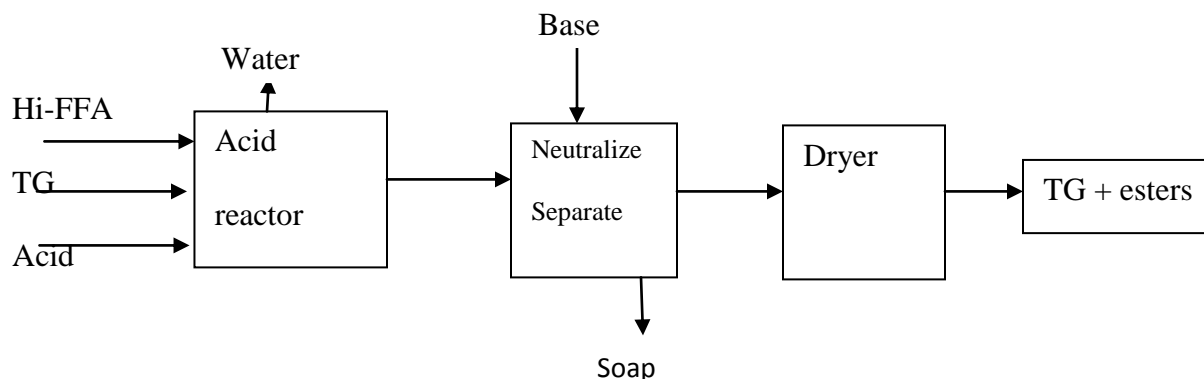


Figure 2.3: Acid Catalyzed Direct Transesterification process (Source; Gerpen, *et al.*, 2004)

This strategy can lead to a waste of material which will result in increased production cost. If the soapstock is discarded, the effective price of the feedstock is increased in inverse proportion to the percentage of remaining oil. The soapstock can, however, be converted into esters by using an acid catalyzed reaction. The problem with this strategy is that the soapstock system contains a large amount of water that must be removed before the product esters can meet the biodiesel standard. The soapstock process is shown in Figure 2.4.

Also reported by Gerpen *et al.* (2004) an alternative procedure for processing high FFA feeds is to hydrolyze the feedstock into pure FFA and glycerin. Typically this is done in a counter current

reactor using sulfuric/sulfonic acids and steam. The output is pure free fatty acids and glycerin. Any contaminants in the feedstock partition mostly into the glycerin and some may leave with the steam/water effluent.

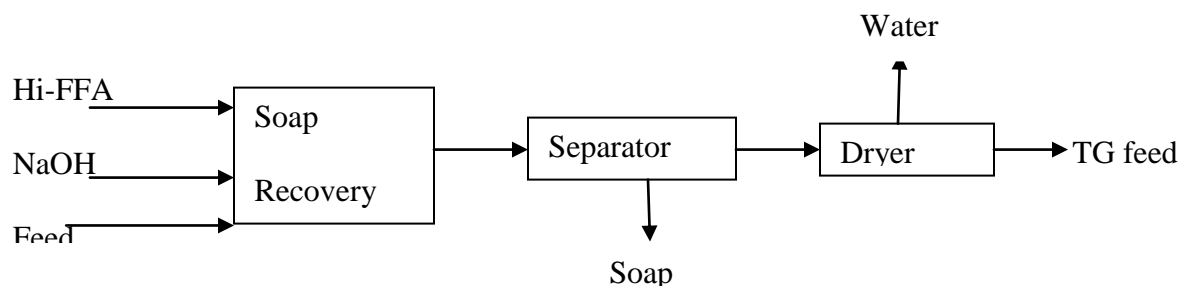


Figure 2.4: Preparation of Soapstock from a High FFA Feed (Source: Gerpen *et al.*, 2004)

Some contaminants continue with the FFA and can be removed or left in, depending on the processes and product specifications. The pure FFAs are then acid esterified in another counter current reactor to transform them into methyl esters. The methyl esters are then neutralized and dried. Yields can exceed 99%. Equipment needs to be acid resistant but generally feedstock costs are extremely low.

2.4 OTHER METHOD OF TRANSESTERIFICATIONS

Other Methods have been discovered to be more effective than base and acid transesterifications. Some of them are highlighted here.

2.4.1. Non-catalyzed System- Supercritical Process

According to Gerpen *et al.* (2004) when a fluid or gas is subjected to temperatures and pressures in excess of its critical point, there are a number of unusual properties exhibited. There is no longer is a distinct liquid and vapor phase, but a single, fluid phase present. Solvents containing a

hydroxyl (OH) group, such as water or primary alcohols, take on the properties of super-acids. Compared to the alkalicatalyzed method, in which the mixing effect is significant in a heterogeneous two-phase system, the mixing is not necessary in supercritical methanol because the reactants are already in a homogeneous phase (Saka and Minami, 2006). The non-catalytic supercritical dimethyl carbonate had successfully been proven to produce biodiesel with non-glycerol by-products such as glycerol in one-step (Ilham and Saka, 2013). Figure 2.4 depicts one conception of a configuration for a supercritical transesterification process by Saka and Minami (2006).

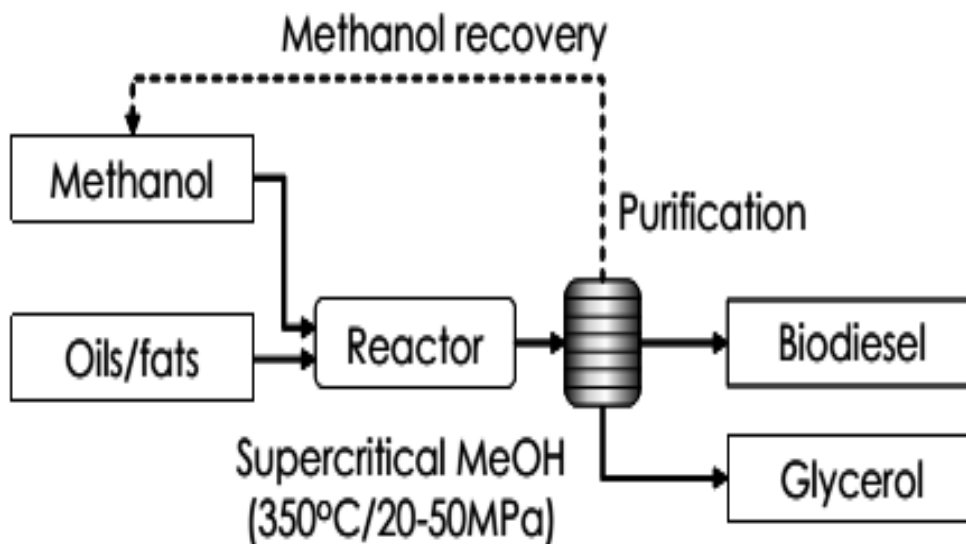


Figure 2.5: One-step supercritical methanol method (Saka and Minami process) for biodiesel production

In the supercritical state, the oil and methanol are in a single phase, and reaction occurs spontaneously and rapidly. The process can tolerate water in the feedstock; free fatty acids are converted to methyl esters instead of soap, so a wide variety of feedstocks can be used. Also the catalyst removal step is eliminated. High temperatures Transesterification by super critical

method of 1 mole of spent fish oil with 41 moles of methanol at 525 K (252°C) and 24 MPa took only 6 minutes and 100% yield was obtained (Ozcimen & Yucel 2011).

Energy consumption and excess amount of alcohol usage are the disadvantages for the biodiesel production in supercritical conditions (Ozcimen and Yucel, 2011). Indeed, the high temperature and pressure requires both an expensive reactor and a sophisticated energy and safety management policy (Ngamprasertsith and Sawangkeaw, 2011).

2.4.1 Continuous oscillatory baffle reactor assembly (COBRA)

Continuous Oscillatory Baffled Reactor Arrangement (COBRA) is a new technology for processing biodiesel. The oscillatory baffle reactor (OBR) generally consists of a column or tube containing periodically spaced orifice baffles with an oscillatory motion superimposed onto the flow (Ni *et al.*, *n.d.*). The oscillatory baffle reactor (OBR) or oscillatory flow reactor (OFR) is provided by generation and cessation of eddies (Ni, *et al.*, *N.d.*) the oscillations of which produce vortices (Abbott *et al.*, *n.d.*). This reactor consists of orifice baffles with an optional restriction ratio equally placed in both the straight section and the bends of the reactor (Abbott *et al.*, *n.d.*). Each baffled cell effectively acts as a continuous stirred tank vessel. A macro-scale OFR containing sharp periodic baffles has developed for a wide variety of reactions including the biodiesel production reaction (Zheng *et al.*, 2007). Uniform mixing is achieved at exceptionally low shear by vortices that form as fluid is forced through each orifice plate (Abbott *et al.*, *n.d.*).

2.4.2 Non-catalyzed systems – biox process

Co-solvent options are designed to overcome slow reaction time caused by the extremely low solubility of the alcohol in the TG phase (Gerpen, *et al.*, 2004). One approach that is nearing commercialization is the Biox Process. This process uses a co-solvent, tetrahydrofuran (THF), to solubilize the methanol. The result is a fast reaction, on the order of 5 to 10 minutes, and no catalyst residues in either the ester or the glycerol phase (Gerpen, *et al.*, 2004). The THF co-solvent is chosen, in part, because it has a boiling point very close to that of methanol. After the reaction is complete, the excess methanol and the tetrahydrofuran co-solvent are recovered in a single step. This system requires a rather low operating temperature, 30 °C. Other co-solvents, such as MTBE, have been investigated (Gerpen, *et al.*, 2004). Co-solvent process is depicted by Figure 2.6. Mohammed-Dabo *et al.*, (2012) transesterified *Jatropha curcas* oil with methanol using tetrahydrofuran as co-solvent at 40°C in 10 minutes and obtained 98% methyl ester yield.

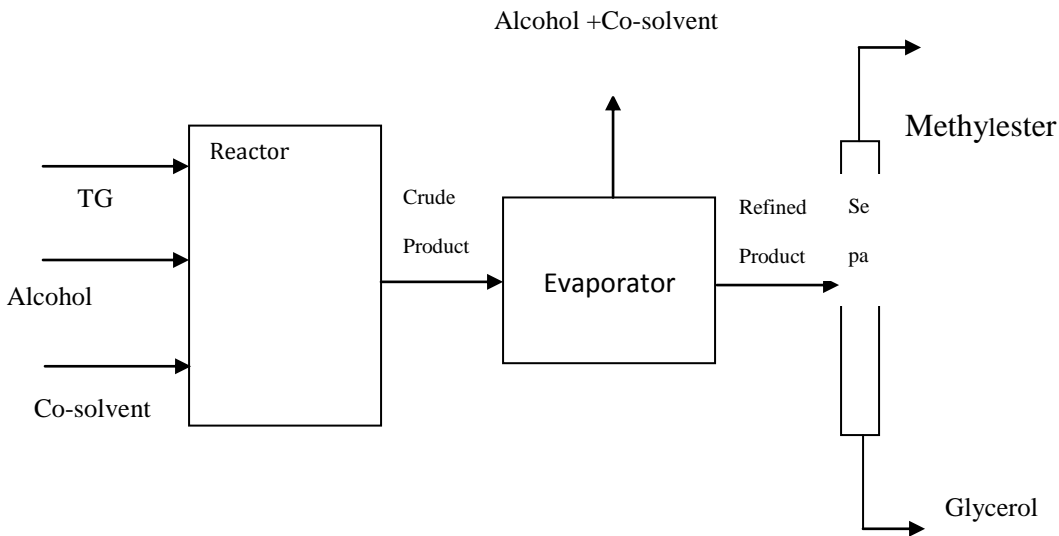


Figure 2.6: Biox Co-Solvent Process (Source; Gerpen *et al.*, 2004)

2.4.3 Ultrasonic reactor method

Ultrasonic reactor method, waves cause the reaction mixture to produce and collapse bubbles constantly. Use of ultrasonic wave as a new technology to speed up transesterification reaction, increase reaction efficiency and reduce the amount of catalyst and energy required to produce biodiesel (Mostafa *et al.*, 2013). This cavitation provides simultaneously the mixing and heating required to carry out the transesterification process. Thus using an ultrasonic reactor for biodiesel production drastically reduces the reaction time, temperatures, and energy input. Low frequency ultrasonic irradiation is widely used for biodiesel production in recent years ((Ozcimen and Yucel, 2011). A record of 98.5% has been achieved using ultrasonic method of biodiesel production from *Jatropha* oil and methanol (1:9) catalyzed by Na/SiO₂ at 70°C for 15 minutes (Ozcimen and Yucel, 2011).

These primary effects on object under ultrasound are; mechanical effects; cavity effects and thermal effects (Guo and Fang, 2011). These three effects of ultrasound radiation not only change the structure of the object, but also lead to chemical reactions. Industrial scale ultrasonic devices allow for the industrial scale processing of several thousand barrels per day.

2.4.4 Microwave method

An alternative heating system microwave irradiation has been used in transesterification reactions in recent years (Ozcimen and Yucel, 2011). According to Gude *et al* (2013) microwave technology has advanced in other food, pharmaceutical and polymer chemistry related research and industry, and it has yet to prove its potential in the biodiesel industry at large scale applications. Microwave assisted method has produced 97.4% conversion of *Jatropha* oil to

methyl esters at 65°C for 2 minutes with 7.5:1 methanol to oil by KOH catalysis (Ozcimen and Yucel, 2011).

Microwave irradiations assisted biodiesel synthesis is a physicochemical process since both thermal and non-thermal effects are often involved, which activates the smallest degree of variance of polar molecules and ions such as alcohol with the continuously changing magnetic field (Guo and Fang, 2011). Microwave irradiation can accelerate the chemical reaction, and high product yield can be achieved in a short time.

2.4.5 Lipase-catalyzed method

Application of lipase for biodiesel production was first reported by Mittelbach (Yucel *et al.*, 2013). Enzyme catalyzed transesterification, using lipase as catalyst does not produce side products and involves less energy consumption but expensive and stricter reaction conditions (Ozcimen and Yucel, 2011). Researchers have found that very good yields could be obtained from crude and used oils using lipases. The use of lipases makes the reaction less sensitive to high FFA content which is a problem with the standard biodiesel process. One problem with the lipase reaction is that methanol cannot be used because it inactivates the lipase catalyst after one batch. However, if methyl acetate is used instead of methanol, the lipase is not in-activated and can be used for several batches, making the lipase system much more cost effective.

2.5 CATALYSTS FOR TRANSESTERIFICATION

Either base or acid can be used to catalyze the alcohol/oil reaction to biodiesel. Strong acid (e.g. H_2SO_4 , HCl or H_3PO_4) catalysts show tolerance to free fatty acids (FFAs) but they catalyze the transesterification reaction very slowly (Chak-Tong and Hongxing, 2008). Reports have shown that strong bases such as sodium hydroxide and potassium hydroxide (also called sodium lye and potassium lye) are bases most suitable for base-catalyzed transesterification mechanism (Gerpen *et al.*, 2004; NBB, 04/2007). However, the alkaline catalysts require anhydrous conditions and feedstock should be low in FFAs content (Chak-Tong and Hongxing, 2008). In other words, the currently employed alkaline catalysts cannot effectively catalyze the transesterification of feedstocks containing high levels of free fatty acids. There are some limitations associated with the use of lye catalysts which include; their hazardous, difficulty in handling, difficulty in maintaining pH and the catalysts are used once after that they must be neutralized (Wayne, 2008) and remove from final product.

According to Marcio *et al.* (2008) transesterification of vegetable oil with alcohol using niobium (V) oxide (Nb_2O_5) of 1.5 wt% calculated on the oil to be processed has been carried out. The transesterification can be carried out with either lower alcohol, such as methanol and ethanol or with alcohols having a longer carbon chain. The catalyst is separated from the product by filtration.

According to Alfred (2009) AMBERLYST™ BD20 is a patent-pending solid-catalyst for esterification technology for the conversion of high free fatty acid (FFA) feedstock materials into valuable biodiesel. It has been proven with crude vegetable oils, animal fats, greases, fatty acid distillate, and recycled materials with an FFA range from 0.5 to 100%. AMBERLYST™ BD20

technology outperforms all current solid catalysts and even conventional sulfuric acid technology in terms of speed, FFA range, and conversion efficiency.

According to Guo and Fang (2011), among the solid catalysts used are ion-exchange resins (e.g. Amberlyst-15), B_2O_3/ZrO_2 , zeolites as well as hafnium and zirconium salts. Hydrated zirconia showed good activity and selectivity in FFAs esterification. Also super acidic sulphated zirconia (SO_4^{2-}/ZrO_2) and tin oxide (SO_4^{2-}/SnO_2) are effective for esterification of fatty acid with alcohol below $150^{\circ}C$, the catalysts deactivate due to sulphate leaching.

2.6 PRETREATMENT OF FEEDSTOCK

Production of high quality biodiesel begins with the quality of the feedstock used. Hence, it is essential that the oil is purified before its processing for biodiesel. This is because the fuel is to be fed into engines which require the best quality possible. As such, careful steps must be taken to remove all undesirable constituents from the feedstock. In the case of vegetable oil extracted from plant seeds such as the *Jatropha*, the most recognizable impurities can be categorized into the following three:

1. Solid (solute) content
2. Water and volatile content
3. Free fatty acid content

Vegetable oil extracted from seeds is regarded as crude and contains a lot of substances that are not required in a high quality biodiesel. Suspended particles are examples of these unwanted elements, and are categorized as solid contents or solute (Agbogun, 2011). Although it is required that oilbearing seeds are dried to remove water before extracting the oil from the seed,

experience has shown that the oil usually contains water and other substances that can be removed by heating the oil. Those other substances that are not water are called the volatile contents. Free fatty acids do not fit directly into this category of impurities. But direct preparation of biodiesel without careful consideration of free fatty acid content of the oil can hamper the process.

2.6.1 Removal of Impurities from Feedstock

Solid contents can be removed by simple filtration. The filter used must be of very small pores like a filter paper in order to be able to trap all the solid materials. When the oil has been completely filtered, the next step is to remove the volatile content and water by heating the oil sample until the bubbling stops. Oil that has been subjected to filtration and heating can finally be put to the crucial free fatty acid removal process.

2.6.2 Removal of Free Fatty Acid from Feedstock

There are two ways of removal of free fatty acid from vegetable oil. They are by:

1. Washing with soap and water
2. Esterification with acid

Washing under soap is the easier of the two methods. It can be carried out with minimum experience and risk. But the problem with this method is that, it results to wastage of usable free fatty acid; hence reduce the quantity of biodiesel. For example, free fatty acid content of rubber seed oil is said to be up to over 30% (Agbogun, 2011). Removal of this amount from the total oil can reduce the quantity of biodiesel obtained by that amount.

Esterification on the other hand, does not remove the fatty acid. Instead, it helps to shield the fatty acids from the attack of alkaline and transform it into a constituent of the final product.

2.6.3 Washing Feedstock with Soap

Vegetable oil without free fatty acid exists as $C_3H_5(COOR)_3$ where R is the alkyl group which could be the same (R) or different groups (R, R', and R"). If R is the same, it implies that the fatty acid components of the oil are of the same type. But if different, it implies that the oil is made up of different type of fatty acids, like in the case of the rubber seed oil and *Jatropha curcas* seed oil.

The general chemical formula for vegetable oil is RCOOR', while that of free fatty acid is RCOOH. Washing oil with soap does not mean that soap will be added to the oil. It requires that the oil is treated with alkaline which could be potassium hydroxide (KOH) or sodium hydroxide (NaOH) to form soap in a process referred to as "Saponification".

If we chose to use KOH as the lye, then KOH can react with the free fatty acid in the oil as expressed in Equation (2.2) to form soap and water.



where, RCOOK is the soap and H_2O is the water formed.

The soap can be removed from the oil by washing the oil several times with clean hot water. At every round of washing, the soap-water is removed (draining the water from the bottom of the oil) by allowing the mixture to settle so that the oil floats on top of the soap-water. Pure oil is eventually obtained when all the soap water is washed off.

2.6.3.1 Determination of free fatty acids in feedstock

Generally, when the free fatty acids in feedstock is less than 1% and certainly, if it less than 0.5%, FFA can be ignored (Gerpen *et al.*, 2004). Soaps may allow emulsification that causes the separation of the glycerol and ester phases to be less sharp if FFA in the feedstock is high. Soap formation also produces water that can hydrolyze the triglycerides and contribute to the formation of more soap. Further, catalyst that has been converted to soap is no longer available to catalyze the reaction.

Free fatty acids (FFAs) of feedstock are determined by titrating the feedstock with sodium hydroxide or potassium hydroxide solution. The lye solution is prepared by dissolving 0.1 mole of potassium in 1 dm³ of distilled water to make 0.1M solution of KOH. 1 g of the oil to be tested is dissolved in 25 ml of propan-2-ol stirred and two to three drops of phenolphthalein indicator is added to the oil/propan-2-ol mixture. This mixture is titrated against 0.1 M KOH until the solution turns pink. A blank titration is also done by titrating only 25 ml of propan-2-ol against 0.1 M KOH until it turns pink.

The formula used in industry for calculation of free fatty acid percentage is as expressed in equation 2.3 (Gerpen *et al.*, 2004):

$$\text{FFA}\% = (v - b) \times N \times \left(\frac{28.2}{w} \right) \quad (2.3)$$

where, v is the volume in ml of titration solution, b is the volume in ml of the blank, N is the normality of the titration solution and w is the weight of the sample of oil in gram. Note that the formula contains 28.2 which is the molecular weight of oleic acid divided by ten. Oils are not made of only oleic acid hence this formula results in small errors, normally accepted (Gerpen *et*

al., 2004). The range of molecular weights encountered in the used oil trade is from 270 for palm to 281 for canola. The acid value of the oil feedstock is expressed as in Equation (2.4).

$$AV = 1.99 \times \% FFA \quad (2.4)$$

2.6.3.2 Esterification of high free fatty acids feedstock

This technique is the better way of removing the free fatty acids from vegetable oil. It involves substituting an alkyl group (R) for the hydrogen of the carboxyl functional group of the acid. In this way, the fatty acid will transform into an ester which will allow almost all of the oil to be available for biodiesel.

If the feedstock is confirmed from titration analysis to contain more than 1% free fatty acids, it is safer to esterify it before using it to produce biodiesel especially if base catalyst (either homogenous or heterogeneous) is employed. The amount of methanol required is $2.25 \text{ g} \times \% FFA \times \text{mass of the oil}$ and the amount of concentrated sulphuric acid is $0.05 \text{ g} \times \% FFA \times \text{mass of the oil}$ (Gerpen *et al.*, 2004) are added to the oil to be esterified after preheated to 60°C . This mixture is stirred and heated at 60°C for about 60 minutes.

At the end of this reaction ester, water and the sulphuric acid are products which can be separated in the separating funnel. After settled in a separating funnel the ester is runoff from the bottom of the funnel leaving behind water/acid mixture. The esterified oil can be tested for FFA and the process is repeated until the final %FFA is less than 1%.

2.7 BIODIESEL QUALITY

2.7.1 Biodiesel Testing

Quality is a prerequisite for the long-term success of a biofuel. Biodiesel quality depends on several factors that reflect its chemical and physical characteristics. The quality of biodiesel can be influenced by a number of factors: the quality of the feedstock; the fatty acid composition of the parent vegetable oil or animal fat; the production process and the other materials used in this process; the post-production parameters; and the handling and storage. Given the fact that most current diesel engines are designed to be powered by diesel fuel, the physicochemical properties of biodiesel should be similar to those of diesel oil (Barabas and Todoruț, 2011).

Biodiesel standards are in place in a number of countries in an effort to ensure that only high-quality biodiesel reaches the consumers. The two most important fuel standards are ASTM D6751 in the United States and EN 14214 (European Committee for Standardization, CEN) in the European Union (Moser, 2009). The European standard EN 14214 and United State standard ASTM 6751 for biodiesel defines the maximum and minimum limits for each of the tests. These limits are set to protect the end users so that the engine will perform and no damage is caused.

2.7.2 Tests that Affect Performance in the Short Term

The following tests for biodiesel affect the performance of diesel engine in the short term, hence standards are set to ensure that biodiesel produced for transportation is save for use.

2.7.2.1 Density

According to Barabas and Todoruț (2011) fuel density is the mass of unit volume, measured in a vacuum. Since density is strongly influenced by temperature, the quality standards state the determination of density at 15°C. Fuel density directly affects fuel performance, as some of the engine properties, such as cetane number, heating value and viscosity are strongly connected to density. The density of the fuel also affects the quality of atomization and combustion. Biofuels generally have a higher density; this will affect the volume of oil delivered into the combustion chamber. The EN standard is 0.86-0.90 g/cm³ (Moser, 2009). The test method at 15⁰C is EN ISO 3675 and EN ISO 12185 (Moser, 2009).

2.7.2.2 Kinematic viscosity

Biodiesel tends to be significantly more viscous than mineral oil; this can lead to poor atomization and incomplete combustion which leads to coking of injector tips. Several structural features influence the kinematic viscosities of Fatty Acid Alkyl Ester (FAAE), such as chain length, degree of unsaturation, double bond orientation, and type of ester head group (Moser, 2009). Viscosity influences the ease of starting the engine, the spray quality, the size of the particles (drops), the penetration of the injected jet and the quality of the fuel-air mixture combustion (Barabas and Todoruț, 2011). The EN and ASTM kinematic viscosity standards are 3.5-5.0 and 1.9-6.0 mm²/s respectively (Biodiesel standard, 2013; Moser; 2009 and Barabas and Todoruț 2011). The standard test methods at 40⁰C are EN ISO 3104 and ISO 3105 (Moser, 2009; Barabas and Todoruț, 2011)

2.7.2.3 Flash point

Flash Point measures the temperature at which enough vapour being given off cause an explosion when it comes into contact with a flame. It is used to classify fuels for transport, storage and distribution according to hazard level (Barabas and Todoruț, 2011). Generally biodiesel has a relatively high flash point compared to mineral oil. But sometimes methanol carries over from the production process and makes the biofuel hazardous. The flash point does not affect the combustion directly; higher values make fuels safer with regard to storage, fuel handling and transportation. The EN and ASTM minimum standard are 120⁰C and 93⁰C respectively (Biodiesel standard,2013; Moser, 2009;Barabas and Todoruț, 2011). The standard methods of testing flash point are EN ISO 3679 and ASTM D93 (Moser, 2009).

2.7.2.4 Sulphur

Sulphur emissions are harmful to human health, high sulphur fuels cause engine wear and shorten the life of catalysts. Biodiesel from rape seed oil contains virtually no sulphur; however, if animal fat is the source the sulphur can be high. The EN and ASTM standards are 10 mg/kg and 15 mg/kg respectively (Biodiesel standard, 2013; Moser, 2009;Barabas and Todoruț, 2011). The test methods for sulphur content are EN ISO 20846, EN ISO 20884 and ASTM D5453 respectively (Moser, 2009;Barabas and Todoruț, 2011).

2.7.2.5 Carbon residue

Carbon residue indicates the presence of impurities and deposits in the engine combustion chamber, and is also an indicator of the quantity of glycerides, free fatty acids, soaps and

transesterification reaction catalyst residues (Barabas and Todoruț, 2011). This is quantity of the material left after the evaporation and burning of the fuel. If it is too high, deposit can occur on injector tips and the combustion chamber. The EN maximum standard is 0.3 (10% dist. Residue) (Biodiesel standard, 2013; Barabas and Todoruț, 2011) and ASTM standard is 0.05% maximum (Moser, 2009). The standard test methods are EN ISO 10370 (Barabas and Todoruț, 2011) and ASTM D4530 (Moser, 2009).

2.7.2.6 Cetane number

This is a measure of the ignition quality of the oil - fuels with low cetane numbers tend to give increased emissions due to incomplete combustion. Cetane number is related to the ignition delay time a fuel experiences once it has been injected into a diesel engine's combustion chamber (Moser, 2009). These limits are given by the two reference fuels used in the experimental determination of the cetane number: a linear-chain hydrocarbon, hexadecane ($C_{16}H_{34}$, also called n-cetane), very sensitive to ignition, having a cetane number of 100, and a strongly branched-chain hydrocarbon, 2,2,4,4,6,8,8-heptamethylnonane (HMN, also called isocetane), having the same chemical formula $C_{16}H_{34}$, with high resistance to ignition, having a cetane number of 15 (Barabas and Todoruț, 2011). The EN and ASTM minimum standards are 51 and 47 respectively (Biodiesel standard, 2013; Moser, 2009; Barabas and Todoruț, 2011). The test methods for measuring cetane number are EN ISO 5165 and ASTM D613 (Moser, 2009).

2.7.2.7 Cloud point

The cloud point is defined as the temperature at which crystal growth is large enough (diameter $\geq 0.5 \mu\text{m}$) to be visible to the naked eye (Moser, 2009). It is the temperature at which

small solid crystals are first visualized as the fuel cooled (Zhiyon *et al.*, 2006). At temperatures below the CP, larger crystals fuse together and form agglomerations that eventually become extensive enough to prevent pouring of the fluid. Below the cloud point these crystals might plug filters or drop to the bottom of a storage tank (Barabas and Todoruț, 2011). The CP is the most commonly used measure of low-temperature operability of the fuel. The biodiesel cloud point is typically higher than the cloud point of conventional diesel. The lowest temperature at which the fluid will pour is defined as the pour point (PP).

2.7.2.8 Pour point

The pour point is the temperature at which the fuel contains so many agglomerated crystals that it is essentially a gel and will no longer flow. It is the temperature at which the fuel is no longer pumpable (Zhiyon *et al.*, 2006). This occurs if the temperature of the biodiesel drops below cloud point (Moser, 2009), when the microcrystals merge and form large clusters, which may disrupt the flow of the biodiesel through the pipes of the engine's fuel system. Similarly to the cloud point, the pour point values also depend on the feedstock the biodiesel was produced (Barabas and Todoruț, 2011).

2.7.2.9 Cold filter plugging point

The Cold Filter Plugging Point (CFPP) is defined as the lowest temperature at which a given volume of biodiesel completely flows under vacuum through a wire mesh filter screen within 60 s. It is the temperature at which fuel will cause a filter plug due to the crystallization of fuel

(Zhiyon *et al.*, 2006). The CFPP is generally considered to be a more reliable indicator of low-temperature operability than CP or PP, since the fuel will contain solids of sufficient size to render the engine inoperable due to fuel filter plugging once the CFPP is reached (Moser, 2009).

2.7.2.10 Lubricity

Lubricity is the fuel quality that prevents or minimizes wear in diesel injection equipment (Zhiyon *et al.*, 2006). According to Moser (2009) Lubricity is determined at 60°C in accordance to ASTM D6079 using a high-frequency reciprocating rig instrument. During the course of the experiment, a ball and disk are submerged in a liquid sample and rubbed at 60°C against each other for 75 minutes at a rate of 50 Hz to generate a wear scar. At the conclusion of the experiment, the maximum length of the wear scar is determined, and this value represents the lubricity of the sample. Shorter wear scar values indicate that the sample has superior lubricity compared to another sample that resulted in a longer wear scar. Lubricity is not prescribed in ASTM D6751 or EN 14214. However, the petro-diesel standards, ASTM D975 and EN 590, contain maximum allowable wear scar limits of 520 and 460 µm, respectively. Biodiesel possesses inherently good lubricity, especially when compared to petro-diesel this gives it an advantage over fossil diesel. The maximum standard for lubricity at 60°C is 520 µm with test method ASTM D6079 (Moser, 2009).

2.7.2.11 Sulphated ash

This measures the amount of contaminants such as catalyst residues remaining within the fuel. After the burning of biodiesel, in addition to CO₂ and H₂O a quantity of ash is formed consisting of unburned hydrocarbons and inorganic impurities (e.g. metal impurities). Metallic ash is very

abrasive and may cause excessive wear of the cylinder walls and the piston ring (Barabas and Todoruț, 2011). Ash is related to engine deposits on combustion. The EN and ASTM maximum standards are 0.02% m/m (Biodiesel standards, 2013; Barabas and Todoruț, 2011). The standard test methods for sulphated ash is ISO 3987 and ASTM D874 (Barabas and Todoruț, 2011).

2.7.2.12 Water content

Water is a constant problem both for producers and users. Excess water promotes bacterial growth and encourages the reversal of biodiesel into free fatty acids (Barabas and Todoruț, 2011). The moisture accumulated in biodiesel leads to the increase of free fatty acid concentration, which can corrode metal parts of the engine's fuel system. Biodiesel is much more hygroscopic (it attracts water) than diesel oil (Barabas and Todoruț, 2011). The biodiesel absorbs water during storage when the temperature is higher and the water absorbed is precipitated at lower temperatures. Following these repeated processes, the accumulated water is deposited on the bottom of the tank. The EN and ASTM maximum standards are 500 mg/kg (Burton 2008; Barabas and Todoruț, 2011). The standard test methods for water content are EN ISO 12937 and ASTM D2708/P40 (Barabas and Todoruț, 2011).

2.7.2.13 Total contamination

This measures the insoluble material; if the values are high the solids will cause filter and injector blockages. The EN maximum standard is 24 mg/kg (Moser, 2009; Barabas and Todoruț, 2011). The European Union test method for total contaminant is EN 12662 (Barabas and Todoruț, 2011).

2.8.2.14 Copper stripe corrosion

This measure the likelihood to cause corrosion to copper, silver and bronze parts, the general culprit tends to be free acids or sulphur compounds. The EN and ASTM maximum standards are 1 and 3(3h/50⁰C) respectively (Moser, 2009; Barabas and Todoruț, 2011). The standard test methods are EN ISO 12937 and ASTM D130 (Moser, 2009;Barabas and Todoruț, 2011).

2.7.2.15 Oxidation stability

The oxidation stability measures the ability of the oil to resist oxidation, this is important in the overall storage ability of the oil. Oxidative stability of biodiesel is determined through measurement of the oil stability index (OSI) by the Rancimat method (EN 14112). The Rancimat method indirectly measures oxidation by monitoring the gradual change in conductivity of a solution of water caused by volatile oxidative degradation products that have been transported via a stream of air (10 l/h) from the vessel (at 110⁰C) containing the biodiesel sample (Moser, 2009). Stability can be improved with the addition of antioxidants. The EN and ASTM minimum standards at 110⁰C are 6 hours and 3 hours respectively (Biodiesel standard, 2013). The standard methods for oxidation stability is EN 14112 (Moser, 2009;Barabas and Todoruț, 2011).

2.7.2.16 Acid value

Acid value (AV) or total acid number is a measure of mineral acids and free fatty acids in a fuel, both are linked to corrosion and engine deposits. Acid number is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize the acidic constituents in one gram of sample (Barabas and Todoruț, 2011). The acid value determination is used to quantify the presence of acid moieties in a biodiesel sample. In a typical procedure, a known amount of

sample dissolved in organic solvent (propanol) is titrated with a solution of potassium hydroxide with known concentration and with phenolphthalein as a color indicator. The EN and ASTM maximum standard is 0.5 mgKOH/g (Biodiesel standard, 2013). The standard test methods for acid value (AV) are EN 14104 and ASTM D664 (Moser, 2009; Barabas and Todoruț, 2011).

2.7.2.17 Iodine value

Iodine number is a measurement of total unsaturation (double bonds) within the biodiesel product. It is measured in g iodine/100 g of biodiesel sample, when formally adding iodine to the double bonds (Barabas and Todoruț, 2011). Biodiesel with high iodine value (IV) is easily oxidized in contact with air. The iodine value highly depends on the nature and ester composition of the feedstocks used in biodiesel production. A high iodine value in a fuel can lead to polymerization and injector fouling. The EN maximum standard is 120 (Biodiesel standard, 2013). The standard test method for iodine value (IV) is EN 14111 (Moser, 2009; Barabas and Todoruț, 2011).

2.7.2.18 Ester content

Ester content measures the degree of reaction conversion in the manufacture of biodiesel. Linoleic and polyunsaturated esters have to be controlled because of the strong negative effect on oxidation stability. The EN minimum standard is 96.5% by mass (Biodiesel standard, 2013). The standard test method for ester content is EN 14103 (Moser, 2009; Barabas and Todoruț, 2011).

2.7.2.19 Methanol content

The methanol has a low flash point which causes a safety risk and it is also a health hazard. Both EN and ASTM maximum standard is 0.2% by mass (Biodiesel standard, 2013; Moser,

2009;Barabas and Todoruț, 2011). The standard test method for methanol content is EN 14110 (Moser, 2009; Barabas and Todoruț, 2011).

2.7.2.20 Glycerides

These must be kept low as they are a measure of low conversion yield highvalue can lead to deposits on valves and injectors. The EN maximum standard for diglycerides and triglycerides is 0.2% by mass (Biodiesel standard, 2013). The standard test method for glycerides is EN 14105 (Moser, 2009;Barabas and Todoruț, 2011).

2.7.2.21 Group I & II metals

Sodium, potassium, calcium and magnesium arise from the addition of catalysts and can lead to high ash levels in the engine. The EN and ASTM maximum standard for group I and group II is 5 mg/kg (Biodiesel standard, 2013, Moser, 2009;Barabas and Todoruț, 2011). The standard test methods for Na, K and group II elements are EN 14108, EN 14109 and EN 14538 respectively (Biodiesel standard, 2013).

In US, the biodiesel component must satisfy the requirements of ASTM D6751 before inclusion in the respective fuels and correspondingly, in the European Union, biodiesel must be satisfactory according to EN 14214 before inclusion petro-diesel (Moser, 2009)

2.8 PROCESS MODELING AND DESIGN

To access the feasibility of the proposed process, complete process modeling were first carried out. Despite some expected differences between process modeling results and actual process

operation, most current modeling software provided reliable information on process operation, because of their comprehensive thermodynamic packages, vast component libraries and advanced calculation techniques (Zhang *et al.*, 2003).

2.9 ECONOMIC EVALUATION OF PROCESS PILOT PLANT

2.9.1 Fixed Capital Investment

This represents the capital necessary to purchase equipment and installation of process equipment with all auxiliaries that were needed for complete process operation. It included the amount require to purchase spare parts, construction of the plant and the acquisition of items necessary for plant operation (Offori-Boateng and Lee, 2011).

2.9.2 Depreciation Cost

This is the amount of economic loss of the fixed assets. This theory is that, fixed asset begins to loss their values from the day they are put into use, and therefore some provision must be made for allocation of these depreciation cost to the business operation during the life time of the asset.

Equation 5.1 gives the expression for depreciation;

$$\text{Depreciation} = \frac{\text{fixed capital cost} - \text{salvage value}}{\text{life span}} \quad \text{Eq. 4}$$

Sometimes salvage value is zero meaning that the equipment is worthless after usage to the period it is replaced. But for this plant not all the items under fixed cost are depreciable. For example, the buildings will not depreciate and the land. Some of the equipment may still be valuable after used. According to Peters and Timmerhaus (1999) a process model to estimate Federal tax regulations generally limit salvage or scrap values to 10% or less of the initial value of the property

2.9.3 PAYBACK PERIOD

According to Lane, (2012 – 2013), Payback Period represents the amount of time that it takes for a capital budgeting project to recover its initial cost. The sum of the manufacturing cost of year 1 and net profit of that year becomes total investment for the second year. Equation 2.5 is an expression for payback period (Lane, 2012-2013);

$$PPB = (\text{Last year with a negative NCF}) + \left(\frac{\text{Absolute value of NCF in that year}}{\text{Total cash flow in the following year}} \right) \quad (2.5)$$

2.9.4 Internal Rate of Return (Irr)

Vaquezet *al* (2011) described Internal Rate of Return as an indicator to quantify the efficiency of an investment. An expression to determine the IRR is expressed in equation 2.6 given by Vaquezet *al* (2011) as;

$$NPV = 0 = -I + \sum_{i=1}^N \frac{CF_n}{(1+r)^n} \quad 2.6$$

where, CF is the cash flow, I is the initial investment, n is the number of period and r is the Internal Rate of Return. Its value is usually obtained by trial and error. It is an interest rate at which net present value NPV is equal to zero.

2.9.5 Net Present Value

Net present value is one of the most important analyses that determine the economic viability of an investment plant. The Net present Value (NPV) greater than zero indicates that the project can be commercially viable (Yeboahet *al.*, 2013).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 MATERIALS

This chapter presents the materials and methods adopted in carrying out this work. The software, equipment and materials used include:

1. Software: Aspen HYSYS, AutoCAD and Excel.
2. Processing equipment: Oven, furnace, peristaltic pump and magnetic stirrer.
3. Analytical equipment: FTIR, SEM, BET, Bomb calorimeter, Flash point tester Pensky-Martins, Viscometer, sulphur analyzer, cloud point and pour point tester.
4. Glass wares: conical flasks, beakers, measuring cylinder, separating funnels, flat bottom flask, and density bottle.
5. Construction materials: Stainless sheet, galvanize iron sheet and plastic tanks.
6. Analytical grade chemicals: methanol, sulphuric acid, KOH, CaO, KNO₃, ethanol, cyclohexane, potassium iodide, toluene, HCl and isopropanol.
7. Raw materials: *Jatropha curcas* seedoil, hydrated lime.

3.2 PROCESS MODELING

The main design and simulation works were done with Aspen HYSYS and AutoCAD employed in some drawing works. Also Microsoft Excel was used in the design calculations and economic evaluation calculations. The process modeling software, Aspen HYSYS^(R) Plant V7.0 and 8.1 were used in this research.

The procedures adopted for process modeling was selecting non-random two liquid (NRTL) thermodynamics fluid package (model), defining the chemical components which were; triolein, methanol, calcium oxide, methyl oleate and glycerol, setting input conditions (temperature, pressure, flow rate and compositions of the chemical components), choosing the proper operating units and determining the plant capacity. In this process, information on triolein, methanol, M-Oleate and glycerol were available in the HYSYS^(R) V7.0 and 8.1 component library except that of calcium oxide which was created using Hypo Manager tool in HYSYS. Regarding the vegetable oil feed stock, *Jatropha curcas* seed oil was considered as the raw material. Due to the fact that oleic acid was the major component of the *Jatropha curcas* seed oil (42-43.5%) (Satish, 2011) triolein (C₅₇H₁₀₄O₆) was chosen to represent *Jatropha* oil in the HYSYS^(R) modeling. Accordingly, methyl oleate (C₁₉H₃₆O₂) was taken as the resulting biodiesel product and its properties were available in HYSYS^(R) component library.

Zhang et al (2003) recommended that for highly polar components such as methanol and glycerol, Non-Random Two Liquid (NRTL) and Universal Quasi-Chemical (UNIQUAL) be selected for thermodynamics fluid package for modeling. Trials modeling were carried out with these two thermodynamics fluid packages and NRTL proved to be better than UNIQUAL, hence NRTL was used for this process modeling.

3.2.1 Process Design

The pilot plant was designed to produce 3.765 litres/h of biodiesel and 1.255 litres/h of glycerol by-product. The main unit operations include; continuous stirred tank reactor (CSTR), mixer,

pumps, valves and storage tanks. The simulation was carried out with a 3:1 molar ratio of methanol to oil, 1.5% calcium oxide catalyst (based on mass of oil), at 60°C and 1 atmosphere. The frequency factor A, and activation energy E, used were $1.88 \times 10^7 \text{s}^{-1}$ and $4.57 \times 10^4 \text{kJ/kgmol}$ respectively. Plate 3.1 shows the input variables in blue colour while HYSYS calculated values in black. Plate 3.2 shows compositions of input variables in the two streams. The values for M.Oleate and glycerol are zero because they were not in input streams.

| Name | Triolein Stream | Methanol Stream | Calciumoxide |
|---------------------------|-----------------|-----------------|--------------|
| Vapour Fraction | 0.0000 | 0.0000 | 0.0000 |
| Temperature [C] | 25.00 | 25.00 | 60.02 |
| Pressure [kPa] | 101.3 | 101.3 | 116.3 |
| Molar Flow [kgmole/h] | 5.000e-003 | 1.500e-002 | 1.299e-003 |
| Mass Flow [kg/h] | 4.427 | 0.4806 | 7.311e-002 |
| Liquid Volume Flow [m3/h] | 4.833e-003 | 6.040e-004 | 3.133e-005 |
| Heat Flow [kJ/h] | -9826 | -3592 | 9.753 |

Plate 3.1: Modeled conditions of feed materials for transesterification

| Name | Methanol Stream | Triolein Stream |
|--------------------------------|-----------------|-----------------|
| Comp Mole Frac (Methanol) | 0.9207 | 0.0000 |
| Comp Mole Frac (Calciumoxide*) | 0.0793 | 0.0000 |
| Comp Mole Frac (Triolein) | 0.0000 | 1.0000 |
| Comp Mole Frac (Glycerol) | 0.0000 | 0.0000 |
| Comp Mole Frac (M-Oleate) | 0.0000 | 0.0000 |

Plate 3.2: Modeled compositions of feed materials for transesterification

After inputting the reaction parameters the simulation converges shows zero balance error as shown in Plate 3.3.



Plate 3.3: Modeled stoichiometry of the transesterification reaction

The kinetic parameters were $1.88 \times 10^7 \text{ s}^{-1}$ frequency factor and $4.57 \times 10^4 \text{ kJ/kgmol}$ activation energy which are displayed in Plate 3.4.

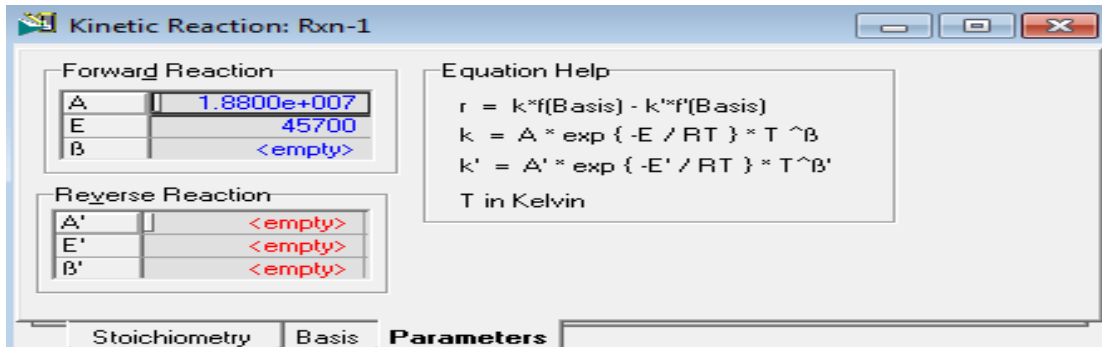


Plate 3.4: modeled kinetic parameters of the transesterification reaction

A Continuous Stirred Tank Reactor CSTR was designed for this operation. The Plate 3.5 shows the connections of the streams to the reactor.

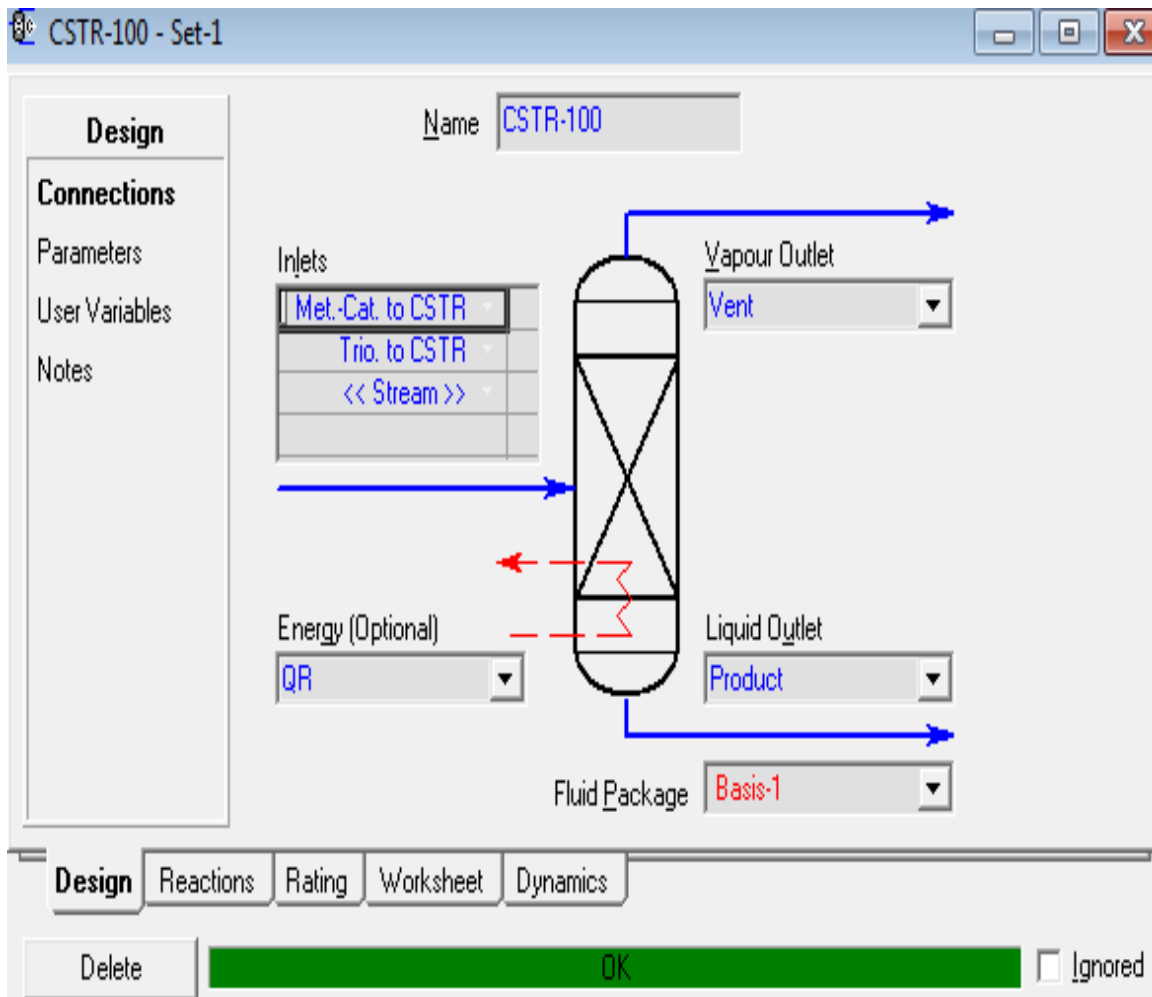


Plate 3.5: Reactor design connections for transesterification of *Jatropha* oil

The reactor was designed with a total volume of 8.933 litres and to occupy 70% liquid of its volume. The reactor operates at atmospheric pressure and a temperature of 60⁰C, hence the HYSYS calculated its heat duty 551.5 kJ/h as shown in Plate 3.6.

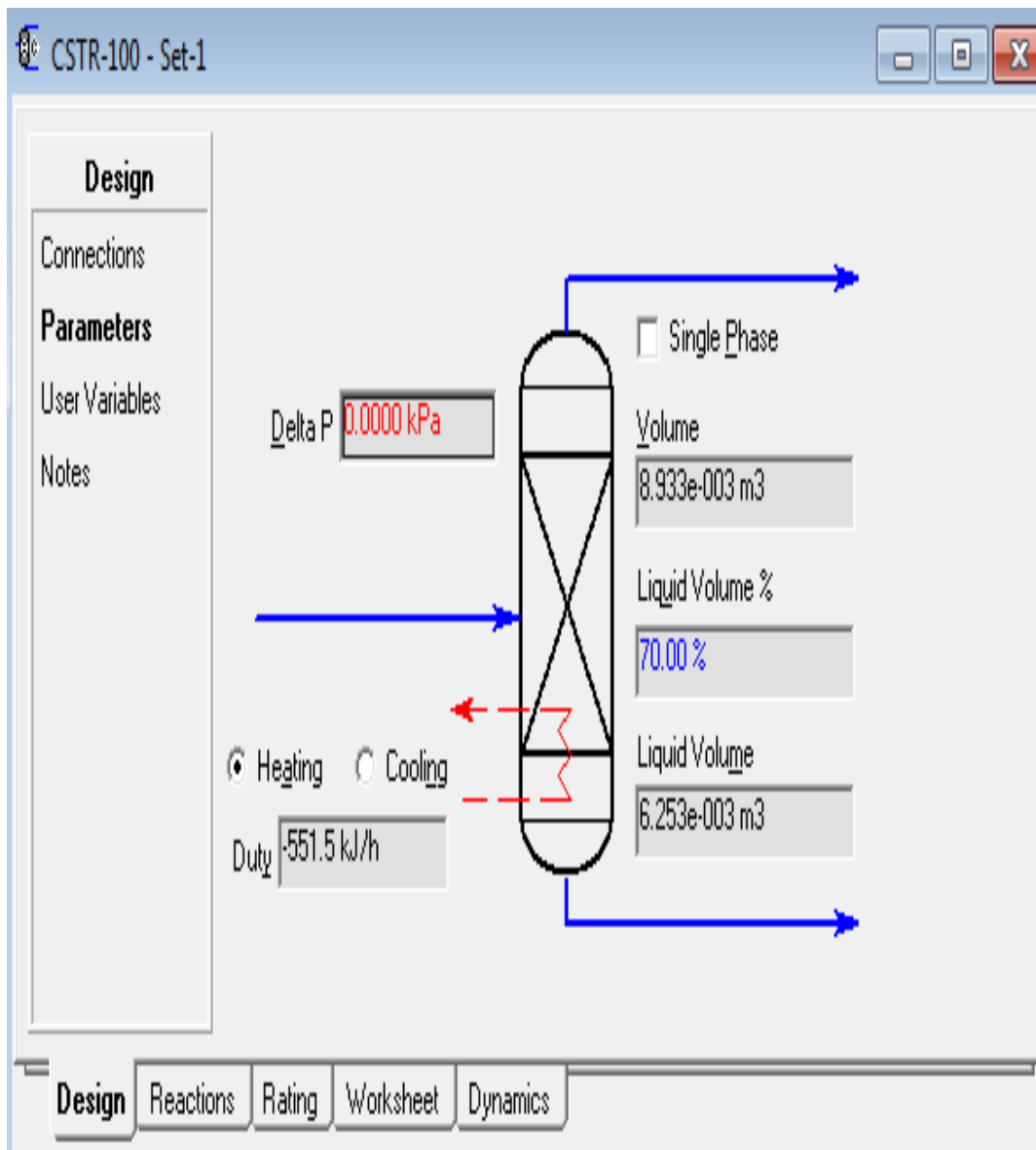


Plate 3.6: Reactor design parameters for transesterification of *Jatropha* oil.

The reactor was simulated at the temperature of 60°C, the mass and volume flow rates of product were 4.98 kg/h and 5.469e-03 m³/h respectively and zero out of the vent, hence there was no need for any unit operation to the vent for recycling or otherwise. This process excluded condenser in its operation. These results are shown in Plate 3.7.

| Worksheet | Name | V1 Out | V2 Out | Product | R Vent | QR |
|------------|-------------------------------|-------------|-------------|-------------|-------------|---------|
| Conditions | Vapour | 0.0000 | 0.0000 | 0.0000 | 1.0000 | <empty> |
| | Temperature [C] | 25.00 | 30.23 | 60.00 | 60.00 | <empty> |
| | Pressure [kPa] | 101.3 | 101.3 | 101.3 | 101.3 | <empty> |
| | Molar Flow [kgmole/h] | 5.000e-003 | 1.630e-002 | 2.130e-002 | 0.0000 | <empty> |
| | Mass Flow [kg/h] | 4.427 | 0.5537 | 4.981 | 0.0000 | <empty> |
| | Std Ideal Liq Vol Flow [m3/h] | 4.833e-003 | 6.353e-004 | 5.469e-003 | 0.0000 | <empty> |
| | Molar Enthalpy [kJ/kgmole] | -1.965e+006 | -2.197e+005 | -6.554e+005 | -2.177e+005 | <empty> |
| | Molar Entropy [kJ/kgmole-C] | 478.7 | 153.6 | 323.4 | 186.8 | <empty> |
| | Heat Flow [kJ/h] | -9826 | -3582 | -1.396e+004 | 0.0000 | -551.5 |
| | | | | | | |

Plate 3.7: Detailed conditions of the transesterification reaction of *Jatropha* oil

The contents of the components in Plate 3.8 indicated that, the product contained 70.42% M.Oleate (biodiesel), 23.47% glycerol, 0.01% unreacted methanol, 0% unreacted triolein (*Jatropha* oil) and 6.09% catalyst. The contents of these component materials were still zero in the vent of the reactor shows that virtually nothing comes out through it.

Conversion obtained at this condition was 99.98% as calculated by HYSYS shown as in Plate 3.8.

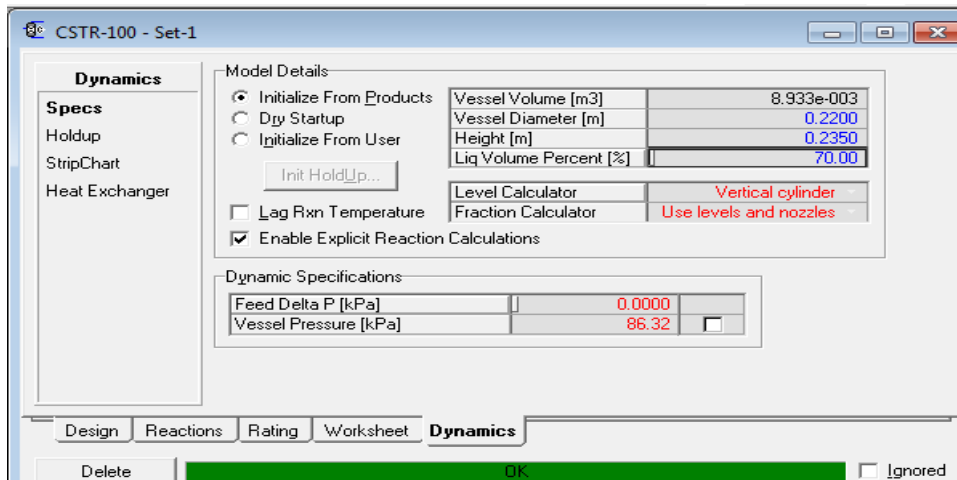


Plate 3.10: Modeled reactor internal dimensions for transesterification pilot plant

A pump was connected to the reactor to pump the product to the separator which separated solid from the solid/liquid mixture. The connection is as shown in Plate 3.11. A pump head of 1.6 m and efficiency of 35% were specified for the pump, pump power of 6.20263×10^{-2} W and pressure drop of 13.79 kPa were calculated by HYSYS. These results are as depicted by Plate 3.12.

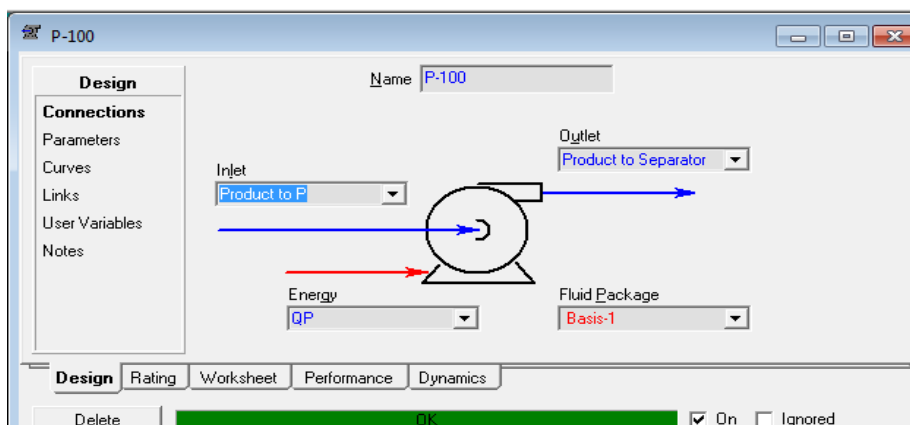


Plate 3.11: Modeled pump connections for the pilot plant

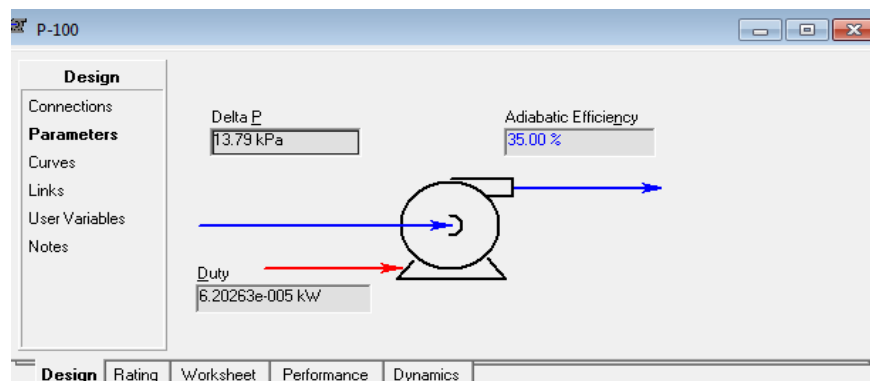


Plate 3.12: Modeled pump parameters for the pilot plant

By specifying the pump height and if efficiency, HYSYS calculated the pump pressure, discharge power and the fluid flow capacity. These results are shown in Plate 3.13.

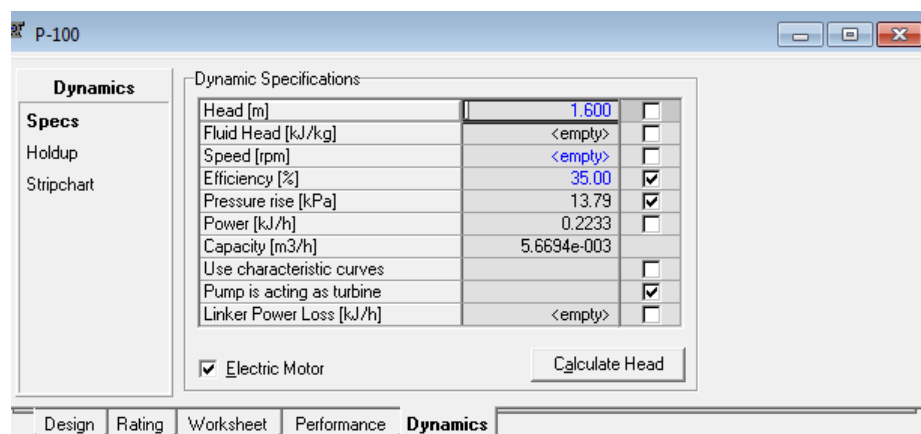


Plate 3.13: Modeled pump dynamic specifications for the pilot plant

A simple solid-liquid separator was simulated for sintered funnels as sintered funnel was not available in HYSYS 7.0 object palette. The connections of the simple solid separator is shown in Plate 3.14. The solid was required to be completely separated out of the liquid products.

The separation specified was 0.1% solid in liquid; ie 99.9% liquid is required to be separated. Plate 3.15 shows the split fractions of the solid in the other phases.

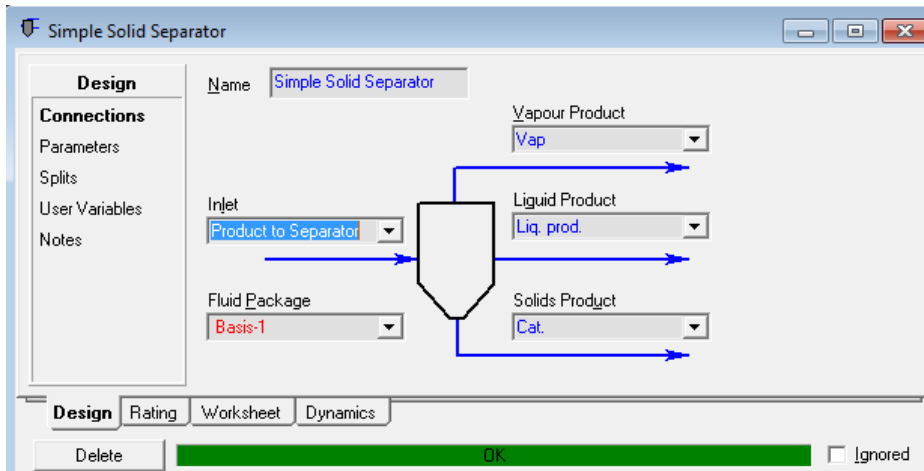


Plate 3.14: Simple solid-liquid separator connections for catalyst and biodiesel separation

The screenshot shows the 'Simple Solid Separator' configuration window with the 'Split Fractions' section active. The 'Type of Fraction' is set to 'Split Fractions'. Below is a table of split fractions:

| Split Fractions | |
|-------------------|---------|
| Solids To Vapour | 0.0000 |
| Solids To Liquid | 0.0010 |
| Solids To Bottoms | 0.9990 |
| Liquid To Bottoms | -0.0000 |

The bottom of the window has tabs for 'Design', 'Rating', 'Worksheet', and 'Dynamics', and buttons for 'Delete', 'OK', and 'Ignored'.

Plate 3.15: Modeled separator split fractions of for pilot plant products

The detail separation indicated that 0.07237kg/h of solid was removed from the mixture leaving 4.908kg/h of liquid containing biodiesel, glycerol and unreacted methanol. The detail separation of solid and liquid is shown in Plate 3.16.

The screenshot shows a software window titled 'Simple Solid Separator' with a 'Worksheet' tab selected. The worksheet contains the following data:

| | Name | Product to Se | Cat. | Vap | Liq. prod. |
|------------|-------------------------------|---------------|------------|-------------|-------------|
| Conditions | Vapour | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| | Temperature [C] | 60.02 | 60.02 | 60.02 | 60.02 |
| Properties | Pressure [kPa] | 95.24 | 95.24 | 95.24 | 95.24 |
| | Composition | | | | |
| | Molar Flow [kgmole/h] | 2.129e-002 | 1.291e-003 | 0.0000 | 2.000e-002 |
| | Mass Flow [kg/h] | 4.980 | 7.237e-002 | 0.0000 | 4.908 |
| | Std Ideal Liq Vol Flow [m3/h] | 5.469e-003 | 3.217e-005 | 0.0000 | 5.437e-003 |
| | Molar Enthalpy [kJ/kgmole] | -6.719e+005 | 8211 | -6.719e+005 | -7.158e+005 |
| | Molar Entropy [kJ/kgmole-C] | 353.2 | 1362 | 353.2 | 288.1 |
| | Heat Flow [kJ/h] | -1.430e+004 | 10.60 | 0.0000 | -1.431e+004 |

At the bottom of the window, there are buttons for 'Design', 'Rating', 'Worksheet', and 'Dynamics'. Below these are 'Delete', 'OK', and 'Ignored' buttons.

Plate 3.16: Detail modeled separation results of the simple–solid separator

A TEE was simulated in place of separating funnel to separate glycerol and biodiesel. The design connections of TEE is as shown in Plate 3.17

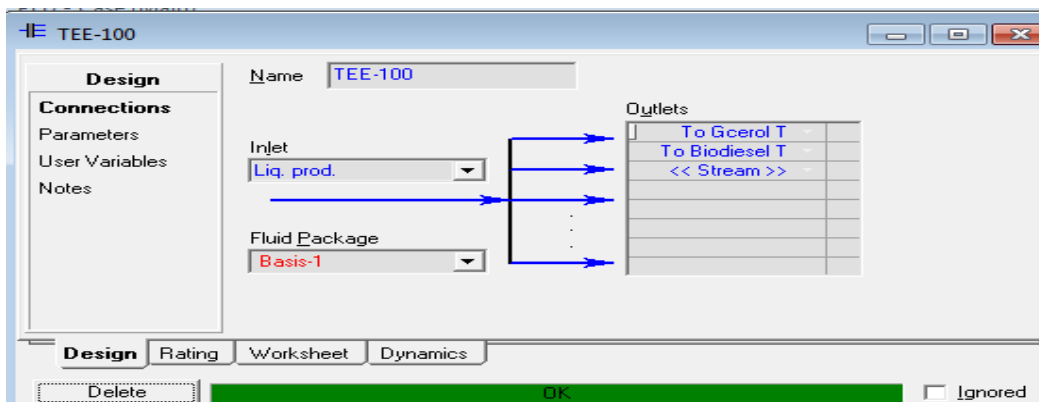


Plate 3.17: Modeled design connections of liquid-liquid separator of the pilot plant

The design parameter indicated the separation of 75% of liquid into biodiesel tank and 15% into glycerol tank as depicted in Plate 3.18.

Plate 3.19 shows the distribution of the products; biodiesel and glycerol into their respective storage tanks; biodiesel tank (B. Tank) and glycerol tank (G. Tank). From the Plate 3.19, 4.073 litres of biodiesel and 1.358 litres of glycerol were collected per hour into their storage tanks.

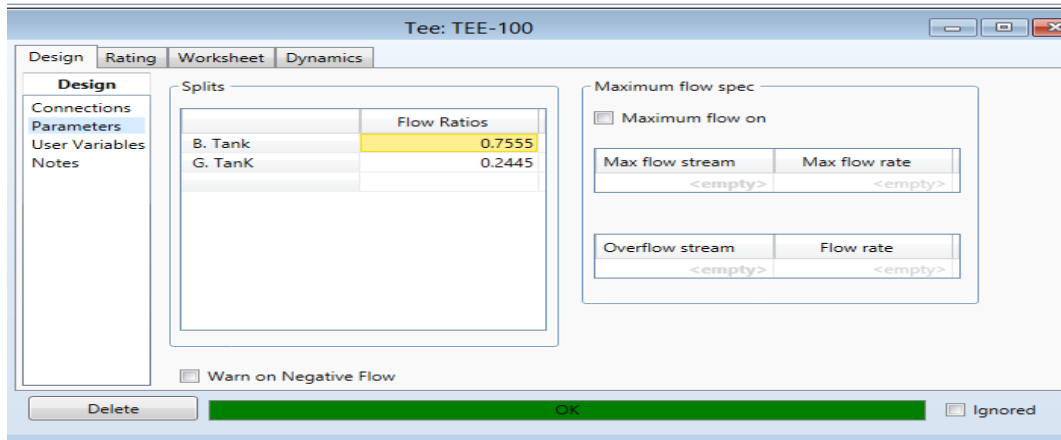


Plate 3.18: Modeled design parameter of liquid-liquid separator of the pilot plant products

| Name | Prod. to TEE | B. Tank | G. Tank |
|-------------------------------|--------------|-------------|-------------|
| Vapour | 0.0000 | 0.0000 | 0.0000 |
| Temperature [C] | 60.02 | 60.02 | 60.02 |
| Pressure [kPa] | 116.3 | 116.3 | 116.3 |
| Molar Flow [kgmole/h] | 2.001e-002 | 1.501e-002 | 5.003e-003 |
| Mass Flow [kg/h] | 4.904 | 3.678 | 1.226 |
| Std Ideal Liq Vol Flow [m3/h] | 5.431e-003 | 4.073e-003 | 1.358e-003 |
| Molar Enthalpy [kJ/kgmole] | -6.970e+005 | -6.970e+005 | -6.970e+005 |
| Molar Entropy [kJ/kgmole-C] | 259.4 | 259.4 | 259.4 |
| Heat Flow [kJ/h] | -1.395e+004 | -1.046e+004 | -3488 |

Plate 3.19: Separated products of the transesterification into storage tanks

Plate 3.20 shows the complete material and energy streams for all the components. This table again shows that nothing come out of the vent of the continuous stirred tank reactor; the molar flow rate, the mass flow rate, the liquid volume flow rate and heat flow were all zero.

| | | | | | | | |
|---------------------------|-----------------|-----------------|--------------|--------------|--------------|------------|-------------|
| Name | Triolein Stream | Methanol Stream | Calciumoxide | TV | Triolein Out | MT | Met-Cat out |
| Vapour Fraction | 0.0000 | 0.0000 | 0.0000 | 1.0000 | 0.0000 | 1.0000 | 0.0000 |
| Temperature [C] | 25.00 | 25.00 | 60.02 | 25.00 | 25.00 | 30.23 | 30.23 |
| Pressure [kPa] | 101.3 | 101.3 | 116.3 | 101.3 | 101.3 | 101.3 | 101.3 |
| Molar Flow [kgmole/h] | 5.000e-003 | 1.500e-002 | 1.299e-003 | 0.0000 | 5.000e-003 | 0.0000 | 1.630e-002 |
| Mass Flow [kg/h] | 4.427 | 0.4806 | 7.307e-002 | 0.0000 | 4.427 | 0.0000 | 0.5537 |
| Liquid Volume Flow [m3/h] | 4.833e-003 | 6.040e-004 | 3.131e-005 | 0.0000 | 4.833e-003 | 0.0000 | 6.353e-004 |
| Heat Flow [kJ/h] | -9826 | -3592 | 9.748 | 0.0000 | -9826 | 0.0000 | -3582 |
| Name | R Vent | Product | V1 Out | V2 Out | P Out | Cat. Out | Liquid |
| Vapour Fraction | 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Temperature [C] | 60.00 | 60.00 | 25.00 | 30.23 | 60.02 | 60.02 | 60.02 |
| Pressure [kPa] | 101.3 | 101.3 | 101.3 | 101.3 | 116.3 | 116.3 | 116.3 |
| Molar Flow [kgmole/h] | 0.0000 | 2.130e-002 | 5.000e-003 | 1.630e-002 | 2.130e-002 | 1.297e-003 | 2.000e-002 |
| Mass Flow [kg/h] | 0.0000 | 4.981 | 4.427 | 0.5537 | 4.981 | 7.296e-002 | 4.908 |
| Liquid Volume Flow [m3/h] | 0.0000 | 5.469e-003 | 4.833e-003 | 6.353e-004 | 5.469e-003 | 3.126e-005 | 5.437e-003 |
| Heat Flow [kJ/h] | 0.0000 | -1.396e+004 | -9826 | -3582 | -1.396e+004 | 9.733 | -1.397e+004 |
| Name | SV | MOleate | Glycerol | Glycerol Out | G. V | B V | MOleate Out |
| Vapour Fraction | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 1.0000 | 1.0000 | 0.0000 |
| Temperature [C] | 60.02 | 60.02 | 60.02 | 60.02 | 60.02 | 60.02 | 60.02 |
| Pressure [kPa] | 116.3 | 116.3 | 116.3 | 116.3 | 116.3 | 116.3 | 116.3 |
| Molar Flow [kgmole/h] | 0.0000 | 1.500e-002 | 5.001e-003 | 5.001e-003 | 0.0000 | 0.0000 | 1.500e-002 |
| Mass Flow [kg/h] | 0.0000 | 3.681 | 1.227 | 1.227 | 0.0000 | 0.0000 | 3.681 |
| Liquid Volume Flow [m3/h] | 0.0000 | 4.078e-003 | 1.359e-003 | 1.359e-003 | 0.0000 | 0.0000 | 4.078e-003 |
| Heat Flow [kJ/h] | 0.0000 | -1.048e+004 | -3492 | -3492 | 0.0000 | 0.0000 | -1.048e+004 |

Material Streams Compositions Energy Streams Unit Ops

Plate 3.20 : Complete modeled material streams of the process intensify pilot plant

The contents of the components all streams are shown Plate 3.21. The simulation results indicated that 70.42% of the product constituted the biodiesel and 23.47% was glycerol (the by-product of the transesterification reaction). There was no unreacted triolein left and unreacted methanol was 0.01% of the product which was less than 0.2% the maximum allowable quantity in biodiesel (Moser, 2009; Barabas and Todoruț, 2011). A detail results of the modeled continuous stirred tank reactor is provided in Appendix I.

| Name | Triolein Stream | Methanol Stream | Calciumoxide | TV | Triolein Out | MT | Met-Cat out | R Vent |
|--------------------------------|-----------------|-----------------|--------------|--------|--------------|-----------|-------------|---------|
| Comp Mole Frac (Triolein) | 1.0000 | 0.0000 | 0.0000 | 1.0000 | 1.0000 | 0.0000 | 0.0000 | 0.0000 |
| Comp Mole Frac (Methanol) | 0.0000 | 1.0000 | 0.0000 | 0.0000 | 0.0000 | 1.0000 | 0.9204 | 0.9529 |
| Comp Mole Frac (M-Oleate) | 0.0000 | 0.0000 | 0.0007 | 0.0000 | 0.0000 | 0.0000 | 0.0001 | 0.0030 |
| Comp Mole Frac (Glycerol) | 0.0000 | 0.0000 | 0.0002 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0441 |
| Comp Mole Frac (Calciumoxide*) | 0.0000 | 0.0000 | 0.9990 | 0.0000 | 0.0000 | 0.0000 | 0.0795 | 0.0000 |
| Comp Mole Frac (Hypo20001*) | xxx | xxx | xxx | xxx | xxx | xxx | xxx | xxx |
| Name | Product | V1 Out | V2 Out | P Out | Cat. Out | Liquid | SV | MOleate |
| Comp Mole Frac (Triolein) | 0.0000 | 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Comp Mole Frac (Methanol) | 0.0001 | 0.0000 | 0.9204 | 0.0001 | 0.0000 | 0.0001 | 0.0001 | 0.0001 |
| Comp Mole Frac (M-Oleate) | 0.7042 | 0.0000 | 0.0001 | 0.7042 | 0.0007 | 0.7498 | 0.7042 | 0.7498 |
| Comp Mole Frac (Glycerol) | 0.2347 | 0.0000 | 0.0000 | 0.2347 | 0.0002 | 0.2499 | 0.2347 | 0.2499 |
| Comp Mole Frac (Calciumoxide*) | 0.0608 | 0.0000 | 0.0795 | 0.0608 | 0.9990 | 0.0001 | 0.0608 | 0.0001 |
| Comp Mole Frac (Hypo20001*) | xxx | xxx | xxx | xxx | xxx | xxx | xxx | xxx |
| Name | Glycerol | Glycerol Out | G. V | B V | MOleate Out | ** New ** | | |
| Comp Mole Frac (Triolein) | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | | | |
| Comp Mole Frac (Methanol) | 0.0001 | 0.0001 | 0.9529 | 0.9529 | 0.0001 | | | |
| Comp Mole Frac (M-Oleate) | 0.7498 | 0.7498 | 0.0030 | 0.0030 | 0.7498 | | | |
| Comp Mole Frac (Glycerol) | 0.2499 | 0.2499 | 0.0442 | 0.0442 | 0.2499 | | | |

Plate 3.21: Complete modeled components in all the streams of the pilot plant

The Process Flow Diagram (PFD) showing the streams, five stage tanks for; mixer, triolein tank, the biodiesel tank and glycerol tank. Valves V1 and V2 were modeled in place of rotameters to control the flow of methanol-catalyst and triolein streams from their storage tanks into the reactor as depicted in Plate 3.22. As shown in the process flow diagram (Plate 3.22), the catalyst separated from the product was recycled back into the methanol/Catalyst stream.

| Workbook - Case (Main) | | | | | | |
|------------------------|-------------------|--|---------------------------|--------------------------|-------------|--|
| Name | Object Type | Inlet | Outlet | Ignored | Calc. Level | |
| V-100 | Tank | Methanol Stream Catalyst Stream | Met.-cat to V1 MV | <input type="checkbox"/> | 500 | |
| V-101 | Tank | Triolein Stream | Trio. to V2 TV | <input type="checkbox"/> | 500 | |
| Biodiesel Tank | Tank | To Biodiesel T | Biodiesel BV | <input type="checkbox"/> | 500 | |
| V-104 | Tank | To Gcerol T | Glycerol GV | <input type="checkbox"/> | 500 | |
| V1 | Valve | Met.-cat to V1 | Met.-Cat. to CSTR | <input type="checkbox"/> | 500 | |
| V2 | Valve | Trio. to V2 | Trio. to CSTR | <input type="checkbox"/> | 500 | |
| V3 | Valve | Product | Product to P | <input type="checkbox"/> | 500 | |
| CSTR-100 | Cont. Stirred Tar | Met.-Cat. to CSTR Trio. to CSTR QR | Product Vent QR | <input type="checkbox"/> | 500 | |
| P-100 | Pump | Product to P QP | Product to Separator | <input type="checkbox"/> | 500 | |
| Simple Solid Separator | Simple Solid Sep | Product to Separator | Cat. Vap Liq. prod. | <input type="checkbox"/> | 500 | |

Plate 3.24 Unit operations and the flows of the streams of the pilot plant

3.3 DESIGN OF CONTINUOUS STIRRED TANK REACTOR FOR TRANSESTERIFICATION

A transesterification reaction of *Jatropha curcas* oil and methanol using solid calcium oxide catalyst was simulated at 60°C and 1 atm. The simulation converged with frequency factor A of $1.88 \times 10^7/s$ and activation energy E of 4.57×10^4 kJ/kgmol. The reaction was first order reaction with respect to triolein (*Jatropha curcas* Oil). Volume of 8.933 litres was calculated for the reactor by HYSYS. The reaction rate was calculated from the Equation (3.1):

$$r_A = k_A C_A \quad (3.1)$$

The rate constant k_A is expressed as in Arrhenius Equation (3.2):

$$k = A \times \exp\left(\frac{-E}{RT}\right) \quad (3.2)$$

where, A is collision frequency or frequency factor, E is activation energy, R is universal gas constant and T is the reaction temperature.

Hence,

$$k = 1.88 \times 10^7 \times \exp\left(\frac{-4.57 \times 10^4}{8.314 \times 10^{-3} \times 333}\right) = 1.275 s^{-1}$$

where, C_A is the concentration of the reactant out of the reactor which is expressed as in Equation (3.3):

$$C_A = \frac{F_{AO}(-X_A)}{\phi} \quad (3.3)$$

where, ϕ is volume flow rate of all the components into the reactor.

$$C_A = \frac{5 \times 1 - 0.9998 \times 10^{-3}}{5.458 \times 10^{-3}} = 0.00018 \text{ kgmol} / \text{m}^3$$

Therefore, r_A is thus;

$$r_A = 1.275 \times 0.00018 = 0.00023 \text{ kgmol} / \text{m}^3 \text{ s}$$

The resident time τ ,

$$\tau = \frac{V}{\phi} \quad (3.4)$$

$$\tau = \frac{8.933 \times 10^{-3}}{5.458 \times 10^{-3}} = 1.64 \text{ h (1 hour, 38 minutes)}$$

According to Walas (1990) the level of the liquid content of a vessel and the dimensions and arrangements of impellers, baffles and other internals are factors that influence the amount of energy required for achieving a needed amount of agitation or quality of mixing. The internal arrangements depend on the objectives of the operation: whether it is to maintain homogeneity of a reacting mixture or to keep a solid suspended or a gas dispersed or to enhance heat or mass transfer. A basic range of design factors, however, can be defined to cover the majority of cases.

Except for very high Reynolds number, baffles are required to prevent vortexing and rotation of the liquid mass as a whole (Walas, 1990). The reactor had four baffles of height equal to the height of the liquid level. Walas (1990) provides detailed specification required for reactors and mixer geometry. The liquid level was equal to the diameter D of the tank (220 mm for this reactor). The width of the baffles was $D/12$ which came to 18 mm. In this design, the diameter of the reactor was 220 mm. It had one impeller of the type with six blades of width $D/3$ located at a level of $D/3$ which was 73 mm off bottom of the reactor. This was more suitable for solids suspension (Walas, 1990). The blade width was $d/8$. The nozzles of the reactor vessel and other tanks were 8 mm and 12 mm respectively. The nozzle of the vent was 8 mm as gas is suspected to pass out through to avoid pressure buildup. Internal features of the continuous stirred tank reactor and the mixer are shown in Figure 3.1 displaying its internal features.

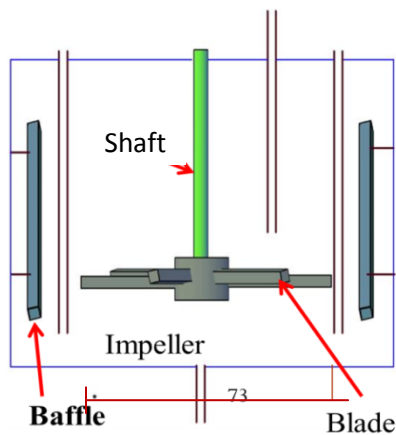


Figure 3.1: Reactor Internal Features the CSTR

Figure 3.8 shows the working drawing of front and plan views of the reactor with its dimensions.

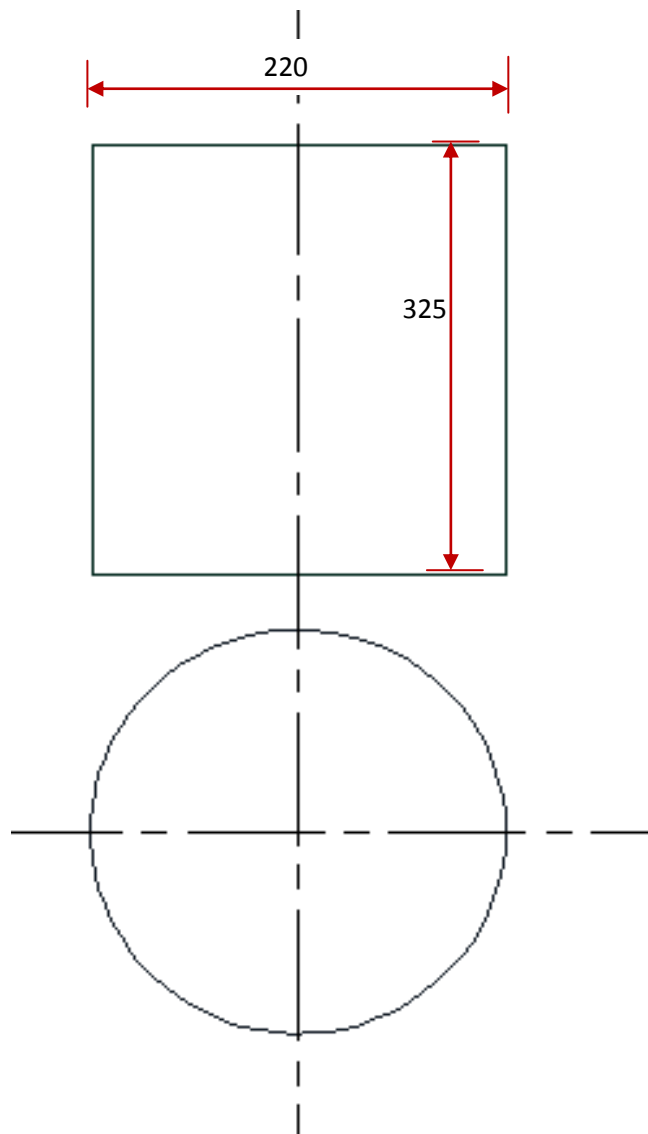


Figure 3.2: Working drawing of plan and front views of the CSTR for the process intensify pilot plant

Table 3.1 has comprehensive dimensions of the reactor and its internal features. The four baffles were joined to the wall of the reactor vessel by supports to give them strength to withstand vibration due the stirring action of the agitator. Due to the presence of solids in suspension and the use of heat transfer jacket, the baffles were offset from the wall of the reactor by a distance equal to one-sixth of the baffle width which was equal to 3 mm. The baffles length extended from one half the impeller diameter from the bottom to the liquid level.

Table 3.1: Reactor Design Specification for process intensify pilot plant

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| <i>l</i> | <i>(8.</i> | <i>t</i> |
| <i>u</i> | <i>93</i> | <i>r</i> |
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A peristaltic (positive displacement) pump was connected to the reactor to pump the product stream to the separation unit as it is more suitable for the designed flow rate. Due to low flow rate of the fluids, 0.06W pump power was required to pump the product to the separator at the height of 1.6 m. The peristaltic pump is a positive displacement chemical dosing device with the ability to vary flow capacity manually or automatically as the process conditions require.

3.3.1 Design of Stirrers for the Continuous Stirred Tank Reactor

According to Walas (1990), a turbine with blades curve at 45° that has two to eight blades is very effective for heat transfer with vessel walls or external coils combines both axial and radial flow. The principle of turbine blades curve at 45° was designed for this work but with flat blades, mostly for its effective combine axial and radial flows. A stirrer that had one impeller with six blades of 8.00 mm blade width was designed for this reactor. The shaft thickness was 10.00 mm and of length 240 mm. The tip speed desired for heat transfer was ranged from 10-15 ft/s (3.048-4.572 m/s). The average of this range was taken for this design, 3.81m/s. Figure 3.3 shows the working drawing reactor stirrer.

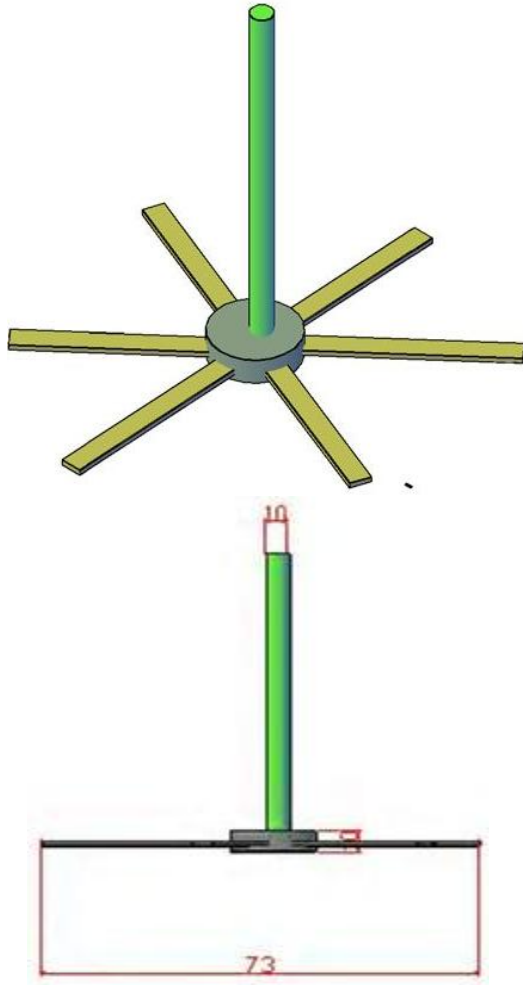
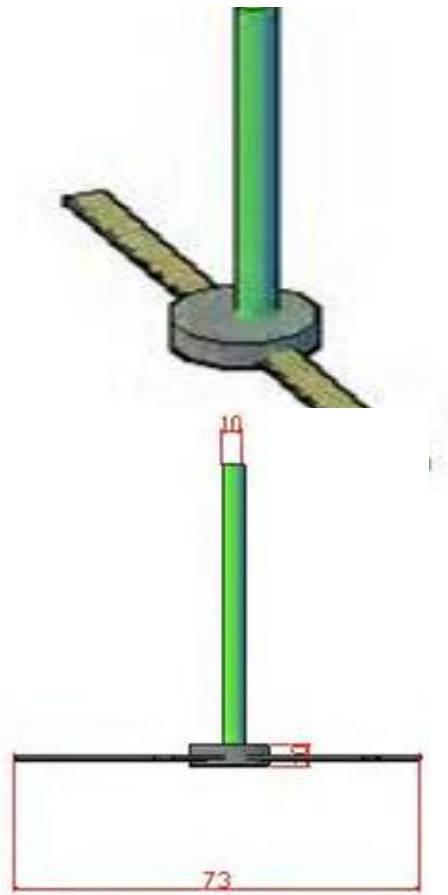


Figure 3.3: working drawings of reactor stirrer of the pilot plant

The power number, N_P and Flow number, N_ϕ for pitch blade turbine 45° with four baffles were in the range of 1.3-1.4 and 0.60-0.87 respectively (Walas, 1990) were recommended. The averages of these values were taken for this stirrer, 1.35 and 0.735 for N_P and N_ϕ respectively. This stirrer possessed a speed of 996.7 rpm. Therefore, the power draw of reactor tank stirrer was 0.06W. The detailed design calculation is in Appendix C1. The stirrer of mixer was designed as a two blades 68 mm blade width. The tank had no baffles since; the mixer was equipped with stirrer just to keep the solid catalyst in suspension. For a non-baffles pitch blades turbine, the recommended power number N_P , and flow number were N_ϕ are 0.7 and 0.3 respectively (Walas, 1990). The speed of the impeller blades was found to be 47.9 rpm. The power draws of the mixer stirrer was $5.6 \times 10^{-4}W$. The total power draw of the two tanks stirrers was 0.06056W. The detailed design calculation and specification are in Appendix IIB and Appendix IIC. Figure 3.4 below shows the working drawing of mixer stirrer.



(a) Auxilliary view

(b) Side view

Figure 3.4: The working drawings of the mixer stirrer

3.3.2 Design of Mixer for Methanol/Catalyst

Figure 3.5 shows the working drawing of the mixer containing its stirrer, motor and the vent. The mixer had no baffles as neither reaction nor heating takes place in it just for keeping the solid catalysts in suspension while the catalyst/methanol mixture flows into the reactor. Its stirrer had the same dimension as that of the reactor since the reactor and the mixer had the same diameter and height, except that it had only two blades.

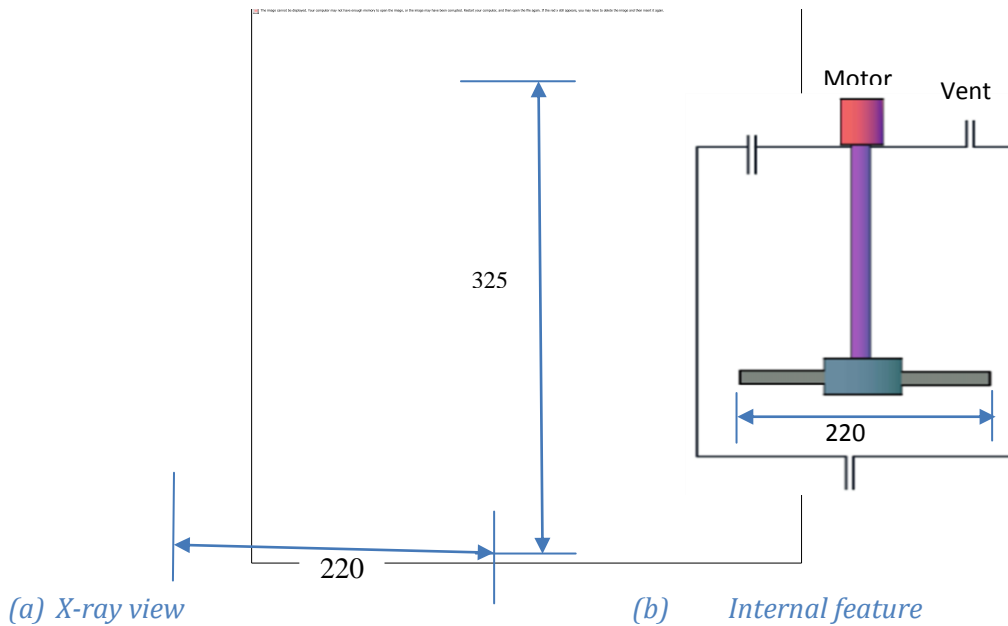


Figure 3.5: The working drawing of the mixer

3.3.3 Hot water jacket design

The hot water jacket was 320 mm tall and 226 mm diameter. A heater was placed at the base of the jacket which was 100 mm below the bottom of the reactor. The heater was controlled by temperature controller to heat the content of the reactor vessel. The whole set up was equipped with two temperature sensors one in the reactor and the second in the jacket to read the temperatures of the reactor fluid and that of hot water in the jacket.

3.3.4 Process Flow Sheet of the Process Intensify Pilot Plant

The whole process pilot plant consisted of four storage tanks, one each for methanol (mixer), triolein and two for products (biodiesel and glycerol). The methanol tank and the reactor were equipped with stirrers for proper mixing of their contents. All the vessels were 8.933 litres capacity, except the biodiesel and glycerol storage tanks. A mixture of methanol and the calcium oxide catalyst flow from the mixer into the reactor where they met with the oil from triolein tank. The hot water was maintained at 60°C by means of a thermostat. The product came out at 60°C,

therefore there was no need for heat exchanger. The product flowed into the separating funnels through the sintered funnels. The catalyst was collected in the sintered funnels. Process flow sheeting in Figure 3.6 describes the process.

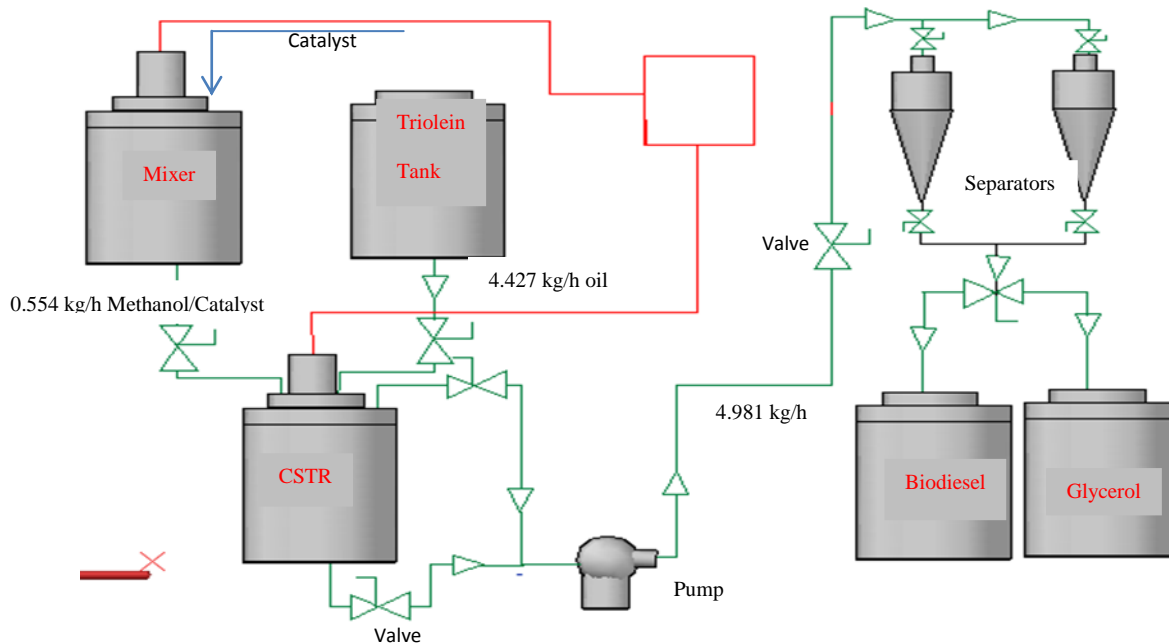


Figure 3.6: Process flows sheeting of the process intensify pilot plant.

3.4 INSTRUMENTATION AND CONTROL OF THE PILOT PLANT

The reactor was equipped with level transmitters to maintain its liquid contents at desired level during operation. The reactor and the hot water jacket were equipped with temperature sensors which read the temperatures of the contents. The sensor for hot water jacket and the heater were joined to the temperature controller to regulate the reactor temperatures at the desired value.

CSTR

3.5 PIPING AND PLANT LAYOUT OF THE PILOT PLANT

The equipment was given adequate space for services when required. The pilot plant was designed to occupy space area of 0.055 m^2 ($\text{Valve}^{\text{Pump}}$) mm by 500 mm. The methanol tank and

triolein tank had gap of 24 cm. The height of the plant was 1400 mm. Figure 3.7 shows the front and isometric views of the plant layout of the pilot plant. The fluid from methanol and triolein tanks were conveyed through polypropylene pipes as the operating temperature and pressure are within its tolerance and also no corrosive chemical in the streams. The product stream from the reactor to the storage tanks via the separator were conveyed with polypropylene pipe with reason same as above. Some pipes specifications are given by Bhachu *et al.* (2005). Appendix D shows detail piping and instrumentation.

The layout was designed in such way that the catalyst/ methanol mixture and oil flowed from their tanks into the reactor by gravity and controlled by valves. The product from the reactor was pumped into the separating funnels through the sintered funnels. The separation of the biodiesel from glycerol was carried out by gravity.

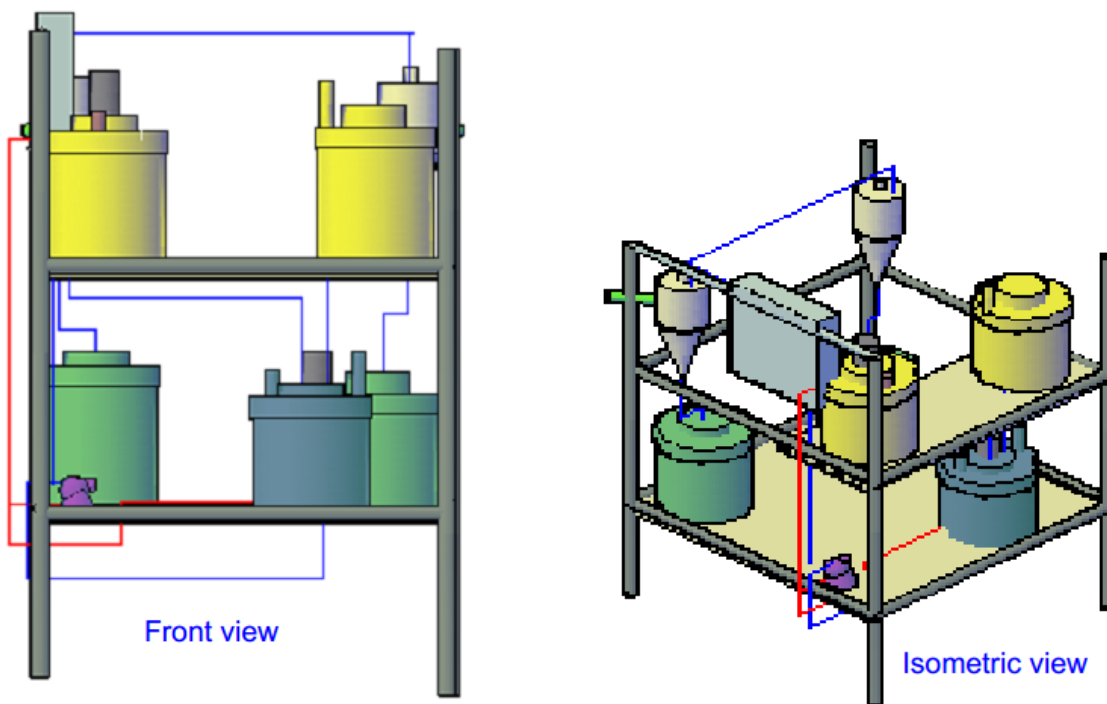


Figure 3.7: Plant layout of the process intensified pilot plant

3.6 FABRICATION AND INSTALLATION OF THE PILOT PLANT

The fabrication of was carried out at Hanigha, Nigeria Limited, Kaduna under the close supervision of the author. This was achieved by locally sourced materials with the exception of the pump which was ordered from China. The component unit operations fabricated were tested for leakage. The components were coupled together and transported to National Research Institute for Chemical Technology NARICT, Zaria. The pieces of equipment constructed were assembled together making a complete pilot plant as shown in Plate 3.25.

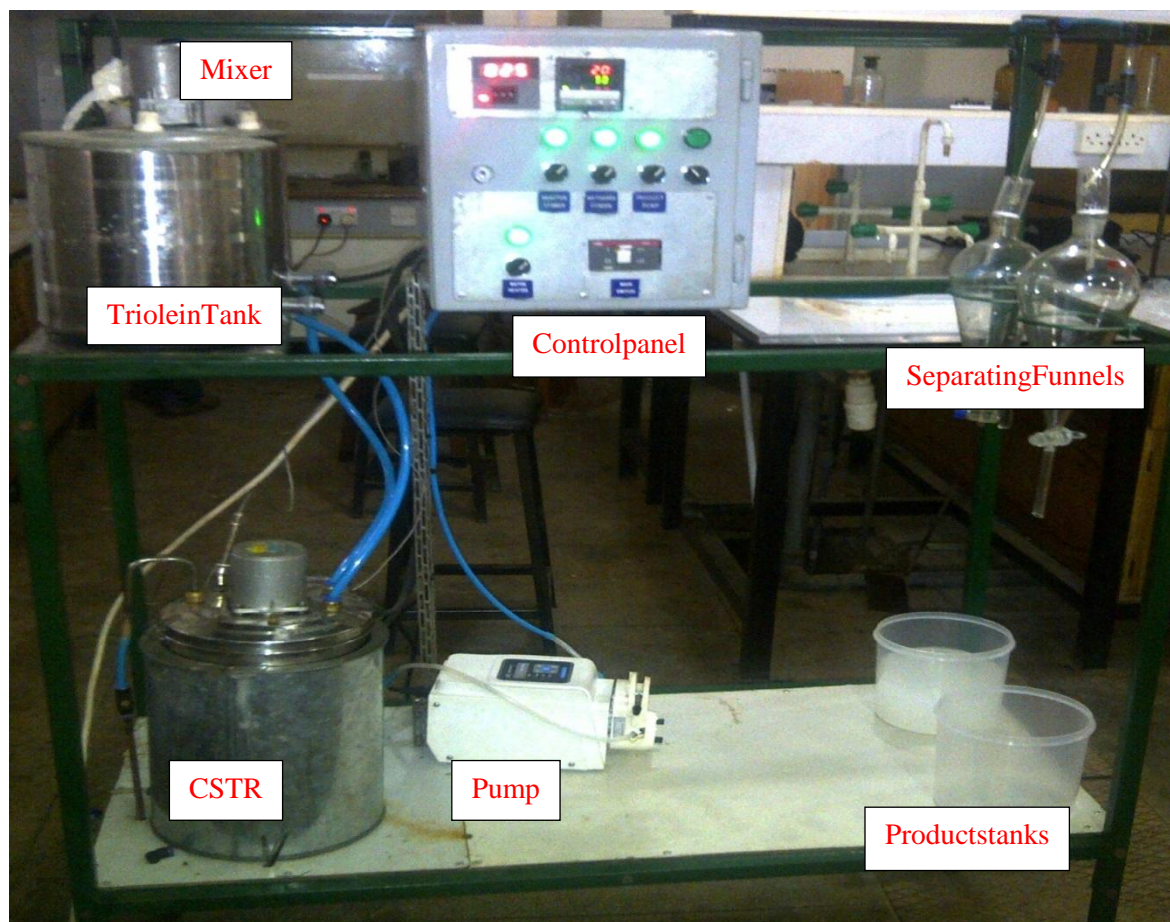


Plate 3.25: Assembled parts of the process intensified pilot plant

3.7 SYNTHESIS OF CATALYSTS

The catalyst simulated and designed for this study was bulk calcium oxide CaO; the author extended it to four other base solid catalysts; super base calcium oxide CaO/(NH₄)₂CO₃ bulk magnesium oxide (MgO), calcium oxide/magnesium oxide (CaO/MgO) and 10% potassium impregnated calcium oxide/magnesium oxide (K-CaO/MgO).

3.7.1 Preparation of Non-Supported Catalyst

At first two calcium oxide catalysts were synthesized for the production of biodiesel without support. These catalysts were tested to determine their efficacy for the production of biodiesel. They included: bulk calcium oxide and super base calcium oxide. However, the catalyst could not be filtered completely from the liquid product despite their high catalytic efficacy. The catalysts were synthesized as follows:

3.7.1.1 Preparation of non-supported bulk calcium oxide (CaO) catalyst

Hydrated lime was collected from the hydrated lime Pilot Plant of National Research Institute for Chemical Technology, NARICT Zaria. 20 g of the hydrated lime was dried in an oven at 110⁰C to constant weight. It was later fired in a muffle furnace for 90 minutes at 900⁰C at the rate 50% power delivery.

3.7.1.2 Preparation of non-supported supper base calcium oxide (CaO/(NH₄)₂CO₃) catalyst

Ammonium carbonate [(NH₄)₂CO₃(500 g)] was purchased from a scientific supply shop in Zaria. A solution was prepared by dissolving 60 g of (NH₄)₂CO₃ in 500 ml distilled water. 60 g of hydrated lime was dissolved in 500 ml of the ammonium solution. The mixture was stirred for 30

minutes and filtered (Hawash *et al.*, 2011). The residue was dried in an oven at 110⁰C to constant weight. The dried powder was calcined in a muffle furnace at 850⁰C for 90 minutes at 50% power rating.

3.7.2 Synthesis of Catalysts with Alumina Support

The earlier catalysts were synthesized without support. For more strength and to reduce leaching of the catalysts in to the liquid products, the following catalysts: bulk calcium oxide, super base calcium oxide, bulk magnesium oxide, calcium oxide/ magnesium oxide and impregnated calcium oxide/magnesium oxide with 10% potassium were synthesized with alumina supports as follows:

3.7.2.1 Synthesis of alumina supported bulk calcium oxide catalyst

Hydrated lime of mass 20 g was dissolved in distilled water; the mixture was stirred and 80 g of alumina was added to it and stirred. This mixture was evaporated over a magnetic stirrer and calcined in a muffle furnace at 900⁰C for 90 minutes.

3.7.2.2 Synthesis of alumina supported super base calcium oxide catalyst

Super base calcium oxide catalyst was prepared by dissolving 20 g of the non-supported catalyst earlier prepared into distilled water, stirred and 80 g of alumina was added to the mixture and stirred. The mixture was evaporated over a magnetic stirrer. This was later calcined at 850⁰C for 90 minutes in a muffle furnace.

3.7.2.3 Synthesis of bulk magnesium oxide catalyst

Magnesium oxide catalyst was prepared by dissolving 20 g of magnesium oxide in distilled water, stirred and 80 g of alumina was added and stirred. The mixture was heated on magnetic stirrer until the water evaporated. The dry residue was calcined in a muffle furnace at 760⁰C for 30 minutes.

3.7.2.4 Synthesis of calcium oxide/magnesium oxide catalyst

10 g of each of calcium oxide and magnesium oxide were dissolved in distilled water contained in a 500 ml beaker to incipient wetness (Jimenez *et al.*, 2005). The slurry thus formed was dried in an oven at 110⁰C to constant weight. The dried sample was dissolved in distilled water in 500 ml beaker, stirred and 80 g of alumina was added and stirred. The beaker with its content placed on a magnetic stirrer and heated until the water evaporated. The residue was transferred into a crucible and calcined at 760⁰C for 30 minutes (Jimenez *et al.*, 2005).

3.7.2.5 Synthesis of calcium oxide/magnesium oxide impregnated on 10%K

20 g mass of each CaO and MgO were mixed and dissolved in distilled water contained in a 500 ml beaker to incipient wetness (Jimenez *et al.*, 2005). The slurry thus formed was dried in oven at 110⁰C to constant weight. The dried mixture was dissolved in a 10% solution of potassium nitrate (KNO₃) in 500 ml beaker and stirred for 30 minutes. It was followed by addition of 160 g of alumina and stirred. The beaker and its content was placed on magnetic stirrer and heated until the water evaporated. The residue was transferred into a crucible and calcined in a muffle furnace at 760⁰C for 30 minutes (Jiménez *et al.*, 2005).

3.7.3 Catalytic Activity of the Unsupported Catalysts

The catalysts prepared were tested to determine their catalytic activities by using them to produce biodiesel. Four of the synthesized catalysts were tested on bench scale batch transesterification on *Jatropha curcas* seed oil and methanol.

3.7.3.1 Pretreatment of oil

Jatropha curcas oil is one of vegetable oils with high free fatty acid content that cannot be transesterified without pretreatment in order to have good yield alkyl esters. 1 g of *Jatropha curcas* oil was dissolved in 25 ml of propan-2-ol. Three drops of phenolphthalein indicator was added to the mixture and it was titrated against 0.1 M KOH to pink colour. The titre value was recorded and this procedure was repeated for two more times. The average value was calculated. A blank titration was performed by titrating 25 ml propan-2-ol without oil against 0.1 M KOH solution to pink. The difference between the oil titre value and blank titre value was calculated as V. The free fatty acid %FFA value was calculated as thus Equation (3.5):

$$\%FFA = \frac{(V - b) \times 0.1 \times 28.2}{w} \quad (3.5)$$

The FFA was calculated as Equation (3.6):

$$FFA = \%FFA \times 1.99 \quad (3.6)$$

The three readings obtained from the titration and blank titration were; 4.8, 4.7, 4.7 and 0.5 ml.

Therefore the titre value was;

$$V = \frac{4.8 + 4.7 + 4.7}{3} - 4.7 \text{ mL}$$

Hence, $V = 4.7 - 0.5 = 4.2$ ml

The FFA has thus;

$$\% FFA = \frac{4.2 \times 0.1 \times 28.2}{1g} = 11.78$$

Hence from Equation 3.6;

$$FFA = 11.78 \times 1.99 = 23.44$$

3.7.3.2 Esterification of the oil

The % FFA was too high for transesterification; hence it was esterified to reduce the acid value to below 1%. The oil was esterified by the following method: for 100 g of oil to be esterified 2.25g x %FFA of methanol and 0.05g x %FFA of concentrated sulphuric acid were required (Gerpen *et al.*, 2004). In this analysis 200 g of *Jatropha* oil was esterified with 53 g of methanol and 1.2 g of concentrated sulphuric acid. The oil was first preheated in a conical flask to 60°C before methanol/sulphuric acid mixture was added to it and then heated at 60°C and stirred by means of magnetic stirrer for 60 minutes. After the esterification the content was transferred into separating funnel where the ester was drawn off below leaving behind water and acid mixture. The separated ester was tested for free fatty Acid by titration method and was found to be 0.58% FFA. This value was acceptable for transesterification with base catalyst (Gerpen *et al.*, 2004).

3.7.4. Trial Transesterification with the Synthesized Catalysts

Four of the five synthesized catalysts were tested for their efficacy by using them to catalyze biodiesel production on bench scale batch process. These investigations were carried out by producing biodiesel using the catalysts varying temperature, and time. The products were analyzed by GC-MS to determine the methyl esters yield. The results of these investigations are presented in Chapter four.

3.7.4.1 Bulk calcium (non-supported) oxide catalyzed transesterification

Five sets of transesterification were carried out with bulk CaO as catalyst. 100 g of *Jatropha curcas* oil was preheated to 60°C and 1.5% CaO w/w of oil was added to 20 g of methanol making 5.5:1 methanol to oil molar ratio. The methanol/catalyst mixture was added to the hot oil at 60°C in a conical flask on the magnetic stirrer. The conical flask was covered with foil paper. The reactions were carried out at 60°C for 50 minutes. Four more reactions were carried out at the same temperature for 60, 70, 80 and 90 minutes. The compositions of alkyl esters were analyzed by GC-MS.

3.7.4.2 Calcium oxide/magnesium oxide catalyzed transesterification

100 g of the esterified oil was transesterified with 20 g of methanol (making a ratio of 5.5:1 methanol to oil) and 1.5 g (1.5% w/w of oil) of CaO/MgO catalyst for 50 minutes at 60°C. Four more transesterifications were carried out for 60, 70, 80 and 90 minutes. The products of these transesterifications were tested for extent of reaction and analyzed with GC-MS.

3.7.4.3 Super base calcium oxide catalyzed transesterification

Transesterification was carried out using super base calcium oxide without and with alumina support catalysts to compare their catalytic efficacy. Methanol (5.4 g) was mixed with 0.2 g of super base calcium oxide catalyst. This was used to transesterify 50 g of *Jatropha curcas* oil in a 250 ml conical flask making a mole ratio of 3:1 (methanol: oil) at 60°C for 60, 50, 40, 30 and 20 minutes on a magnetic stirrer. The catalyst was 0.4% percentage of oil (w/w). The same procedure was repeated for alumina supported catalyst.

3.7.4.4 Transesterification catalyzed by 10% potassium impregnated calciumoxide/magnesium oxide catalyst

0.4 g of this catalyst was used to produce biodiesel from 100 g of *Jatropha* oil and 10.8 g of methanol making 3:1 methanol to oil molar ratio. The transesterifications were carried out at 60°C for 60, 50, 40, 30 and 20 minutes in 250 ml conical flask covered with foil paper on a magnetic stirrer.

3.8 PLANT COMMISSIONING AND PRODUCTION

The plant commissioning was preceded by pre-commissioning which was operated to ensure that all constructions and installation activities (electrical and mechanical) have been carried out as designed.

3.8.1 Pilot Plant Operation Procedure

The following were the operating steps of the pilot plant from raw materials to the finished products:

1. Charging the raw materials
2. Transesterification
3. Separation of products

3.8.1.1 Charging raw materials

First, all the valves were checked to ensure they were closed and all the pipes were also connected appropriately. Raw materials namely *Jatrophacurcas* seed oil, methanol and catalyst were measured based on requirement and were charged into triolein tank (oil) and mixer

(mixture of methanol and catalyst). The mixer stirrer was switched on. The valves of the two tanks were opened and adjusted to the required flow rate; 80.6 ml/min and 10.6ml/min for oil and methanol/catalyst flows respectively. These flows were in accordance to molar ratio of 1:3 (oil to methanol)

3.8.1.2 Transesterification

Following the flows of the reactants into the reactor, the reactor stirrer was switched on. The heater was also switched on and set at 60⁰C to heat the reactor content. When the reactor temperature reached 60⁰C, it was maintained for 70 minutes and at this time the level of the liquid in the reactor had reached the maximum. After about 70 minutes, the pump was switched on to pump the products to the separating funnels via the sintered funnels. The catalysts were collected in the sintered funnels while the liquid product; biodiesel was collected in the separating funnels.

3.8.1.3 Separation of the products

When the first separating funnel was filled with the product, its valve was closed and the valve of the second opened. The first funnel was left for the two liquids glycerol and biodiesel to separate out under gravity. After several hours the liquid remained uniform no distinct layer partition was observed to indicate existence of two immiscible liquids.

3.8.2 Start Up and Short Down Procedure

The commissioning of the pilot plant was done following the procedure below.

3.8.2.1 Startup of the plant

The following were the steps for starting up the pilot plant:

- 1) All the components of the plant were ensured to be in good condition before proper connections were made.
- 2) All the valves were properly closed.
- 3) The hot water jacket was filled with water.
- 4) The triolein tank was filled with oil.
- 5) The mixer was filled with methanol/catalyst mixture.
- 6) The plant main power switch was on.
- 7) The mixer agitator was switched on.
- 8) The triolein tank valve and that of mixer were opened to the required flow rates.
- 9) The reactor agitator was switched on.
- 10) The heater was switched on and set to desired temperature.
- 11) And finally the pump was connected to the reactor and the separating funnels; this indicated the full operation has begun.

3.8.2.2 Shut down procedure

When the plant was required to be shut down, the following steps were followed:

- 1) The mixer stirrer was switched off.
- 2) The valves of triolein tank and mixer were closed.
- 3) The pump was left to continue pumping the products to the separator.
- 4) When the reactor content was empty, its agitator was switched off.
- 5) Then the pump was switched off.
- 6) The heater was switched off.

- 7) The plant main switch was closed
- 8) And finally the entire valves were closed.

3.8.3 Characterization of the Biodiesel Samples

The biodiesel and the glycerol obtained were characterized to determine their physicochemical properties in accordance with ASTM and EN standard.

3.8.3.1 Methyl esters content analysis with GC-MS

Biodiesel sample was diluted with n-hexane. 2 ml of the solution was collected into a sample bottle and injected into the GC-MS machine. The methyl esters content was calculated from area% of the GC-MS analysis. This analysis was performed on GCMS-QP2010 PLUS SHIMADZU/JAPAN in the Quality Control Unit of NARICT, Zaria.

3.8.3.2 Viscosity

Biodiesel sample was measured into 200 ml beaker and heated to 40°C. A spindle of a viscometer was adjusted until it submerged into the sample. The viscometer was switched on after spinning; reading was taking from the scale. This analysis was carried with Brookfield SYNCHRO ELECTRIC VISCOMETER in the Department of Chemical Engineering, Ahmadu Bello University, Zaria.

3.8.3.3 Density

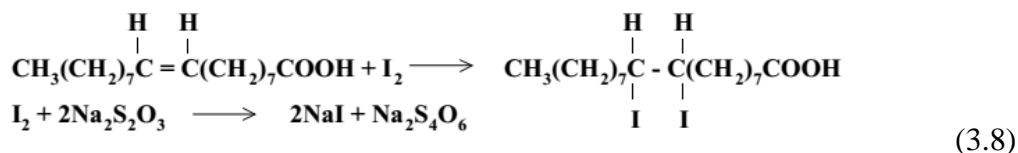
The densities of the biodiesel samples produced were measured with relative density bottle at 15 °C by cooling the biodiesel sample with ice block to 15⁰C before taking the measurement in accordance with ISO 3675.

3.8.3.4 Iodine value

Iodine value analysis was carried out in accordance to ASTM D1959-97 as presented by KEM Application Note (n.d a). 0.3g sample of biodiesel was measured into in a 250ml conical flask with stopper. 10ml cyclohexane was added, and dissolved then followed by 20 ml Wijs (0.1mol/L iodine monochloride acetic acid solution) reagent and stirred. The flask was plugged with stopper, and left for 30 minutes in a dark room at room temperature. Then, 20ml of 100g/l potassium iodide solution was added and 100ml pure water. The solution was titrated with 0.1mol/l sodium thiosulfate solution, to obtain iodine value. A blank level titration was performed beforehand by performing blank test likewise. This was done by titrating as above except without biodiesel sample. Iodine value was calculated from Equation (3.7).

$$\text{Iodine value (g/100g)} = \frac{(\text{BLI} - \text{EPI}) \times \text{TF} \times \text{CI}}{s} \quad (3.7)$$

where, BLI is blank titration (40.6), EPI is the titration volume, TF is factor of titration (1.003), CI is concentration conversion coefficient (1.269) and s is the sample weight (g). The Equation (3.8) expresses the reactions during the titration (KEM Application, puff)



3.8.3.5 Saponification value

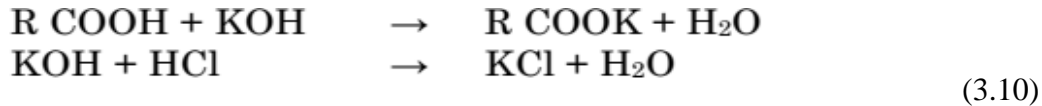
Saponification value analysis was carried out in accordance to ASTM D5558 as presented by KEM Application Note (b) (pdf). 2.0g biodiesel sample was delivered into a 250ml conical flask, 25.0ml of 0.5mol/l potassium hydroxide Ethanol was added, and a cooling pipe was fixed to the flask. The mixture was heated under reflux for 30 minutes to saponify the biodiesel sample. Two

drops of phenolphthalein were added to the saponified sample and was titrated against 0.5 N HCl.

A blank test was performed by titrating 25 ml of 0.5 KOH ethanol solution without biodiesel sample and also not heated under reflux against 0.5 N HCl with two drops of phenolphthalein indicator.

$$\text{saponification value} = \frac{\text{blank titre} - \text{sample titre}}{\text{mass of sample}} \times \text{normality} \times 56.1 \quad (3.9)$$

Saponification reaction equations is given by (KEM Application Note (n.d b) is expressed as Equation (3.10):



3.8.3.6 Cetane number analysis

The cetane numbers of the biodiesel samples were determined from the values of their saponification values and iodine numbers by calculation using Krisnagkura equation (Fadhilet al., 2012). The Krisnagkura equation is expressed in Equation (3.11)

$$CI = 46.3 + (5458 / SV) - (0.225 \times IN) \quad (3.11)$$

where, CI is cetane index, SV is saponification value and IN is iodine number.

The cetane number, CN is expressed as in Equation (3.12):

$$CN = CI \times 0.72 + 10 \quad (3.12)$$

where, CI is cetane index calculated from Equation (3.12)

3.8.3.7 Acid value

The volumetric standard sample, potassium hydroxide, the titration solvent and indicator solution were prepared as detailed in ASTM D974 (Mahajan *et al.*, 2006). Using a 10ml glass syringe, biodiesel samples were withdrawn from the sample containers, placed in 250ml conical flasks, and accurately weighed with analytical balance prior to analysis. Samples were then dissolved in 10 ml of the titration solvent (500 ml of toluene, 495 ml of isopropyl alcohol and 5 ml of water) (MacFarlane *et al.*, 2008) and then titrated with 0.02-N potassium hydroxide solution as per ASTM D664. The titration was deemed complete when a colour change from orange to green that held for at least 15s was observed in the titration mixture (Mahajan *et al.*, 2006).

The acid number was calculated as from Equation (3.13) (Mahajan *et al.*, 2006):

$$\text{Acid value} \left[\frac{\text{mgKOH}}{\text{g sample}} \right] = \frac{\text{volume KOH (ml)} \times \text{N KOH (mmol/ml)} \times 56.1\text{mg/mmol}}{\text{Sample weight g}} \quad (3.13)$$

3.8.3.8 Flash point

The flash points of the samples were determined in the temperature range 120-215⁰C by a digital Pensky-Martens closed-cup apparatus. The cup was filled with the sample fuel, inserted into the apparatus and closed in accordance with ASTM standard D93 (Babara and Todorut, 2011). This analysis was performed on Multiple Flash Point Tester Pensky-Martens STANHOPE-SETA 34100-2 in the Department of Chemical Engineering, Ahmadu Bello University, Zaria.

3.8.3.9 Energy content

The energy content of the samples were determined in a bomb calorimeter in accordance to ASTM 51900 standard. The bomb calorimeter was inserted into a metal tank that can be assumed to be adiabatic. The tank was filled with water brought to a suitable temperature. The fuel sample to be investigated was inserted into the bomb calorimeter, ignited by arcing, and combusted. The calorific value was read from the screen. This test was performed on Parr 6100 Calorimeter in the Department of Chemical Engineering, Ahmadu Bello University, Zaria.

3.8.3.10 Pour point

The sample tube was filled to the mark with the biodiesel fuel sample, corked with thermometer. The tubes were inserted into STANHOPE-SETA Cloud and Pour point tester. The samples were checked from time to time until they could no longer flow, this temperature was read and recorded as pour point. This test was carried out in the Quality control department of Kaduna Refinery and Petrochemical Company, Kaduna.

3.8.3.11 Dissolved group I&II metals

The biodiesel samples were analyzed for dissolved group I and II metals with AAS machine in accordance with EN 14108 EN 14109 and EN 14538 (Moser, 2009) in the Quality Control Unit of NARICT, Zaria.

3.8.3.12 Sulphur content

The sulphur content analyses of the samples were performed on Horiba (sulphur in oil analyzer SLFA-2800) in accordance with ASTM standard D5453 (Moser, 2009; Babara and Todorut,

2011) in the Quality Control Department of Kaduna Refining and Petrochemical Company, Kaduna.

3.8.4 Study of Optimum Quantity of Methanol for Biodiesel Production

Following the success of the simulation and design of this plant to produce biodiesel from the reactants (methanol and oil) at the stoichiometric quantity, an investigation was carried out to compare the yield of stoichiometric quantity and higher quantities of methanol. 50 g of *Jatropha curcas* seed oil was transesterified with 5.4 g of methanol (in the ratio of 3 moles of methanol to one mole of oil) and 0.2 g of calcium oxide catalyst at 60⁰C for 60 minutes. This production was carried in 250 ml conical flask covered with foil paper on magnetic stirrer. Using the same quantity of the same sample oil and also same method six more productions were carried out with 8.1 g, 10.8, 13.5 g, 16.2 g, 18.9 g and 21.6 g, of methanol. At the end of the reaction the products were filtered to remove the catalyst. The filtrates were analyzed with GC-MS to determine the conversions.

3.8.5 Biodiesel Production by Transesterification: Effect of Time and Temperature on Glycerol Yield

Following the complete conversion of feedstock to biodiesel without glycerol the co-product in three of the reactions carried out with pilot plant, optimization study was carried out to determine the best conditions to produce complete biodiesel without glycerol. *Jatropha curcas* oil of 50 g in 250 ml conical flask was heated on a magnetic stirrer to 60⁰C. 5.4 g of methanol was mixed with 0.2 g (0.4% w/w of oil) bulk calcium oxide catalyst. When the oil was at 60⁰C the methanol/catalyst mixture was then added to the oil making methanol to oil ratio 3:1 and covered

with foil paper. The transesterification was carried out at 65⁰C for 50, 60, 70, 80 and 90 minutes. The same procedure was repeated for 60⁰C, 55⁰C, 50⁰C and 45⁰C. The biodiesel samples produced were analyzed with GC-MS to determine biodiesel and glycerol compositions.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

This chapter presents the results and discussion of all the analyses carried out in this study.

4.1 CATALYSTS FOURIER TRANSFORM INFRA-RED (FTIR) SPECTRUM

ANALYSIS

All the catalysts had hydroxyl (-OH) functional group though not very strong indicating that they do not contribute to transesterification reaction which they catalyzed. The super base calcium

oxide catalyst had carbonyl (C=O) functional group in addition to hydroxyl group as shown in Table 4.1. Figure 4.1 shows FTIR spectra of the five catalysts.

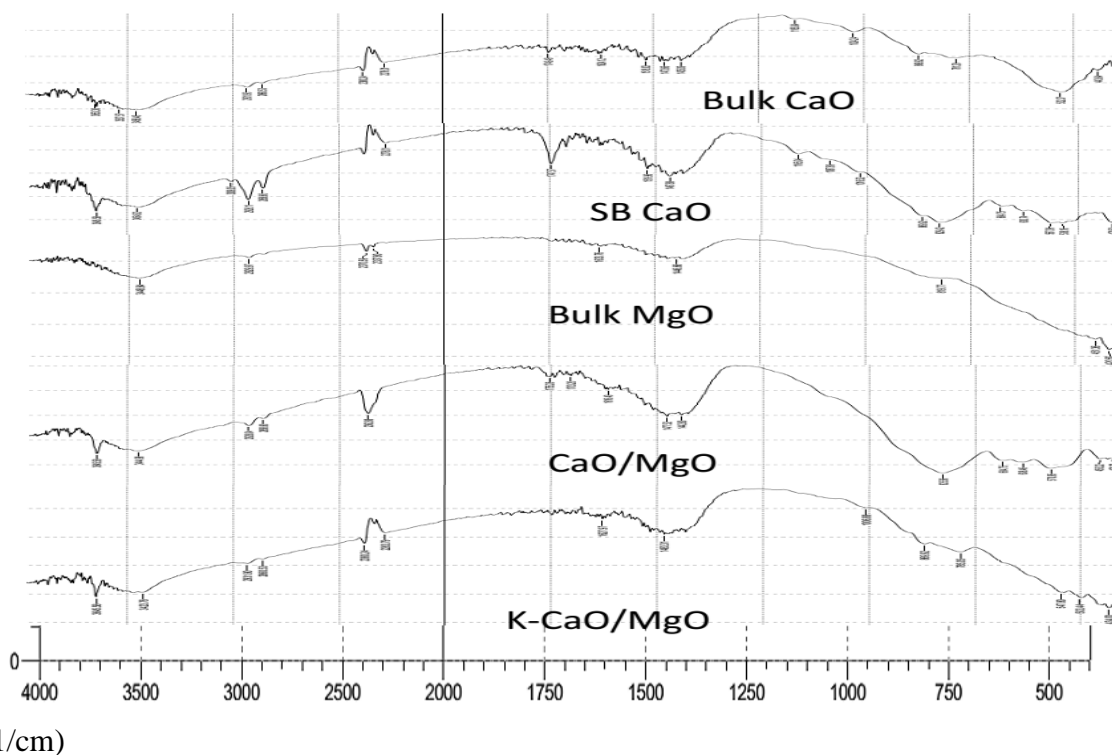


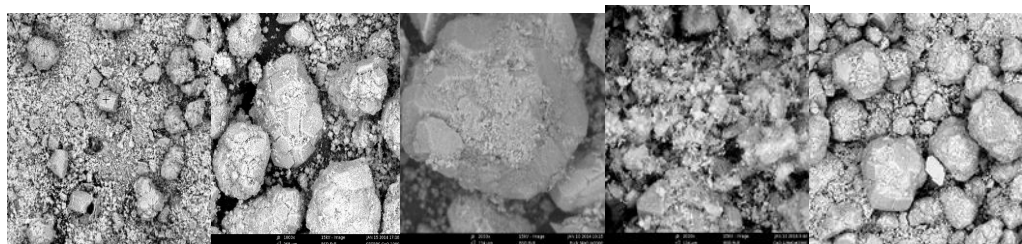
Figure 4.1: FTIR spectra of the five catalysts.

Table 4.1: Functional groups found in the prepared catalysts analyzed by FTIR

| Catalyst | Bulk CaO | Super Base CaO | Bulk MgO | CaO/MgO | K-CaO/MgO |
|---------------------------|----------|----------------|----------|---------|-----------|
| Functional groups present | -OH | -OH, C=O | -OH | -OH | -OH |
| Intensity | Broad | C=O, strong | Broad | Broad | Broad |

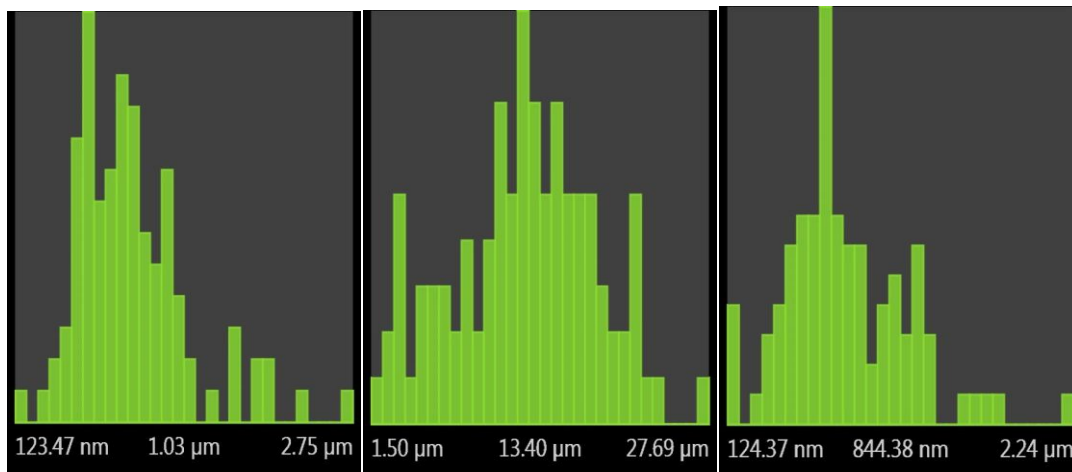
4.2 SCANNING ELECTRON MICROSCOPE AND BET ANALYSES OF THE SYNTHESIZED CATALYSTS

Scanning Electron Microscope photo images of the catalysts are shown in Plate 5.1. Plates 5.2 and 5.3 show the particle size histograms and pore areas distribution by scanning electron microscope catalysts. The particle sizes of three catalyst; namely, bulk calcium oxide, bulk magnesium oxide and CaO/MgO were in Nano size while that of super base CaO and 10% potassium impregnated CaO/MgO were larger as shown in Table 5.2. CaO/MgO had the highest BET specific surface area followed by bulk MgO with bulk CaO the least. The pore volumes of the catalysts followed the same trend. Compared to literature values, the catalysts possessed good catalytic properties. Bulk CaO catalyst synthesized in this study calcined at 900°C for 90 minutes had 23.68m²/g specific surface area which is higher than that synthesized by Wei *et al.* (2002)with specific surface area of 12.706 and 12. 166 m²/g calcined at 800°C for 2 hours and at 900°C for 1 hour respectively from CaCO₃.



a) CaO b) super base CaO c) MgO d) CaO/MgO e) 10K-CaO/MgO

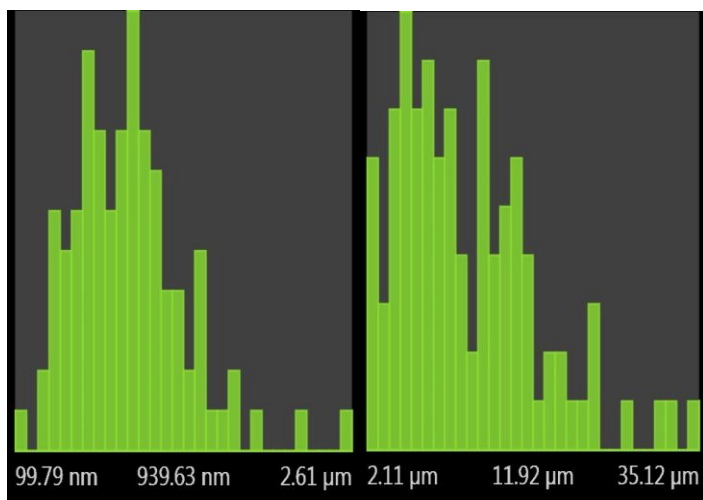
Plate 4.1: Particle structures of the synthesized catalysts’ analyzed by SEM



a) CaO

b) super base CaO

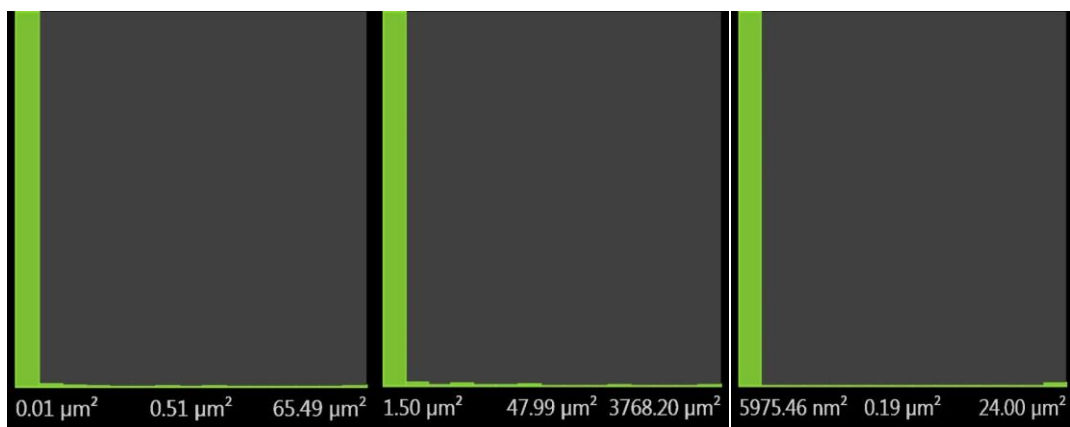
c) Bulk MgO



d) CaO/MgO

e) 10% K-CaO/MgO

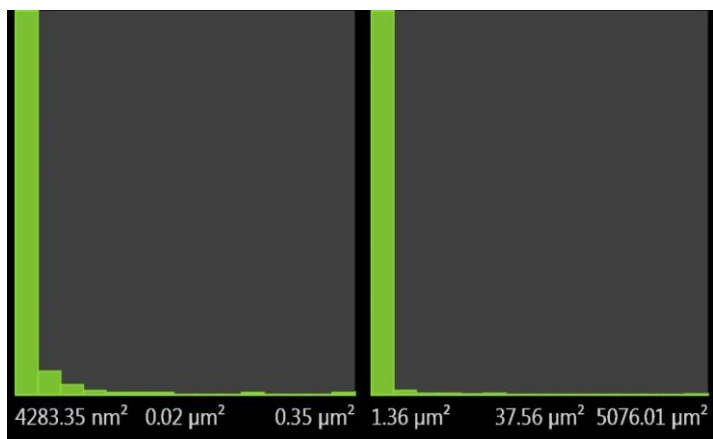
Plate 4.2: particle size distribution of the synthesized catalysts' analyzed by SEM



a) CaO

b) super base CaO

c) MgO



d) CaO/MgO

e) 10% K-CaO/MgO

Plate 4.3: Pore areas distribution of the synthesized catalysts analyzed by SEM

Table 4.2: Summary of the synthesized catalysts analyses by SEM and BET

| Catalyst/analyzed results | Bulk CaO | Super Base CaO | Bulk MgO | CaO/MgO | 10% K- CaO/MgO |
|--|-------------|-------------------|-------------|----------|-------------------|
| Average Grain size (μm) | 62.25 | 14.20 | 484.38 | 519.71 | 7.02 |
| Pore surface area ($\mu\text{m}^2/\text{g}$) | 0.0100 | 1.500 | 0.000598 | 0.000428 | 1.360 |

| | | | | | |
|--------------------------------------|----------|----------|----------|----------|----------|
| BET Surface Area (m ² /g) | 23.68 | 36.78 | 49.62 | 58.22 | 34.27 |
| BET Pore Volume (cm ³ /g) | 0.007835 | 0.012522 | 0.016216 | 0.020460 | 0.011632 |

4.3.1 Efficacy of Bulk Calcium oxide Catalyst

All the five biodiesel samples produced dissolved completely in the methanol. This confirmed that the transesterification reactions were complete. The results showed an increase in the yield of biodiesel from 50 minutes to 70 minutes but a decrease at 80 minutes and a rise again at 90 minutes; 94.76% at 50 minutes, 98.67% at 60 minutes, 100%, at 70 minutes, 89.92% at 80 minutes and 99.08% at 90 minutes indicates that the catalyst was good enough for biodiesel production from *Jatropha curcas* oil. It is interesting to note that only three methyl esters were common products to all the samples of biodiesel; Methyl hexadecanoate, Methyl 14-methylpentadecanoate and Methyl octadecanoate as shown in Appendix V-A1. This indicates that using the same feed stock, different methyl esters can be produced with different reaction times.

The products at 70 minutes and 90 minutes had no glycerol as shown in Figure 4.2. Complete conversion to biodiesel without glycerol co-product was obtained by 70 minutes reaction time. It was made possible to produce biodiesel without glycerol with this catalyst. This process reduced the time waste for separation of biodiesel and glycerol which normally takes a minimum of one hour. The yields increased from 94.76% to 100% from 50 to 70 minutes but fall to 89.6% for 80 minutes reaction and rose again to 99% for 90 minutes as shown in Figure 4.2. This fall would not have occurred if the heating source (the magnetic stirrer) had proper control. The glycerol

line remains almost flat on the horizontal line. The other impurities rose when the biodiesel fall. The detailed result is presented in Appendix VA1 and VA2.

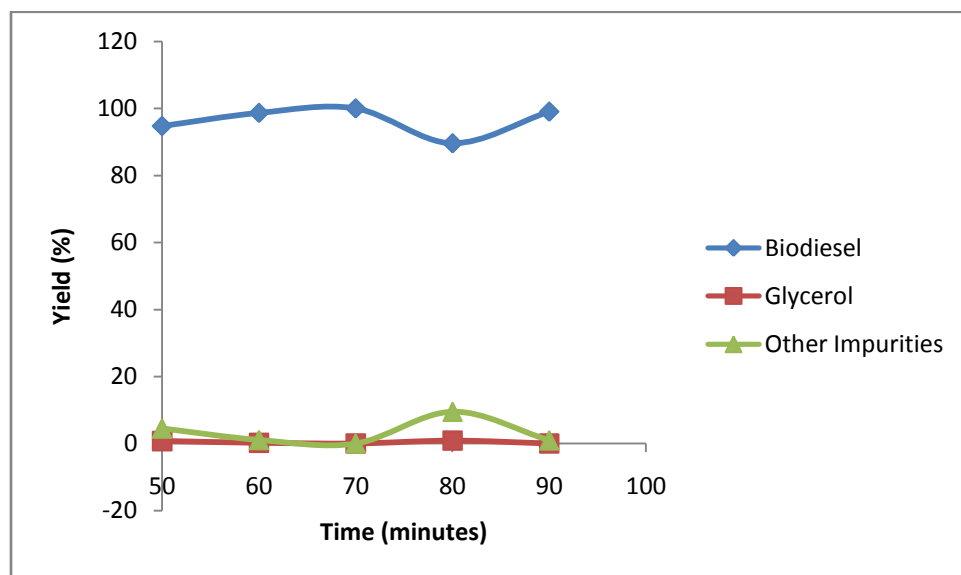


Figure 4.2: Efficiency of bulk CaO Catalyst for transesterification of *Jatropha* oil

4.3.2 Efficacy of Calcium oxide/Magnesium oxide Catalyst

Two samples have the highest yield; 98.995% and 100.00% as shown in Figure 5.3 were products of 60 and 90 minutes runs. These products had no ethyl esters as do others produced for 50, 70 and 80 minutes. Glycerol was not found in any of the products as shown in Figure 4.3. Also the other impurities or side products were very low. This indicated that this catalyst was good for biodiesel production without glycerol.

All the productions contained methyl 10-undecanoate except that of 90 minutes. The following methyl esters were found in all productions at average of 0.72% methyl palmitoleate, 12.4% methyl hexadecanoate 8.3% methyl-14-methylpentadecanoate, 8.83% methyl 9-octadecanoate,

2.21% methyl-16-methylpentadecanoate, and 17.84% methyl oleate. The following methyl esters were found only in 90 minutes production; methyl laurate, methyl tridecanoate and methyl myristate. The 50 minutes production had 12%, 70 minutes production had 13.88% and 80 minutes production had 0.9% ethyl esters respectively.

Earlier works showed longer production time and higher reaction temperature; three hours and at 100⁰C (Vazquez *et al.*, 2011) but less yield when compared to the results shown here where we had 99% yield for just 60 minutes and 100% for 90 minutes reaction times. With effective reaction conditions such as, temperature, time, stirring rate, active catalyst, refined feedstock and adequate methanol, complete conversion to biodiesel without glycerol and side products is possible as obtained here in 90 minutes production time. This has been achieved by Endalewet *al.* (2011) and Ilham and Saka (2013). The detail results are presented in Appendix VB1 and VB2. Endalewet *al.* (2011) got 100% biodiesel each by one step esterification and transesterification of *Jatropha curcas* oil and methanol 6:1 (methanol to oil molar ratio), catalyzed by 3% mixture of CaO and Fe₂(SO₄)₃, and Li-CaO and Fe₂(SO₄)₃, at 60⁰C, for 3 hours and 300 rpm. Ilham and Saka (2013) got 100% biodiesel by transesterification of rapeseed oil with dimethyl carbonate using super critical method.

The biodiesel yields remained almost flat around 100% and glycerol on zero line because its quantity was zero for all reaction times. Also other impurities were flat on zero line because its quantities were negligible as shown Figure 4.3.

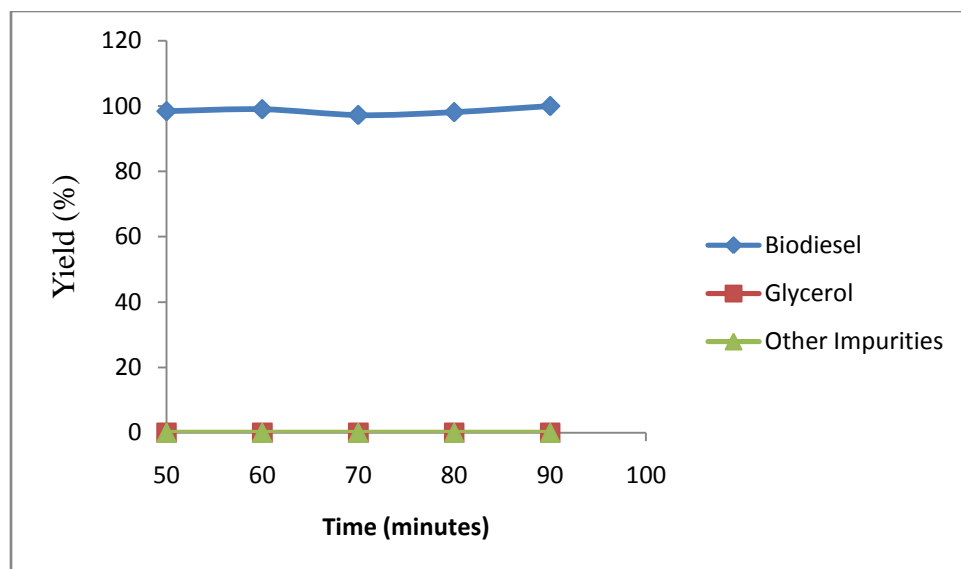


Figure 4.3: Efficiency of CaO/MgO Catalyst for transesterification of *Jatropha* oil

4.3.3 Efficacy of non-alumina support super base calcium oxide catalyst

The products of the transesterification catalyzed by super base calcium oxide, $\text{CaO}/(\text{NH}_4)_2\text{CO}_3$ without support had methyl esters below the EN standard for biodiesel 96.5%. This was due to high acid content of the feedstock. The acid content of the feedstock was 1.22. Transesterification catalyzed by a solid base catalyst would not yield very high methyl ester if the free fatty acid of the feedstock is up to 1 as confirmed from this study. The free fatty acids may appear in the product or converted to other side products as shown in Appendix VC1 and VC2.

However, fourteen methyl esters were found common to all the products as the same refined oil was used for the five runs. The common methyl esters were, Methyl decanoate, methyl tridecanoate, Methyl linoelaidate, Methyl 15-methylhexadecanoate, Methyl 14-methylpentadecanoate, Methyl hexadecanoate, methyl n octadecanoate, Methyl-5-

(undecyclopropyl) pentaanoate, Methyl eicosanoate, Methyl docosanoate, Methyl henicosanoate, Methyl heptacosanoate, Methyl-15-tetracosanoate and Methyl heptacosanoate. The highest yield obtained was 88.4% and no glycerol found in any of the products as shown in Figure 4.4 but the catalyst was not completely separated from the products. The products looked cloudy due to the inability to completely filter the solid catalyst. This problem was resolved by supporting the catalyst with alumina in the next production. The other impurities or side products were high due to low methyl ester yield. The detail results are presented in Appendix VC1 and VC2.

The biodiesel yield rose from 84 to 88% (20 to 40 minutes) and fell to 56.7% (50 minutes) and rose again to 80% (60 minutes). Likewise the other impurities fell from the time of 20 to 40 minutes and its value rose from 11.7% to 43.2% 50 minutes reaction time and finally fell to 19.5% for a reaction time of 60 minutes as shown Figure 4.4

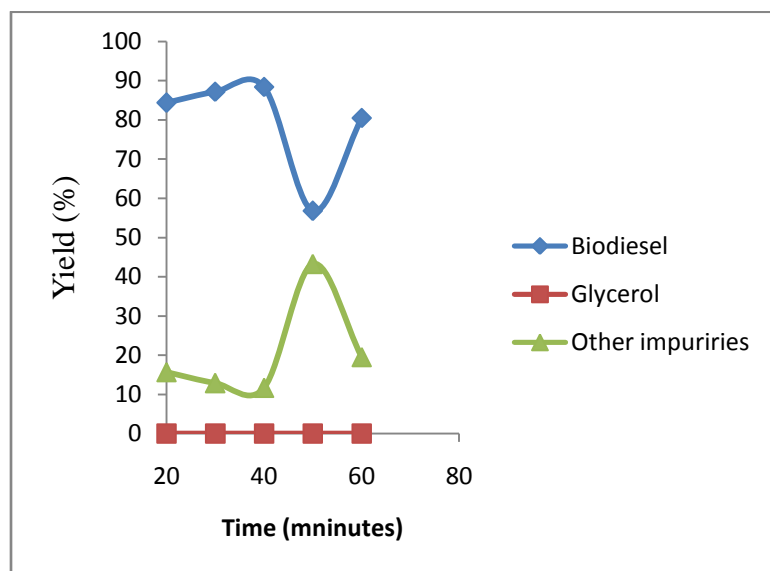


Figure 4.4: Efficiency of non-supported super base CaO Catalyst for transesterification of *Jatropha* oil

4.3.4 Efficacy of alumina supported super base calcium oxide catalyst

The results of transesterification with alumina supported super base calcium oxide catalyst are shown in Figure 4.5. Two out of the five runs met EN biodiesel standard of 96.5% methyl ester content (Hillionet *et al.*, 2003). This production had a lot of products common to all the runs; Methyl decanoate, Methyl tridecanoate, Methyl hexadecanoate, Methyl 14-methylpentadecanoate, Methyl 15-methylhexadecanoate, Methyl oleate, Methyl n-octadecanoate, Methyl-11 -octadecenoate, Methyl-15 -octadecenoate, Methyl-16 -octadecenoate, Methyl henicosoate, and Methyl hexacosanoate. The difference in methyl ester contents could be due to the malfunction of the magnetic stirrer used for the production. Its temperature and stirring rate could not be controlled only by switch on and off the heating which was not effectively done for all the productions.

These results showed that as low as 0.4% catalyst loading by mass of oil was enough for good biodiesel. These productions are a very cost effective for biodiesel processing in the sense that good biodiesel was produced at very small amount of methanol and catalyst for very short time of just 20 minutes. A previous work recorded 96% conversion for transesterification for 3 hours, at 70°C with mole ratio of 12:1 and 1.5% catalyst dosages (Hawash *et al.*, 2011). The productions of 20 and 50 minutes had no glycerol while the rest had very little as shown in Figure 4.5. This means that catalyst has the ability to select or suppress a product in the reaction. They all have small quantity of impurities except that of 50 minutes. After filtration the liquid products were very clear unlike the ones catalyzed by non-supported super base CaO. The detail

result is presented in Appendix VD1 and VD2. The biodiesel yield was almost flat if not for a fall from reaction times of 40 to 50 minutes as can be seen in Figure 4.5. Likewise the other impurities rose from 40 to 50 minutes and fell back to almost zero. The glycerol line remained at zero because its values were negligible.

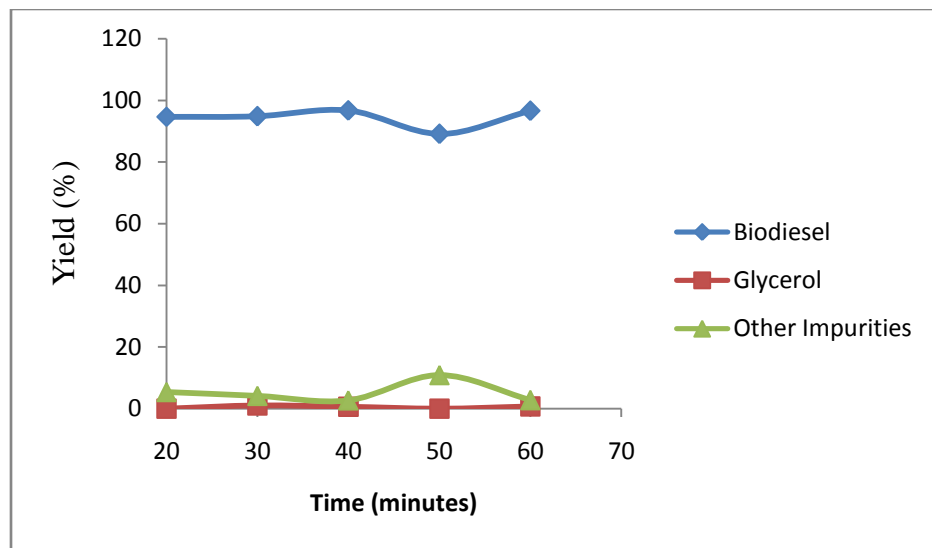


Figure 4.5: Efficiency of alumina supported super base CaO Catalyst for transesterification of *Jatropha* oil

4.3.5 Efficacy of 10% potassium impregnated CaO/MgO catalyst

The methyl esters yields of the productions catalyzed by 10% potassium impregnated calcium oxide/magnesium oxide were low compared to that catalyzed by bulk CaO, alumina supported super base CaO and CaO/MgO. This could be due to high FFA of the feedstock. Its feedstock had 1.22 FFA. All the products had zero glycerol. The highest methyl ester yield was that of 20 minutes run with 94% and approximately 5.9% other impurities. The other impurities increases with decrease methyl esters yield as shown in Figure 4.6.

The biodiesel yield fell from the reaction times of 20 to 40 minutes and then remains through to 60 minutes; likewise the other impurities rose from 20 to 40 and remained as shown in Figure 4.6. Again like that catalyzed by CaO/MgO the glycerol yield was zero throughout, hence its line lied horizontally on zero line. The detail result is shown in Appendix VE1 and VE2.

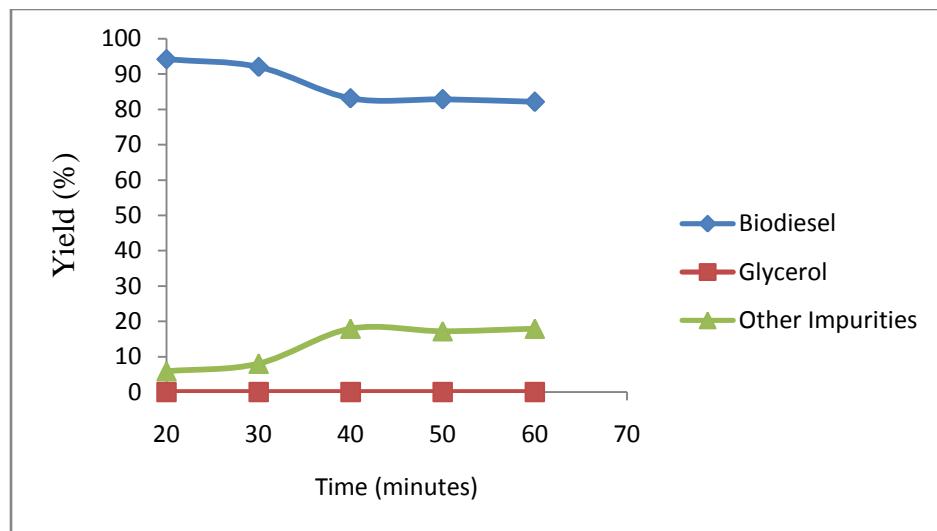


Figure 4.6: Efficiency of 10% K-CaO/MgO Catalyst for transesterification of *Jatropha* oil

4.3.6 Productions from the pilot plant

The table of reaction temperature profiles is shown Appendix VIA. The plant was designed for 98 minutes resident time but due to the capacity of the reactor the residence time was reduced to 70 minutes during production as the agitation of the reactor content by the impeller caused the overflow. Figure 4.7 shows the reaction profiles. The methyl esters yields were quite impressive. The one catalyzed by CaO/MgO had the highest methyl esters yield of 99.99% followed by that of 10%K-CaO/MgO 98.25% and the least was that catalyzed by bulk MgO catalyst which was 95.76%.

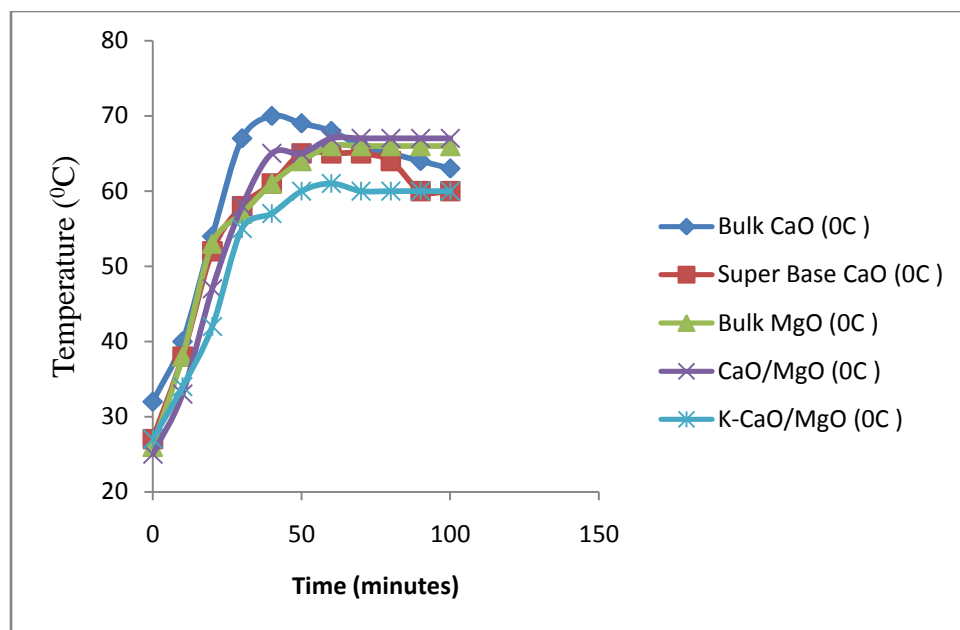


Figure 4.7: Reaction temperature profile of the heterogeneous catalytic transesterifications of *Jatropha curcas* oil

All the products met EN biodiesel methyl ester content 96.5% (Hillion *et al.*, 2003) except that catalyzed by bulk MgO. Three productions catalyzed by bulk MgO, CaO/MgO and 10%K-CaO/MgO had no glycerol except that catalyzed by bulk CaO and super base CaO which had 0.412% and 0.612% respectively. Figure 4.8 shows the products yields distribution of the five productions. The low yields of the first three productions were due to the high feedstocks acid content. Their acid contents were above 1. Transesterification with solid base catalysts produces lower yield with high free fatty acid feedstock than that of low free fatty acid as observed in this study. The acids either appeared in the products or converted into other compounds such as aldehydes, ketones etc. which constituted other impurities.

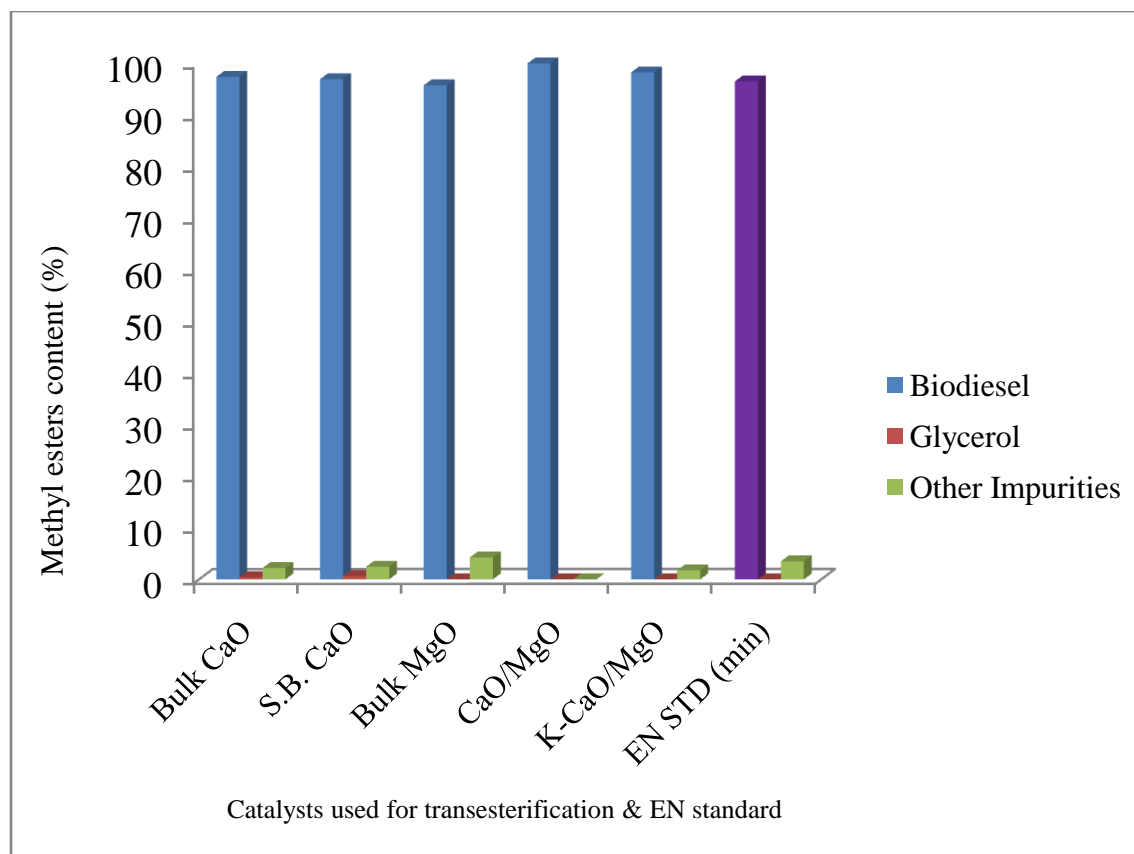


Figure 4.8: Pilot plant methyl esters content in the products compared to EN standard

The free fatty acid content of the feedstock catalyzed by CaO/MgO and 10%K-CaO/MgO were lower than 1 and consequently their biodiesel acid values were also lower. The results obtained from the pilot plant productions indicated that the five catalysts were good for transesterification of low free fatty acid feedstocks. The detail results are presented in Appendix VIB.

5.3.7 Iodine Number

The iodine numbers of all the products were quite low compared to international standard, 120 EN (Moser, 2009). The highest iodine value of the products was 69.58 from that catalyzed by bulk MgO and the lowest was 42 that catalyzed by 10% potassium impregnated CaO/MgO as

shown in Table 4.3. This meant that the fuel consisted of few unsaturated methyl esters. Figure 4.9 shows the comparison of sample fuels iodine numbers with the standard.

Table 4.3: Analysis of Iodine Value of the pilot plant biodiesel product

| Parameter | CaO | SB CaO | MgO | CaO/MgO | K-CaO/MgO |
|--------------------|-------|--------|-------|---------|-----------|
| Titre (ml) | 0.70 | 0.70 | 0.80 | 0.60 | 0.50 |
| Mass of sample (g) | 0.40 | 0.40 | 0.40 | 0.30 | 0.50 |
| Iodine value | 51.87 | 51.87 | 69.73 | 69.58 | 42.00 |

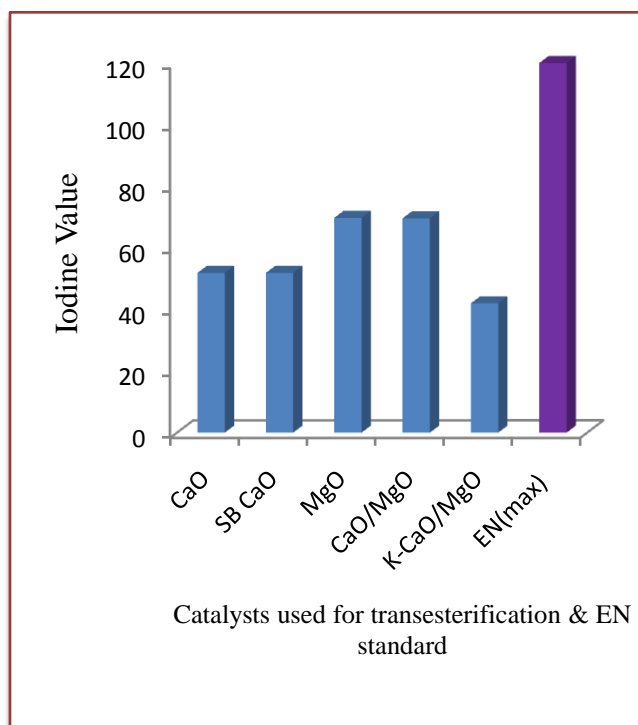


Figure 4.9: Iodine value of the biodiesel samples compared with and EN standard

4.3.8 Saponification value analysis

The saponification values of the sample products are presented in Table 4.4. That catalyzed by bulk MgO had the highest value of 239.8 and least was that catalyzed by super base CaO which was 196.4.

Table 4.4: Saponification analysis of the pilot plant biodiesel products

| Parameter | CaO | SB CaO | MgO | CaO/MgO | K-CaO/MgO |
|--------------------|------------|---------------|------------|----------------|------------------|
| Titre (ml) | 21.50 | 22.80 | 19.70 | 19.80 | 21.40 |
| Mass of sample (g) | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Saponification | 214.58 | 196.35 | 239.83 | 238.43 | 215.99 |

4.3.9 Products cetane value

The cetane numbers (values) of the pilot plant products are shown in Table 4.5. The cetane numbers were calculated from their saponification values and iodine numbers using Krisnagkura equation (Fadhil *et al.*, 2012). The product from the catalysis of bulk MgO had the least cetane number of 48.4 and that of super base CaO the highest 54.9. All the products had cetane number higher than U.S. standard 47 (Barabás and Todoruț, 2011) but the ones catalyzed by Bulk MgO and CaO/MgO had lower cetane number than EN standards 51 (Moser, 2009) as shown in Figure 4.10.

Table 4.5: Cetane number analysis of the pilot plant biodiesel products

| Sample | SV | IN | C | 5458/SV | 0.225*IN | CI | CN |
|-----------|----------|-------|------|----------|----------|----------|-------|
| CaO | 214.583 | 51.87 | 46.3 | 25.43538 | 11.67075 | 60.06463 | 53.25 |
| SBC | 196.35 | 51.87 | 46.3 | 27.7973 | 11.67075 | 62.42655 | 54.95 |
| MgO | 239.8275 | 69.73 | 46.3 | 22.75802 | 15.68925 | 53.36877 | 48.43 |
| CaO/MgO | 238.425 | 69.58 | 46.3 | 22.89189 | 15.6555 | 53.53639 | 48.55 |
| K-CaO/MgO | 215.985 | 42.00 | 46.3 | 25.27027 | 9.45 | 62.12027 | 54.73 |

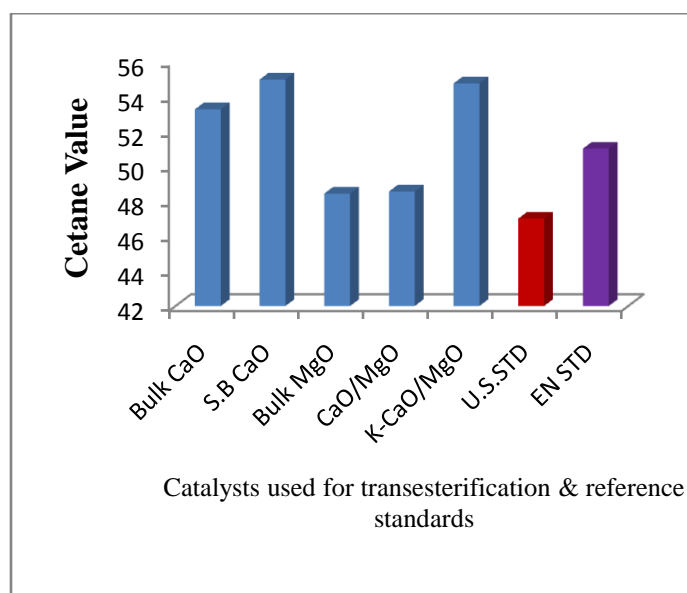


Figure 4.10: Comparison of cetane value of the pilot plant products with ASTM & EN standards

4.3.10 Acid value

The acid values of the biodiesel samples produced from the pilot plant are presented in Table 4.6. They had acid value lower than minimum ASTM standard 0.8 (Barabas and Todurut, 2011). Those ones that their feedstock had FFA greater than 1 had acid value greater than EN standard 0.5 (Moser, 2009). The comparison of samples acid value with international standard is shown Figure 4.11.

Table 4.6: Acid Value Analysis

| Parameter | CaO | SB CaO | MgO | CaO/MgO | K-CaO/MgO |
|-----------------|------|--------|------|---------|-----------|
| Titre (ml) | 1.30 | 1.10 | 0.90 | 0.80 | 0.61 |
| Sample mass (g) | 2.40 | 2.30 | 1.80 | 2.10 | 1.90 |
| Acid value | 0.61 | 0.54 | 0.56 | 0.48 | 0.34 |

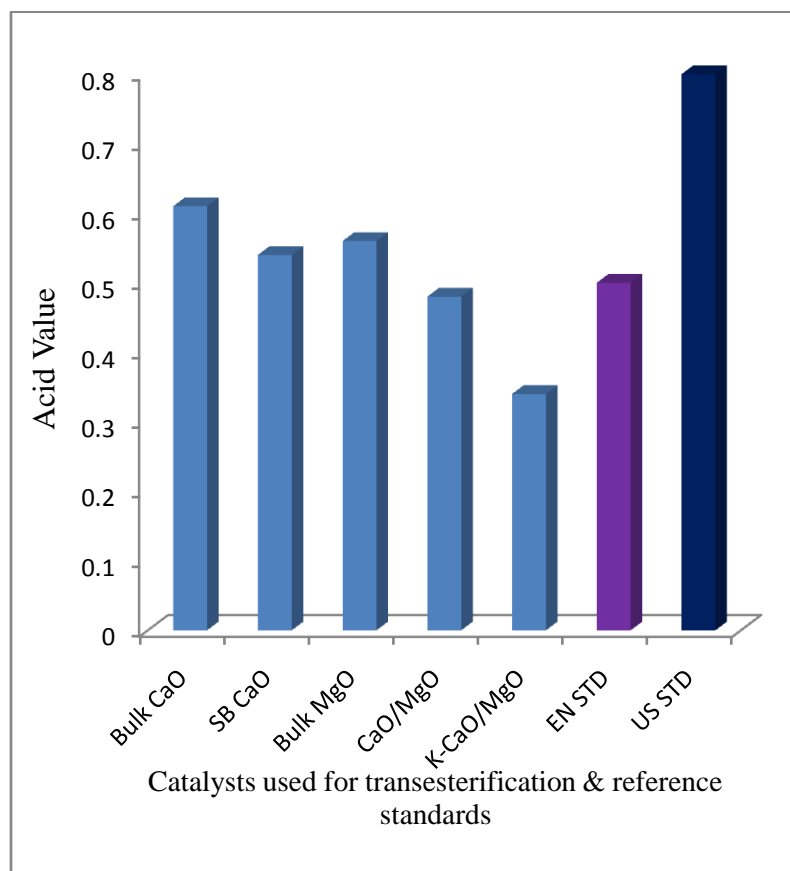


Figure 4.11: Comparison of pilot plant biodiesel acid values with standards

4.3.11 Comprehensive Properties of Biodiesel Samples Produced

Due to the limited analytical equipment, not all the properties of biodiesel were analyzed but the most important ones were carried out. These biodiesel characteristic properties are shown in

Table 4.7. Their viscosities fall within limit of U.S standard 1.9-6.0 mm²/s (Barabas and Todurut, 2011). The one that had the highest viscosity was that catalyzed by bulk CaO (6 mm²/s) and that catalyzed by bulk MgO was the least (3.5 mm²/s). Figure 4.12 shows the comparative viscosity of biodiesel samples and the international standards.

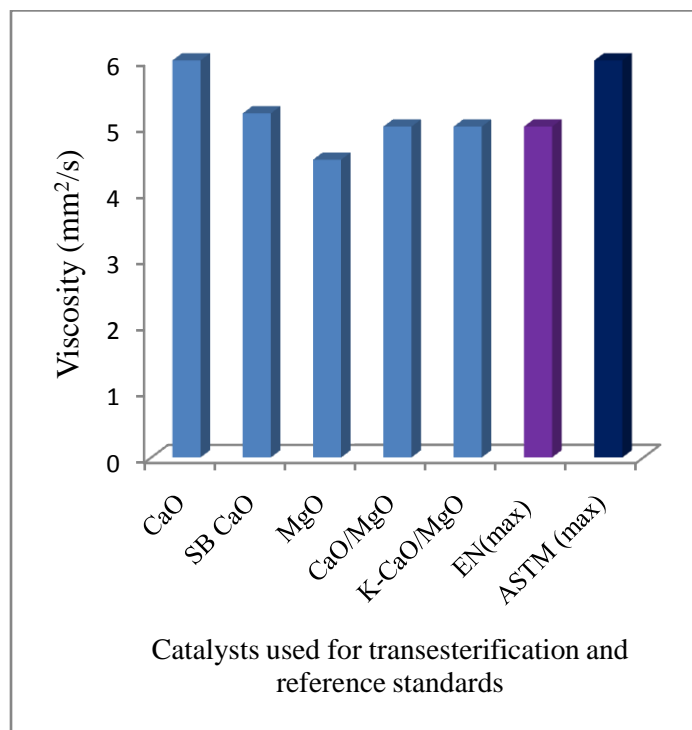


Figure 4.12: Comparison of viscosity of pilot plant biodiesel samples with standards

Two products had density slightly greater than U.S standard of 0.9 g/cm³ (Barabas and Todurut, 2011) upper limit. They were products from the catalysis of bulk MgO and CaO/MgO which were 0.913 and 0.905 respectively. Figure 4.13 shows the comparative density of the samples product with that of international standards.

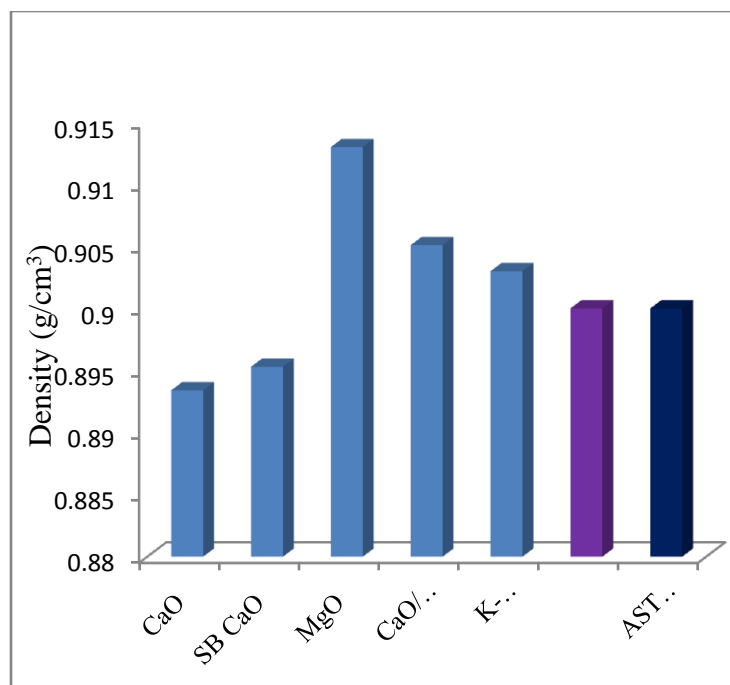


Figure 4.13: Comparison of pilot plant biodiesel density and International standards

They all had flash point values above the ASTM minimum standard for biodiesel of 130⁰C (Barabas and Todurut, 2011 and Moser, 2009) as shown in Figure 4.14. This indicated that the products were safe for storage, fuel handling and transportation as claimed by Barabas and Todurut, (2011).

All the products had very low dissolved metals of both group I and II elements as shown in Table 4.6. The highest was 1.559 mg/kg of group I metals found from that catalyzed by CaO/MgO which is lower than EN maximum allowable standard 5 mg/kg (Moser, 2009). They had energy content higher than International standard; EN of 37.5 MJ/kg (Flech *et al*, 2012). The one catalyzed by bulk MgO had the least energy content of 39.43 MJ/kg and that catalyzed by CaO/MgO had the highest value of 50.36 MJ/kg as shown in Table 4.7. The comparison of samples' energy content with international standards is presented in Figure 4.15.

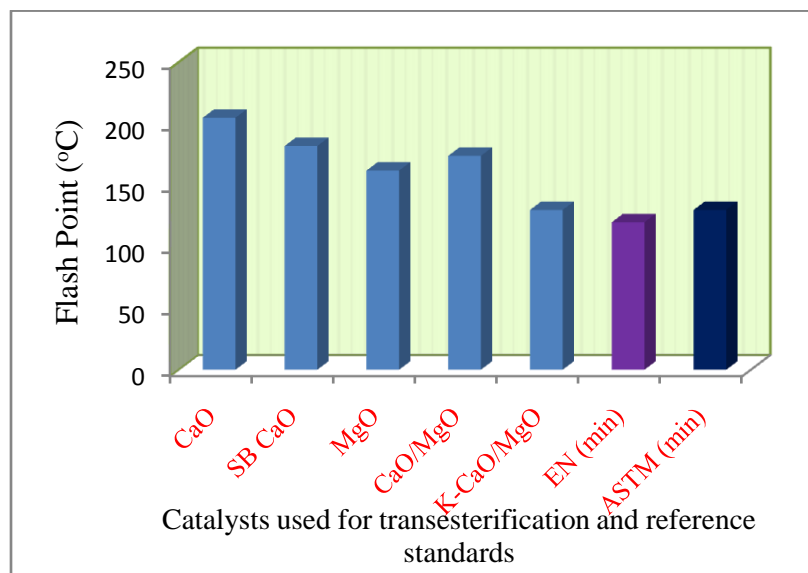


Figure 4.14: Flash points biodiesel pilot plant compared with the standards

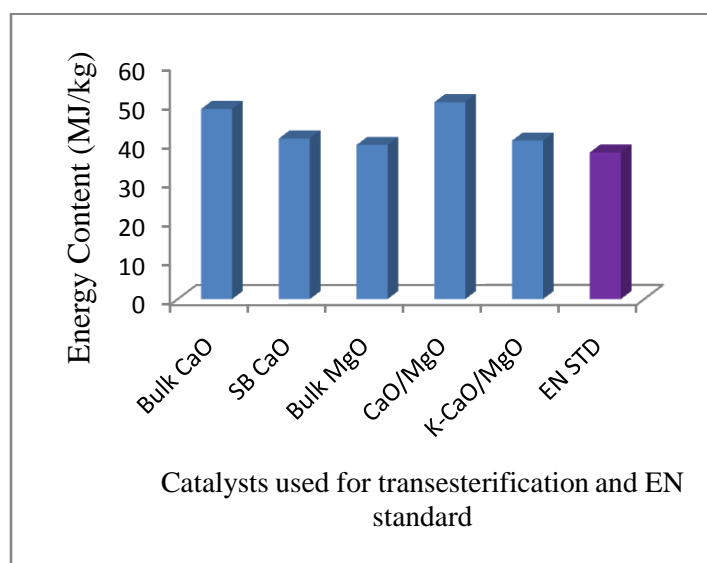


Figure 4.15: Comparison of pilot plant biodiesel energy content with the standard

The pour point values of the sample are presented in Table 4.7; were with the standard limit of ASTM or EN to compare with. The sulphur content were low in negative values indicating the values were negligible.

Table 4.7: Summary of the pilot plant biodiesel characterizations

| Parameters | Bulk | S B | Bulk | CaO | K-CaO | STD |
|--------------------------------|-------------|------------|-------------|-------------|--------------|----------------|
| | CaO | CaO | MgO | /MgO | /MgO | Max/min |
| Methyl ester content(%) | 97.40 | 96.94 | 95.76 | 99.99 | 98.25 | 96.5 |
| Density (g/cm ³) | 0.8934 | 0.8953 | 0.9130 | 0.9051 | 0.9030 | 0.9 |
| Viscosity (mm ² /s) | 6.0 | 5.2 | 4.5 | 5.0 | 5.0 | 0.6 |
| Saponification value | 214.58 | 196.35 | 139.83 | 238.43 | 215.99 | - |
| Iodine value | 51.87 | 51.87 | 69.73 | 69.58 | 42 | 120 |
| Cetane number | 53 | 55 | 48 | 49 | 54 | 47 |
| Flash point (°C) | 205 | 182 | 162 | 174 | 130 | 130 |
| Pour point (°C) | -13 | -11 | -12 | -13 | -15 | - |
| FFA (mgKOH/g) | 0.61 | 0.54 | 0.56 | 0.48 | 0.34 | 0.8 |
| Group I metals (mg/g) | 0.0672 | - | 0.2131 | 1.5590 | 1.5019 | 5 |
| Group II metals (mg/g) | 0.1559 | 0.7857 | 0.7137 | 0.5236 | 0.6485 | 5 |
| Sulphur content (-%) | 0.0069 | 0.0060 | 0.0062 | 0.0067 | 0.0065 | +0.0015 |
| Specific energy (MJ/kg) | 48.63 | 41.07 | 39.43 | 50.36 | 40.54 | 37.5 |

These results indicate that transesterification was more of an irreversible reaction. The reaction is supported by only forward reaction kinetics. Many researchers used higher mole ratio of

methanol to oil (6:1 and above) in order to achieve complete reaction but it has been established by the results in this investigation that it was not cost effective to use mole ratio higher than 3:1 (i.e. methanol to oil) provided the reaction temperature was not too high above methanol boiling point(65⁰C). If production of biodiesel using higher mole ratio was a condition of reversible reaction hence, transesterification was not a reversible reaction since it could be carried out at stoichiometric quantity. The reaction was first order (Urrejola *et al.*, 2012;Thananchayan *et al.*, 2013) with respect to triglyceride but going by the results of this investigation it was not reversible as claimed by Urrejola *et al.* (2012) and (Romero *et al.*, (2011).

4.4 Optimum Quantity of Methanol for Transesterification

When the methanol to oil ratio was 3:1, 93.3% yield was achieved (though from previous reactions 100% yield had been recorded) while the highest yield of 97.89% at 9:1 mole ratio as shown in figure 4.16. From the previous results and this very one, it could be deduced that it was not worthy of using methanol in excess of stoichiometric quantity for biodiesel production. Even at stoichiometric quantity, there was still excess methanol to be recovered due to earlier esterification of the oil before transesterification. This is because the triglycerides that were oxidized to acids after esterification were no longer available for transesterification anymore. The comparison of the yield of ratio 3:1 with those of higher ones is shown in Figure 4.16. The variation in the yields was due to the malfunctioning of the magnetic stirrer used in the production process.

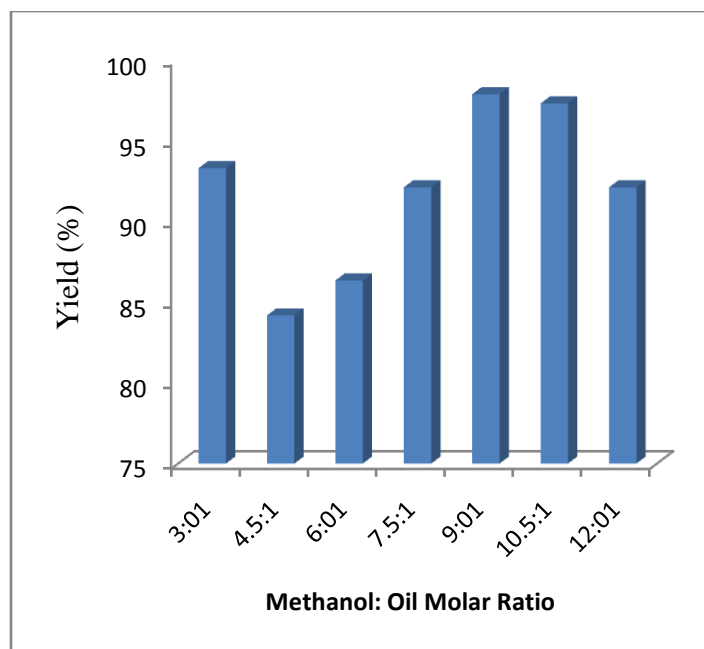


Figure 4.16: Optimum quantity of methanol for biodiesel production

4.5 Biodiesel Production by Transesterification: Effect of Time and Temperature on Glycerol Yield

All the productions at 65⁰C had glycerol and high other impurities as shown in Figure 4.17. All had low yield except the batch produced in 80 minutes. This was because, methanol boils at 65⁰C, and hence it was been lost as the reaction progresses. As there was no much methanol to react with the radicals that were created from the cleavage of triglycerides, these radicals re-arranged and form possible products as the conditions suit. At this temperature we required more methanol quantity than stoichiometric due to losses by evaporation.

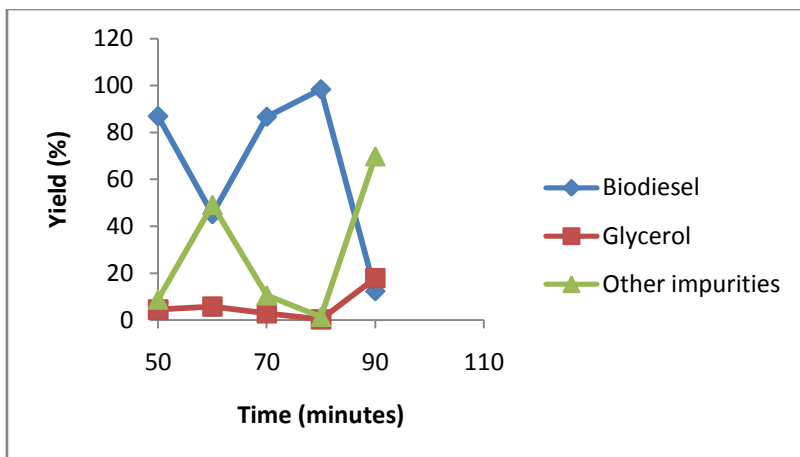


Figure 4.17: Products yield comparison at 65°C Transesterification

At 60°C there was no glycerol in all the products but the other impurities were high except that of 90 minutes that was completely converted to biodiesel as shown Figure 4.18. This temperature is close to methanol boiling temperature, any slight increase in temperature above 60°C causes loss of methanol. Using a heating source whose temperature and stirring rate can be controlled effectively, complete conversion of feedstock to biodiesel is possible without glycerol and other impurities. The detail results are presented in Appendix VIIB1 and VIIB2.

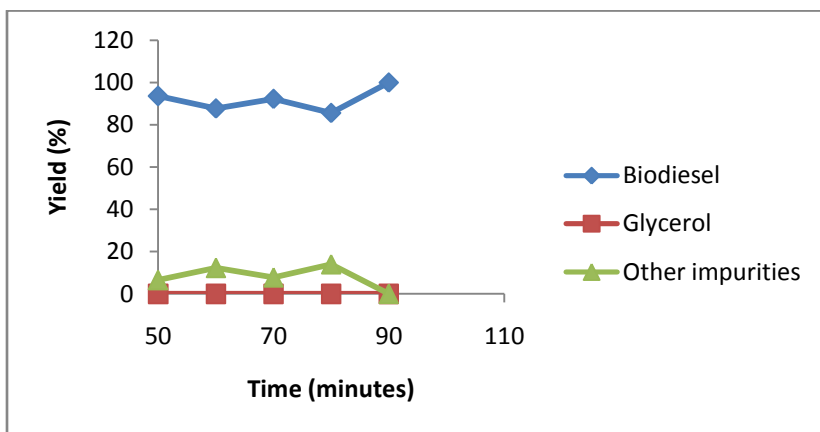


Figure 4.18: Products yield comparison at 60°C transesterification

So many things happened during transesterification depending on the reaction conditions such as temperature, time and stirring rates and also the quality of the feedstock causing the formation of many side products as obtained in Appendix VIIA2 and VIIB2.

At 55°C there was no glycerol except the production at 90 minutes run and the other impurities were lower than that of 60 minutes production as shown in Figure 4.19. Glycerol free biodiesel production could be possible at this temperature with bulk calcium oxide catalyst. The detail results are presented in Appendix VIIC1 and VIIC2.

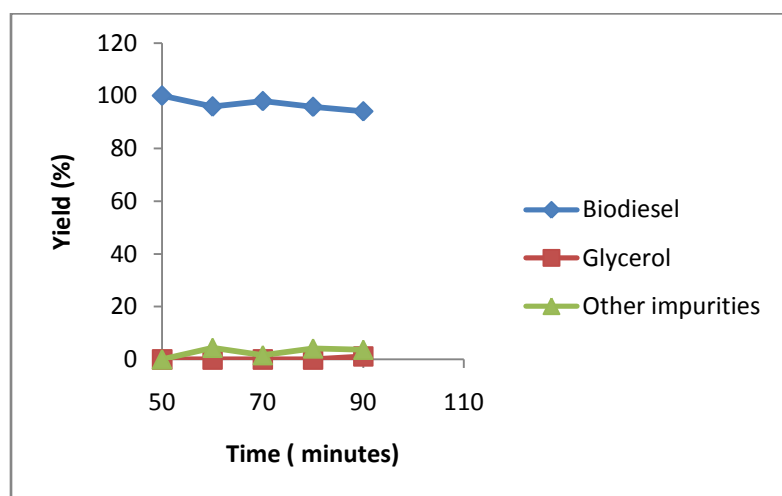


Figure 4.19: Products yield comparison at 55°C transesterification

At 50°C glycerol was found only in 50 minutes run, high biodiesel yield and low other impurities were achieved as shown Figure 4.20. The products at 50°C had lower molecular weight methyl esters; methyl 4-methylpentanoate ($C_7H_{14}O_2$), methyl 6-methylheptanoate ($C_9H_{18}O_2$), methyl 4-decenoate ($C_{11}H_{20}O_2$) and methyl decanoate ($C_{11}H_{22}O_2$). The detail results are presented in Appendix VIID1 and VIID2. Dioxygen formed in Appendix VIID2 could be from the reduction of fatty acid.

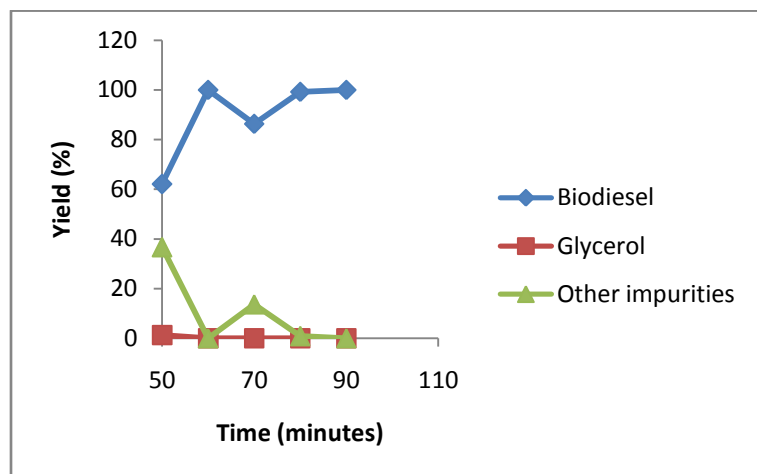


Figure 4.20: Products yield comparison at 50°C transesterification

Productions at 45°C were all glycerolfree as shown in Figure 4.21. The products at 45°C had also lower molecular weight methyl esters which include; methyl 4-methylpentanoate ($C_7H_{14}O_2$), methyl octanoate ($C_9H_{18}O_2$), methyl 3-ethylhexanoate ($C_9H_{18}O_2$), methyl 4-decenoate ($C_{11}H_{20}O_2$) and methyl tridecanoate ($C_{14}H_{28}O_2$). It shows that good biodiesel could be produced at low temperature; as low as 45°C. This saves energy and material cost. The detail results are presented in Appendix VIIE1 and VIIE2.

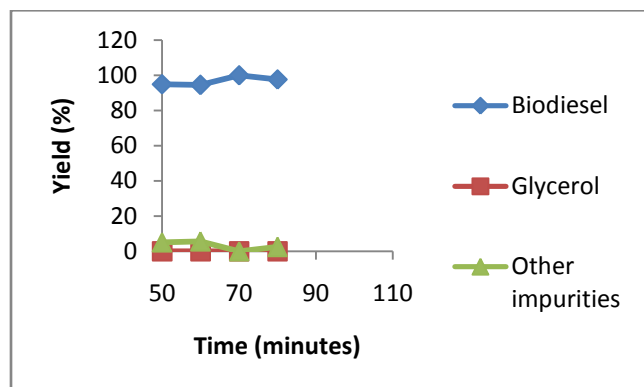


Figure 4.21: Products yield comparison at 45°C transesterification

The highest biodiesel average yields were 96.72% and 96.75% obtained at 45°C and 55°C respectively as shown Figure 4.22. At these temperatures the glycerol yields were approximately zero and 0.24%. Also the other impurities were lowest 2.29% and 3.79% respectively. Figure 4.22 also showed the fall in biodiesel yield with increase in temperature, rise in glycerol yield with increase in temperature. The rise in other impurities with increase in temperature was also observed.

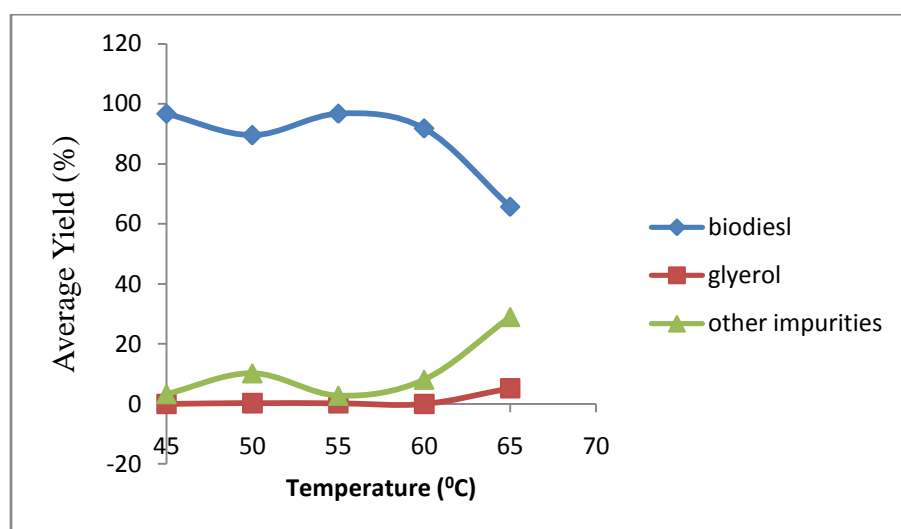


Figure 4.22: Comparison of the products average yields with temperature

The oxidation of triglycerides to fatty acids could also lead to formation of biodiesel without glycerol. If there was no oxidation at all at favourable conditions glycerol was formed as shown in route 1 Figure 4.23. This was achieved in Appendix VIIA2; Glycerol-1, 2-dipalmitate, Glycerin-1,3-dipalmitate, Glycerin-1-monoleate, glycerol 2-monoleate and Glycerol-1-monopalmitate Appendix VIIC2; Glycerol 2-monoleate and Appendix VIID2 with Glycerol-1-monopalmitate. If one of the triglycerides is oxidized, then glycol is formed as in route 2. This was achieved in Appendix VIID2; Diethyleneglycol. If two of the triglycerides were oxidized a mono-alcohol is formed as in route 3. This was achieved in Appendix VIIA2; 1,2-

Cyclododecanediol, 14-methyl-8-hexadecen-1-ol, cis-9-Octadecen-1-ol, 14-methyl-8-hexadecyn-1-ol, Humulane-1,6-dien-3-ol, 1,4-Methanoazulen-9-ol, decahydro-1,5,5,8a-tetramethyl, Lupan-3-ol, Methyl-3,13-octadecadienol, Appendix VIID2; Methoxyethanol, and n-1-Eicosanol and Appendix VIIE2; 3-Decen-1-ol. If all the triglycerides were oxidized no alcohol is formed as in route 4.

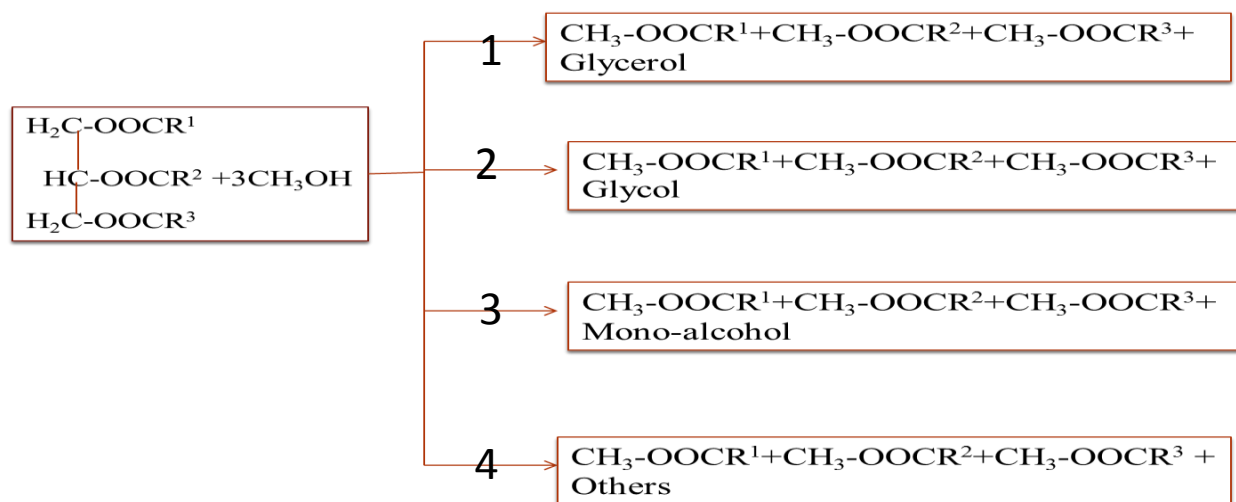


Figure 4.23: Transesterification reaction routes

Depending on the reaction temperature, time, stirring rate and quality of feedstock, many different products are formed with CaO catalyst at the expense of glycerol.

4.6 ECONOMIC EVALUATION OF BIODIESEL PROCESS INTENSIFY PILOT PLANT

Based on the cost of fabrication of the plant equipment and current local costs of raw materials and also banks interest charge in Nigeria, the financial estimate for capital and production costs and accrued revenue were obtained. It was assumed that the present raw material cost and interest rate remain unchanged throughout the life span of the plant. The exchange rate of naira to dollar as at the time of this analysis was N165/\$. The materials of construction were sourced

locally in Kaduna except the pump which was imported from China. The fabrication of the plant was done in Kaduna by Hanigha Nigeria Limited located at Kaduna South.

4.6.1 Fixed Capital Investment

The fixed capital cost of this investment amounted to 18.70% of total capital investment. The equipment cost amount to 40% of the fixed capital and the rest was for physical plant capital cost which includes piping, installation, instrument, land and building, which are direct costs. There were also indirect costs which were neither directly involved in the material and labour or installation nor in the complete facility. They included engineering and supervision cost, construction expenses, contractor fees and contingency fee.

4.6.2 Purchase Equipment Cost

The total purchase equipment cost (PEC) was estimated to be N400, 000 (\$2,424) based on the actual cost of materials of construction and fabrication of the pilot plant by Hanigha Nigeria limited. Purchase equipment cost is ranged 15-40% of total fixed capital cost (Peters and Timmerhaus, 1999). Taking purchase equipment cost to be 40% of total fixed cost, then the total fixed cost was found to be

$$TFC = \frac{400000}{0.4} = N1000\ 000 \quad \text{€6060.61}$$

4.6.3 Depreciation Cost

Assuming the salvage value is 10% the total fixed capital after the life period of the plant (10 years). Hence, the depreciation of this plant was N90 000 (\$545.45). The summary of the fixed capital cost is presented in Table 4.8.

4.6.4 Manufacturing Cost

This is the cost of processing and sales of products. This includes the cost of raw materials. This generally consists of the variable cost, fixed costs and general expenses. Variable cost consists of direct and indirect costs. Generally, variable cost may include costs of raw materials, utilities, miscellaneous materials, shipping and packaging. Fixed costs also include the cost of maintenance, operating labour, supervision, plant overheads, capital charges, Insurance rates and Royalties. General expenses are made up of administrative costs, engineering and legal costs, office maintenance and communications, distribution and selling cost.

Table 4.8: Summary of Fixed Capital Cost of the pilot plant

| Item | %TFC | Cost (N) | Cost (\$) |
|--|-------------|-----------------|------------------|
| Total Fixed Cost TFC | | 1000000 | 6060.61 |
| Purchase Equipment Cost | 40 | 400000 | 2424.24 |
| Instrumentation & Control Installation Cost (ICIC) | 5 | 50000 | 303.03 |
| Piping & Installation Cost (PIC) | 7 | 70000 | 424.24 |
| Electrical Installation Cost (EIC) | 5 | 50000 | 303.03 |
| Building Process & Auxiliary Cost (BPAC) | 5 | 50000 | 303.03 |
| Service Facility Cost (SFC) | 8 | 80000 | 484.85 |
| Yard Improvement Cost (YIC) | 3 | 30000 | 181.82 |
| Land Cost (LC) | 1 | 10000 | 60.61 |
| Total Direct Cost | | 740000 | 4484.85 |
| Indirect Cost | | | |
| Engineering & Supervision Cost (ESC) | 10 | 100000 | 606.06 |
| Construction Expenses | 6 | 60000 | 363.64 |
| Contractor Fee (CF) | 3 | 30000 | 181.82 |
| Contingency Fee (CgC) | 7 | 70000 | 424.24 |

Total Indirect Cost**260000****1575.76**

Assuming the plant is run for 250 days/yr taking the remaining days for maintenance and holidays and 12 hours per day. The plant was designed to consume 4.427kg/h (4.833 L/h) of *Jatropha* oil, 0.4806kg/h (0.604 L/h) of methanol and 0.07311kg/h of calcium oxide catalyst. Therefore, annual quantities of raw materials required were found to be 13 281 kg (14499 litres) of *Jatropha* oil, 1 441.8 kg (1 812 litres) of methanol and 219.33 kg of calcium oxide. A litre of methanol from Methanex Asian Posted Contract Price was US \$0.368 (N60.73). Annual cost of methanol was found to be N110 042.76. Actual market price of *Jatropha curcas* seed is not fixed in Nigeria but international price was N247.50/L (\$1.50/L) as claimed by Satish (accessed 2014). Therefore the annual cost of *Jatropha* oil was found to be N3 588 502.50.

4.6.5 Total Investment

This is the total cost of money invested into the business. It is the sum total of total fixed capital investment and the manufacturing cost. For this investment, the total investment cost was found to be N5 323 305.26 (\$32 395.79). Out of this total investment 18.79% was for total fixed capital investment while the remaining 81.21% was for production cost. The raw materials was 69.73% of the total investment cost and 85.85% of total production (or manufacturing) cost. As shown in Table 4.9, the leading cost in the production cost was *Jatropha curcas* seed oil. The investment will yield more profit and cash flow than what was obtained in Table 4.10 when the price of *Jatropha curcas* seed oil falls.

4.6.6 Income

The plant was simulated and designed to produce 3.85 litres/h of biodiesel and 1.28litres/h of glycerol making 11 550 litres per annul and 3 840 litres per annul respectively, but the actual production was 97.398% biodiesel out of the total 5.469 L/h. The glycerol was only 0.412% making a total of 0.023 L/h which can be neglected. Hence; the plant income depended only on the sales of biodiesel alone. Therefore, the annual production of biodiesel was found to be 15 980.09 litres. Let the selling price of biodiesel be fixed at N370/L (\$2.24/L). Based on the sales of biodiesel the income, profits, cash flow, returns on investment and payback period of the investment transaction were prepared in Table 4.10.

Table 4.9: Summary of manufacturing cost for the pilot plant

| Item | %TFC | Cost (N) | Cost (\$) |
|-------------------------------|-------------|-------------------|------------------|
| Fixed charges | | | |
| Depreciation cost | | 90000 | 678.79 |
| Insurance | 0.5 | 8000 | 48.48 |
| Rent | 10 | 160000 | 969.70 |
| Maintenance cost, (MC) | 1 | 16000 | 96.97 |
| Local taxes (LT) | 0.1 | 1600 | 9.70 |
| Operating Labour Cost (OLC) | 12 | 192000 | 1163.64 |
| Plant Overhead Cost (POC) | 9 | 144000 | 872.73 |
| Total Fixed charges | | 633600 | 3840 |
| Variable cost | | | |
| Jatropha oil | | 3588502.50 | 21748.50 |
| Methanol | | 110042.76 | 666.93 |
| Catalyst | | 13160 | 79.76 |
| Raw materials | | 3711705.26 | 22495.18 |
| Utilities | 12 | 192000 | 1163.64 |
| Operating Supplies Cost | 16%MC | 2560 | 15.52 |
| Salaries and wages | 40% OLC | 76800 | 465.45 |
| General & Administrative cost | 0.5 | 8000 | 48.48 |
| Cost of sales | 28.5POC | 41040 | 248.73 |

| | | | |
|---|---------|---------------------|------------------|
| Direct Supervisory and Electrical Labour Cost | 18% OLC | 34560 | 209.45 |
| Total Variable Cost | | 3711705.26 | 22495.18 |
| Total Manufacturing Cost | | 4,323,305.26 | 26,335.18 |

A total income of N5 912633.30 (\$35 834.14) was generated from the sales of biodiesel as the only product of the investment. For 30% income tax, the profit after tax was found to be N412 529.63 (\$2 500.18). The return on investment was found to 07.75%. The payback period was found to be 13 years as shown in Table 4.10. This is a pilot plant not a commercial venture; hence the analyses obtained here are in order. When it is required for a profit investment, it can be scaled up.

Table 4.10: Revenue Accrue for the pilot plant

| Item | N/year | \$/year | % | Years |
|-------------------------------|------------|----------|------|-------|
| Total Income | 5912633.30 | 35834.14 | | |
| Total Investment | 5323305.26 | 32262.46 | | |
| Profit Before Tax PBT | 589328.04 | 3571.69 | | |
| Income Tax (30%) | 176798.41 | 1071.51 | | |
| Profit After Tax (PAT) | 412529.63 | 2500.18 | | |
| Return On Investment (ROI) | | | 7.75 | |
| Internal Rate of Return (IRR) | | | | |
| Net present value (NPV) | 0 | | | |
| Payback period (PBP) | | | | 13.05 |

4.6.7 PAY BACK PERIOD

By using excel spread sheet cash flow table was prepared as in Table 4.11 hence the payback period was calculated from the Table 4.11. The payback period was calculated from Table 4.11 using equation 2.5 to be 13 years for this project. Thus the project will recoup its initial investment in 13 years after the start of the investment as shown in Figure 4.24. For this investment IRR was ignored since it was not for making profit. The net present value of this investment was also ignored for the same reason as internal rate of return.

Table 4.11: Cash Flow of Investment for the pilot plant

| Year | Income (N) | Investment (N) | Net Profit | Cash Flow (N) | Cumulated Cash Flow (N) |
|-------------|-------------------|-----------------------|-------------------|----------------------|--------------------------------|
| 0 | 0 | 5323305.26 | -5345305.26 | -5345305.26 | -5345305.26 |
| 1 | 5718826.84 | 5323305.26 | 395521.58 | 395521.58 | -4949783.68 |
| 2 | 6143735.68 | 5718826.84 | 424908.83 | 424908.83 | -4524874.85 |
| 3 | 6600215.24 | 6143735.68 | 456479.56 | 456479.56 | -4068395.28 |
| 4 | 7090611.23 | 6600215.24 | 490395.99 | 490395.99 | -3577999.29 |
| 5 | 7617443.64 | 7090611.23 | 526832.41 | 526832.41 | -3051166.88 |
| 6 | 8183419.71 | 7617443.64 | 565976.06 | 565976.06 | -2485190.82 |
| 7 | 8791447.79 | 8183419.71 | 608028.08 | 608028.08 | -1877162.73 |
| 8 | 9444652.36 | 8791447.79 | 653204.57 | 653204.57 | -1223958.16 |
| 9 | 10146390.03 | 9444652.34 | 701737.67 | 701737.67 | -522220.49 |
| 10 | 10900266.81 | 10146390.03 | 753876.78 | 753876.78 | 231656.29 |

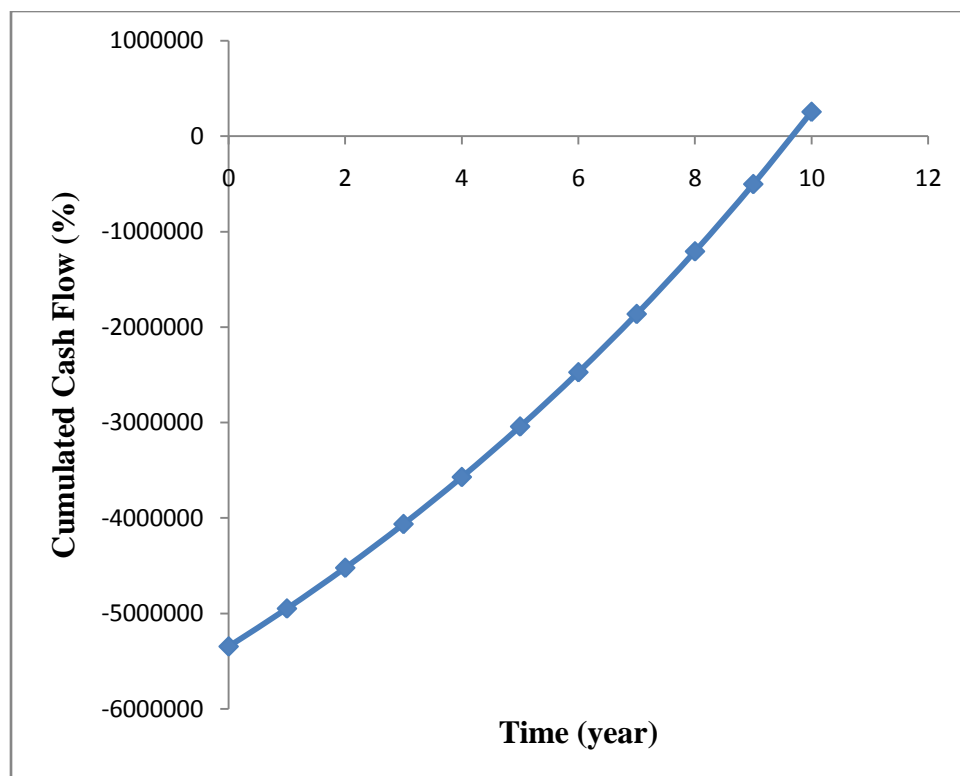


Figure 4.24: Graph of cumulated cash flow against period for the pilot plant

CHAPTER FIVE

5.0 SUMMARY, CONCLUSIONS, RECOMMENDATIONS AND CONTRIBUTIONS TO KNOWLEDGE

5.1 SUMMARY OF THE STUDY

An intensified pilot plant was successfully modeled, designed and constructed for the production of biodiesel from *Jatropha curcas* seed oil without the following equipment; neutralizer, washer, dryer, distillation columns, condenser and heat exchanger. This was aimed at studying process intensification on biodiesel production.

Five solid base catalysts namely; bulk calcium oxide (CaO), super base calcium oxide (CaO/(NH₄)₂CO₃), bulk magnesium oxide (MgO), calcium oxide/magnesium oxide/

(CaO/MgO) and 10% potassium impregnated calcium oxide/magnesium oxide (K-CaO/MgO) were synthesized and characterized.

The efficacies of the four out of five of the catalysts namely; bulk CaO, super base CaO, bulk MgO, CaO/MgO and 10% K-CaO/MgO were investigated for biodiesel production on batch bench scale.

The pilot plant was used to produce biodiesel with *Jatropha curcas* seed oil and methanol in the stoichiometric quantity using the synthesized catalysts. The biodiesel samples produced were analyzed.

Investigation into the optimization of methanol quantity for biodiesel production was carried out.

The effect of temperature and time on glycerol yield by transesterification was also investigated.

And finally, the financial feasibility of the pilot plant was evaluated.

5.2 CONCLUSIONS

The following conclusions may be drawn from this study:

1. Process intensify pilot plant was modeled, designed and constructed to produce 15, 980.09 L/annum of biodiesel from *Jatropha curcas* seed oil.
2. Four out of the five synthesized catalysts were tested for their efficacy on bench scale batch process namely; bulk calcium oxide, super base calcium oxide, calcium oxide/magnesium oxide

and 10% potassium impregnated calcium oxide/magnesium oxide and were found suitable for the catalysis of *Jatropha curcas* oil with methanol to produce biodiesel.

3. The pilot plant developed was used to produce biodiesel with the five synthesized catalysts from *Jatropha curcas* seed oil and methanol at stoichiometric quantity at 60⁰C and 70 minutes which resulted in 95.76 to 99.99% methyl esters content.
4. High quality and same quantity biodiesel was produced from this pilot plant despite the absence of the following units; neutralizer, washer, dryer, condenser, distillation columns and heat exchanger.
5. All the five catalysts were capable of producing about 100% biodiesel without glycerol and other impurities provided the feedstock was highly refined.
6. High yield biodiesel (96.58%) was produced at 60⁰C and 20 minutes reaction temperature and time with super base calcium oxide catalyst.
7. High yield biodiesel (100%) was also produced at 45⁰C and 60 minutes reaction temperature and time with bulk calcium oxide catalyst.
8. After refining of high acidic oil it will require less quantity of methanol than stoichiometric quantity for transesterification because after esterification much of the component of the triglycerides had been converted to methyl esters.
9. CaO/MgO and 10% impregnated CaO/MgO catalysts were capable of suppressing the formation of glycerol at low reaction temperature (below 65⁰C).
10. Biodiesel was produced with 0-0.612% glycerol the co-product from the pilot plant using the process adopted in this study.

11. This new process technology is capable of saving a minimum of 1585.98 MJ/annul of energy required to recover excess methanol from products as by using conventional technology that has the same capacity.
12. This new technology is capable of saving a minimum of N13 744.00 (\$83.30) per annum of equivalent convectional plant capacity for methanol recovery.
13. This study confirmed that transesterification using solid base catalysts did not support the reversibility of the reaction. The kinetic parameters used for this study were for first order irreversible reaction.
14. The return on investment ROI of the plant was 7.75%, very low resulting payback period of 13 years.

5.3 RECOMMENDATIONS

The following recommendations are made from this study;

1. This pilot plant was good for scale up to commercial biodiesel production for its smaller, cleaner, safer, cheaper and more energy efficiency biodiesel process.
2. For production of biodiesel from other vegetable oils and compare their yields with that of *Jatropha curcas* seed oil.
3. For biodiesel production with solid acid catalysts and compare the results with that of solid base catalysts that has been established here.
4. The project is recommended for commercial venture with the hope that as more farmers engage in *Jatropha* farming, raw materials cost will fall.
5. Government should subsidize the products for consumers to encourage them to buy the fuel.
6. Government should give the producers tax free to attract more producers into the business.

7. More investigation should be carried out on biodiesel production without glycerol using bulk MgO, CaO/MgO and 10% K-CaO/MgO catalysts.

5.4 CONTRIBUTION TO KNOWLEDGE

1. High quality biodiesel (99.99% methyl esters) was produced with continuous stirred tank reactor (CSTR) and solid base catalyst in stoichiometric quantity for the first time from a process intensified pilot plant.
2. Process intensify pilot plant was simulated, design, constructed and was used to produce biodiesel yielded of 99.99% methyl esters in stoichiometric quantity for the first time.

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APPENDICES

Appendix I: Detail Results of CSTR Aspen HYSYSYS Simulation

LEGENDS, Case Name: CONTINUOUS HETEROGENEOUS CATALYTIC
TRANSESTERIFICATION.HSC
Burlington, MA,
USA, Unit Set: SI
Date/Time: Wed Feb 05 10:57:05 2014

CSTR (Cont. Stirred Tank Reactor): Design, Reactions, Rating, Worksheet, Dynamics, Notes
Cont. Stirred Tank Reactor: CSTR,

CONNECTIONS

Inlet Stream Connections

| | |
|--------------|---------------------|
| Stream Name, | From Unit Operation |
| V1 Out, | V1 Valve |
| V2 Out, | V2 Valve |

Outlet Stream Connections

| | |
|--------------|-------------------|
| Stream Name, | To Unit Operation |
| R Vent, | |

Product, Pump: Pump

Energy Stream Connections

Stream Name, From Unit Operation

QR,

PARAMETERS

Physical Parameters, Optional Heat Transfer: Heating

| Delta P | Vessel Volume | Duty | Energy Stream |
|---------|---------------|------|---------------|
|---------|---------------|------|---------------|

| | | | |
|-------------|---------------|--------------|----|
| 0.0000 kPa, | 8.933e-003 m3 | -551.5 kJ/h, | QR |
|-------------|---------------|--------------|----|

User Variables

REACTION DETAILS

Reaction: Rxn-1

| Component, | Mole Weight, | Stoichiometric Coeff.* |
|----------------|--------------|------------------------|
| Triolein, | 885.4 | -1* |
| Methanol, | 32.04 | -3* |
| Calciumoxide*, | 56.08 | 0* |
| M-Oleate, | 296.5 | 3* |
| Glycerol, | 92.10 | 1 |

REACTION RESULTS FOR: Set-1

Extents

| | Act. % Conv. | Base Comp. | Rxn Extent (kgmole/h) |
|--------|--------------|------------|-----------------------|
| Rxn-1, | 99.98 | Triolein, | 4.999e-003 |

Balance

| Total Inflow | Total Rxn, (kgmole/h) | Total Outflow (kgmole/h) | (kgmole/h) |
|---------------|--------------------------|-----------------------------|------------|
| Triolein, | 5.000e-003 | -4.999e-003 | 9.743e-007 |
| Methanol, | 1.500e-002 | -1.500e-002 | 2.923e-006 |
| M-Oleate, | 9.738e-007 | 1.500e-002 | 1.500e-002 |
| Glycerol, | 3.246e-007 | 4.999e-003 | 4.999e-003 |
| Calciumoxide* | 1.297e-003 | 0.0000 | 1.297e-003 |

RATING

Sizing

| | | |
|----------------------------------|--------------------|------------------------|
| Cylinder | Vertical | Reactor has a Boot: No |
| Volume 8.933e-003 m ³ | Diameter 0.2200 m* | Height 0.2350* |

Nozzles

Base Elevation Relative to Ground Level 0.0000 m* Diameter 0.2200 m* Height 0.2350*

| | V1 Out | V2 Out | R Vent |
|-----------------------------|------------|------------|------------|
| Diameter (m) | 5.000e-002 | 5.000e-002 | 5.000e-002 |
| Elevation (Base) (m) | 0.1175 | 0.1175 | 0.2350 |
| Elevation (Ground) (m) | 0.1175 | 0.1175 | 0.2350 |
| Elevation (% of Height) (%) | 50.00 | 50.00 | 100.00 |

Product.

| | |
|-----------------------------|------------|
| Diameter (m) | 5.000e-002 |
| Elevation (Base) (m) | 0.0000 |
| Elevation (Ground) (m) | 0.0000 |
| Elevation (% of Height) (%) | 0.00 |

CONDITIONS

| Name | V1 Out | V2 Out | Product. | R Vent | QR |
|--|-------------|-------------|-------------|-------------|-------------|
| Vapour | 0.0000 | 0.0000 | 0.0000 | 1.0000 | |
| Temperature (C) | 25.0000 | 30.2317 | 60.0000* | 60.0000 | |
| Pressure (kPa) | 101.3200* | 101.3200* | 101.3200 | 101.3200 | |
| Molar Flow (kgmole/h) | 0.0050 | 0.0163 | 0.0213 | 0.0000 | |
| Mass Flow (kg/h) | 4.4272 | 0.5537 | 4.9810 | 0.0000 | |
| Std Ideal Liq Vol Flow (m ³ /h) | 0.0048 | 0.0006 | 0.0055 | 0.0000 | |
| Molar Enthalpy (kJ/kgmole) , | -1.965e+006 | -2.198e+005 | -6.554e+005 | -2.177e+005 | |
| Molar Entropy (kJ/kgmole-C) | 478.7 | 153.5 | 323.4 | 186.8 | |
| Heat Flow (kJ/h) | -9.8264e+03 | -3.5818e+03 | -1.3960e+04 | 0.0000e-01 | -5.5154e+02 |

PROPERTIES

| Name | V1 Out | V2 Out | Product. | R Vent |
|--|-------------|------------|------------|------------|
| Molecular Weight | 885.4 | 33.97 | 233.9 | 35.47 |
| Molar Density (kgmole/m ³) | 1.774 | 25.19 | 3.758 | 3.658e-002 |
| Mass Density (kg/m ³) | 1571 | 855.7 | 878.8 | 1.298 |
| Act. Volume Flow (m ³ /h) | 2.819e-003 | 6.470e-004 | 5.668e-003 | 0.0000 |
| Mass Enthalpy (kJ/kg) | -2220 | -6469 | -2803 | -6138 |
| Mass Entropy (kJ/kg-C) | 0.5406 | 4.519 | 1.383 | 5.265 |
| Heat Capacity (kJ/kgmole-C) | 115.8 | 125.5 | 499.5 | 51.36 |
| Mass Heat Capacity (kJ/kg-C) | 0.1307 | 3.693 | 2.136 | 1.448 |
| Lower Heating Value (kJ/kgmole) | 1.417e+008 | | 7.060e+005 | |
| Mass Lower Heating Value (kJ/kg) | 1.600e+005 | | 1.990e+004 | |
| Phase Fraction [Vol. Basis] | | | | |
| Phase Fraction [Mass Basis] | 2.122e-314, | 2.122e-314 | 2.122e-314 | 122e-314 |
| Partial Pressure of CO2 (kPa) | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

| | | | | |
|--|------------|------------|------------|------------|
| Cost Based on Flow (Cost/s) | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Act. Gas Flow (ACT_m3/h) | 0.0000 | | | |
| Avg. Liq. Density (kgmole/m ³) | 1.034 | 25.65 | 3.895 | |
| Specific Heat (kJ/kgmole-C) | 115.8 | 125.5 | 499.5 | 51.36 |
| Std. Gas Flow (STD_m ³ /h) | 0.1182 | 0.3854 | 0.5036 | 0.0000 |
| Std. Ideal Liq. Mass Density (kg/m ³) | 916.0 | 871.5 | 910.9 | 832.8 |
| Act. Liq. Flow (m ³ /s) | 7.829e-007 | 1.711e-007 | 1.566e-006 | 0.0000 |
| Z Factor | 2.304e-002 | | | |
| Watson K | | | | |
| User Property | | | | |
| Partial Pressure of H2S (kPa) | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Cp/(Cp - R) | 1.077 | 1.071 | 1.017 | 1.193 |
| Cp/Cv | 1.077 | 1.071 | 1.017 | 1.193 |
| Heat of Vap. (kJ/kgmole) | 5.252e+004 | | 4.517e+004 | |
| Kinematic Viscosity (cSt) | 1.124 | | 4.680 | |
| Liq. Mass Density (Std. Cond) (kg/m ³) | 1585 | 872.2 | 994.7 | 811.7 |
| Liq. Vol. Flow (Std. Cond) (m ³ /h) , | 2.794e-003 | 6.348e-004 | 5.008e-003 | 0.0000 |
| Liquid Fraction | 1.000 | 1.000 | 1.000 | 0.0000 |
| Molar Volume (m ³ /kgmole) | 0.5637 | 3.970e-002 | 0.2661 | 27.34 |
| Mass Heat of Vap. (kJ/kg) | 59.32 | | | 1273 |
| Phase Fraction [Molar Basis] | 0.0000 | 0.0000 | 0.0000 | 1.0000 |
| Surface Tension (dyne/cm) | 2.941e+004 | 28.78 | | |
| Thermal Conductivity (W/m-K) | 0.1039 | | | 1.516e-002 |
| Viscosity (cP) | 1.765 | | | 6.072e-003 |
| Cv (Semi-Ideal) (kJ/kgmole-C) | 107.4 | 117.1 | 491.2 | 43.04 |
| Mass Cv (Semi-Ideal) (kJ/kg-C) | 0.1214 | 3.448 | 2.100 | 1.213 |
| Cv (kJ/kgmole-C) | 107.4 | 117.1 | 491.2 | 43.04 |
| Mass Cv (kJ/kg-C) | 0.1214 | 3.448 | 2.100 | 1.213 |

| | | | | | |
|--|------------|------------|------------|--|-------|
| Cv (Ent. Method) (kJ/kgmole-C) | | | | | |
| Mass Cv (Ent. Method) (kJ/kg-C) | | | | | |
| Cp/Cv (Ent. Method) | | | | | |
| Reid VP at 37.8 C (kPa) | | | | | 30.47 |
| True VP at 37.8 C (kPa) | 1.929e-022 | 32.07 | 8.772e-003 | | 30.47 |
| Liq. Vol. Flow - Sum (Std. Cond) (m ³ /h) | 2.794e-003 | 6.348e-004 | 5.099e-003 | | 0000 |
| Viscosity Index | 0.2414 | | | | |

DYNAMICS

Vessel Parameters: Initialize From Products

| | | | |
|---------------------------------|------------|-----------------------|------------------------|
| Vessel Volume (m ³) | 8.933e-003 | Level Calculator | Vertical cylinder |
| Vessel Diameter (m) | 0.2200* | Fraction Calculator | Use levels and nozzles |
| Vessel Height (m) | 0.2350* | Feed Delta P (kPa) | 0.0000 |
| Liquid Level Percent (%) | 1.00* | Vessel Pressure (kPa) | 101.3 |

Holdup: Vessel Levels

| Phase | Level, (m) | Percent (%) | Volume (m3) |
|-------|---------------|----------------|----------------|
|-------|---------------|----------------|----------------|

Vapour 0.0000

Liquid 0.0000

Aqueous 0.0000

Holdup: Details

| Phase | Accumulation, (kgmole/h) | Moles* (kgmole)* | Volume (m3) |
|---------|-----------------------------|---------------------|----------------|
| Vapour | 0.0000 | 0.0000* | 0.0000 |
| Liquid | 0.0000 | 0.0000 | 0.0000 |
| Aqueous | 0.0000 | 0.0000 | 0.0000 |
| Total | 0.0000 | 0.0000 | 0.0000 |

Duty Valve Source: Direct_Q

| SP | Min. Available | Max. Available |
|--------|----------------|----------------|
| (kJ/h) | (kJ/h) | (kJ/h) |
| -551.5 | , | |

Liquid Heater Height as % of Vessel Volume

Top of Heater: 5.00 % Bottom of Heater: 0.00 %

Heat Flow into the PFR: Heating

NOTES

Hyprotech Ltd., Aspen HYSYS Version 7 (22.0.0.7020),

LEGENDS, Case Name: CONTINUOUS HETEROGENEOUS CATALYTIC

TRANSESTERIFICATION.HSC

Burlington, MA,

USA Unit Set: SI

Date/Time: Wed Feb 05 11:02:19 2014

Pump (Pump): Design, Rating, Worksheet, Performance, Dynamics, Notes

Pump: Pump,

CONNECTIONS

Inlet Stream

Stream Name, From Unit Operation

Product, CSTR Cont. Stirred Tank Reactor

Outlet Stream

Stream Name, To Unit Operation

P Out, Simple Solid-Liquid Separator Simple Solid Separator

Energy Stream

Stream Name, From Unit Operation

QP,

PARAMETERS

Adiabatic Efficiency (%): 35.00* Delta P: 15.00 kPa*, Duty: 6.748e-005 kW

CURVES

Delta P: 15.00 kPa* Duty: 6.748e-005 kW

Coefficient A: 0.0000* Coefficient B: 0.0000 Coefficient C: 0.0000*

Parameter Preferences Units for Delta P: m Flow Basis Act. Vol. Flow Units for Flow: m³/h

User Variables

RATING

Characteristic Curves

Speed:

Flow, Head, Efficiency (%)

NPSH

NPSH Required NPSH Available, Enable NPSH Curves: No

NPSH Curves

Nozzle Parameters

Base Elevation Relative to Ground Level 0.0000 m*

| | Product. | P Out |
|------------------------|------------|------------|
| Diameter (m) | 5.000e-002 | 5.000e-002 |
| Elevation (Base) (m) | 0.0000 | 0.0000 |
| Elevation (Ground) (m) | 0.0000 | 0.0000 |

Inertia

Rotational inertia (kg-m²) 0.5000, Radius of gyration (m) 0.1000, Mass (kg) 50.00,
m²/s) 5.000e-002

Friction loss factor (kg-

Start Up

Design Flow Typical Operating Capacity 10.00 m³/h

CONDITIONS

| Name | Product. | P Out | QP |
|--|-------------|-------------|----------|
| Vapour | 0.0000 | 0.0000 | |
| Temperature (C) | 60.0000* | 60.0228 | |
| Pressure (kPa) | 101.3200 | 116.3200 | |
| Molar Flow (kgmole/h) | 0.0213 | 0.0213 | |
| Mass Flow (kg/h) | 4.9810 | 4.9810 | |
| Std Ideal Liq Vol Flow (m ³ /h) | 0.0055 | 0.0055 | |
| Molar Enthalpy (kJ/kgmole) | -6.554e+005 | -6.554e+005 | |
| Molar Entropy (kJ/kgmole-C) | 323.4 | 324.5 | |
| Heat Flow (kJ/h) | -1.3960e+04 | -1.3959e+04 | 4292e-01 |

PROPERTIES

| Name | Product. | P Out |
|--|------------|------------|
| Molecular Weight | 233.9 | 233.9 |
| Molar Density (kgmole/m ³) | 3.758 | 3.758 |
| Mass Density (kg/m ³) | 878.8 | 878.8 |
| Act. Volume Flow (m ³ /h) | 5.668e-003 | 5.668e-003 |
| Mass Enthalpy (kJ/kg) | -2803 | -2803 |
| Mass Entropy (kJ/kg-C) | 1.383 | 1.388 |
| Heat Capacity (kJ/kgmole-C) | 499.5 | 499.6 |
| Mass Heat Capacity (kJ/kg-C) | 2.136 | 2.136 |

| | | |
|--|------------|------------|
| Lower Heating Value (kJ/kgmole) | | |
| Lower Heating Value (kJ/kg) | | |
| Phase Fraction [Vol. Basis] | | |
| Phase Fraction [Mass Basis] | 2.122e-314 | 2.122e-314 |
| Partial Pressure of CO2 (kPa) | 0.0000 | 0.0000 |
| Cost Based on Flow (Cost/s) | 0.0000 | 0.0000 |
| Act. Gas Flow (ACT_m ³ /h) | | |
| Avg. Liq. Density (kgmole/m ³) | 3.895 | 3.895 |
| Specific Heat (kJ/kgmole-C) | 499.5 | 499.6 |
| Std. Gas Flow (STD_m ³ /h) | 0.5036 | 0.5036 |
| Std. Ideal Liq. Mass Density (kg/m ³) | 910.9 | 910.9 |
| Act. Liq. Flow (m ³ /s) | 1.566e-006 | 1.566e-006 |
| Z Factor | | |
| Watson K | | |
| User Property | | |
| Partial Pressure of H2S (kPa) | 0.0000 | 0.0000 |
| Cp/(Cp - R) | 1.017 | 1.017 |
| Cp/Cv | 1.017 | 1.017 |
| Heat of Vap. (kJ/kgmole) | | |
| Kinematic Viscosity (cSt) | | |
| Liq. Mass Density (Std. Cond) (kg/m ³) | 994.7 | 994.7 |
| Liq. Vol. Flow (Std. Cond) (m ³ /h) | 5.008e-003 | 5.008e-003 |
| Liquid Fraction | 1.000 | 1.000 |
| Molar Volume (m ³ /kgmole) | 0.2661 | 0.2661 |
| Mass Heat of Vap. (kJ/kg) | | |
| Phase Fraction [Molar Basis] | 0.0000 | 0.0000 |
| Surface Tension (dyne/cm) | | |
| Thermal Conductivity (W/m-K) | | |

Viscosity (cP)

Cv (Semi-Ideal) (kJ/kgmole-C) 491.2 491.2

Mass Cv (Semi-Ideal) (kJ/kg-C) 2.100 2.101

Cv (kJ/kgmole-C) 491.2 491.2

Mass Cv (kJ/kg-C) 2.100 2.101

Cv (Ent. Method) (kJ/kgmole-C)

Mass Cv (Ent. Method) (kJ/kg-C)

Cp/Cv (Ent. Method)

Reid VP at 37.8 C (kPa)

True VP at 37.8 C (kPa) 8.772e-003 8.772e-003

Liq. Vol. Flow - Sum(Std. Cond) (m3/h) , 5.099e-003 5.099e-003

Viscosity Index

PERFORMANCE

Results

Total Head Velocity Head 4.242e-013 m*

Total Fluid Head

Pressure Head 1.741 m* Delta P excluding Static Head Results

DYNAMICS

Dynamic Specifications

Head (m) Not Active Power (kJ/h) 0.2429 Not Active

Fluid Head (kJ/kg) Not Active

Adiabatic Efficiency (rpm) Not Active Capacity (m3/h) 5.469e-003

Polytropic Efficiency (%) 35.00* Active Use Characteristic Curves Not Active

Pressure Increase (kPa) 15.00* Active Pump is Acting as a Turbine Not Active

Holdup Details

| Phase | Accumulation, (kgmole/h) | Moles* (kgmole)* | Volume (m3) |
|---------|-----------------------------|---------------------|----------------|
| Vapour | 0.0000 | 0.0000* | 0.0000 |
| Liquid | 0.0000 | 0.0000 | 0.0000 |
| Aqueous | 0.0000 | 0.0000 | 0.0000* |
| Total, | 0.0000 | 0.0000 | 0.0000 |

NOTES

Hyprotech Ltd. , Aspen HYSYS Version 7 (22.0.0.7020),
LEGENDS, Case Name: CONTINUOUS HETEROGENEOUS CATALYTIC
TRANSESTERIFICATION.HSC
Burlington, MA
USA, Unit Set: SI

Date/Time: Wed Feb 05 11:04:19 2014

Simple Solid-Liquid Separator (Simple Solid Separator): Design, Worksheet, Notes

Simple Solid Separator: Simple Solid-Liquid Separator,

CONNECTIONS

Inlet Stream

STREAM NAME, FROM UNIT OPERATION

P Out, Pump

Outlet Stream

STREAM NAME, TO UNIT OPERATION

SV,

Liquid,

TEE-100 Tee

Cat. Out,

RCY-1 Recycle

PARAMETERS

Physical Properties

Pressure Drop: 0.0000 kPa*,

Splits: Stream Fractions

Basis: Mole, Solids In Vapour: 0.0000*, Solids In Liquid: 0.0001*, Liquid In Bottoms: 0.0010*

User Variables

CONDITIONS

| Name | P Out | , Cat. Out | SV | Liquid |
|--|-------------|------------|-------------|-------------|
| Vapour | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Temperature (C) | 60.0228 | 60.0228 | 60.0228 | 60.0228 |
| Pressure (kPa) | 116.3200 | 116.3200 | 116.3200 | 116.3200 |
| Molar Flow (kgmole/h) | 0.0213 | 0.0013 | 0.0000 | 0.0200 |
| Mass Flow (kg/h) | 4.9810 | 0.0730 | 0.0000 | 4.9081 |
| Std Ideal Liq Vol Flow (m ³ /h) | 0.0055 | 0.0000 | 0.0000 | 0.0054 |
| Molar Enthalpy (kJ/kgmole) | -6.554e+005 | 7506 | -6.554e+005 | -.984e+005 |
| Molar Entropy (kJ/kgmole-C) | 324.5 | 1361 | 324.5 | 257.3 |
| Heat Flow (kJ/h) | -1.3959e+04 | 9.7327e+00 | 0.0000e-01 | -1.3969e+04 |

PROPERTIES

| Name | Out | Cat. Out | SV | Liquid |
|--|-------|----------|-------|--------|
| Molecular Weight | 233.9 | 56.27 | 233.9 | 245.4 |
| Molar Density (kgmole/m ³) | 3.758 | 41.46 | 3.758 | 3.548 |

| | | | | | |
|--|------------|------------|------------|------------|------------|
| Mass Density (kg/m ³) | 878.8 | 2333 | 878.8 | 870.7 | , |
| Act. Volume Flow (m ³ /h) | 5.668e-003 | 3.128e-005 | 0.0000 | 5.637e-003 | |
| Mass Enthalpy (kJ/kg) | -2803 | 133.4 | -2803 | -2846 | |
| Mass Entropy (kJ/kg-C) | 1.388 | 24.19 | 1.388 | 1.049 | , |
| Heat Capacity (kJ/kgmole-C) | 499.6 | 234.8 | 499.6 | 516.7 | |
| Mass Heat Capacity (kJ/kg-C) | 2.136 | 4.173 | 2.136 | 2.106 | |
| Lower Heating Value (kJ/kgmole) | | | | | |
| Mass Lower Heating Value (kJ/kg) | | | | | |
| Phase Fraction [Vol. Basis] | | | | | |
| Phase Fraction [Mass Basis] | | 2.122e-314 | 2.122e-314 | 2.122e-314 | 2.122e-314 |
| Partial Pressure of CO2 (kPa) | | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Cost Based on Flow (Cost/s) | 0.0000 | 0.0000 | 0.0000 | 0.0000 | |
| Act. Gas Flow (ACT_m ³ /h) | | | | | |
| Avg. Liq. Density (kgmole/m ³) | 3.895 | 41.47 | | 3.679 | |
| Specific Heat (kJ/kgmole-C) | 499.6 | 234.8 | 499.6 | 516.7 | |
| Std. Gas Flow (STD_m ³ /h) | 0.5036 | 3.066e-002 | 0.0000 | 0.4729 | |
| Std. Ideal Liq. Mass Density (kg/m3) | 910.9 | | 2334 | 910.9 | 902.7 |
| Act. Liq. Flow (m ³ /s) | 1.566e-006 | 1.015e-010 | 0.0000 | 1.566e-006 | |
| Z Factor | | | | | |
| Watson K | | | | | |
| User Property | | | | | |
| Partial Pressure of H2S (kPa) | 0.0000 | 0.0000 | 0.0000 | 0.0000 | |
| Cp/(Cp - R) | 1.017 | 1.037 | 1.017 | 1.016 | |
| Cp/Cv | 1.017 | 1.037 | 1.017 | 1.016 | |
| Heat of Vap. (kJ/kgmole) | | | | | |
| Kinematic Viscosity (cSt) | | | | | |
| Liq. Mass Density (Std. Cond) (kg/m ³) | 994.7 | 2336 | 994.7 | 986.2 | |
| Liq. Vol. Flow (Std. Cond) (m ³ /h) | 5.008e-003 | 3.123e-005 | 0.00004 | 9.77e-003 | |

| | | | | |
|--|------------|------------|------------|------------|
| Liquid Fraction | 1.000 | 1.000 | 1.000 | 1.000 |
| Molar Volume (m ³ /kgmole) | 0.2661 | 2.412e-002 | 0.2661 | 0.2818 |
| Mass Heat of Vap. (kJ/kg) | | | | |
| Phase Fraction [Molar Basis] | 0.0000 | 0.0000 | 0.0000 | 0.0000 , |
| Surface Tension (dyne/cm) | | | | |
| Thermal Conductivity (W/m-K) | | | | |
| Viscosity (cP) | | | | |
| Cv (Semi-Ideal) (kJ/kgmole-C) | 491.2 | 226.5 | 491.2 | 8.4 |
| Mass Cv (Semi-Ideal) (kJ/kg-C) | 2.101 | 4.025 | 2.101 | 72 |
| Cv (kJ/kgmole-C) | 491.2 | 226.5 | 491.2 | 508.4 |
| Mass Cv (kJ/kg-C) | 2.101 | 4.025 | 2.101 | 0.072 |
| Cv (Ent. Method) (kJ/kgmole-C) | 257.0 | | | |
| Mass Cv (Ent. Method) (kJ/kg-C) | 4.568 | | | |
| Cp/Cv (Ent. Method) | 0.9134 | | | |
| Reid VP at 37.8 C (kPa) | | | | |
| True VP at 37.8 C (kPa) | 8.772e-003 | 8.772e-003 | 8.772e-003 | 772e-003 |
| Liq. Vol. Flow Sum (Std. Cond) (m ³ /h) | 5.099e-003 | 3.124e-005 | 0.0000 | 5.068e-003 |

Viscosity Index

NOTES

Hyprotech Ltd. , Aspen HYSYS Version 7 (22.0.0.7020),

Appendix II: Stirrers Design

Appendix II A: Reactor stirrer design

For reaction with heat transfer, the speed of the tip is between 10-15 ft/s (3.048-4.572 m/s) (Stanley, 1990). Taking the average of this range for this work, we have 3.81m/s. The power number N_Q for pitch blade 45° with four baffles is in the range of 1.3-1.4. For this work the average range is taken given $N_p = 1.35$.

The tip speed in revolutions per second is thus calculated as follows;

$$\omega = \frac{vN}{r} = \frac{3.81 \times N}{0.0365} = 104.38 \text{ rad / s}$$

$$N = \frac{\omega}{2\pi} = \frac{104.38}{2 \times \pi} = 16.61 \text{ rps} \quad \text{or} \quad 996.79 \text{ rpm}$$

The power P, draws by the stirrer is thus;

$$P = N_p \times N^3 \times \rho \times d^5$$

$$P = 1.35 \times 16.61^3 \times 912.6 \times 0.073^5 = 11.704 \text{ W}$$

The Flow Rate of Fluid by Stirrer

The flow for pitch blade turbine 45^0 is in the range of 0.60-0.87. Taking the average of this taking for this design, N_Q is 0.735.

The flow rate is thus;

$$\phi = N_\phi \times N \times d^3$$

Where, d is the diameter of the blade.

$$\phi = 0.735 \times 16.61 \times 0.073^3 = 0.00475 \text{ m}^3 / \text{s}$$

$$\text{Or } 17.097 \text{ m}^3/\text{h}$$

The Reactor Stirrer Design Specification

| Stirrer Parameter | Value | Unit |
|---------------------------|----------------------------------|---|
| Impeller diameter $d=D/3$ | 0.073 | M |
| Power | 18.106 | W |
| Blade width, $d/8$ | 0.008 | M |
| stirrer speed, N | 16.61/(996.79) | rps/(rpm) |
| Flow rate | 4.75×10^{-3} , (17.097) | m^3/s , (m^3/h) |

Appendix IIB: Reactor Pump Rating

The Pump power is given as;

$$P = \frac{\phi \times g \times \rho \times h}{\text{Pump Efficiency}}$$

Hence,

$$P = \frac{5.469 \times 10^{-3} \times 9.81 \times 887.4 \times 1.6}{3.6 \times 10^3 \times 0.35} = 0.0604 \text{ W}$$

Appendix IIC: Mixer Stirrer Design

The Power number of pitch turbine blade 45° is 0.7 and when uniform solid distribution must be approached a velocity of 0.6 ft/s (0.183 m/s) will be sufficient. Hence, a tip velocity of 0.183m/s was used for the design of this stirrer. The power draw was therefore;

The angular frequency, ω is;

$$\omega = \frac{vN}{r} = \frac{0.183}{0.365} = 5.0137 \text{ rad / s}$$

The speed in rps, N was thus;

$$N = \frac{\omega}{2 \times \pi} = \frac{5.0137}{2 \times \pi} = 0.798 \text{ rps or } 47.877 \text{ rpm}$$

Therefore the power drawn is;

$$P = N_p \times N^3 \times \rho \times d^5$$

$$P = 0.7 \times 0.798^3 \times 875.3 \times 0.073^5 = 6.45 \times 10^{-4} \text{ W}$$

The Mixer Flow Rate ϕ

The flow number, N_ϕ of a pitch blade turbine without baffles is 0.3, hence, the flow can be calculated as thus;

$$\phi = N_\phi \times N \times d^3$$

$$\phi = 0.3 \times 0.798 \times 0.073^3 = 9.31 \times 10^{-5} \text{ m}^3 / \text{s or } 0.335 \text{ m}^3 / \text{h}$$

The Mixer Stirrer Design Specification

| Stirrer Parameter | Value | Unit |
|---------------------------|---------------|-----------|
| Impeller diameter $d=D/3$ | 0.073 | m |
| Power | 7.995e-004 | W |
| Blade width, $d/8$ | 9 | mm |
| stirrer speed, N | 0.857/(51.42) | rps/(rpm) |

| | | |
|-----------|---------------------------------|--|
| Flow rate | 1.00 x10 ⁻⁴ , (0.36) | m ³ /s, (m ³ /h) |
|-----------|---------------------------------|--|

Appendix III: Piping Data and Specification

| PVC 1120 type 1 | |
|------------------------------|---|
| Density (g/cm ³) | 1.039 |
| Temperature Limit (°C) | -18-60 |
| Pressure limit (atm) | 30.6 @ 23 ⁰ C and 9.4 @ 60 ⁰ C for schedule 80 |
| Cost estimate | |
| chemical corrosion | Not suitable for high concentrated H ₂ SO ₄ and alkali (50% Not for sulphur compounds, may be damage by ketone, aromatics and chlorine compounds. |
| | Chlorinated (polyvinyl chloride) CPVC4120 type 18 grade |
| Density (g/cm ³) | 1.52 |
| Temperature Limit (°C) | -18-99 |
| Pressure limit (atm) (1" ID) | 30.6 @ 23 ⁰ C and 6.12 @ 60 ⁰ C for schedule 40, 42.8 @ 23 ⁰ C, 8.58 @ 60 ⁰ C for schedule 80 |
| Cost estimate | |

| | |
|--------------------|---|
| chemical corrosion | Not suitable for vegetable oil and petro-diesel, may be damage by ketone, aromatics and chlorine compounds. |
|--------------------|---|

Carbon Steel, Schedule 40

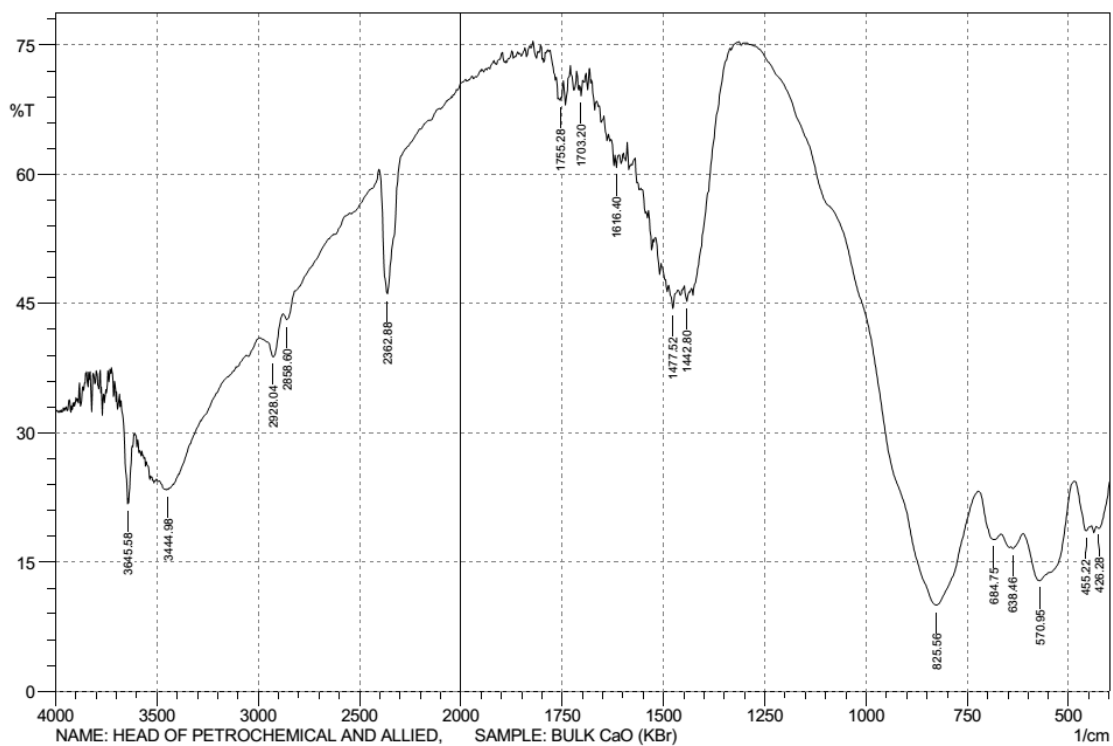
| | |
|------------------------------|--|
| Density (g/cm ³) | 7.84 |
| Temperature Limit (°C) | Does not pose a problem |
| Pressure limit (atm) (1" ID) | Does not a problem |
| Cost estimate | |
| chemical corrosion | Not suitable in handling alkaline, aqueous acids and may deteriorate on exposure to H ₂ S |
| | Stainless Steel 304 Schedule 10 |
| Density (g/cm ³) | 8.03 |
| Temperature Limit (°C) | Not a problem |
| Pressure limit (atm) (1" ID) | Not a problem |
| Cost estimate | |
| chemical corrosion | Can be tarnished by oxidizing acids |

Polypropylene

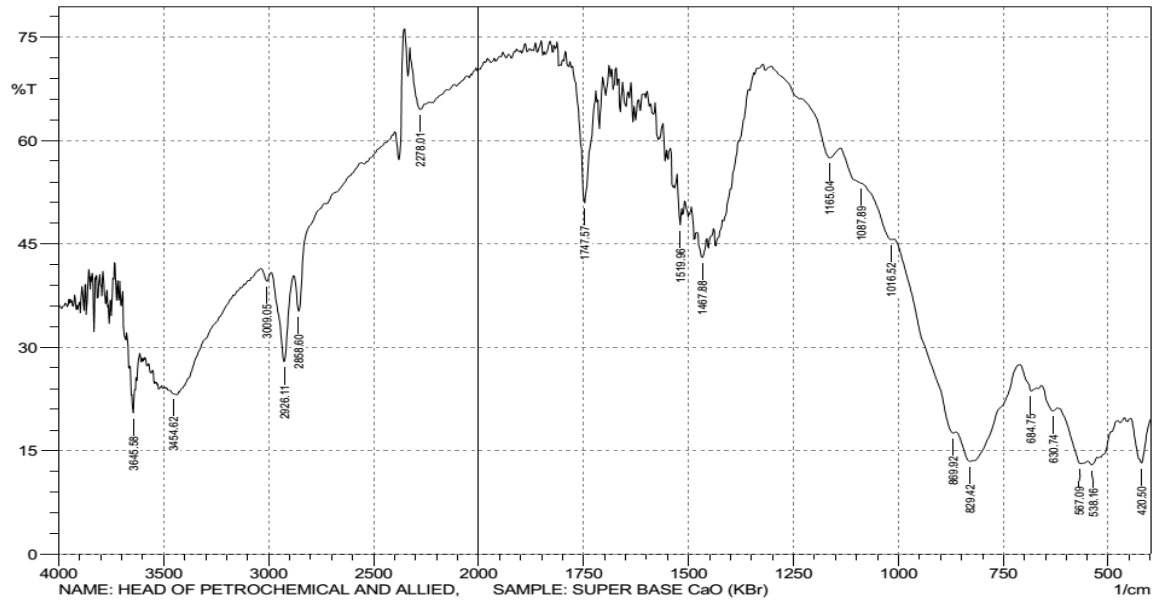
| | |
|------------------------------|---|
| Density (g/cm ³) | 0.90 |
| Temperature Limit (°C) | 0°C to 135°C |
| Pressure limit (atm) (1" ID) | Not a factor |
| Cost estimate | |
| chemical corrosion | excellent resistance to dilute and conc. H ₂ SO ₄ , alcohols, bases and mineral oils and minor attacks to aliphatic hydrocarbons and vegetable oils |

Appendix IV: Characterization of the Synthesized Catalysts

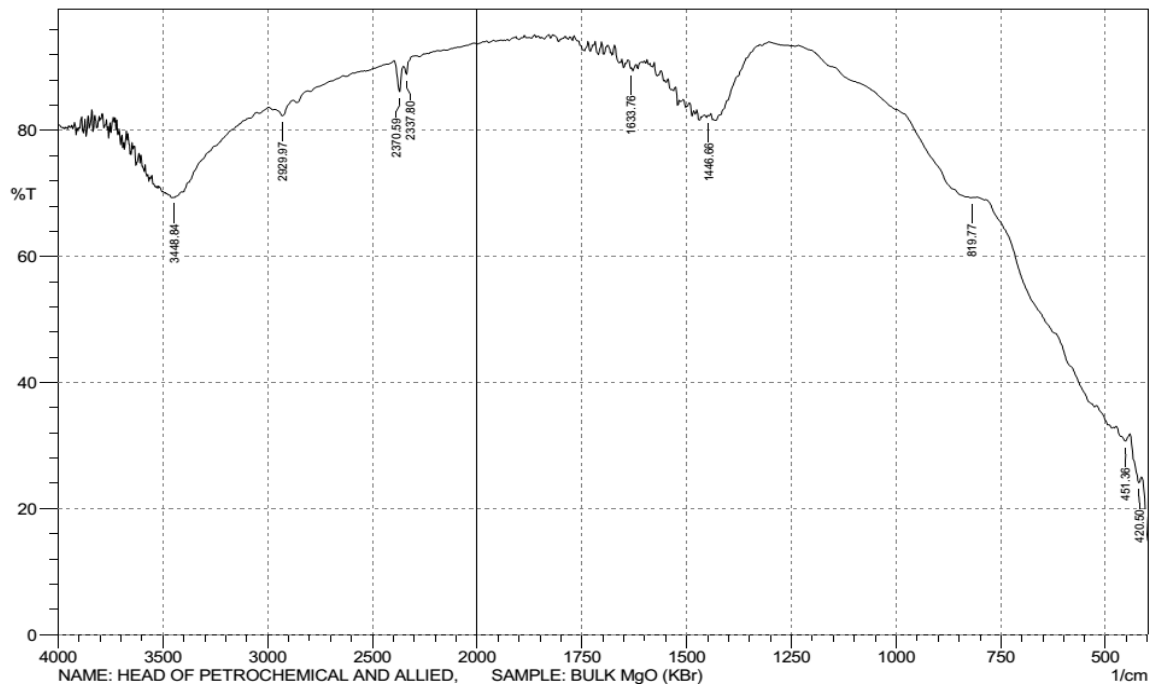
Appendix IVA Fourier Transform Infra-Red (FTIR) Analysis



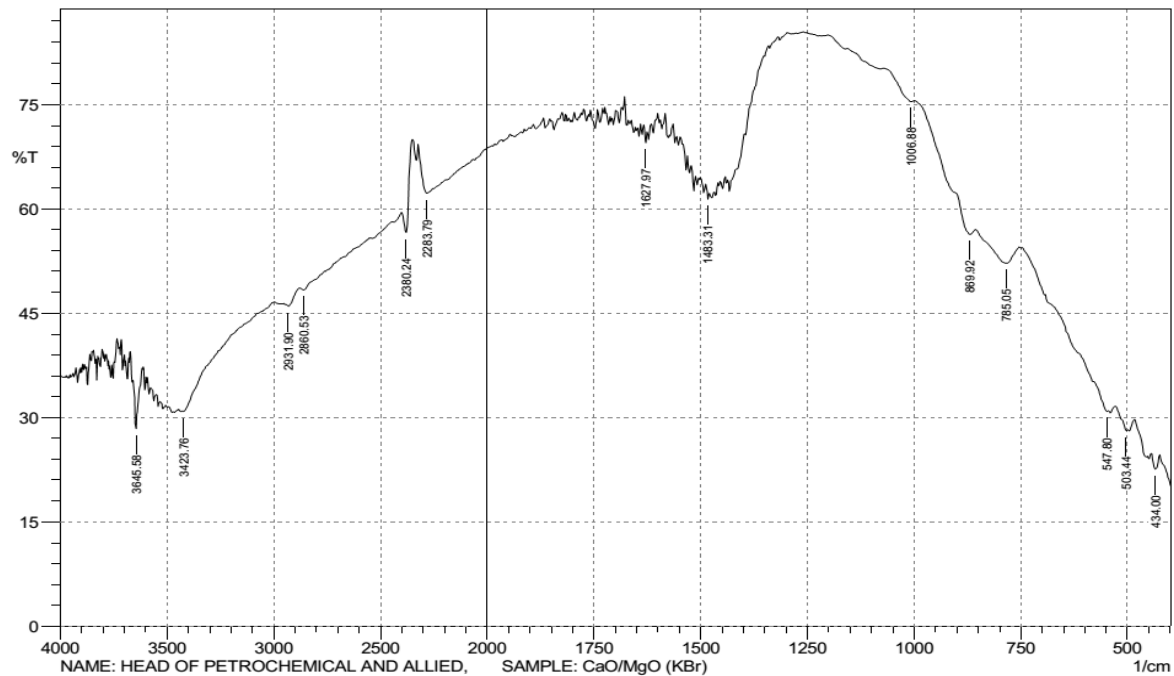
Appendix IVA1: FTIR Spectrum of bulk CaO Catalyst



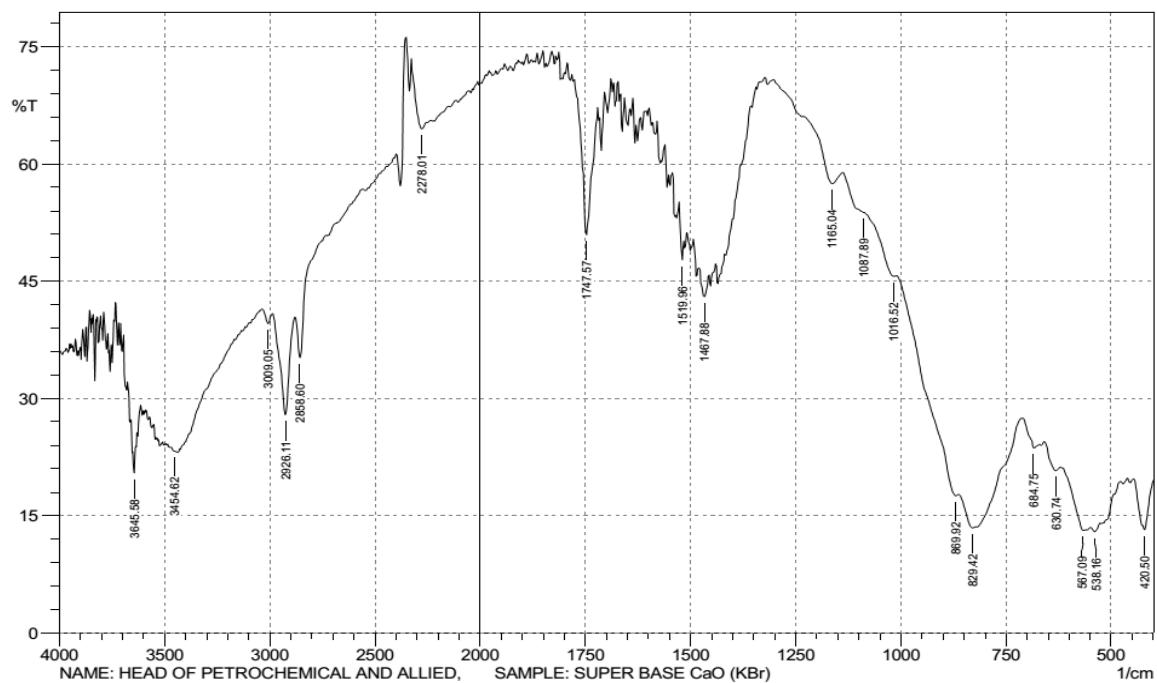
Appendix IVA2: FTIR Spectrum of Super base CaO Catalyst



Appendix IVA3: FTIR Spectrum of MgO Catalyst

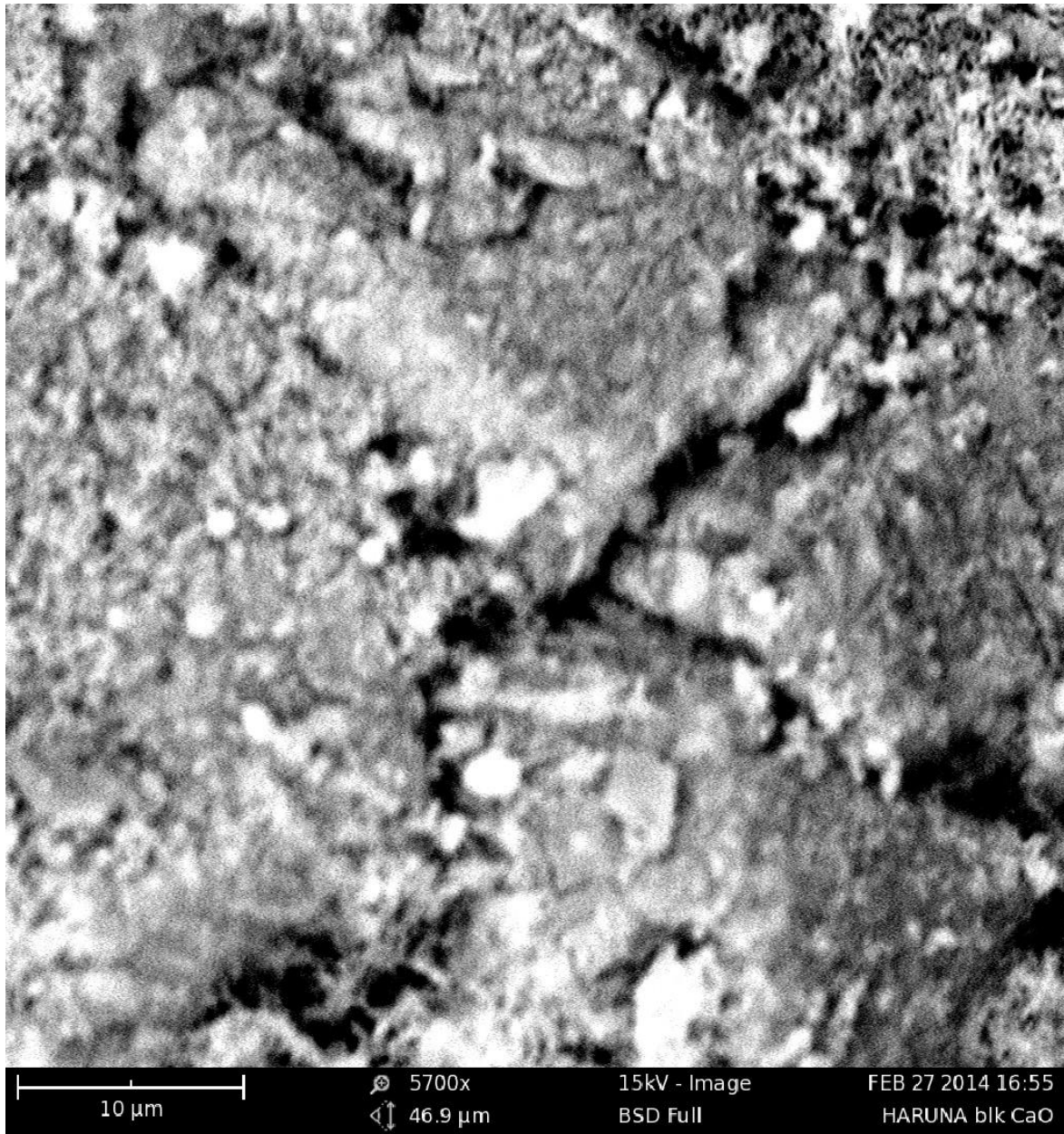


Appendix IVA4: FTIR Spectrum of CaO/MgO Catalyst

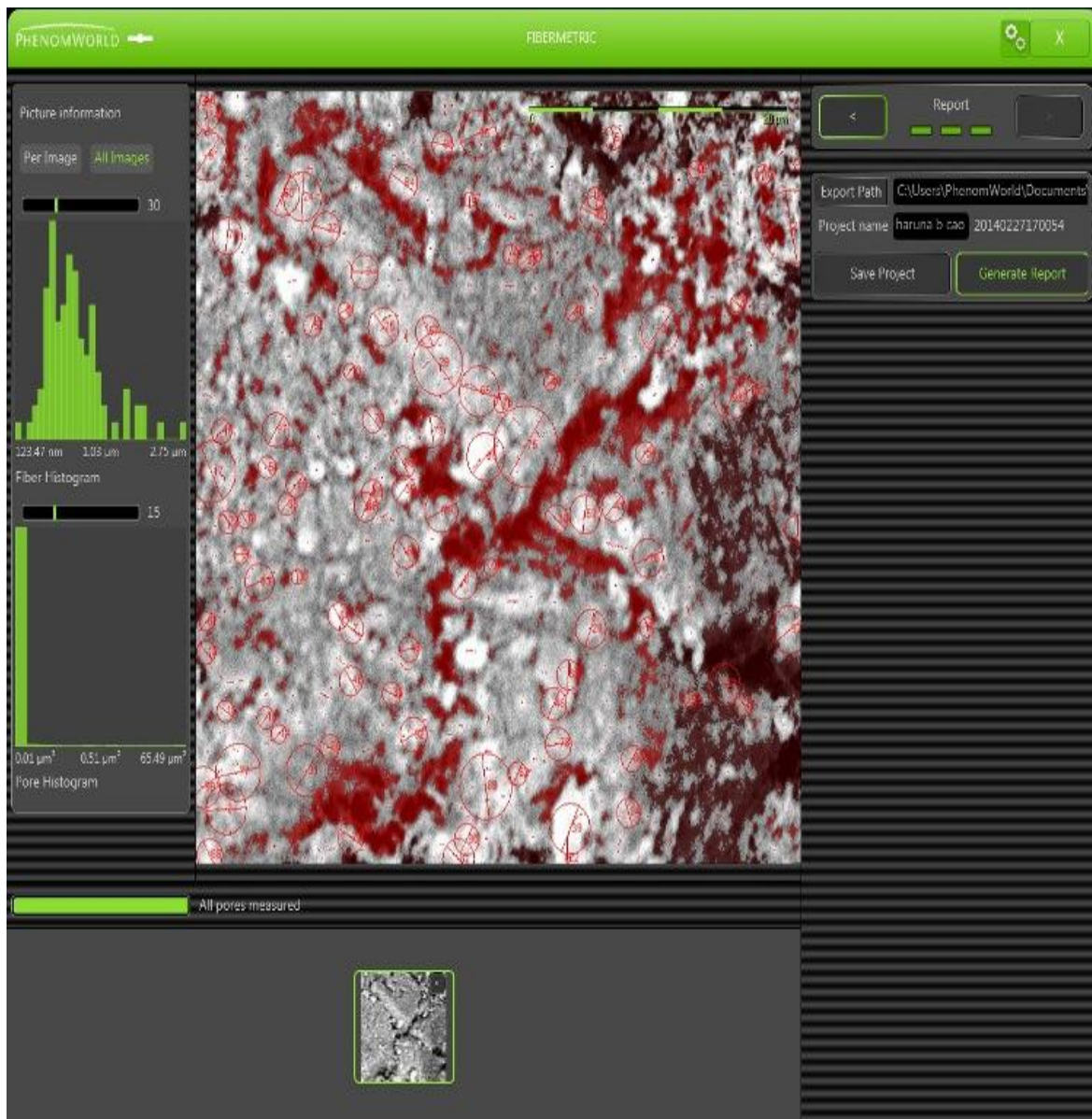


Appendix IVA5: FTIR Spectrum of 10%K- CaO/MgO Catalyst

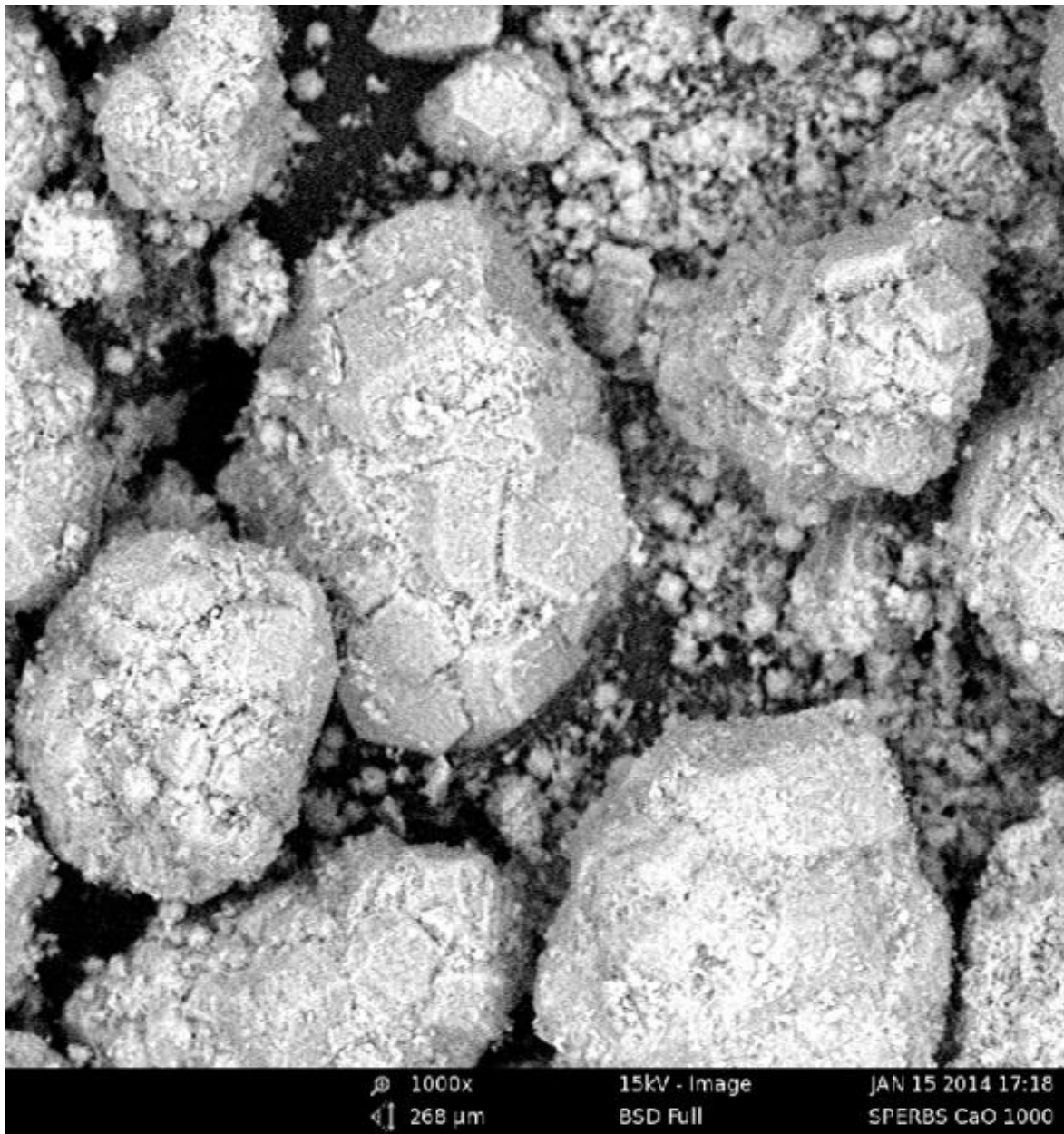
Appendix IVB Scanning Electron Microscope (SEM) Analysis of the synthesized catalysts



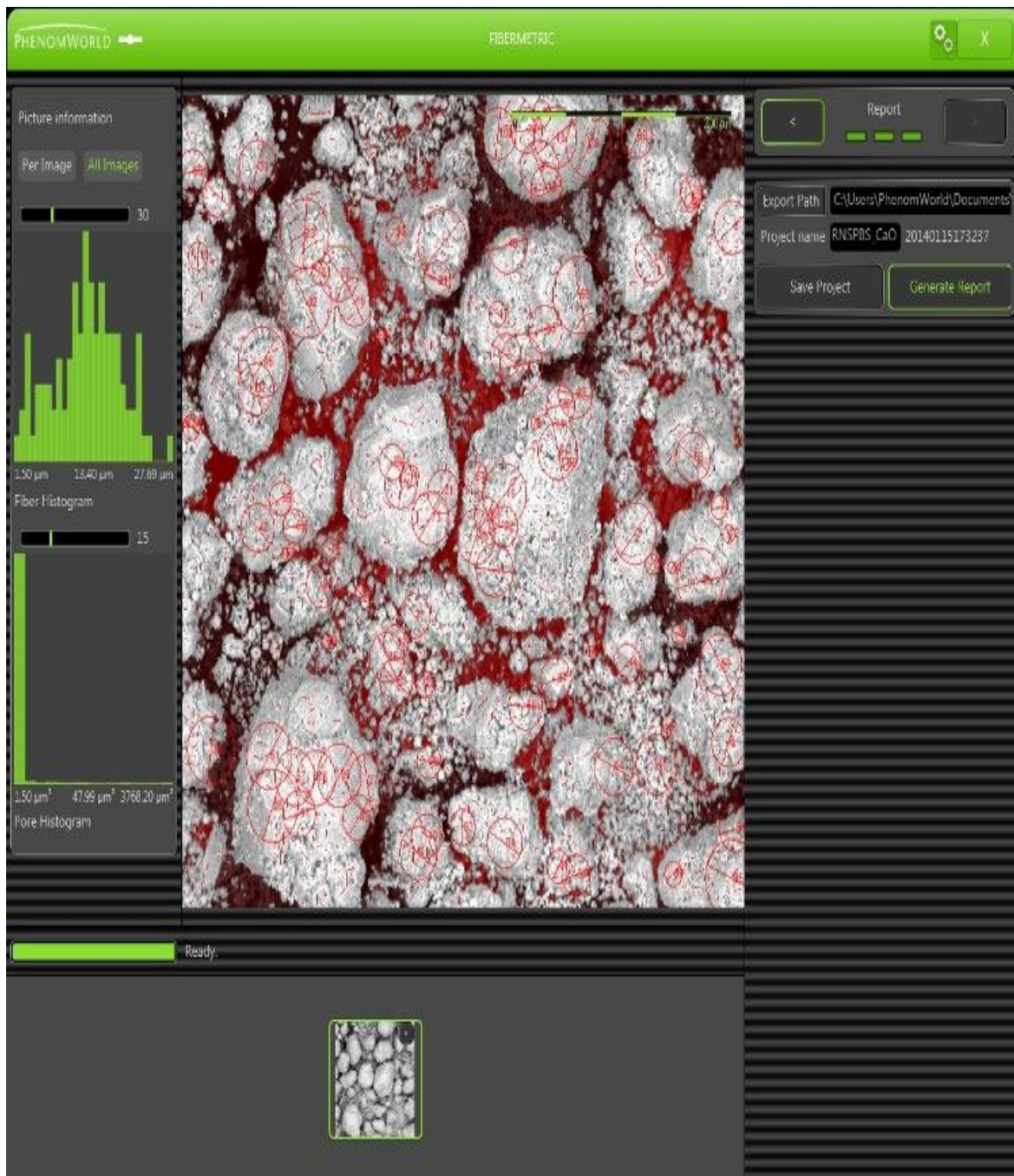
Appendix IVB1: A SEM grain particles of Calcium oxide Catalyst metric image



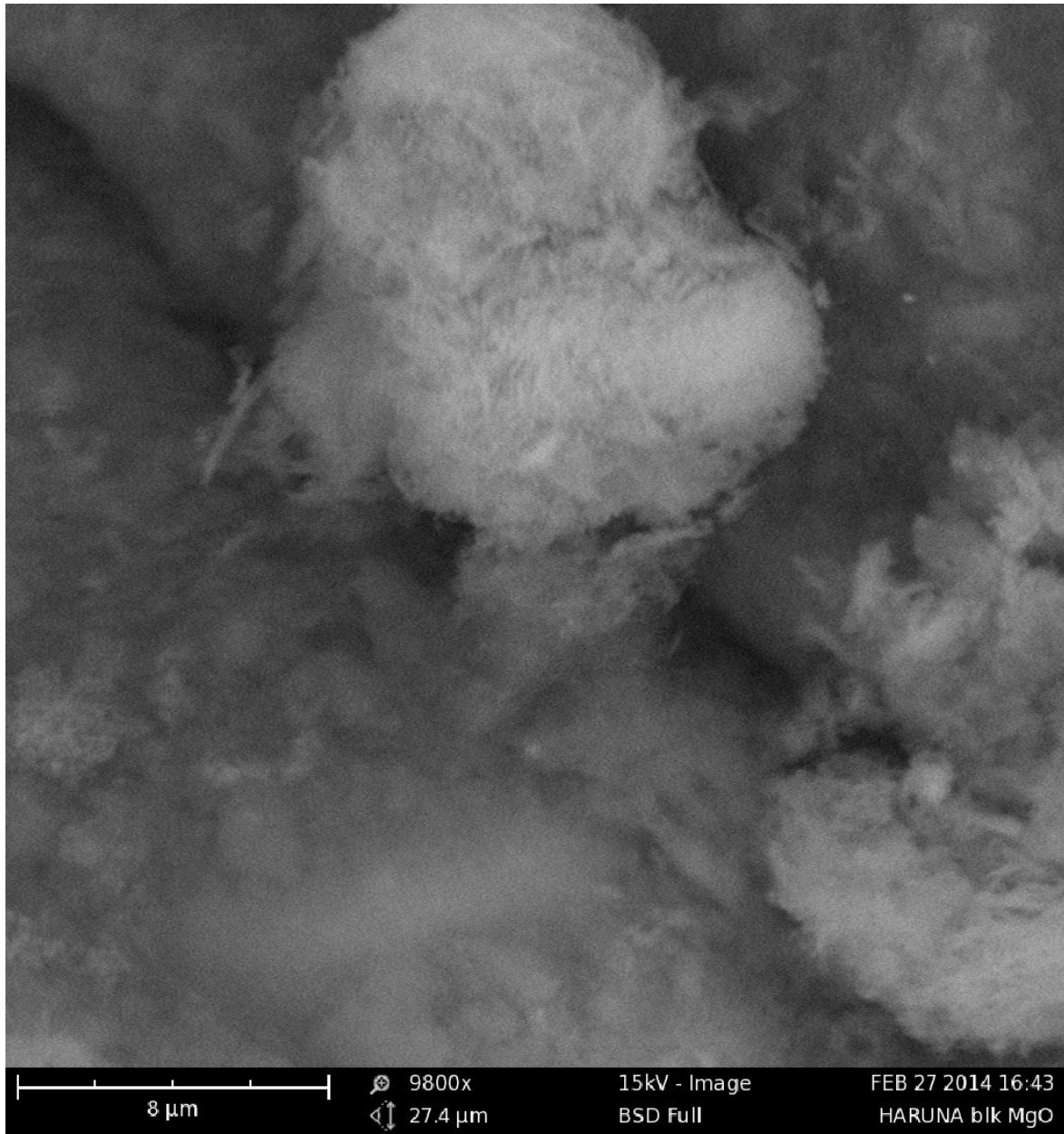
Appendix IVB2: Screenshot of bulk calcium oxide catalyst



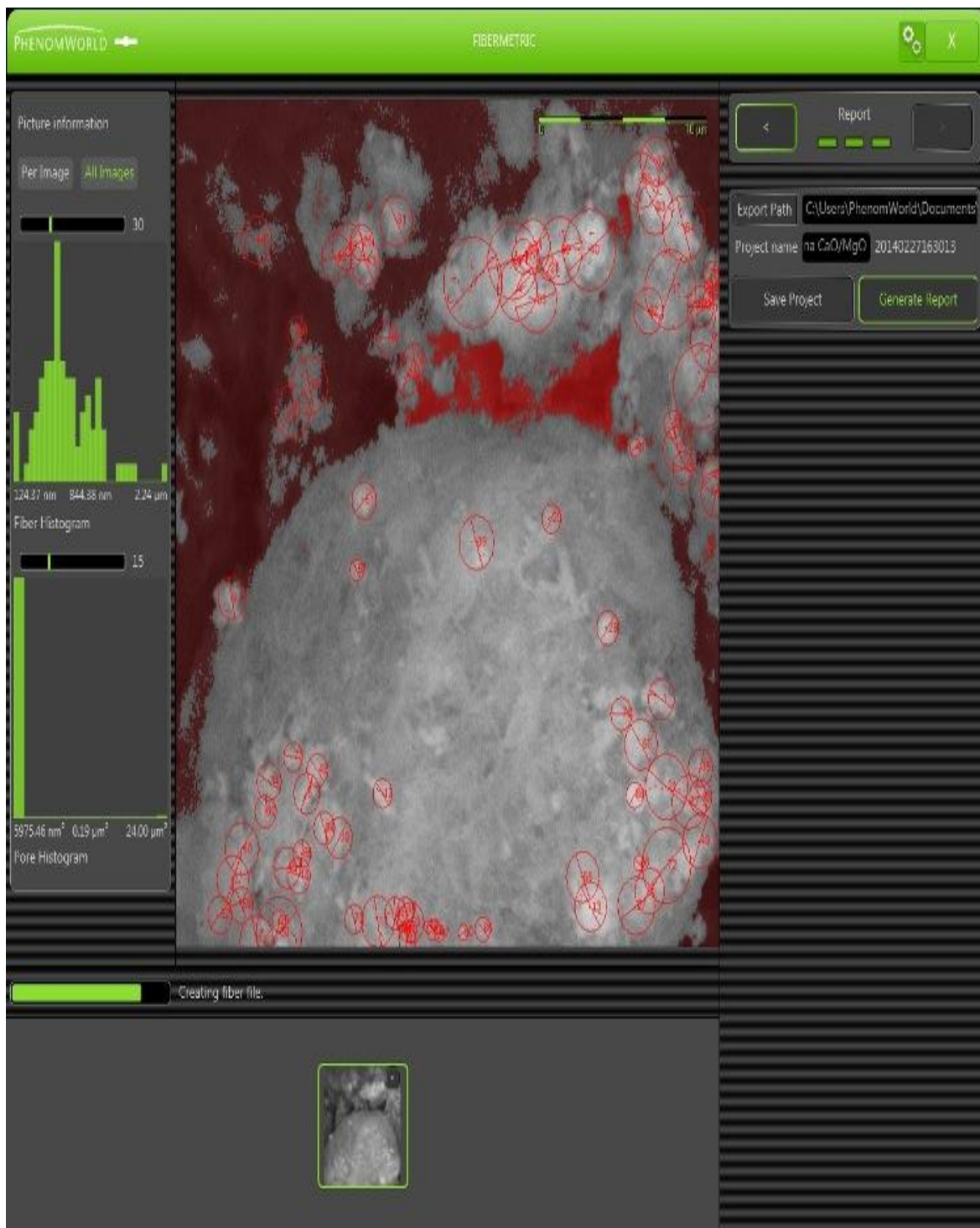
Appendix IVB3: SEM grain particles of super base calcium oxide catalyst



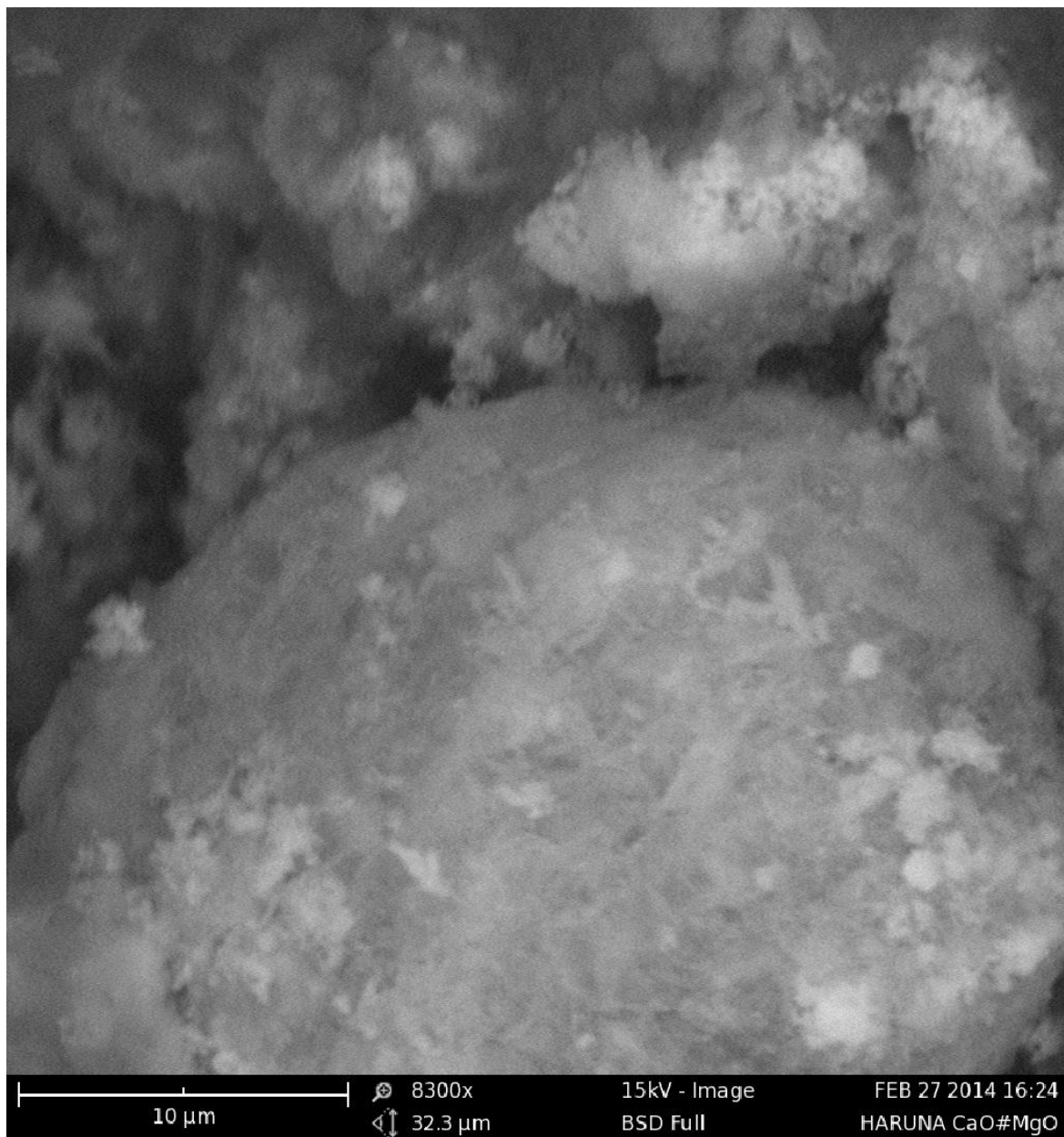
Appendix IVB4: Screenshot of super base calcium oxide catalyst



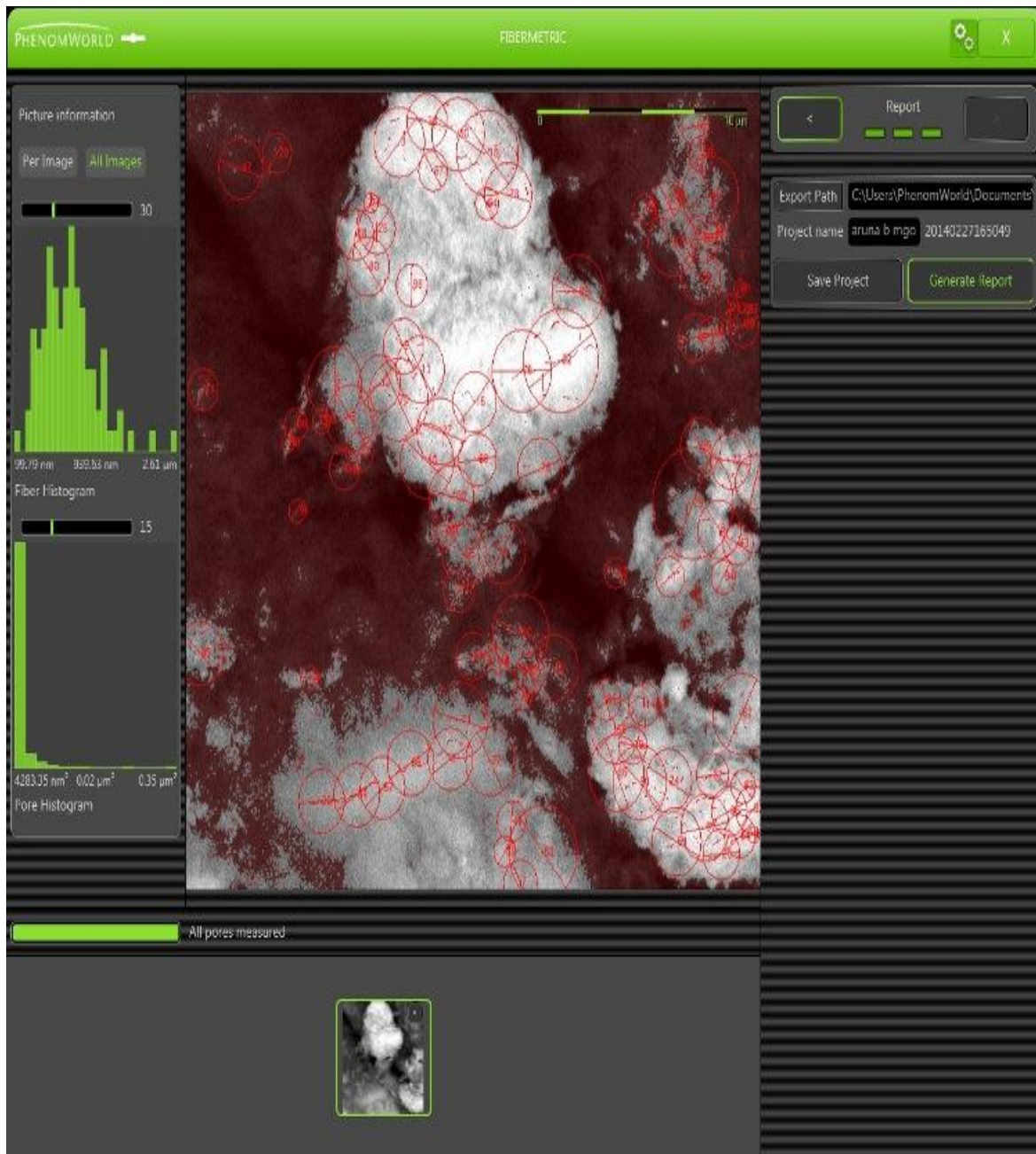
Appendix IVB5: SEM grain particles of Bulk magnesium oxide catalyst



Appendix IVB6: Screenshot of magnesium oxide catalyst



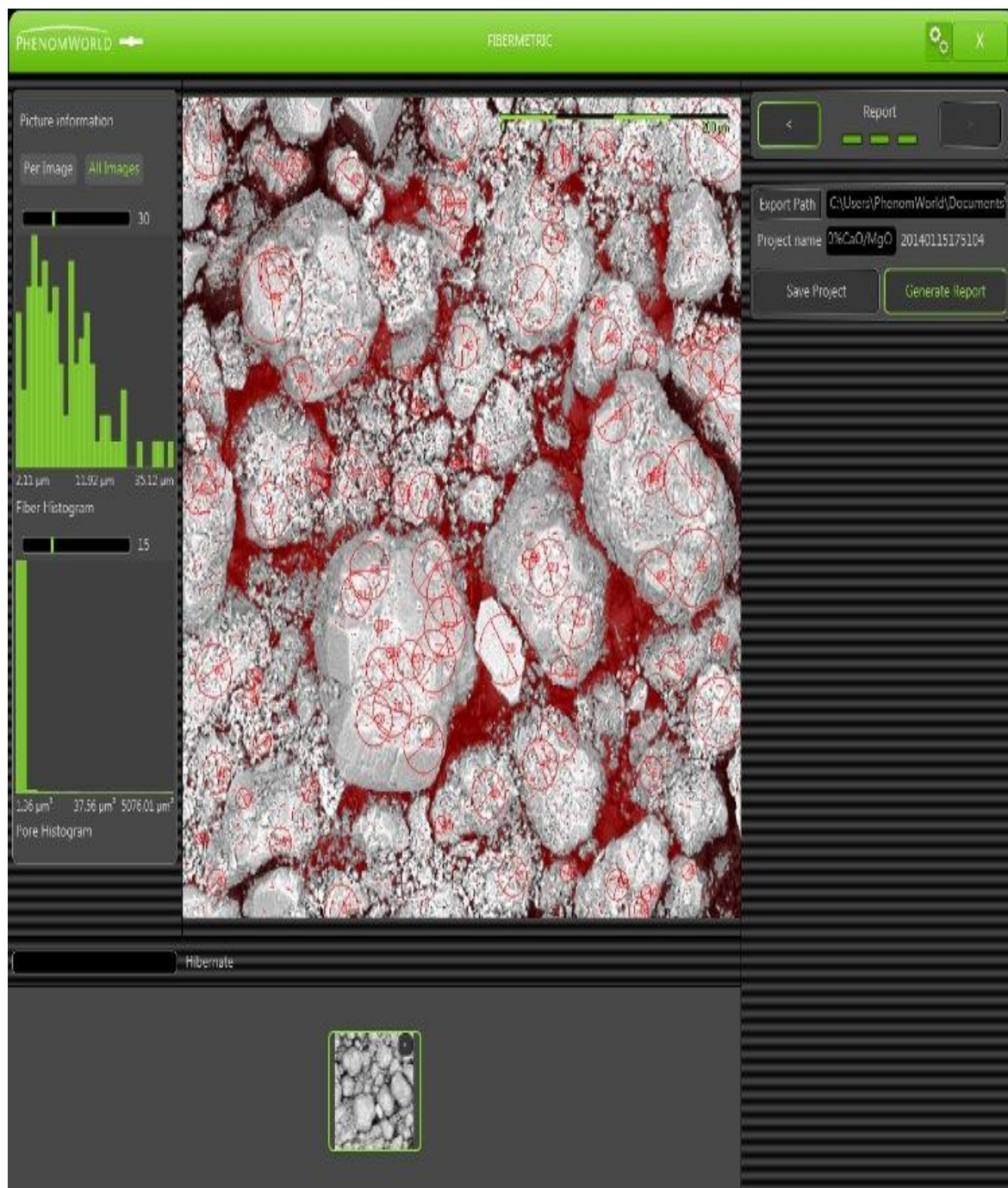
Appendix IVB7: grain particles of Calcium oxide/ magnesium oxide catalyst



Appendix IVB8: Screenshot of calcium oxide/magnesium oxide catalyst



Appendix IVB9: grain particles of 10%K impregnated calcium oxide/magnesium oxide catalyst



Appendix IVB10: Screenshot of 10% potassium impregnated calcium oxide/magnesium oxide

Appendix V Efficacies of the prepared Catalysts

Appendix VA1: Efficacy of bulk CaO catalyst for transesterification of *Jatropha* oil

| Methyl ester composition | MF | Transesterification at 60 ⁰ C (min) | | | | |
|---|--|--|---------------|---------------|---------------|--------------|
| | | 50 | 60 | 70 | 80 | 90 |
| Methyl 10-undecenoate | C ₁₂ H ₂₂ O ₂ | | 0.632 | | | 0.188 |
| Methyl tridecanoate | C ₁₄ H ₂₈ O ₂ | | | | | 0.114 |
| Methyl myristate | C ₁₅ H ₃₀ O ₂ | | | | | 0.362 |
| Methyl palmitoleate | C ₁₇ H ₃₂ O ₂ | | 0.224 | | | 1.800 |
| Methyl -7-hexadecenoate | C ₁₇ H ₃₂ O ₂ | | 0.112 | | | 0.900 |
| Methyl hexadecanoate | C ₁₇ H ₃₄ O ₂ | 6.088 | 8.544 | 5.892 | 7.764 | 11.032 |
| Methyl 14-methylpentadecanoate | C ₁₇ H ₃₄ O ₂ | 7.130 | 8.544 | 5.892 | 5.676 | 2.758 |
| Methyl heptadecanoate | C ₁₈ H ₃₆ O ₂ | | | | | 0.412 |
| Methyl 8-(2-hexylcyclopropyl)ocitanoate | C ₁₈ H ₃₄ O ₂ | | 0.112 | | | |
| Methyl isoheptadecanoate | C ₁₈ H ₃₆ O ₂ | | 4.272 | | | |
| Methyl 15-methylhexadecanoate | C ₁₈ H ₃₆ O ₂ | 4.464 | | 4.142 | 1.048 | |
| Methyl oleate | C ₁₉ H ₃₆ O ₂ | 12.688 | | 31.716 | 7.188 | 0.900 |
| Methyl octadecanoate | C ₁₉ H ₃₈ O ₂ | 4.260 | 7.720 | 4.784 | 4.192 | 11.392 |
| Methyl -7-octadecenoate | C ₁₉ H ₃₆ O ₂ | 0.228 | | 15.858 | 7.188 | 12.940 |
| Methyl -9-octadecenoate | C ₁₉ H ₃₆ O ₂ | | | | 14.376 | |
| Methyl linoleate | C ₁₉ H ₃₆ O ₂ | | 26.588 | | 17.752 | |
| Methyl-8,11-Octadecadienote | C ₁₉ H ₃₆ O ₂ | | 13.294 | | 8.876 | |
| Methyl-10,13-Octadecadienote | C ₁₉ H ₃₆ O ₂ | | 13.294 | | | |
| Methyl-9,11-Octadecadienote | C ₁₉ H ₃₆ O ₂ | | | | 8.876 | |
| Methyl-9,12-Octadecadienote | C ₁₉ H ₃₆ O ₂ | | 13.294 | | | |
| Methyl 7-octadecenoate | C ₁₉ H ₃₆ O ₂ | 4.464 | | | | |
| Methyl 8-octadecenoate | C ₁₉ H ₃₆ O ₂ | 12.688 | | 15.858 | 7.188 | 25.880 |
| Methyl olaidate | C ₁₉ H ₃₆ O ₂ | 4.260 | 0.112 | | | 25.880 |
| Methyl -6-octadecenoate | C ₁₉ H ₃₆ O ₂ | | | 15.858 | | |
| Methyl 16-methylheptadecanoate | C ₁₉ H ₃₈ O ₂ | | 1.930 | | | 2.848 |
| Methyl hydrosterculate | C ₂₀ H ₃₈ O ₂ | | | | | 0.900 |
| Methyl eicosanoate | C ₂₁ H ₄₂ O ₂ | | | | | 0.412 |
| Total | | 94.76 | 98.672 | 100.00 | 89.624 | 99.08 |

Appendix VA2: Efficacy of bulk CaO catalyst for transesterification of *Jatropha* oil

| Transesterification at 60 ⁰ C (min) | | | | | | |
|--|--|-------------|--------------|----------|-------------|-------------|
| Non- methyl esters | MF | 50 | 60 | 70 | 80 | 90 |
| Glycerol-2-monoleate | C ₂₁ H ₃₄ O ₄ | 0.266 | 0.234 | | 0.302 | |
| Glycerol-1-monoleate | C ₂₁ H ₄₀ O ₄ | 0.492 | | | 0.604 | |
| Propylene glycol monoleate | C ₂₁ H ₃₄ O ₄ | | 0.234 | | | |
| Linoleic acid chloride | C ₁₈ H ₃₁ ClO | 0.266 | 0.234 | | | |
| 6-Octadecenoic acid | C ₁₈ H ₃₄ O ₂ | 0.492 | | | | |
| Linoleic acid | C ₁₈ H ₃₂ O ₂ | | 0.234 | | | 0.14 |
| Tetradecanoic acid | C ₁₄ H ₂₈ O ₂ | 0.29 | | | | |
| 9-Octadecenoic acid | C ₁₆ H ₃₀ O ₂ | 0.492 | | | | |
| Palmitic acid | C ₁₆ H ₃₂ O ₂ | 0.58 | | | | |
| Oleic acid | C ₁₈ H ₃₄ O ₂ | 0.492 | | | | |
| Octadecanoic acid | C ₁₈ H ₃₆ O ₂ | 0.29 | | | | |
| Eicosanoic acid | C ₂₀ H ₄₀ O ₂ | 0.29 | | | | |
| 13-Docosenoic acid | C ₂₂ H ₄₀ O ₂ | 0.492 | | | | |
| Methyl ricinoleate | C ₁₉ H ₃₆ O ₃ | | 0.158 | | | 0.78 |
| 7-Tetradecenal | C ₁₄ H ₂₆ O | | 0.234 | | | |
| Oleic acid chloride | C ₁₈ H ₃₃ ClO | | | | 0.302 | |
| 9-Hexadecenal | C ₁₆ H ₃₀ O | 0.266 | | | | |
| 9-Octadecenal | C ₁₈ H ₃₄ O | 0.266 | | | | |
| 9-Octadecenoate | C ₁₇ H ₃₂ O ₂ | 0.266 | | | 0.302 | |
| Total | | 5.24 | 1.328 | 0 | 1.51 | 0.92 |

Appendix VB1: Efficacy of CaO/MgO catalyst for transesterification of *Jatropha* oil

| Methyl ester composition | MF | Transesterification at 60 ⁰ C (min) | | | | |
|--|--|--|--------|--------|--------|--------|
| | | 50 | 60 | 70 | 80 | 90 |
| Methyl 10-undecenoate | C ₁₂ H ₂₂ O ₂ | 0.228 | 0.300 | 0.422 | 0.403 | |
| Methyl laurate | C ₁₃ H ₂₆ O ₂ | | | | | 1.296 |
| Methyl tridecanoate | C ₁₄ H ₂₈ O ₂ | | | | | 0.324 |
| Methyl myristate | C ₁₅ H ₃₀ O ₂ | | | | | 0.864 |
| Methyl palmitoleate | C ₁₇ H ₃₂ O ₂ | 0.588 | 0.682 | 0.880 | 0.884 | 0.548 |
| Methyl-11-hexadecenoate | C ₁₇ H ₃₂ O ₂ | 0.294 | | 0.440 | | 0.548 |
| Methyl hexadecanoate | C ₁₇ H ₃₄ O ₂ | 12.003 | 12.480 | 12.822 | 12.960 | 11.904 |
| Methyl 14-methylpentadecanoate | C ₁₇ H ₃₄ O ₂ | 8.002 | 8.320 | 8.548 | 8.640 | 7.936 |
| Methyl -7-hexadecenoate | C ₁₇ H ₃₂ O ₂ | 0.228 | 0.341 | 0.440 | 0.403 | |
| Methyl 15-methylhexadecanoate | C ₁₈ H ₃₆ O ₂ | | | | 0.132 | |
| Methyl heptadecanoate | C ₁₈ H ₃₆ O ₂ | | | | 0.264 | |
| Methyl 8-(2-hexylcyclopropyl) ocatanoate | C ₁₈ H ₃₄ O ₂ | | 0.300 | | 0.442 | |
| Methyl 9-octadecenoate | C ₁₉ H ₃₆ O ₂ | 14.97 | 13.040 | 12.050 | 11.778 | 12.948 |
| Methyl 7-octadecenoate | C ₁₉ H ₃₆ O ₂ | | 13.040 | | 12.220 | 12.948 |
| Methyl trans-8-octadecenoate | C ₁₉ H ₃₆ O ₂ | | | | 11.778 | |
| Methyl 8-octadecenoate | C ₁₉ H ₃₆ O ₂ | | 13.040 | | | 12.948 |
| Methyl trans-9-octadecanoate | C ₁₉ H ₃₆ O ₂ | | | 12.050 | | |
| Methyl cis-9-octadecenoate | C ₁₉ H ₃₆ O ₂ | | 26.080 | | | |
| Methyl cis-octadec-11-enoate | C ₁₉ H ₃₆ O ₂ | | | 12.050 | | |
| Methyl-12-octadecenoate | C ₁₉ H ₃₆ O ₂ | 12.97 | | 12.050 | | |
| Methyl n-octadecanoate | C ₁₉ H ₃₈ O ₂ | 8.312 | 8.552 | 9.192 | 9.048 | 9.072 |

| | | | | | | |
|--------------------------------|--|---------------|---------------|---------------|---------------|---------------|
| Methyl 16-methylheptadecanoate | C ₁₉ H ₃₈ O ₂ | 2.078 | 2.138 | 2.298 | 2.262 | 2.268 |
| Methyl oleate | C ₁₉ H ₃₆ O ₂ | 26.238 | 0.341 | 12.490 | 23.998 | 26.180 |
| Methyl dihydrostercolate | C ₂₀ H ₃₈ O ₂ | | 0.341 | | | |
| Methyl-10-nonadecenoate | C ₂₀ H ₃₈ O ₂ | 0.298 | | | | |
| Methyl eicosanoate | C ₂₁ H ₄₂ O ₂ | | | | 0.264 | |
| Methyl tricosanoate | C ₂₄ H ₄₈ O ₂ | | | | 0.112 | |
| Methyl pentacosanoate | C ₂₆ H ₅₂ O ₂ | | | | 0.112 | |
| ethyl-9-hexadecenoate | C ₁₈ H ₃₄ O ₂ | 0.240 | | 0.296 | 0.300 | |
| Ethyl-9-octadecenoate | C ₂₀ H ₃₈ O ₂ | 0.480 | | 0.596 | | |
| Ethyl Oleate | C ₂₀ H ₃₈ O ₂ | 0.480 | | 0.596 | 0.600 | |
| Total | | 98.416 | 98.995 | 98.312 | 98.134 | 100.00 |

Appendix VB2: Efficacy of CaO/MgO catalyst for transesterification of *Jatropha* oil

| Transesterification at 60⁰C (min) | | | | | | |
|---|---|--------------|------------|--------------|--------------|-----------|
| Non- methyl esters | MF | 50 | 60 | 70 | 80 | 90 |
| Methyl ricinoleate | C ₁₉ H ₃₆ O ₃ | 0.456 | 0.6 | 0.844 | | |
| Methyl-12-hydroxy-9-octadecenoate | C ₁₈ H ₃₆ O ₃ | 0.228 | 0.3 | 0.422 | | |
| Supraene | C ₃₀ H ₅₀ | 0.9 | | 1.1 | 1.13 | |
| Ricinolic acid | C ₁₈ H ₃₄ O ₃ | | | 0.422 | | |
| 9-Hexadecenal | C ₁₆ H ₃₀ O | | | | 0.3 | |
| 2,3-Bis-9-octadecenoyloxypropyl-9-octadecenoate | C ₅₇ H ₁₀₄ O ₆ | | | | 0.3 | |
| Methyl-10-hydroxyoctadecanoate | C ₁₉ H ₃₈ O ₃ | | | | 0.224 | |
| Methyl-10-hydroxyl-11-dodecenoate | C ₁₃ H ₂₄ O ₃ | | | | 0.112 | |
| Total | | 1.584 | 0.9 | 2.788 | 2.066 | 0 |

Appendix VC1: Efficacy of non-supported super base CaO catalyst for transesterification of *Jatropha* oil

| Transesterification at 60⁰C (min) | | | | | | |
|---|--|-----------|-----------|-----------|-----------|-----------|
| Methyl ester composition | MF | 20 | 30 | 40 | 50 | 60 |
| Methyl decanoate | C ₁₁ H ₂₂ O ₂ | 5.496 | 4.036 | 5.764 | 8.752 | 6.89 |
| methyl tridecanoate | C ₁₄ H ₂₈ O ₂ | 5.496 | 7.14 | 5.764 | 8.752 | 6.89 |
| Pentanoic acid 10-undecenyl ester | C ₁₆ H ₃₂ O ₂ | 0.972 | | 1.07 | | |
| Methyl-9,12-hexadecadienoate | C ₁₇ H ₃₀ O ₂ | 9.576 | | | | |
| Methyl hexadecanoate | C ₁₇ H ₃₂ O ₂ | 5.496 | 4.036 | 5.764 | 5.86 | 4.712 |
| Methyl 14-methylpentadecanoate | C ₁₇ H ₃₄ O ₂ | 5.496 | 7.14 | 5.764 | 8.752 | 6.89 |
| Methyl 15-methylhexadecanoate | C ₁₈ H ₃₆ O ₂ | 8.468 | 7.352 | 5.764 | 8.752 | 6.89 |
| Methyl linoelaidate | C ₁₉ H ₃₄ O ₂ | 19.152 | 8.64 | 9.76 | 7.986 | 12.08 |
| Methyl-5-octadecenoate | C ₁₉ H ₃₆ O ₂ | | 0.932 | | | |

| | | | | | | |
|---|--|---------------|---------------|---------------|---------------|---------------|
| methyl-6-Octadecenoate | C ₁₉ H ₃₆ O ₂ | | 5.878 | 3.958 | | |
| Methyl elaide | C ₁₉ H ₃₆ O ₂ | | 5.878 | | | |
| Methyl Oleate | C ₁₉ H ₃₆ O ₂ | | 5.878 | 3.958 | | 4.822 |
| Methyl 7-octadecenoate | C ₁₉ H ₃₆ O ₂ | | 5.878 | 3.958 | | |
| Methyl-8-octadecenoate | C ₁₉ H ₃₆ O ₂ | | 5.878 | 3.958 | | |
| Methyl-9-octadecenoate | C ₁₉ H ₃₆ O ₂ | | | 3.958 | | 0.744 |
| methyl octadecanoate | C ₁₉ H ₃₈ O ₂ | 2.832 | 3.104 | 12.488 | 2.892 | 2.176 |
| Methyl-10 -octadecenoate | C ₁₉ H ₃₈ O ₂ | | | | | 4.822 |
| Methyl-11-octadecynoate | C ₁₉ H ₃₄ O ₂ | | | 4.88 | | |
| Methyl-11-octadecenoate | C ₁₉ H ₃₆ O ₂ | 0.68 | 0.932 | 0.696 | 0.962 | 5.56 |
| Methyl-16-octadecenoate | C ₁₉ H ₃₆ O ₂ | | | | | 4.822 |
| Methyl-15-Octadecenoate | C ₁₉ H ₃₆ O ₂ | | | | | 4.822 |
| Methyl-13,16-octadecadienoate | C ₁₉ H ₃₄ O ₂ | | 4.32 | 0.696 | 0.962 | |
| Methyl-5-(undecyclopropyl) pentaanoate | C ₂₀ H ₃₈ O ₂ | 0.68 | 0.932 | 0.696 | 0.962 | 0.744 |
| Methyl-11,14-icosadienoate | C ₂₁ H ₃₈ O ₂ | 9.576 | 4.32 | 4.88 | | 6.044 |
| Methyl eicosanoate | C ₂₁ H ₄₂ O ₂ | 2.972 | 0.212 | 0.154 | 0.464 | 0.34 |
| Methyl docosanoate | C ₂₃ H ₄₆ O ₂ | 2.972 | 0.212 | 0.154 | 0.232 | 0.168 |
| Methyl henicosanoate | C ₂₂ H ₄₄ O ₂ | 0.14 | 0.212 | 3.274 | 0.232 | 0.168 |
| Methyl 12-(2-octycyclopropyl) dodecanoate | C ₂₄ H ₄₆ O ₂ | 0.68 | | | | |
| Methyl hexacosanoate | C ₂₇ H ₅₄ O ₂ | | 3.104 | | | |
| methyl heptacosanoate | C ₂₈ H ₅₆ O ₂ | 2.972 | 0.212 | 0.154 | 0.232 | 0.168 |
| Methyl-15-tetracosanoate | C ₂₅ H ₄₈ O ₂ | 0.68 | 0.932 | 0.696 | 0.962 | 0.744 |
| Methyl triacontanoate | C ₃₁ H ₆₂ O ₂ | | | 0.154 | | |
| Total | | 84.336 | 87.158 | 88.362 | 56.754 | 80.496 |

Appendix VC2: Efficacy of non-supported super base CaO catalyst for transesterification of *Jatropha* oil

| Non-methyl esters | MF | Transesterification at 60 ^o C (min) | | | | |
|---------------------------|--|--|------|------|-------|-------|
| | | 20 | 30 | 40 | 50 | 60 |
| 9,12-Octadecadien-1-ol | C ₁₈ H ₃₀ O | 9.576 | | | | 6.044 |
| 2-Octadecadien-1-ol | C ₁₈ H ₃₆ O | 0.972 | | | | |
| 10-Pentadecen-1-ol | C ₁₅ H ₃₀ O | | | | 1.376 | |
| 10-Undecyn-1-ol | C ₁₁ H ₂₂ O | | | | 9.356 | |
| 11-Tridecen-1-ol | C ₁₃ H ₂₆ O | | | | | 1.114 |
| 2-Dodecyl-1,3-propanediol | C ₁₅ H ₃₂ O ₂ | | 1.24 | 1.07 | | 1.114 |
| Tetradecen-1-ol acetate | C ₁₆ H ₃₀ O ₂ | | 1.24 | | | |

| | | | | | | |
|---------------------------------------|--|---------------|---------------|--------------|--------------|--------------|
| Linoleic acid chloride | C ₁₈ H ₃₁ ClO | | 4.32 | 4.88 | | 6.044 |
| 3,3-dimethyl-2-hexone | C ₈ H ₁₆ O | 0.306 | 0.28 | 0.36 | 0.692 | 0.218 |
| Methyl isopropyl ketone | C ₅ H ₁₀ O | 0.306 | 0.28 | | 0.692 | |
| 9-Octadenal | C ₁₈ H ₃₄ O | 0.972 | 1.24 | 1.07 | 1.376 | 1.114 |
| 3-Butyl propyl ether | C ₇ H ₁₄ O | 0.306 | 0.28 | 0.36 | 0.692 | 0.218 |
| Acetic acid ally ester | C ₅ H ₈ O ₂ | 0.306 | 0.28 | 0.36 | | 0.218 |
| Methyl butanone | C ₅ H ₁₀ O | | | 0.36 | | 0.218 |
| 1-Isopropoxyacetne | C ₆ H ₁₂ O ₂ | 0.306 | | | 0.692 | |
| 4-Hydroxy-5-methyl-3-propy-2-hexanone | C ₁₀ H ₂₀ O | | | | 0.692 | |
| Ally-3-oxobutanoate | C ₇ H ₁₀ O ₃ | | 0.28 | 0.36 | | |
| Oleic acid | C ₁₈ H ₃₄ O ₂ | 1.652 | 2.172 | 1.77 | 2.338 | 1.854 |
| 9-Octadecanoic acid | C ₁₈ H ₃₄ O ₂ | | | | | |
| Docosenoic acid | C ₂₂ H ₄₂ O ₂ | 0.972 | 1.24 | 1.07 | | |
| 1,3-Docosenoic acid | C ₂₂ H ₄₂ O ₂ | | | | 1.376 | 1.114 |
| 4-Methyl-1-octene | C ₉ H ₁₈ | | | | | 0.22 |
| 1,6,11-Dodecatriene | C ₁₂ H ₂₀ | | | | 7.986 | |
| 1,3,11-Dodecatriene | C ₁₂ H ₂₀ | | | | 7.986 | |
| 13-Tetradecatriene | C ₁₄ H ₂₄ | | | | 7.986 | |
| Total non-methyl esters | | 15.674 | 12.852 | 11.66 | 43.24 | 19.49 |

Appendix VD1: Efficacy of alumina supported super base CaO Catalyst for transesterification of *Jatropha* oil

| Methyl esters | MF | Transesterification at 60°C |
|---------------|----|-----------------------------|
|---------------|----|-----------------------------|

| | | 20 | 30 | 40 | 50 | 60 |
|--|--|--------------|--------------|--------------|-------------|--------------|
| Methyl-4-decanoate | C ₁₁ H ₂₀ O ₂ | 0.236 | | | | |
| Methyl decanoate | C ₁₁ H ₂₂ O ₂ | 3.612 | 4.666 | 5.314 | 3.586 | 3.444 |
| Methyl tridecanoate | C ₁₄ H ₂₈ O ₂ | 3.612 | 3.278 | 3.816 | 3.586 | 3.444 |
| Methyl palmitoleate | C ₁₇ H ₃₂ O ₂ | | 0.188 | 0.254 | 0.254 | |
| Methyl hexadecanoate | C ₁₇ H ₃₄ O ₂ | 3.612 | 3.278 | 3.816 | 3.586 | 3.444 |
| Methyl -7-hexadecenoate | C ₁₇ H ₃₄ O ₂ | 0.236 | | 0.254 | 0.254 | |
| Methyl 14-methylpentadecanoate | C ₁₇ H ₃₄ O ₂ | 3.612 | 3.278 | 3.816 | 3.586 | 4.86 |
| Methyl 15-methylhexadecanoate | C ₁₈ H ₃₆ O ₂ | 5.108 | 4.666 | 5.314 | 5.094 | 4.86 |
| Methyl 8-(2-hexylcyclopropyl) octanoate* | C ₁₈ H ₃₄ O ₂ | | 0.188 | | 0.254 | |
| Methyl 9-octadecenoate | C ₁₉ H ₃₆ O ₂ | | 12.964 | | | |
| Methyl-6-octadecenoate | C ₁₉ H ₃₆ O ₂ | 0.236 | | 0.254 | 0.254 | |
| Methyl cis-6-octadecenoate | C ₁₉ H ₃₆ O ₂ | | 0.188 | | | 0.168 |
| Methyl 7-octadecenoate | C ₁₉ H ₃₆ O ₂ | | 0.188 | | | 0.168 |
| Methyl elaidate | C ₁₉ H ₃₆ O ₂ | 0.236 | | | | |
| Methyl oleate | C ₁₉ H ₃₆ O ₂ | 13.972 | 12.964 | 13.768 | 13.612 | 13.896 |
| Methyl n-octadecanoate | C ₁₉ H ₃₈ O ₂ | 1.496 | 1.388 | 1.498 | 3.016 | 1.416 |
| Methyl-10 -octadecenoate | C ₁₉ H ₃₈ O ₂ | 13.972 | | 14.022 | 13.612 | 14.064 |
| Methyl-11 -octadecenoate | C ₁₉ H ₃₆ O ₂ | 0.236 | 0.188 | 0.254 | 0.254 | 0.168 |
| Methyl cis-octadec-11 enoate | C ₁₉ H ₃₆ O ₂ | 13.972 | 12.964 | 13.768 | 13.612 | 13.896 |
| Methyl-15 -octadecenoate | C ₁₉ H ₃₆ O ₂ | 13.972 | 12.964 | 13.768 | 13.612 | 13.896 |
| Methyl-16 -octadecenoate | C ₁₉ H ₃₆ O ₂ | 13.972 | 12.964 | 13.768 | 13.612 | 13.896 |
| Methyl heneicosanoate | C ₂₂ H ₄₄ O ₂ | 1.496 | 1.388 | 1.498 | 1.508 | 1.416 |
| Methyl-13 -docosenoate | C ₂₃ H ₄₄ O ₂ | | | | | 0.168 |
| Methyl docosenoate | C ₂₃ H ₄₆ O ₂ | 1.496 | 1.388 | 1.498 | 1.508 | 1.416 |
| Methyl hexacosanoate | C ₂₇ H ₅₄ O ₂ | 1.496 | | | | |
| Total methyl esters | | 96.58 | 89.09 | 96.68 | 94.8 | 94.62 |

Appendix V D2: Efficacy of alumina supported super base CaO catalyst for transesterification of *Jatropha*oil

| Non-methyl esters | MF | Transesterification at 60 ^o C | | | | |
|--------------------------------|--|--|--------------|-------------|-------------|-------------|
| | | 20 | 30 | 40 | 50 | 60 |
| Glycerol-2-monoleate | C ₂₁ H ₄₀ O ₄ | 0.686 | | 0.642 | 1.042 | |
| 9,12-Octadecadien-1-ol | C ₁₈ H ₃₄ O | 0.686 | | | | |
| 13-tetradec-11-yn-1-ol | C ₁₄ H ₂₄ O | 0.686 | | | | |
| Cyclododecene epoxide | C ₁₂ H ₂₂ O | | 2.182 | 0.642 | 1.042 | 2.152 |
| 13-tetradecanal | C ₁₄ H ₂₆ O | | 2.182 | | | |
| 7-tetradecanal | C ₁₄ H ₂₆ O | 0.686 | 2.182 | 0.642 | 1.042 | 1.076 |
| 9-hexadecenal | C ₁₆ H ₃₀ O | | 2.182 | | 1.042 | 1.076 |
| 1,2-15,16-Diepoxihexadecane | C ₁₆ H ₃₀ O ₂ | | | 0.642 | | |
| Linoleic acid chloride | C ₁₈ H ₁₃ ClO | 0.686 | 2.182 | 0.642 | 1.042 | 1.076 |
| Total non-methyl esters | | 3.43 | 10.91 | 3.21 | 5.21 | 5.38 |

Appendix VE1: Efficacy of %K impregnated CaO/MgO catalyst for transesterification of *Jatropha*oil

| Methyl ester composition | MF | Transesterification at 60 ^o C (min) | | | | |
|--|--|--|--------|--------|-------|--------|
| | | 20 | 30 | 40 | 50 | 60 |
| Acetic acid ally ester | C ₅ H ₈ O ₂ | 0.594 | | 0.37 | 0.582 | 0.734 |
| Methyl decanoate | C ₁₁ H ₂₂ O ₂ | 4.258 | 5.104 | 4.666 | 6.3 | 6.022 |
| methyl tridecanoate | C ₁₄ H ₂₈ O ₂ | 4.258 | 5 | 4.666 | 6.3 | 6.022 |
| Pentanoic acid 10-undecenyl ester | C ₁₆ H ₃₂ O ₂ | | 0.948 | | | |
| Methyl-7,10-hexadecadienoate | C ₁₇ H ₃₀ O ₂ | 12.296 | 10.142 | | | |
| Methyl-9,12-hexadecadienoate | C ₁₇ H ₃₀ O ₂ | 12.296 | 10.142 | 11.094 | 7.99 | 8.572 |
| Methyl hexadecanoate | C ₁₇ H ₃₂ O ₂ | 4.258 | 5 | 4.666 | 6.3 | 6.022 |
| Methyl 14-methylpentadecanoate | C ₁₇ H ₃₄ O ₂ | 4.258 | 5 | 4.666 | 6.3 | 6.022 |
| Methyl 15-methylhexadecanoate | C ₁₈ H ₃₆ O ₂ | 6.272 | 7.626 | 7.228 | 9.628 | 9.198 |
| Methyl linoelaidate | C ₁₉ H ₃₄ O ₂ | 24.592 | 20.284 | 22.188 | 15.98 | 17.144 |
| methyl octadecanoate | C ₁₉ H ₃₈ O ₂ | 1.914 | 2.626 | 2.476 | 3.328 | 3.072 |
| Methyl-11-octadecenoate | C ₁₉ H ₃₆ O ₂ | 0.276 | 0.424 | 0.394 | 0.522 | 0.454 |
| Methyl-5-(undecyclopropyl) pentaanoate | C ₂₀ H ₃₈ O ₂ | 0.276 | 0.424 | 0.394 | 0.522 | 0.454 |
| Methyl-11,14-icosadienoate | C ₂₁ H ₃₈ O ₂ | 12.296 | 10.142 | 11.094 | 7.99 | 8.572 |
| Methyl eicosanoate | C ₂₁ H ₄₂ O ₂ | 1.914 | 2.73 | 2.572 | 3.57 | 3.175 |
| Methyl hencosanoate | C ₂₂ H ₄₄ O ₂ | | 2.73 | 0.096 | 0.126 | 0.104 |
| Methyl-13-docosenoate | C ₂₃ H ₄₄ O ₂ | | 0.424 | 0.394 | | |

| | | | | | | |
|--|--|---------------|---------------|---------------|---------------|---------------|
| Methyl docosanoate | C ₂₃ H ₄₆ O ₂ | 1.914 | 2.73 | 2.572 | 3.454 | 3.176 |
| Methyl 12-(2-octacyclopropyl dodecanoate | C ₂₄ H ₄₆ O ₂ | 0.276 | 0.424 | | 0.522 | 0.454 |
| Hexyl-9-octadecenoate | C ₂₄ H ₄₆ O ₂ | 0.66 | | 0.394 | | |
| Methyl-15-tetracosanoate | C ₂₅ H ₄₈ O ₂ | 0.276 | | | 0.522 | 0.454 |
| methyl heptacosanoate | C ₂₈ H ₅₆ O ₂ | 1.914 | 0.104 | 2.572 | 3.454 | 3.176 |
| Total | | 94.794 | 92.004 | 82.502 | 83.392 | 82.824 |

Appendix VE2: Efficacy of %K impregnated CaO/MgO Catalyst

| Non-methyl esters | MF | 20 | 30 | 40 | 50 | 60 |
|--|--|--------------|--------------|---------------|---------------|---------------|
| 2-Octadecadien-1-ol | C ₁₈ H ₃₆ O | | 0.948 | 0.904 | | 1.042 |
| 2-Dodecyl-1,3-propanediol | C ₁₅ H ₃₂ O ₂ | 0.66 | | 0.904 | 1.152 | 1.042 |
| Tetradecen-1-ol acetate | C ₁₆ H ₃₀ O ₂ | 0.66 | | | | |
| 11-Tridecen-1-ol | C ₁₃ H ₂₆ O | | | | 1.152 | |
| Linoleic acid chloride | C ₁₈ H ₃₁ ClO | | | 11.094 | | |
| 3,3-dimethyl-2-hexanone | C ₈ H ₁₆ O | 0.594 | 0.758 | 0.37 | 0.582 | 0.734 |
| Methyl isopropyl ketone | C ₅ H ₁₀ O | 0.594 | 0.758 | 0.37 | 0.582 | 0.734 |
| 3-Butenyl propyl ether | C ₇ H ₁₄ O | 0.594 | 0.758 | 0.37 | 0.582 | 0.734 |
| Methyl propyl ketone | C ₅ H ₁₀ O | 0.594 | | | 0.582 | |
| 4-Hydroxy-5-methyl-3-propyl-2-hexanone | C ₁₀ H ₂₀ O | | 0.758 | | | |
| Ally-3-oxobutanoate | C ₇ H ₁₀ O ₃ | | | 0.37 | | 0.734 |
| Oleic acid | C ₁₈ H ₃₄ O ₂ | 0.936 | 1.372 | 1.342 | 1.674 | 1.496 |
| 9-Octadecenal | C ₁₈ H ₃₄ O | 0.66 | 0.948 | 0.904 | 1.152 | 1.042 |
| 2-Tridecenal | C ₁₃ H ₂₄ O | | | 0.904 | 1.152 | |
| 9-Octadecanoic acid | C ₁₈ H ₃₄ O ₂ | | 0.948 | | | |
| Docosenoic acid | C ₂₂ H ₄₂ O ₂ | | | | | 1.042 |
| 4-Methyl-1-octene | C ₉ H ₁₈ | | 0.758 | | | |
| 1,11,13-Octadecatriene | C ₁₈ H ₃₂ | | | | | 8.572 |
| 1,3,11-Dodecatriene | C ₁₂ H ₂₀ | | | | 7.99 | |
| Total non-methyl esters | | 5.292 | 8.006 | 17.532 | 16.500 | 17.176 |

Appendix VIA: Reaction temperatures profile

| Time (minutes) | Bulk CaO (°C) | Super Base CaO (°C) | Bulk MgO (°C) | CaO/MgO (°C) | K-CaO/MgO (°C) |
|-----------------------|----------------------|----------------------------|----------------------|---------------------|-----------------------|
| 0 | 32 | 27 | 26 | 25 | 27 |
| 10 | 40 | 38 | 38 | 33 | 34 |
| 20 | 54 | 52 | 53 | 47 | 42 |
| 30 | 67 | 58 | 57 | 58 | 55 |
| 40 | 70 | 61 | 61 | 65 | 57 |

| | | | | | |
|-----|----|----|----|----|----|
| 50 | 69 | 65 | 64 | 65 | 60 |
| 60 | 68 | 65 | 66 | 67 | 61 |
| 70 | 66 | 65 | 66 | 67 | 60 |
| 80 | 65 | 64 | 66 | 67 | 60 |
| 90 | 64 | 60 | 66 | 67 | 60 |
| 100 | 63 | 60 | 66 | 67 | 60 |

Appendix VIB: Biodiesel yields from the pilot plant

| Methyl ester composition | MF | Bulk CaO | Super CaO | MgO | CaO/MgO | K-CaO/MgO |
|--|--|----------|-----------|--------|---------|-----------|
| Methyl decanoate | C ₁₁ H ₂₂ O ₂ | | | | | 3.222 |
| Methyl 10-undecenoate | C ₁₂ H ₂₂ O ₂ | 0.552 | | | | |
| Methyl 11-dodecenoate | C ₁₃ H ₂₄ O ₂ | 0.276 | | | | |
| Methyl tridecanoate | C ₁₄ H ₂₈ O ₂ | | | | | 3.222 |
| Methyl palmitoleate | C ₁₇ H ₃₂ O ₂ | | | 0.416 | | |
| Methyl hexadecanoate | C ₁₇ H ₃₄ O ₂ | 12.456 | 12.786 | 4.844 | 5.272 | 3.222 |
| Methyl-7-hexadecenoate | C ₁₇ H ₃₄ O ₂ | | | | | 0.26 |
| Methyl 14-methylpentadecanoate | C ₁₇ H ₃₄ O ₂ | 8.304 | 8.524 | 4.844 | 7.01 | 5.064 |
| Methyl 15-methylhexadecanoate | C ₁₈ H ₃₆ O ₂ | | | 4.072 | 4.374 | 5.064 |
| Methyl 8-(2-hexylcyclopropyl) octanoate* | C ₁₈ H ₃₄ O ₂ | | | 0.208 | | 0.26 |
| Methyl -3-octadecenoate | C ₁₉ H ₃₆ O ₂ | | | | 15.624 | |
| Methyl 9-octadecenoate | C ₁₉ H ₃₆ O ₂ | | 12.742 | 14.872 | 15.624 | |
| Methyl-6-octadecenoate | C ₁₉ H ₃₆ O ₂ | 13.218 | 25.484 | 14.872 | | 0.26 |
| Methyl cis-octadec-11-enoate | C ₁₉ H ₃₆ O ₂ | | | | | 0.26 |
| Methyl 7-octadecenoate | C ₁₉ H ₃₆ O ₂ | 13.218 | 12.742 | 14.872 | | |
| Methyl 8-octadecenoate | C ₁₉ H ₃₆ O ₂ | 26.436 | 12.742 | 14.872 | 15.624 | |
| Methyl elaidate | C ₁₉ H ₃₆ O ₂ | 13.218 | | 0.208 | 31.248 | 14.586 |
| Methyl oleoate | C ₁₉ H ₃₆ O ₂ | | | 14.872 | | |
| Methyl-14-octadecenoate | C ₁₉ H ₃₆ O ₂ | | | | | 14.326 |
| Methyl-15-octadecenoate | C ₁₉ H ₃₆ O ₂ | | | | | 14.326 |
| Methyl-16-octadecenoate | C ₁₉ H ₃₆ O ₂ | | | | | 14.326 |
| Methyl n-octadecanoate | C ₁₉ H ₃₈ O ₂ | 7.776 | 9.536 | 4.95 | 5.214 | 1.842 |
| Methyl-10 -octadecenoate | C ₁₉ H ₃₈ O ₂ | | | 0.208 | | 14.326 |
| Methyl 16-methylheptadecanoate | C ₁₉ H ₃₈ O ₂ | 1.944 | 2.384 | 1.65 | | |
| Ricinoleic acid methyl ester | C ₁₉ H ₃₆ O ₃ | 0.552 | | | | |
| Methyl heneicosanoate | C ₂₂ H ₄₄ O ₂ | | | | | 1.842 |

| | | | | | | |
|--------------------|--|--------------|--------------|--------------|--------------|--------------|
| Methyl docosanoate | C ₂₃ H ₄₆ O ₂ | | | | | 1.842 |
| Total | | 97.95 | 96.94 | 95.76 | 99.99 | 98.25 |

Appendix VIC: Non-methyl esters in the products from the pilot plant

| Non-methyl esters | MF | Bulk CaO | Super Base CaO | MgO | CaO/MgO | K- CaO/MgO |
|--------------------------------|---|---------------------|-------------------------------|-------------|----------------|-----------------------|
| Glycerol-2-monooleate | C ₂₁ H ₄₀ O ₄ | 0.412 | 0.612 | | | |
| 9-Octadecenoate | C ₅₇ H ₁₀₄ O ₆ | 0.412 | 0.612 | | | |
| 9-Hexadecenal | C ₁₆ H ₃₀ O | 0.824 | 0.612 | 1.26 | | 0.35 |
| 9-Octadecenal | C ₁₈ H ₃₄ O | | 0.612 | 0.63 | | |
| n-Undecylenic aldehyde | C ₁₁ H ₂₀ O | | | | | 0.35 |
| Cyclododecane epoxide | C ₁₂ H ₂₂ O | | | | | 0.35 |
| 13-Tetradecenal | C ₁₄ H ₂₆ O | 0.412 | 0.612 | | | |
| 7-Tetradecenal | C ₁₄ H ₂₆ O | | | | | 0.35 |
| 9-Octadecenoic acid | C ₁₈ H ₃₄ O ₂ | | | 0.63 | | |
| 9-Hexadecenoic acid | C ₁₆ H ₃₀ O ₂ | | | 1.066 | | |
| Myristic acid | C ₁₄ H ₂₈ O ₂ | | | 0.218 | | |
| Eicosanoic acid | C ₂₀ H ₄₀ O ₂ | | | 0.218 | | |
| Linoleoyl chloride | C ₁₈ H ₃₁ ClO | | | | | 0.35 |
| n-Octadecenoic acid | C ₁₈ H ₃₄ O ₂ | | | 0.218 | | |
| Total non-methyl esters | | 2.060 | 3.06 | 4.24 | 0 | 1.75 |

Appendix VIIA1: Methyl esters content at 65⁰C transesterification

| Methyl ester composition | MF | Transesterification time (minutes)@ 65 ⁰ C | | | | |
|--------------------------|--|---|----|----|----|-------|
| | | 50 | 60 | 70 | 80 | 90 |
| methyl tridecanoate | C ₁₄ H ₂₈ O ₂ | | | | | 0.256 |

| | | | | | | | |
|--|--|--------------|---------------|--------------|--------------|---------------|-------|
| methyl myristic | C ₁₅ H ₃₀ O ₂ | | | | | | 0.128 |
| Methyl palmitoleate | C ₁₇ H ₃₂ O ₂ | | 0.324 | 0.576 | | | |
| Methyl-7 hexadecenoate | C ₁₇ H ₃₂ O ₂ | | 0.162 | 0.288 | | | |
| Methyl hexadecanoate | C ₁₇ H ₃₂ O ₂ | 7.96 | 5.982 | 15.888 | 8.04 | | |
| Methyl 14-methylpentadecanoate | C ₁₇ H ₃₄ O ₂ | 7.96 | 3.988 | 3.972 | 8.04 | 0.128 | |
| Methyl 15-methylhexadecanoate | C ₁₈ H ₃₆ O ₂ | 3.98 | | 0.248 | 6.236 | 0.128 | |
| Methyl 8-(2-hexylcyclopropyl) octanoate | C ₁₈ H ₃₄ O ₂ | | 0.162 | 0.288 | | | |
| methyl-6-Octadecanoate | C ₁₉ H ₃₆ O ₂ | | 11.276 | 31.458 | 26.956 | | |
| Methyl 7-octadecenoate | C ₁₉ H ₃₆ O ₂ | 11.67 | 5.638 | 10.486 | 13.478 | | |
| Methyl 8-octadecenoate | C ₁₉ H ₃₆ O ₂ | 11.67 | 5.638 | | 13.478 | | |
| Methyl 9-octadecenoate | C ₁₉ H ₃₆ O ₂ | 11.67 | 5.638 | | | | |
| methyl oleate | C ₁₉ H ₃₆ O ₂ | 11.67 | | | 13.478 | | |
| methyl octadecanoate | C ₁₉ H ₃₈ O ₂ | 8.48 | 3.684 | 7.008 | 8.864 | | |
| Methyl-10 -octadecenoate | C ₁₉ H ₃₈ O ₂ | | | 0.288 | | | |
| Methyl-11-octadecenoate | C ₁₉ H ₃₆ O ₂ | 11.67 | | | | | |
| Methyl 16-methylheptadecanoate | C ₁₉ H ₃₈ O ₂ | 2.12 | 2.456 | 4.672 | | | |
| methyl-14,17-Octadecadienoate | C ₁₉ H ₃₄ O ₂ | | | 10.486 | | 0.678 | |
| Methyl -10-nondecenoate | C ₂₀ H ₃₈ O ₂ | | 0.162 | | | | |
| methyl eicosanoate | C ₂₁ H ₄₂ O ₂ | | | 0.744 | | | |
| Methyl henicanoate | C ₂₂ H ₄₄ O ₂ | | | 0.248 | | | |
| methyl-8,11,14-docosatrienoate | C ₂₃ H ₄₀ O ₂ | | | | | 0.678 | |
| methyl-8,11,14-docosatrienoate | C ₂₃ H ₄₀ O ₂ | | | | | 0.678 | |
| 3-Hydropropyl-9-octadecenoate | C ₂₁ H ₄₀ O ₃ | | 0.484 | | | 8.932 | |
| methyl-8-[2-((2-ethylcyclopropyl) methyl)cyclopropyl]cyclopropyl octanoate | C ₂₂ H ₃₈ O ₂ | | | | | 0.678 | |
| Total | | 88.85 | 45.594 | 86.65 | 98.57 | 12.284 | |

Appendix VIIA2: Non-Methyl esters content at 65⁰C transesterification

| Non-methyl esters | MF | Transesterification time (minutes) at 65 ⁰ c (min) | | | | |
|-------------------|---|---|----|-------|-------|----|
| | | 50 | 60 | 70 | 80 | 90 |
| 9-octadecanoate | C ₅₇ H ₁₀₄ O ₆ | | | 2.458 | 0.286 | |

| | | | | | | |
|--|---|---------------|---------------|--------------|-------------|---------------|
| 9-Octadecanoic acid, 3-hydroxypropyl ester | C ₅₇ H ₁₀₄ O ₆ | 2.228 | | | | |
| 9-Octadecanoic acid, 1,2,3-propanetriyl ester | C ₅₇ H ₁₀₄ O ₆ | | 2.344 | | | |
| Glycerol-1,2-dipalmitate | C₃₅H₆₈O₅ | | 1.472 | 0.21 | | |
| Glycerin-1,3-dipalmitate | C ₃₅ H ₆₈ O ₅ | | 0.936 | | | |
| Glycerin-1,3—disterate | C ₃₉ H ₇₆ O ₅ | | 0.936 | | | |
| Glycerin-1-monoleate | C ₂₁ H ₄₀ O ₄ | | 1.86 | | | 8.932 |
| glycerol 2-monoleate | C ₂₁ H ₄₀ O ₄ | 2.228 | | | 0.286 | 8.932 |
| Glycerol-1-monopalmitate | C ₁₉ H ₃₈ O ₄ | | | 0.21 | | |
| Propyleneglycol monoleate | C ₂₁ H ₄₀ O ₃ | | | 2.458 | | |
| Palmitin beta monoglyceride | | | 0.568 | | | |
| palmitin-1,2-di,2-aminoethyl hydrogen phosphinate | C ₃₇ H ₇₄ NO ₈ P | | 0.936 | | | |
| 2-Hydroxyl-1-(hydroxymethyl) ethyl ester | C ₁₈ H ₃₆ O ₄ | | | 0.21 | | |
| 2-Hydroxycyclopentadecanote | C ₁₅ H ₂₈ O ₂ | | 3.82 | | | |
| Alpha-monolein | C ₂₁ H ₄₀ O ₄ | 2.228 | | | | |
| Alpha-monostearin | C ₂₁ H ₄₂ O ₄ | | | 0.21 | | |
| Ascorbic acid2,6-dihexadecanoate | C ₃₈ H ₆₈ O ₈ | | 1.174 | | | |
| Longiborneol | C ₁₅ H ₂₆ O | | 0.15 | | | 0.298 |
| 1,4-Methanoazulen-9-ol,decahydro-1,5,5,8a-tetramethyl | C ₁₅ H ₂₆ O | | 0.15 | | | |
| Globulol | C ₁₅ H ₂₆ O | | 0.15 | | | |
| 7,10-Hexadecadienal | C ₁₆ H ₂₈ O | | 1.02 | | | |
| 8,10-Hexadecadienal | C ₁₆ H ₂₈ O | | 1.22 | | | |
| 14-Methyl-8-hexadecenal | C ₁₇ H ₃₂ O | | 1.86 | 2.458 | | |
| 13-Octadecenal | C ₁₈ H ₃₄ O | | 3.72 | | | |
| 9-Hexadecenal | C ₁₆ H ₃₀ O | | 1.704 | | 0.286 | 3.336 |
| 9-Octadecenal | C ₁₈ H ₃₄ O | | 0.514 | 2.458 | 0.286 | 1.668 |
| 13-Octadecenal | C ₁₈ H ₃₄ O ₂ | | 3.72 | | | |
| 13-Tetradecenal | C ₁₄ H ₂₆ O ₂ | 2.228 | 1.22 | 2.458 | | |
| 1-Pentadecancarboxyl acid | C ₁₆ H ₃₂ O ₂ | | 2.348 | | | 0.596 |
| n-Pentadecanoic acid | C ₁₅ H ₃₀ O ₂ | | 1.174 | | | |
| n-Hexadecanoic acid | C ₁₆ H ₃₂ O ₂ | | 2.348 | | | |
| n-Octadecanoic acid | C ₁₈ H ₃₆ O ₂ | 3.738 | 6.158 | | | |
| 9-Octadecanoic acid | C ₁₈ H ₃₄ O ₂ | | 7.644 | | | |
| 6-Octadecenoic acid | C ₁₈ H ₃₄ O ₂ | | 3.822 | | | |
| Oleic acid | C ₁₈ H ₃₄ O ₂ | | 3.822 | | | 1.668 |
| Linoleic acid | C ₁₈ H ₃₂ O ₂ | | | | | 2.346 |
| 14-methyl-8-hexadecen-1-ol | C ₁₇ H ₃₀ O | | 1.22 | | | |
| 1,2-Cyclododecanediol | C ₁₂ H ₂₄ O ₂ | | | | | 8.932 |
| 9-Octadecanoyl chloride | C ₁₈ H ₃₃ ClO | | 0.484 | | 0.286 | |
| 9-Octadecenoyl chloride | C ₁₈ H ₃₃ ClO | | 0.484 | | | |
| Oleic acid chloride | C ₁₈ H ₃₃ ClO | | | | | 8.932 |
| Linoleic acid chloride | C ₁₈ H ₃₁ ClO | | | | | 0.678 |
| Hexadecanoyl glyceride | C ₁₉ H ₃₈ O ₄ | | | 0.21 | | |
| cis-9-Octadecen-1-ol | C ₁₈ H ₃₆ O | | | | | |
| Lupeyl acetate | C ₃₂ H ₅₂ O ₂ | | 0.15 | | | 8.296 |
| Thunbergol | C ₂₀ H ₃₄ O | | | | | 5.396 |
| Humulane-1,6-dien-3-ol | C ₁₅ H ₂₆ O | | 0.1 | | | 8.296 |
| Ergost-25-ene3,5,6,12-tetrol | C ₂₈ H ₄₈ O ₄ | | | | | 8.296 |
| Viridiflorol | C ₁₅ H ₂₆ O | | | | | 2.9 |
| Tricyclo[20,8,0,0(7,16)]triacontane,i(22),7(16) diepoxy- | C ₃₀ H ₅₂ O ₂ | | | | | 2.9 |
| Lupan-3-ol, acetate | C ₃₂ H ₅₄ O ₂ | | | | | 5.396 |
| 9-Octadecanoic acid, 2-(2-hydroxyethoxy) ethyl ester | C ₂₂ H ₄₀ O ₄ | | 1.246 | | | |
| n-Eiconoic acid | C ₂₀ H ₄₀ O ₂ | | | | | 0.596 |
| Total | | 14.878 | 54.406 | 13.34 | 1.43 | 88.394 |

Appendix VIIB1: Methyl esters at 60⁰C transesterification

| Methyl ester composition | MF | Transesterification time (minutes) at 60°C | | | | |
|---|--|--|--------------|--------------|---------------|--------------|
| | | 50 | 60 | 70 | 80 | 90 |
| Methyl palmitoleate | C ₁₇ H ₃₂ O ₂ | | | | 0.264 | 0.356 |
| Methyl-7 hexadecenoate | C ₁₇ H ₃₂ O ₂ | | | | 0.132 | 0.178 |
| Methyl hexadecanoate | C ₁₇ H ₃₂ O ₂ | 5.508 | 6.06 | 5.892 | 6.24 | 7.5 |
| Methyl 14-methylpentadecanoate | C ₁₇ H ₃₄ O ₂ | 5.508 | 6.06 | 5.892 | 6.24 | 7.5 |
| Methyl 15-methylhexadecanoate | C ₁₈ H ₃₆ O ₂ | 4.348 | 4.206 | 4.224 | 4.568 | 3.75 |
| Methyl 8-(2-hexylcyclopropyl) octanoate | C ₁₈ H ₃₄ O ₂ | | | | 0.132 | 0.178 |
| Methyl -3-octadecenoate | C ₁₉ H ₃₆ O ₂ | | | | 12.078 | 14.458 |
| methyl-6-Octadecenoate | C ₁₉ H ₃₆ O ₂ | | | 14.222 | | |
| Methyl 9-octadecenoate | C ₁₉ H ₃₆ O ₂ | 14.356 | 13.338 | | 12.078 | 14.458 |
| Methyl elaide | C ₁₉ H ₃₆ O ₂ | | | 14.222 | 24.156 | 28.916 |
| Methyl 7-octadecenoate | C ₁₉ H ₃₆ O ₂ | 14.356 | | 14.222 | | |
| methyl oleate | C ₁₉ H ₃₆ O ₂ | 28.712 | 13.338 | 28.444 | | |
| Methyl-12-octadecenoate | C ₁₉ H ₃₆ O ₂ | | 13.338 | | | |
| Methyl-15-octadecenoate | C ₁₉ H ₃₆ O ₂ | | 13.338 | | | |
| Methyl 8-octadecenoate | C ₁₉ H ₃₆ O ₂ | 14.356 | | | 12.078 | 14.458 |
| methyl octadecanoate | C ₁₉ H ₃₈ O ₂ | 6.376 | 4.704 | 5.112 | 4.344 | 6.448 |
| Methyl-11-octadecenoate | C ₁₉ H ₃₆ O ₂ | | 13.338 | | | |
| Methyl 16-methylheptadecanoate | C ₁₉ H ₃₈ O ₂ | | | | 1.448 | 1.612 |
| Methyl -10-nondecenoate | C ₂₀ H ₃₈ O ₂ | | | | 0.132 | 0.178 |
| 9-Hexadecenoate | C ₁₈ H ₃₈ O ₂ | | | | 0.416 | |
| 9-Octadecenoate | C ₂₀ H ₃₈ O ₂ | | | | 0.832 | |
| ethyl docosanoate | C ₂₄ H ₄₈ O ₂ | | | | 0.416 | |
| Total | | 93.52 | 87.72 | 92.23 | 85.554 | 99.99 |

Appendix VIIB2: Non methyl esters at 60⁰C Transesterification

| Non-methyl esters | Transesterification time (minutes) at 60 ⁰ C | | | | | |
|--|---|-------------|--------------|-------------|--------------|-------------|
| | MF | 50 | 60 | 70 | 80 | 90 |
| 9-octadecen-1-ol | C ₁₈ H ₃₆ O | | 2.122 | 1.296 | | |
| 6-Pentadecen-1-ol | C ₁₅ H ₃₀ O | 0.49 | | | | |
| 9-Hexadecenal | C ₁₆ H ₃₀ O | | 4.244 | 1.296 | 4.404 | |
| 9-Octadecnal | C ₁₈ H ₃₄ O | | | | 2.202 | |
| 13-Tetradecenal | C ₁₄ H ₂₆ O ₂ | | 2.122 | | | |
| Oleic acid | C ₁₈ H ₃₄ O ₂ | | | 1.296 | 2.202 | |
| 6- octadecenoic acid | C ₁₈ H ₃₄ O ₂ | | | | 2.202 | |
| Arachidic acid | C ₂₀ H ₄₀ O ₂ | | 0.334 | | 0.602 | |
| 1-Tridecancarboxylic acid | C ₁₄ H ₂₈ O ₂ | | | 0.258 | | |
| n-Pentadecanoic acid | C ₁₅ H ₃₀ O ₂ | | 0.334 | 0.258 | 0.602 | |
| 1-Pentadecancarboxyl acid | C ₁₆ H ₃₂ O ₂ | | 0.668 | 0.516 | 1.204 | |
| 9-Hexadecenoic acid | C ₁₆ H ₃₀ O ₂ | 0.49 | | 1.296 | | |
| n-octadecanoic acid | C ₁₈ H ₃₆ O ₂ | | 0.334 | | | |
| n-octadecanoic acid | C ₁₈ H ₃₆ O ₂ | | 0.334 | | | |
| n-Octadecenoic acid | C ₁₈ H ₃₄ O ₂ | | | 0.258 | 0.602 | |
| n-octadecanoic acid | C ₁₈ H ₃₆ O ₂ | | 0.334 | | | |
| Linoleic acid | C ₁₈ H ₃₂ O ₂ | 0.98 | 2.122 | 1.296 | | |
| Cypermethrin | C ₂₂ H ₁₉ Cl ₂ NO ₃ | 0.808 | | | | |
| Alpha Cypermethrin | C ₂₂ H ₁₉ Cl ₂ NO ₃ | 1.616 | | | | |
| Cyclopentacarboxylic acid, 3-(2,2-dichloroethyl-2,2-dimethyl,ethyl ester | C ₁₀ H ₁₄ Cl ₂ O ₂ | 0.808 | | | | |
| Methyl-3-(2,2-dichlorovinyl-2,2-dimethyl-(1-cyclopropane) carboxylate | C ₉ H ₁₂ Cl ₂ O ₃ | 0.808 | | | | |
| 9-Octadecyne | C ₁₈ H ₃₄ | 0.49 | | | | |
| Total | | 6.49 | 12.28 | 7.77 | 14.02 | 0.00 |

Appendix VIIC1: Methyl esters at 55⁰C transesterification

| Methyl ester composition | Transesterification time (minutes) at 55 ⁰ C | | | | | |
|---|---|-------|--------|-------|--------|-------|
| | MF | 50 | 60 | 70 | 80 | 90 |
| Methyl Octanoate | C ₉ H ₁₈ O ₂ | | 0.342 | | | |
| Methyl-4-decenoate | C ₁₁ H ₂₀ O ₂ | | | | | 0.25 |
| Methyl decanoate | C ₁₁ H ₂₂ O ₂ | 3.89 | 3.614 | 3.57 | | |
| methyl tridecanoate | C ₁₄ H ₂₈ O ₂ | 3.89 | 3.614 | 3.57 | 3.552 | 3.64 |
| Methyl palmitoleate | C ₁₇ H ₃₂ O ₂ | | 0.338 | 0.21 | | 0.25 |
| Methyl-7 hexadecenoate | C ₁₇ H ₃₂ O ₂ | 0.27 | 0.338 | 14.43 | | 0.25 |
| Methyl hexadecanoate | C ₁₇ H ₃₂ O ₂ | 3.89 | 3.614 | 3.57 | | 7.28 |
| Methyl 14-methylpentadecanoate | C ₁₇ H ₃₄ O ₂ | 5.52 | 3.956 | 5.16 | 5.094 | 3.64 |
| Methyl 15-methylhexadecanoate | C ₁₈ H ₃₆ O ₂ | 5.52 | 3.614 | 5.16 | 5.094 | 5.16 |
| Methyl 8-(2-hexylcyclopropyl) octanoate | C ₁₈ H ₃₄ O ₂ | 0.27 | | | | |
| methyl-6-Octadecenoate | C ₁₉ H ₃₆ O ₂ | 0.27 | 15.298 | 28.65 | 0.25 | 0.25 |
| Methyl 9-octadecenoate | C ₁₉ H ₃₆ O ₂ | | | | 0.5 | |
| Methyl elaide | C ₁₉ H ₃₆ O ₂ | | | 14.43 | | |
| methyl oleate | C ₁₉ H ₃₆ O ₂ | 14.21 | 14.96 | | 13.868 | |
| Methyl-15-octadecenoate | C ₁₉ H ₃₆ O ₂ | 14.21 | 14.96 | | 13.868 | 13.41 |
| methyl octadecanoate | C ₁₉ H ₃₈ O ₂ | 15.84 | | 1.59 | 8.646 | 3.04 |

| | | | | | | |
|--------------------------|--|---------------|---------------|--------------|--------------|--------------|
| Methyl-10 –octadecenoate | C ₁₉ H ₃₈ O ₂ | | 14.96 | | | 13.41 |
| Methyl-11-octadecenoate | C ₁₉ H ₃₆ O ₂ | 14.48 | 15.298 | 14.43 | 14.118 | 13.66 |
| Methyl-16-octadecenoate | C ₁₉ H ₃₆ O ₂ | 14.21 | | | 13.868 | 13.41 |
| methyl-14-Octadecenoate | C ₁₉ H ₃₄ O ₂ | | | | | 13.41 |
| Methyl -10-nondecenoate | C ₂₀ H ₃₈ O ₂ | | | | 13.868 | |
| Methyl docosanoate | C ₂₃ H ₄₆ O ₂ | 1.63 | | 1.59 | 1.542 | 1.52 |
| Methyl henicanoate | C ₂₂ H ₄₄ O ₂ | 1.63 | | 1.59 | 1.542 | 1.52 |
| Methyl-13-docosanoate | C ₂₃ H ₄₄ O ₂ | | 0.342 | | | |
| Methyl-15-tetracosanoate | C ₂₅ H ₄₈ O ₂ | 0.27 | 0.338 | | | |
| Total | | 100.00 | 95.586 | 97.97 | 95.81 | 94.08 |

Appendix VIIC2: Non-Methyl esters at 55⁰C transesterification

| Non-methyl esters | Transesterification time (minutes) at 55 ⁰ C | | | | | |
|------------------------|---|----|-------|-------|-------|-------|
| | MF | 50 | 60 | 70 | 80 | 90 |
| Glycerol 2-monoleate | C ₂₁ H ₄₀ O ₄ | | | | | 1.186 |
| 9-Octadecnal | C ₁₈ H ₃₄ O | | | | 0.25 | |
| 9-Hexadecenal | C ₁₆ H ₃₀ O | | | | | 1.186 |
| Decanhydrazide | C ₁₀ H ₂₂ N ₂ O | | 0.342 | | | |
| Octadecanohydrazide | C ₁₈ H ₃₈ N ₂ O | | 0.342 | | | |
| Linoleic acid chloride | C ₁₈ H ₃₁ ClO | | 0.746 | 0.406 | 0.786 | 1.186 |
| 10-undecenyl aldehyde | C ₁₁ H ₂₀ O | | 0.746 | 0.406 | 1.572 | |

| | | | | | |
|----------------------------|-------------------|-------------|--------------|--------------|-------------|
| Methyl-3,13-octadecadienol | $C_{19}H_{39}O$ | | | 0.786 | |
| Cyclododocene epoxide | $C_{12}H_{22}O_2$ | 0.746 | 0.406 | | 1.186 |
| 1,2-15,16-Diepoxyldecane | $C_{16}H_{30}O_2$ | 0.746 | | | |
| 7-Tetradecenal | $C_{16}H_{26}O$ | 0.746 | | | |
| 9-Tetradecenal | $C_{14}H_{26}O$ | | | 0.786 | |
| 9,17-Octadecadienal | $C_{18}H_{32}O$ | | 0.406 | | 1.186 |
| Total | | 0.00 | 4.414 | 1.624 | 4.18 |

Appendix VIID1: Methyl esters at 50⁰C transesterification

| Methyl ester composition | Transesterification time (minutes) at 50 ⁰ C | | | | | |
|--|---|-------|--------|-------|--------|-------|
| | MF | 50 | 60 | 70 | 80 | 90 |
| Methyl-4-methylpentanoate | C ₇ H ₁₄ O ₂ | | | | 1.34 | |
| Methyl-6-Methyl heptanoate | C ₉ H ₁₈ O ₂ | | | 1.97 | | |
| Methyl-4-decenoate | C ₁₁ H ₂₀ O ₂ | | | | 0.57 | |
| Methyl decanoate | C ₁₁ H ₂₂ O ₂ | 3.356 | 3.896 | 3.80 | 2.928 | 5.21 |
| methyl tridecanoate | C ₁₄ H ₂₈ O ₂ | 2.388 | 3.896 | 3.802 | 2.928 | 3.66 |
| Methyl -12-methyl tetradecanoate | C ₁₆ H ₃₂ O ₂ | | | | 1.34 | |
| methyl 11-cyclopentylundecaoate | C ₁₇ H ₃₂ O ₂ | | | | 1.34 | |
| Methyl palmitoleate | C ₁₇ H ₃₂ O ₂ | | 0.26 | | | |
| Methyl-7 hexadecenoate | C ₁₇ H ₃₂ O ₂ | | 14.514 | 4.32 | 15.572 | 14.56 |
| Methyl hexadecanoate | C ₁₇ H ₃₂ O ₂ | 2.388 | 3.896 | 1.832 | 2.928 | 3.66 |
| Methyl-9,12-hexadecadienoate | C ₁₇ H ₃₀ O ₂ | | | 8.3 | | |
| Methyl 14-methylpentadecanoate | C ₁₇ H ₃₄ O ₂ | 3.356 | 5.486 | 3.802 | 2.928 | 5.21 |
| Methyl 15-methylhexadecanoate | C ₁₈ H ₃₆ O ₂ | 3.356 | 5.486 | 4.644 | 2.928 | 3.66 |
| Methyl 8-(2-hexylcyclopropyl) octanoate | C ₁₈ H ₃₄ O ₂ | 0.138 | 0.26 | | | |
| Methyl-13,16-octadecadienoate | C ₁₉ H ₃₄ O ₂ | | | | 0.57 | |
| methyl-6-Octadecenoate | C ₁₉ H ₃₆ O ₂ | 0.138 | 28.508 | 4.32 | 15.572 | 29.35 |
| Methyl elaide | C ₁₉ H ₃₆ O ₂ | 8.91 | 14.514 | 4.32 | 15.002 | 14.56 |
| Methyl-5-octadecenoate | C ₁₉ H ₃₆ O ₂ | | | | | 0.23 |
| Methyl-15-octadecenoate | C ₁₉ H ₃₆ O ₂ | 8.91 | | | | |
| methyl octadecanoate | C ₁₉ H ₃₈ O ₂ | 0.968 | 1.59 | 0.842 | | 1.55 |
| Methyl-10 –octadecenoate | C ₁₉ H ₃₈ O ₂ | 9.048 | | 4.32 | | |
| Methyl-11-octadecenoate | C ₁₉ H ₃₆ O ₂ | 9.048 | 14.514 | 4.32 | 15.572 | 14.79 |
| Kemester9718 | C ₁₉ H ₃₈ O ₂ | | | | | |
| Methyl-16-octadecenoate | C ₁₉ H ₃₆ O ₂ | 8.91 | | | | |
| Methyl-9,12-octadecadienoate | C ₁₉ H ₃₄ O ₂ | | | 8.3 | | |
| Methyl linoleate | C ₁₉ H ₃₄ O ₂ | | | 16.6 | | |
| Methyl linoleaidate | C ₁₉ H ₃₄ O ₂ | | | 8.3 | | |
| Methyl -10-nondecenoate | C ₂₀ H ₃₈ O ₂ | | | | 15.002 | |
| Methyl-5(-2undecylcyclopropyl)pentanoate | C ₂₀ H ₃₈ O ₂ | | | | | 0.23 |
| methyl eicosanoate | C ₂₁ H ₄₂ O ₂ | | | 0.842 | 1.34 | |
| Methyl docosanoate | C ₂₃ H ₄₆ O ₂ | 0.968 | 1.59 | 0.842 | | 1.55 |
| Methyl hencosanoate | C ₂₂ H ₄₄ O ₂ | | 1.59 | 0.842 | | 1.55 |
| Methyl-15-tetracosanoate | C ₂₅ H ₄₈ O ₂ | 0.138 | | | | 0.23 |
| Methyl heptacosanoate | C ₂₈ H ₅₆ O ₂ | | | | 1.34 | |

| | | | | | |
|--------------|--------------|---------------|--------------|--------------|---------------|
| Total | 62.02 | 100.00 | 86.32 | 99.20 | 100.00 |
|--------------|--------------|---------------|--------------|--------------|---------------|

Appendix VIID2: Non-methyl esters of transesterification at 50°C

| Non-methyl esters | Transesterification time (minutes) at 50°C | | | | | |
|---|---|--------------|-------------|--------------|-------------|-------------|
| | MF | 50 | 60 | 70 min | 80 | 90 |
| Glycerol-1-monopalmitate | C ₁₉ H ₃₈ O ₄ | 1.322 | | | | |
| Hexacarbonohydrazide | C ₁₆ H ₃₄ N ₂ O | | | | 0.162 | |
| Hadrazine | C ₂ H ₆ N ₄ O | | | | 0.162 | |
| Ethanehydrazonic acid | C ₂ H ₆ N ₂ O | | | | 0.162 | |
| Hydroxypropanohydrazide | C ₃ H ₈ N ₂ O ₂ | | | | 0.162 | |
| Dioxygen | O ₂ | | | | 0.162 | |
| Diethyleneglycol | C ₄ H ₁₀ O ₃ | | | 10.936 | | |
| Methoxyethanol | C ₃ H ₈ O ₂ | | | 2.734 | | |
| Linoleic acid chloride | C ₁₈ H ₃₁ ClO | 5.076 | | | | |
| 1,12-Tridecadiene | C ₁₃ H ₂₄ | 5.076 | | | | |
| Epoxydodecane | C ₁₂ H ₂₂ O | 5.076 | | | | |
| 10-Undecenal aldehyde | C ₁₁ H ₂₀ O | 5.076 | | | | |
| 7-Tetradecenal | C ₁₄ H ₂₆ O | 5.076 | | | | |
| Vinyl stearyl ether | C ₂₀ H ₄₀ O | 1.198 | | | | |
| n-Decyl flouride | C ₁₀ H ₂₁ F | 1.198 | | | | |
| Octadecyl octadecanoate | C ₃₆ H ₇₂ O ₂ | 1.198 | | | | |
| n-1-Eicosanol | C ₂₀ H ₄₂ O | 1.198 | | | | |
| Palmitin, 1,2-di-,2-aminoethyl hydrogen phosphate | C ₃₇ H ₇₄ NO ₈ P | 2.52 | | | | |
| Palmitic acid beta monoglyceride | C ₁₉ H ₃₈ O ₄ | 1.322 | | | | |
| 2-Hydroxy-1-(dihydroxymethyl)ethyl pentadecanoate | C ₁₈ H ₃₆ O ₄ | 1.322 | | | | |
| 2,3-Dihydroxypropylpalmitate | C ₁₉ H ₃₈ O ₄ | 1.322 | | | | |
| Total non-methyl esters | | 37.98 | 0.00 | 13.67 | 0.81 | 0.00 |

Appendix VIIIE1: methyl esters of transesterification at 45⁰C

| Methyl ester composition | transesterificationtime (minutes) at45 ⁰ C | | | | |
|--------------------------------|---|-------|-------|--------|--------|
| | MF | 50 | 60 | 70 | 80 |
| Methyl-4-methyl pentanoate | C ₇ H ₁₄ O ₂ | 0.508 | | | |
| Methyl Octanoate | C ₉ H ₁₈ O ₂ | 0.508 | | | |
| Methyl-3-ethylhexanoate | C ₉ H ₁₈ O ₂ | 0.508 | | | |
| Methyl-4-decenote | C ₁₁ H ₂₀ O ₂ | 0.642 | | 0.208 | |
| Methyl decanoate | C ₁₁ H ₂₂ O ₂ | 2.874 | 4.93 | 3.566 | 3.566 |
| methyl tridecanoate | C ₁₄ H ₂₈ O ₂ | 2.874 | 3.5 | 3.566 | 3.566 |
| Methyl-12-methyl tetradecanote | C ₁₆ H ₃₂ O ₂ | 0.508 | | | |
| Methyl palmitoleate | C ₁₇ H ₃₂ O ₂ | | 0.194 | | |
| Methyl-7 hexadecenoate | C ₁₇ H ₃₂ O ₂ | 0.642 | | 14.716 | 14.204 |
| Methyl hexadecanoate | C ₁₇ H ₃₂ O ₂ | 2.874 | 3.5 | 3.566 | 3.566 |
| Methyl 14-methylpentadecanoate | C ₁₇ H ₃₄ O ₂ | 2.874 | 3.5 | 5.08 | 5.088 |
| Methyl 15-methylhexadecanoate | C ₁₈ H ₃₆ O ₂ | 2.874 | 4.93 | 5.08 | 5.088 |

| | | | | | |
|---|-------------------|--------------|---------------|---------------|--------------|
| Methyl -3-octadecenote | $C_{19}H_{36}O_2$ | | | | |
| methyl-6-Octadecenoate | $C_{19}H_{36}O_3$ | 0.642 | | 29.642 | 14.434 |
| Methyl-(-3-pentyl-2-oxiranyl)undcenoate | $C_{19}H_{36}O_2$ | | 0.194 | 0.208 | |
| Methyl elaide | $C_{19}H_{36}O_2$ | | | 14.716 | 14.204 |
| Methyl Oleate | $C_{19}H_{36}O_2$ | | 13.758 | | |
| Methyl 7-octadecenoate | $C_{19}H_{38}O_2$ | | | | 0.226 |
| methyl octadecanoate | $C_{19}H_{38}O_2$ | | 1.43 | 1.51 | 1.518 |
| Methyl-10 -octadecenoate | $C_{19}H_{36}O_2$ | 14.954 | 13.948 | | 14.434 |
| Methyl-11-octadecenoate | $C_{19}H_{36}O_2$ | 15.596 | 13.948 | 14.926 | 14.434 |
| Methyl-16-octadecenoate | $C_{19}H_{36}O_2$ | 14.954 | 13.758 | | |
| methyl-14-Octadecenoate | $C_{19}H_{36}O_2$ | 14.954 | | | |
| Methyl-15-Octadecenoate | $C_{19}H_{36}O_2$ | | 13.758 | | |
| Methyl-13-octadecenoate | $C_{23}H_{46}O_2$ | 14.954 | | | |
| Methyl docosanoate | $C_{22}H_{44}O_2$ | | 1.43 | 1.51 | 1.518 |
| Methyl hencosanoate | $C_{28}H_{56}O_2$ | | 1.43 | 1.51 | 1.518 |
| methyl heptacosanoate | $C_{25}H_{48}O_2$ | 0.508 | | | |
| Methyl-15-tetracosanoate | | 0.642 | 0.194 | 0.208 | 0.226 |
| Total | | 94.89 | 94.402 | 100.00 | 97.59 |

Appendix VIIE2: Non-methyl esters of transesterification at 45⁰C

| Non-methyl esters | Transesterification time (minutes) at 45 ⁰ C | | | | |
|----------------------------------|---|-------|-------|----|-------|
| | MF | 50 | 60 | 70 | 80 |
| 3-Decen-1-ol | $C_{10}H_{20}O$ | | | | 0.486 |
| 2-Methyl-Z,Z-3,13-Octadecadienol | $C_{19}H_{36}O$ | | 1.118 | | |
| Methyl-3,13-octadecadienol | $C_{19}H_{39}O$ | | | | |
| Linoleic acid chloride | $C_{18}H_{31}ClO$ | 1.022 | 1.118 | | 0.486 |

| | | | | | |
|--------------------------------|-------------------|-------------|-------------|-------------|-------------|
| 10-undecenyl aldehyde | $C_{10}H_{20}O$ | 2.044 | 1.118 | | 0.486 |
| Cyclododocene epoxide | $C_{12}H_{22}O_2$ | 1.022 | 1.118 | | 0.486 |
| 7-Tetradecenal | $C_{14}H_{26}O$ | 1.022 | 1.118 | | 0.486 |
| Total non-methyl esters | | 5.11 | 5.59 | 0.00 | 2.43 |

ABSTRACTS OF PUBLICATIONS

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