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Arnold Paintsil
The University of Western Ontario

Supervisor
Professor E.K. Yanful
The University of Western Ontario

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OPTIMISATION OF THE TRANSESTERIFICATION STAGE OF BIODIESEL PRODUCTION USING STATISTICAL METHODS

by

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The school of Graduate and Postdoctoral studies
The University of Western Ontario
London, Ontario, Canada

Abstract

The present research examines solely the transesterification stage of the biodiesel production process. Six process variables that affect the yield of biodiesel at this stage are examined using the 12 run Plackett-Burman Design. To study the effect of FFA[1] and to replicate real life situations where oil (feedstock) contain varying amounts of FFA, linoleic acid is used as FFA and intentionally added to high oleic acid canola oil containing less than 0.07% FFA. The process is catalyzed with potassium carbonate and evaluated at varying temperatures, stirring rates, reaction times and methanol oil ratios. The yields at the end of these reactions are measured and the active factors determined with the PB[2] design in Minitab software. At the end of the experimental design, it was found that the FFA amount affects the yield of biodiesel the most and methanol-oil ratio the least for the range of values studied.

The Box-Behnken method was then applied in optimising the amount of free fatty acid, the amount of catalyst and the stirring speed. The relationship between the yield and the three (3) factors was determined using analysis of variance (ANOVA) and subsequently optimised.

The optimised factor combination for a percentage yield greater than 98% was found for a 1 hour reaction to be 0.5 wt% FFA, 400 rpm stirring rate and 4 wt% catalyst at 60˚C temperature and 6:1 methanol-oil ratio for 100 g of Canola oil.

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[1] FFA refers to Free Fatty Acid

[2] PB = Plackett-Burman Design

Keywords

Transesterification, Plackett-Burman design, biofuel, biodiesel, ANOVA, Free fatty acid, Optimisation, Canola Oil, Potassium carbonate, factorial design, Active factors.

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Acronyms

ANOVA – Analysis of Variance

TAG – Triacylglycerol

FAME – Fatty Acid Methyl Esters

GC – Gas Chromatography

C19 – Methyl nonadecanoate

DF – Degrees of freedom

SEQ SS – Sequential Sum of Squares

ADJ SS – Adjusted Sum of Squares

ADJ MS – Adjusted mean squares

COEFF – Coefficient

SE COEFF – Standard Error of the coefficient

S.D. – Standard deviation

C.I. – Confidence Interval

Chapter 1

1 Introduction

1.1 Background of research

Crude oil has been the world's sole energy source for a long time. With the increase in population and advances in technology comes increase in the world's dependence on oil. The increased dependence on oil suggests natural oil reserves are likely to be depleted in the near future. Worldwide energy consumption has increased 17 folds in the last century. Known petroleum reserves are estimated to be depleted in less than 50 years at the present rate of consumption (Demirbas, 2006).

Biofuels are an alternative to the sole dependence on oil. It presents another source to rely on if there is a break in the supply of oil and, also, it relieves the stress on oil consumption. Increase in biofuel production would mean an increase in plant and animal production since more feedstock would be required, which would also increase jobs. This is very important, especially for developing countries where the rate of unemployment is high.

Biodiesel is one such biofuel that is produced using the transesterification process. Biodiesel is a diesel replacement fuel for use in compression-ignition engines. It is manufactured from plant oils (soybean oil, cotton seed oil, canola oil), recycled cooking greases or oils (e.g., yellow grease), or animal fats (beef tallow, pork lard). The biodiesel manufacturing process converts oils and fats into long-chain mono alkyl esters, or biodiesel.

Biodiesel typically has a higher cetane rating than petroleum diesel. Biodiesel also has better lubricity than current low-sulphur petroleum diesel and much better lubricity than the ultra-low-sulphur petroleum diesel. The energy content of biodiesel is roughly 10% lower than that of petroleum diesel. Biodiesel dramatically reduces most emissions, including carbon dioxide. A recent analysis of biodiesel emissions found a life-cycle greenhouse gas reduction of 41% (Detchon, 2007).

In the transesterification reaction, triacylglycerol (TAG) is reacted with an alcohol (methanol, ethanol), in the presence of a catalyst (base or acid) to produce glycerol and fatty acid alkyl esters. The whole biodiesel production is summarized by this reaction and hence various reaction parameters are monitored to ensure that maximum yield (and/or conversion) and purity is achieved. These include;

- The alcohol to oil molar ratio
- Reaction temperature
- Catalyst concentration
- Reaction time

Various experiments have been conducted that propose the optimum values for the parameters stated above. These parameters (60°C reaction temperature and 6:1 methanol: oil molar ratio, 1wt% catalyst) have become a standard for methanol-based transesterification (Knothe, et al., 2005). Some reports also state that the transesterification reaction is more dependent on the alcohol to oil ratio, catalyst concentration and reaction time than on temperature(Joshi et al., 2009; Kuwornu & Ahiekpor, 2010).

Several researches have focussed on determining what yields of biodiesel can be obtained for a particular feedstock. Though this is necessary, it is equally important that the process be optimised and cost reduced to the minimum so as to make biodiesel competitive to petrodiesel. This research further sought to use statistical methods to determine the optimum parameters for the production of biodiesel. The transesterification stage was studied with no emphasis on a particular feedstock. Canola oil was used as feedstock for this particular research because it has been studied extensively in North America and has its properties are well known. The idea was to use Canola oil to obtain a model equation that could be used to predict the effect of the factors on yield of biodiesel for any feedstock. The use of statistical methods greatly reduced the time spent on experiments as a few experiments were used to arrive at a meaningful conclusion, thereby reducing the cost of production. Also, the designed experiments helped reduce the variations that could have been obtained in the results. Potassium carbonate was used as the catalyst because of its cost and efficiency and methanol, as alcohol.

The specific objectives were;

- To determine the factors that affect the yield of biodiesel the most.
- Determine the maximum amount of free fatty acid (FFA) that could be tolerated for Canola oil. This was done by intentionally adding FFA to the canola oil.
- Optimise the biodiesel production process using Potassium Carbonate as catalyst
- Analyse effect of reaction parameters on above process (temperature, catalyst amount and methanol-oil molar ratio, reaction time and speed of stirring)
- Obtain a model equation relating the factors to the yield of biodiesel obtained.

Baroi et al., (2009) studied the production of biodiesel from *Jatropha curcas* using Potassium carbonate. They reported that a 6wt% potassium carbonate (wt. % of the oil) was the optimum catalyst amount when 6:1 methanol oil ratio was used at a temperature of 60°C for 10 hours reaction time. They recommended that further research be done using the best parameter combination, to obtain a shorter time as required for commercial operation. The proposed methods are the;

- Factorial design of experiments
- Response surface methodology

The optimisation is done to find the best combination of factors at the least cost as possible. The research method is selected to include the optimisation of the amount of FFA in the oil sample also. Linoleic acid is used as the FFA.

Summarised below are the experimental plan and procedure.

1.2 Experimental Plan

- Performed a fractional factorial experiment (Plackett-Burman design) with an initial twelve runs (3 replicates, 36 in total) using various reaction parameters for potassium carbonate.
- Determined which factors influence the yield the most using the Pareto plot.
- Determined how much the amount of FFA and the other factors affect the yield of biodiesel
- Determined the maximum amount of FFA that can be tolerated without affecting the yield
- Optimised the process using the response surface method.

1.3 Experimental procedure

- A fractional factorial experiment was run. 12 runs for a start to determine which factors were more important.
- Yields were measured for each run of the experiment.
- Several experiments were run at the center and axial points to account for curvature
- Surface response design was used to determine optimum conditions.
- The experiment was then carried out at these optimum values to find the percentage yield.

Chapter 2

2 Literature review

Biofuels are an alternative to the sole dependence on oil. They present another source to rely on if there should be a break in the supply of oil and also relieve the stress on oil consumption.

Biofuels are classified as first-generation or second-generation fuels. There are no strict technical definitions for these terms. The main distinction between them is the feedstock used. A first-generation fuel is generally one made from sugars, grains, or seeds, i.e. one that uses only a specific (often edible) portion of the above ground biomass produced by a plant, and relatively simple processing is required to produce a finished fuel. First-generation fuels are already being produced in significant commercial quantities in a number of countries. Second-generation fuels are generally those made from non-edible lignocellulosic biomass, either non-edible residues of food crop production (e.g. corn stalks or rice husks) or non-edible whole plant biomass (e.g. grasses or trees grown specifically for energy). Second-generation fuels are not yet being produced commercially in any country. (Lawson, 2008)

Edible oils are in use in developed nations such as USA and European nations but developing countries are not self-sufficient in the production of edible oils and hence have emphasized in the application of a number of the non-edible oils (Sharma, et al., 2008). It is imperative to develop feedstocks that will replace the use of foods to produce fuels. While the use of food for fuel can but replace a small proportion of the fossil/mineral fuel used, and thus cannot have a major effect on fuel prices, it has a major effect on food and feed prices (Gressel, 2008). Biofuels of the second generation seem promising and is a venture worth pursuing, especially with their ability to be blended and used without engine modification (Festel, 2008).

A sustainable biofuel has two favourable properties which are its availability from renewable raw materials, and its lower negative environmental impact than that of fossil fuels (Demirbas, 2006). Only second generation and beyond biofuels will make a real dent in the amount of fossil petroleum used. The biofuel crops will only be cost effective in the long run if they are altered genetically to remove toxins and environmental contaminants, and to be more productive and have the right properties as fuels, as well as have residues that have value **(**Gressel**,** 2008**)**.

Biodiesel can be produced from a great variety of feedstock. These feedstock include most common vegetable oils (e.g., soybean, cottonseed, palm, peanut, rapeseed/canola, sunflower, safflower, coconut) and animal fats (usually tallow) as well as waste oils (e.g., used frying oils). The choice of feedstock depends largely on geography. (Knothe, et al., 2005). Biodiesel production from algae is another promising area that is been explored by many scientists the world over. Various experiments have been conducted that show the prospects of some of the proposed feedstock for biodiesel. Chhetri et al. (2008) reports over 97% conversion to biodiesel for Jatropha oil and Soap-nut oil. Over 90% conversion is also reported by Sharma et al. (2008) for neat canola oil, used frying oil, soybean oil and waste cooking oil.

U.S. biodiesel production is growing rapidly, from 28 million gallons in 2004 to 91 million gallons in 2005. That is still only 0.15% of the U.S. diesel market and less than 10% of the 1 billion gallons produced in Europe, but production in 2006 was estimated at 245 billion gallons (Detchon, 2007). Even though biodiesel can be made from a range of feedstock, the use of these feedstock is influenced by the price and availability of the feedstock. A report on biodiesel production in Canada mentions Canola oil as the mostly used feedstock, but further mentions that canola oil and soybean oil are apt to be relatively high cost feedstock for biodiesel production while yellow grease, tallow and palm oil are low-cost. This is attributed to the fact that canola ad soybean are priced as food oils on the international markets while yellow grease, tallow and palm oil as classed as feed and industrial oils. The price of palm oil has fallen drastically since there is rapid and significant increase in production rate (Stiefelmeyer, et al., 2006).

The oil as it is from these feedstock has a high kinematic viscosity and hence cannot be used directly in an engine. The kinematic viscosity of vegetable oils is about an order of magnitude greater than that of conventional, petroleum-derived diesel fuel. High viscosity causes poor atomization of the fuel in the engine's combustion chambers and ultimately results in operational problems, such as engine deposits (Knothe, et al., 2005). Two very common engines types are the spark-ignited (gasoline) engine and the diesel engine. The spark-ignited engine usually runs on gasoline while the diesel engine runs on diesel. These engines are both internal combustion engines that convert fuel into energy through a series of small explosions or combustions. The major difference between diesel and gasoline is the way these explosions happen. In a gasoline engine, fuel is mixed with air, compressed by pistons and ignited by sparks from spark plugs. The fuel and air are close to the chemically correct, or stoichiometric, mixture are inducted into the engine cylinder, compressed, and then ignited by a spark. The power of the engine is controlled by limiting the quantity of fuel-air mixture that enters the cylinder using a flow-restricting valve called a throttle (Knothe et. al., 2005; Brain, 2011). In a diesel engine, also known as a compression-ignited engine, only air enters the cylinder through the intake system. This air is compressed to a high temperature and pressure, and then finely atomized fuel is sprayed into the air at high velocity. When it contacts the high temperature air, the fuel vaporizes quickly, mixes with the air, and undergoes a series of spontaneous chemical reactions that result in self-ignition or auto ignition.

Simply, in a diesel engine, the air is compressed first, and then the fuel is injected. Because air heats up when it's compressed, the fuel ignites (Knothe et. al., 2005; Brain, 2011).

The performance of biodiesel in diesel engines have been documented and compared to that of petroleum diesel. Summarized below are some of these findings, as mentioned in (Ciolkosz & Perez, 2009).

- Engine power: engine power and torque tend to be 3 to 5 percent lower when using biodiesel. This is due to the fact that biodiesel fuel has less energy per unit volume than traditional diesel fuel
- Fuel efficiency: fuel efficiency tends to be slightly lower when using biodiesel due to the lower energy content of the fuel. Typically, the drop-off is in the same range as the reduction in peak engine power (3–5%)
- Engine wear: short-term engine wear when using biodiesel has been measured to be less than that of petroleum diesel. While long-term tests have not been published, engines are expected to experience less wear in the long run when using biodiesel
- Deposits and clogging: deposits and clogging due to biodiesel have been widely reported but are generally traceable to biodiesel that is either of low quality or has become oxidized. If fuel quality is high, deposits in the engine should not normally be a problem
- Pollution from engine exhaust: biodiesel results in much less air pollution due to its higher oxygen content and lack of both “aromatic compounds” and sulphur. The one exception to this is nitrogen oxide (NO_x) emissions, which tend to be slightly higher when using biodiesel. Proper tuning of the engine can minimize this problem, however.
- Cold-weather performance: similar to petroleum diesel, engines tested in cold weather typically experience significant problems with operation caused primarily by clogging of

> the filters and/or coking of the injectors. The use of flow-improving additives and “winter blends” of biodiesel and kerosene has proved effective at extending the range of operating temperatures for biodiesel fuel. Pure biodiesel tends to operate well at temperatures down to about 5°C (this varies noticeably depending on the type of oil used). Additives typically reduce that range by about 5 to 8 degrees, while winter blends have proved effective at temperatures as low as -20°C and below.

Similar findings on the comparison in performance of biodiesel and petrol diesel are published in (Knothe et. al., 2005).

Depending on the conversion of biomass, three main pathways come into consideration (Zinoviev et. al., 2007);

- the thermo-chemical pathway (Pyrolysis)
- the physical-chemical conversion pathway (Transesterification)
- The bio-chemical conversion pathway (Fermentation)

Of all these pathways, four methods to reduce the high viscosity of vegetable oils to enable their use in common diesel engines without operational problems such as engine deposits have been investigated: blending with petrodiesel, pyrolysis, micro-emulsification (co-solvent blending), and transesterification (Knothe et. al., 2005).

2.1 Blending with petrodiesel

Various mixtures of vegetable oils and petrodiesel have been tried and experimented on to see their performance in diesel engines. When vegetable oil is used as diesel fuel, its advantages include;

- Liquid nature portability
- Heat content (80% of diesel fuel)

- Readily available
- Renewability

It should however be realised that vegetable oils have a higher viscosity, lower volatility, and have very reactive unsaturated hydrocarbon chains (Ma & Hanna, 1999; Knothe, Gerpen et. al., 2005). Most studies have concluded that vegetable oil/petrodiesel blends are not suitable for long-term fueling of direct injection diesel engines. The problems include (Ma & Hanna, 1999) ;

- Coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices
- Carbon deposits
- Oil ring sticking
- Thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils.

2.2 Micro-emulsification

When diesel is mixed with low molecular weight alcohols, the hybrid diesel fuels formed have a lower viscosity than the parent diesel.

Microemulsions are clear, stable, two-phase nano-dispersions which readily form upon mixing water with an oil phase. Water-in-oil (w/o) microemulsions are comprised of a continuous non-polar hydrocarbon phase and a discontinuous aqueous phase. Because of the small droplet size (2 to 200 nanometers) of the discontinuous phase, these microemulsions appear to be clear, one-phase systems. Microemulsion diesel fuel technology uses a microemulsifier to make a diesel or biodiesel fuel and a water phase compatible. The microemulsifier typically contains a surfactant and an oxygenate. The resulting microemulsion fuel, when utilized in conventional diesel engines, is “clean-burning”, gives no power loss or increase in fuel consumption, and is thermal and shear stable in the fuel handling system.

The purpose of the oxygenate is to help solubilize the surfactant in the fuel, adjust the properties (i.e. viscosity) of the fuel, and possibly contribute to improving the ignition properties of the water-containing microemulsion fuel (Kesling, et al., 2006).

Micro-emulsion fuels present an opportunity to replace up to 50% of the petroleum in diesel fuels with biomass and by-product materials, including alcohols, vegetable oil fatty acids, and aromatic alcohols. The technology is expected to be driven by lowered NO_x and particulate emissions, although petroleum sparing and energy security are major energy related objectives. Major factors in the adoption of this and other market fuel technologies include cetane rating, emissions decreases, and appropriate physical chemical properties, e.g. cloud point, vaporization (Griffith & Compere, 2003). Boruff et. al. (1982) also documented similar findings in their evaluation of diesel fuel-ethanol microemulsions.

2.3 Pyrolysis

Pyrolysis refers to the thermochemical conversion of biomass into energy. Usually, the biomass is heated in the absence of air (oxygen) to achieve decomposition. The application of heat to biomass will yield pyrolytic products with gaseous, liquid, and solid fractions, the proportions of which are heavily dependent on the pyrolysis conditions. The liquid or oil fraction is commonly called pyrolytic oil or bio-oil. Slow pyrolysis, which employs lower process temperatures and longer reaction times, favors charcoal production. The liquid pyrolytic product can be easily stored and transported, readily upgraded and refined to produce high quality fuels, and may contain chemicals in economically recoverable amounts (Maher & Bressler, 2007).

The crude pyrolysis liquid or bio-oil, is dark brown in color, approximates to biomass in elemental composition and is a complex mixture of oxygenated hydrocarbons and an appreciable amount of water.

One of the main drawbacks of the bio-oil is that the composition of the pyrolytic oils is very similar to that of the original biomass and is very different from petroleum derived fuels and chemicals. The primary disadvantages of using the bio-oil as a diesel fuel most notably include the low HHV (Higher heating value) which is approximately 40% less than that of fuel oil, its high viscosity, and substantial solids content. As well, bio-oil typically contains up to 25 wt. % water that cannot be readily separated. This causes miscibility problems with conventional fuel oils and as a result, blends cannot be achieved. Pyrolysis oils have also been described as acidic, corrosive, polar, thermally unstable, and highly oxygenated (Knothe, Gerpen, & Krahl, 2005; Maher & Bressler, 2007). It should also be noted that, these disadvantages aside, pyrolysis has a lower operational cost and feedstock for pyrolysis are readily available.

2.4 Transesterification

Transesterification is the most used method of conversion and refers to the reaction of a vegetable oil or animal fat with an alcohol in the presence of a catalyst to produce alkyl esters and glycerol. The alkyl esters are what are called biodiesel.

The purpose of the transesterification process is to lower the viscosity of the oil. The transesterification reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH)/ sodium hydroxide (NaOH) and sulfuric acid, or heterogeneous catalysts such as metal oxides or carbonates.

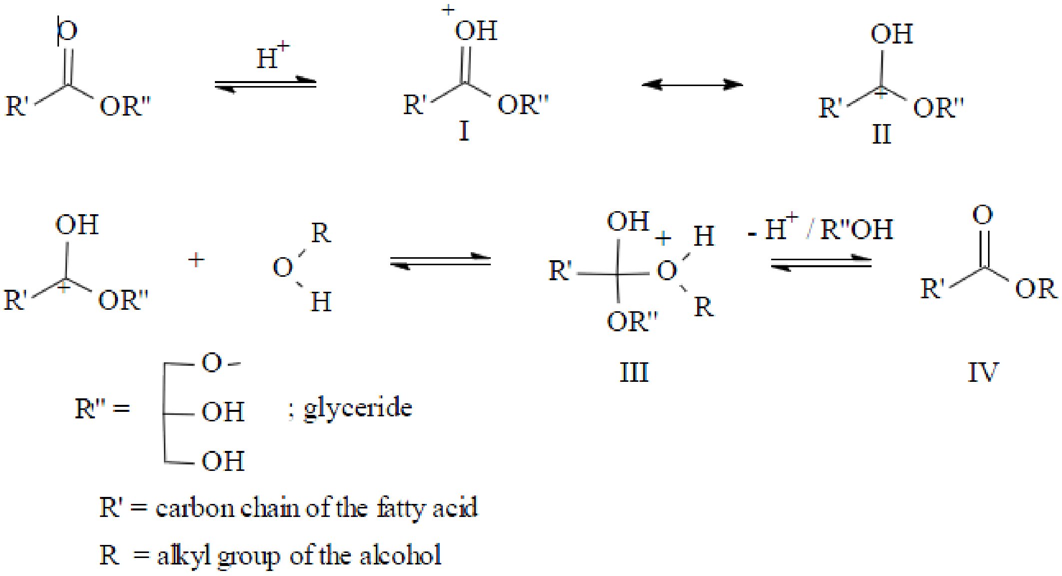
Transesterification is the general term used to describe he important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis. The term transesterification is synonymous to alcoholysis of carboxylic esters. The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of a catalyst (typically a strong acid or base) accelerates considerably the adjustment of the equilibrium. In order to achieve a high ester yield, alcohol has to be used in excess. In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol. The overall process is a sequence of three consecutive and reversible reactions, in which di- and mono-glycerides are formed as intermediates. The stoichiometric reaction requires one (1) mole of a triglyceride and three (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. Several factors, including the type of catalyst (alkaline or acid), alcohol-oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content affect the transesterification process. The types of catalysts often used are discussed below.

2.4.1 Acid-Catalyzed Processes

The transesterification process is catalyzed by Bronsted acids, preferably by sulphonic and sulphuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100 °C and more than 3 hr to reach complete conversion. Pryde *et al*. (1983) showed that the methanolysis of soybean oil, in the presence of 1 mol% of H_2SO_4, with an alcohol/oil molar ratio of 30:1 at 65 °C, takes 50 h to reach complete conversion of the vegetable oil (> 99%), while the butanolysis (at 117 °C) and ethanolysis (at 78 °C), using the same quantities of catalyst and alcohol, take 3 and 18 hrs., respectively.

The alcohol/vegetable oil molar ratio is one of the main factors that influence the transesterification. An excess of the alcohol favours the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ratio has to be established empirically, considering each individual process.

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown below for a monoglyceride. However, it can be extended to di- and triglycerides (Schuchardi et al., 1998).



R' = carbon chain of the fatty acid

R = alkyl group of the alcohol

Scheme 1: Mechanism of Acid catalyzed transesterification of Vegetable Oil (Schuchardi et. al, 1998)

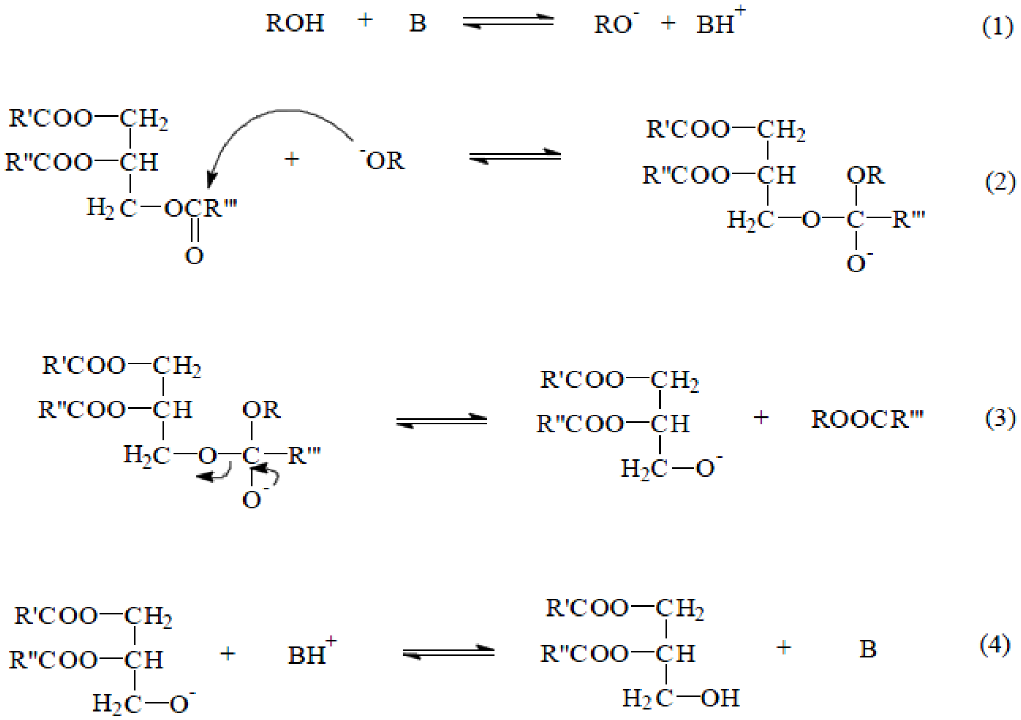
The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H+.

According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.

2.4.2 Base-Catalyzed Processes

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reactions. Due to this reason, together with the fact that the alkaline catalysts are less corrosive than acidic compounds, industrial processes usually favour base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates.

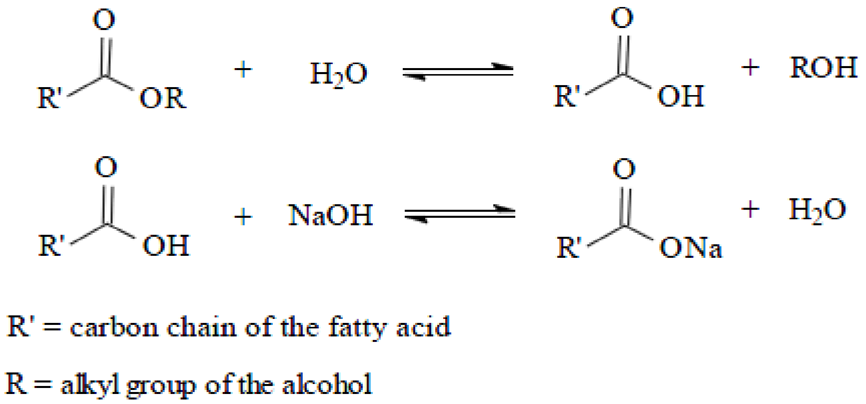
The mechanism of the base-catalyzed transesterification of vegetable oils is as shown.



Scheme 2: Mechanism of base catalyzed transesterification of vegetable oil (Schuchardi et al., 1998)

The first step is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate from which the alkyl ester and the corresponding anion of the diglyceride are formed; the latter deprotonates the catalyst, thus regenerating the active species which is now able to react with a second molecule of the alcohol, starting another catalytic cycle.Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields (> 98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water which makes them inappropriate for typical industrial processes. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol%. However, even if a water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation. This undesirable saponification reaction reduces the ester yields and considerably makes difficult the recovery of the glycerol due to the formation of emulsions (Schuchardi et al., 1998).



Scheme 3: hydrolysis of esters and further reaction to form soap

Potassium carbonate, used in a concentration of 2 or 3 mol% gives high yields of fatty acid alkyl esters and reduces the soap formation. This can be explained by the formation of bicarbonate instead of water, which does not hydrolyse the esters (R = the alkyl group of the alcohol).

$$K_2CO_3 + ROH \rightleftharpoons ROK + KHCO_3$$

Scheme 4: reaction for bicarbonate formation

2.4.3 Choice of Catalyst (K_2CO_3)

Hartman (2012), compares the efficiency of several catalysts. This comparison was based on the amount of glycerol set free and the degree of soap formation. He mentioned that sodium methoxide ensured a practically complete alcoholysis, but since it is known to promote migration of double bonds and other secondary reactions, its use is not always advisable. Potassium carbonate was found to produce comparable efficiencies to sodium methoxide.

Aside being available commercially for a relatively cheap price, potassium carbonate can also be produced simply and inexpensively by burning organic materials (which mostly contain Carbon and potassium) and using the ash that is produced. This can also be undertaken through a refining process to obtain the white crystalline potassium carbonate. This makes potassium carbonate a viable and more favourable catalyst especially for regions where cost is a major concern.

2.5 Design of experiment

Montgomery (2003), mentions that by designed experiments, engineers can determine which subset of the process variables has the greatest influence on process performance. The results of such an experiment can lead to

1. Improved process yield

2. Reduced variability in the process and closer conformance to nominal or target requirements
3. Reduced design and development time
4. Reduced cost of operation.

Several approaches can be considered in running an experiment. There is the best-guess approach which is based on the selection of arbitrary combinations of factors and then running tests with them. The response for this combination is measured. This approach can be repeated indefinitely, switching the levels of one (or two) factors for the next test based on the outcome of the previous test. This method is however flawed, in that, for a case where the initial best guess does not produce the desired results, the experiment would have to be repeated with a new guess at the correct combination. This could be time consuming is the correct combination is not found. Also, if the initial guess produces an acceptable result, this could lead the experimenter into thinking that the best solution has been found; which could be wrong.

The one-factor-at-a-time approach is also used extensively. This method consists of selecting a starting point or baseline set of levels, for each factor, then successively varying each factor over its range with the other factors held constant at the baseline level. A major disadvantage of this approach is that it fails to consider any possible interactions between the factors. Dunn (2012) explains that changing one variable at a time, leads into thinking an optimum has been reached, when all that has been done is found a sub-optimal solution.

A factorial experiment is recommended. This is an experimental strategy in which factors are varied together, instead of one at a time. In this method, two levels of the factors are considered and several experiments run (randomly, based on the total number of factors under study). This helps the experimenter to investigate the individual effects of each factor (or the main effects) and to determine whether the factors interact.

Response surface methods usually accompany factorial designs. These are a collection of mathematical and statistical techniques that are useful for modeling and analysis in applications where a response of interest is influenced by several variables and the objective is to optimise this response. The response surface of the response variable is mapped out and the process is moved as close to the optimum as possible, taking into account all constraints.

Several experiments have been performed and reports written on the use of factorial and surface designs for the optimisation of biodiesel.

Vicente et. al (1998), investigated the application of these methods to the optimisation of biodiesel. They experimented using Sunflower Oil and methanol. Stirring was fixed at 600 rpm, time at 4 minutes, methanol-oil ratio fixed at 6:1 at atmospheric pressure. The factors investigated were temperature and catalyst concentration. They found that the conversion of trans-glycerides was strongly dependent on these two factors with the conversion increasing at low temperatures and high catalyst concentrations. They further noted that the conversion decreased at very high temperature and pressures. This they explained to be a result of an increase in side reactions at these elevated conditions. Similar results were obtained by Joshi et. al (2008), when they investigated how the catalyst (KOH) concentration affects, ethanol oil ratio and temperature affects the yield of biodiesel. In their report, catalyst and Ethanol-Oil molar ratio were found to be the main factors that affect the yield using the response surface design.

Research shows that plant oils or greases used in CI engines at concentrations as low as 10% to 20% can cause long-term engine deposits, ring sticking, lube oil gelling and other maintenance problems and can reduce engine life. These problems are caused mostly by the greater viscosity, or thickness, of the raw oils (around $40mm^2/s$) compared with that of the diesel fuel, for which the engines and injectors were designed (1.3 to $4.1mm^2/s$). Through the process of converting plant oils or greases to biodiesel by transesterification, the viscosity of the fuel is reduced to values similar to conventional diesel fuel (biodiesel values are typically 4 to $5mm^2/s$) (NRE, 2009)

This report aims to use the factorial design and response surface designs to investigate the factors that affect the production of biodiesel from "Canola Oil (with added FFA) using the novel catalyst K_2CO_3". A Plackett-Burman design is initially employed to determine which factors affect the yield the most. Subsequent designs focus on determining the optimum conditions for producing the biodiesel from this feedstock. Six factors are considered for the initial design and are listed below;

1. FFA Content (A)
2. Methanol Oil Ratio (B)
3. Catalyst Amount (C)
4. Reaction Time (D)
5. Temperature (E)
6. Stirring Speed (F)

This thesis follows the integrated manuscript format. Chapters 3 and 4 are technical papers that have been prepared for publishing. Formulae and short notes are provided in the appendix for quick reference.

Chapter 3

3 Effect of process variables on transesterification: a Plackett-Burman design application

3.1 Introduction

A sustainable biofuel has two favourable properties, namely, availability from renewable raw materials, and lower negative environmental impact than that of fossil fuels (Demirbas, 2006).

Biodiesel can be produced from a great variety of feedstock. These feedstock include most common vegetable oils (e.g., soybean, cottonseed, palm, peanut, rapeseed/canola, sunflower, safflower, coconut) and animal fats (usually tallow) as well as waste oils (e.g., used frying oils). The choice of feedstock depends largely on geography (Knothe, et al., 2005).

Various experiments have been conducted that show the potential of some of the proposed feedstock for biodiesel production. Chhetri et al. (2008) reports over 97% conversion to biodiesel for Jatropha oil and Soapnut oil. Over 90% conversion is also reported by Sharma, et al. (2008) for neat canola oil, used frying oil, soybean oil and waste cooking oil.

Even though biodiesel can be made from a range of feedstock, their use is influenced by price and availability. A report on biodiesel production in Canada has shown that the prices of a number of feedstock have fallen drastically because there has been a rapid and significant increase in production rate (Stiefelmeyer, et al., 2006).

U.S. biodiesel production is growing rapidly, from 28 million gallons in 2004 to 91 million gallons in 2005. That is still only 0.15% of the U.S. diesel market and less than 10% of the 1 billion gallons produced in Europe, but production in 2006 was estimated at 245 billion gallons (Detchon, 2007). It is thus necessary that cheaper, simpler and alternative methods be sought to increase production.

Depending on the conversion of biomass, the following three pathways may be considered (Zinoviev, et al., 2007):

- the thermo-chemical pathway (Pyrolysis)
- the physico-chemical conversion pathway (Transesterification)
- The bio-chemical conversion pathway (Fermentation)

In all these pathways, four methods to reduce the high viscosity of vegetable oils to enable their use in common diesel engines without operational problems, such as engine deposits, have been investigated: blending with petrodiesel, pyrolysis, micro-emulsification (co-solvent blending), and transesterification (Fukuda, et al., 2001; Knothe, et al., 2005).

Over the years, extensive research has been conducted on these methods of biodiesel production. Biodiesel production via transesterification remains one of the most widely used processes. Transesterification is the reaction of a vegetable oil or animal fat with an alcohol in the presence of a catalyst to produce alkyl esters and glycerol. The course of transesterification is influenced very much by the type of catalysis used. The choice is often between a base and an acid catalyst.

Several factors influence the outcome of this stage of the biodiesel process. They include the amount of free fatty acid, methanol-Oil ratio, amount of catalyst, reaction time, effect of stirring, pressure and temperature (Freedman, et al., 1984). Eventhough the effects of these factors have been documented (Feuge & Gros, 1949; Meher, et al., 2006; Freedman, et al., 1984), there has been no attempt to quantitatively determine how each one of these factors affect the yield of biodiesel.

The experiment in the present research focusses on the transesterification stage of biodiesel production and uses the Packett-Burman design to model the process. This design is a two-level and 12-run experiment. The primary goal is to find a relationship between six of the factors listed above (except pressure) and the yield of biodiesel produced. This design approach helps to quantitatively determine how the investigated factors affect the yield of biodiesel in the ranges chosen. A qualitative representative is given in the pareto plot. The experimenter seeks to use the least expensive and most common materials in biodiesel production and hence reduce the cost of production.

Montgomery (2003) has noted that, by using experimental design, engineers can determine which subset of the process variables has the greatest influence on process performance. The results of such experiments can lead to improved process yield, reduced variability in the process and closer conformance to nominal or target requirements, reduced design, development time and cost of operation.

Several approaches can be considered when running an experiment but the one that leads to the most optimum result is always sought. Factorial experiments have been recommended and used for several decades. They allow the experimenter to investigate the individual effects of each factor (or the main effects) and to determine if the factors interact.

Complete runs are expensive, so screening methods are employed. Screening methods give the least number of experiments that can provide substantial information. In these experiments, many factors are considered and the objective is to identify those factors (if any) that have large effects. The factors that are identified as more important are then investigated more thoroughly in subsequent experiments (Barrentine, 1999; Montgomery, 2001;).

Thus screening methods help identify the “active factors”[3] in an experiment. The most popular screening methods used are the fractional factorial methods (2^{k-p} designs) and the Plackett Burman designs (Plackett & Burman, 1946). Where as fractional factorials restrict the number of runs to be a power of 2, the Plackett-Burman designs allow the number of runs to be a power of 4. This allows for a more economical screening. This method has been used extensively in the determination and optimisation of active factors in the biological sciences (Giordaus et al., 2011), with applications in the production of biodiesel from algae (Lu et al., 2011) amongst others but no work has been done using it on the transesterification of biodiesel.

Canola oil is the chosen feedstock for this experiment. It is relatively inexpensive in North America and its properties and characteristics are very well known (Przybylski, et al., 2005). It has also been used in many experiments. The canola oil used in the present study had a high amount of oleic acid and a 0.07% free fatty acid amount. Linoleic acid was intentionally added as a source of free fatty acid to mimic real life situation.

Potassium carbonate, a base, was chosen as the catalyst. Base-catalysis was preferred because transesterification of vegetable oils proceeds faster than the acid-catalyzed reactions and, also, alkaline catalysts are less corrosive. Even though it is necessary that they are used in the absence of water, alkaline metal alkoxides are the most active catalysts, since they give very high yields (> 98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). (Schuchardi et al., 1998). The potassium carbonate used is produced by a simple and inexpensive process and it has efficiencies comparable to sodium methoxide (Hartman, 1956). Methanol was used for alcoholysis.

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[3] Active factors are the factors that individually or interactively produce a change in the response.

3.2 Materials

Canola oil (certified organic) with FFA concentration of less than 0.10% was obtained from Sigma-Aldrich in Oakville, Canada. Anhydrous potassium carbonate (min. 99 %) supplied by Caledon labs was obtained from the chemical store. Anhydrous grade methanol (99.8%) and technical grade linoleic acid (about 65%) were also purchased from Sigma-Aldrich in Oakville, Canada. Analytical grade methyl nonadecanoate (≥98.0%) and toluene were purchased for the GC analysis from Sigma Aldrich in Milwaukee, USA

3.3 Method

3.3.1 Experimental Set-Up

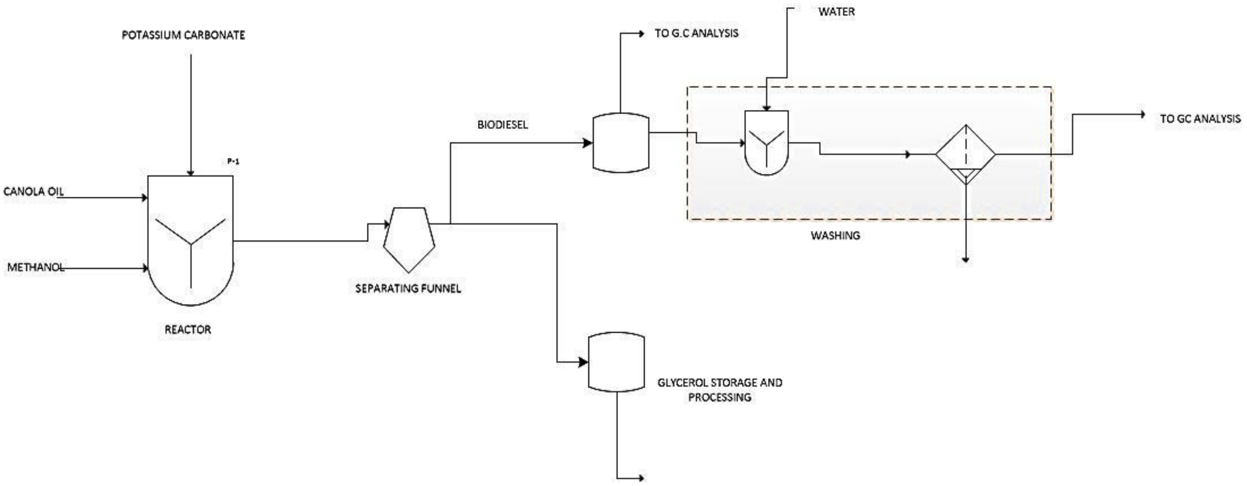

Figure 3-1: Process flow diagram; Transesterification stage

The reactor was a 250-mL Erlenmeyer flask. The opening was fitted with a 24/40 Liebig condenser. To make the process water tight, the other opening of the condenser was fitted with a bent tube which was filled with (drierite) calcium sulphate and cotton. These materials were chosen to minimize any pressure build up that may accompany sealing the condenser.

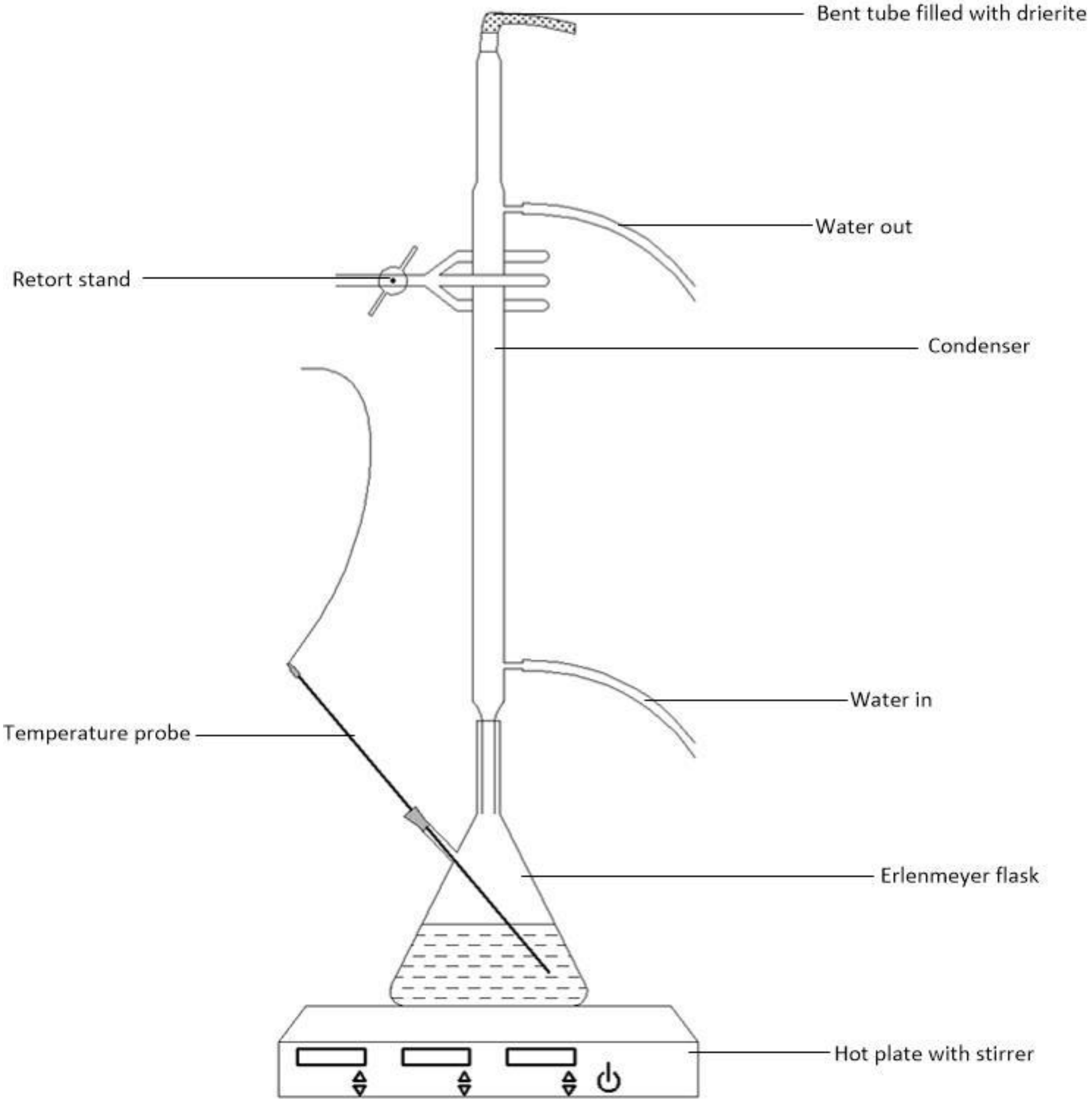

Figure 3-2: Experimental set-up

This set up was mounted on a VWR 800 series advanced digital hot plate with stirrer. The hot plate also comes equipped with a temperature probe to ensure efficient measuring of temperature. To use the probe, an opening was made on the flask (reactor). This opening was made at a 60° angle to the surface of the flask. It was fitted with a septum and the probe passed through the septum.

The septum prevents airflow into the system. The stirrer also had a stop watch that measured the reaction time and automatically ended the reaction at the desired reaction time.

The reaction mixture was allowed to settle overnight by gravity in the separating funnel, and the two resulting phases were decanted into separated bottles. The glycerol was stored, tested for free fatty acids and later disposed of, while the fatty acid methyl esters (FAME) phase is taken for further testing (washing and methyl ester determination in the GC).

3.3.2 Experimental Design (Plackett-Burman Design)

Exactly 100 g of canola oil was measured out and poured into the reactor. The reaction parameters were modified for each run from the design. The design is as shown in table 1 below.

The -1 (s) and 1 (s) are coded variables used to denote the high and low amounts of each variable. The actual values are given in *Table 2* below. The values used for each of the factors is based on previous work done in the lab and from literature (Ma et. al. 1999; Feuge & Gros, 1949; Freedman et al. 1984; Knothe et. al. 2005; Baroi et. al. 2009).

Three replicates of each run was done and the corresponding yield determined. The runs were also randomised to remove any correlations that may be present.

Table 3-1: Plackett-Burman Design

Standard Order	**A / Temp**	**B / Stir**	**C / Catalyst**	**D / MeOH**	**E / FFA**	**F/ Time**
1	1	-1	1	-1	-1	-1
2	1	1	-1	1	-1	-1

3	-1	1	1	-1	1	-1
4	1	-1	1	1	-1	1
5	1	1	-1	1	1	-1
6	1	1	1	-1	1	1
7	-1	1	1	1	-1	1
8	-1	-1	1	1	1	-1
9	-1	-1	-1	1	1	1
10	1	-1	-1	-1	1	1
11	-1	1	-1	-1	-1	1
12	-1	-1	-1	-1	-1	-1

The amounts to use for each run was calculated based on how the reaction proceeds. The reaction may be represented as follows:

TAG + (x+y) MeOH = x FAME + GLYCEROL + y MeOH

Table 3-2: factor notations and amounts

NOTATION	FACTORS	LOW	HIGH
A	Temperature (°C)	30	60
B	Stirrring Speed (rpm)	400	800

C	Catalyst Amount (wt % oil)	1	4
D	MeOH-Oil Ratio	3:1	6:1
E	FFA amount (wt % oil)	0.5	6
F	Reaction Time (hr)	1	3

Applying the equation above, the factor values shown in *Table 3* were obtained.

The molecular weights of Canola oil, and methanol used in the calculations were calculated as 883.370 g/mol, 0.340 g/mol respectively.

Table 3-3: factor calculations

FACTOR	AMOUNT	CALCULATED AMOUNT
Methanol	3:1	10.88 g
	6:1	21.76 g
Catalyst	1 wt %	1.00 g
	4 wt %	4.00 g
FFA	0.5 wt %	0.50 g
	6 wt %	6.00 g

The procedure followed is as outlined in *Figure 1*.

At the end of each run, the mixture was transferred into a separating funnel and then left to settle (by gravity) overnight. The resulting layers are then decanted into separate bottles for analysis.

3.3.3 Gas Chromatography Analysis

Yield was determined using gas chromatography. The approach taken is as outlined in EN 14103 (Determination of total FAME in B100 biodiesel).

Exactly 100 mg of each sample was measured using a high precision balance and placed in a 12 mL vial. This was followed by the addition of 100 mg of internal standard (C19) to each sample. The masses in each case were recorded to the nearest 0.1 mg. The sample and standard were then dissolved in 10 mL of toluene. The resulting mixture was allowed to settle; it was then mixed thoroughly for 15 minutes after which three samples were drawn from each vial for GC analysis. The GC was fitted with a Carbowax™ column.

The yield of FAME was computed as:

$$C = \frac{\Sigma A - A_{IS}}{A_{IS}} x \frac{C_{IS} x V_{IS}}{m} x 100\ \% \qquad \text{... Equation 3-1}$$

Where ΣA: total peak area from C14 to C24

A_{IS} : Internal standard peak area

C_{IS}: Concentration of internal standard in mg/mL

V_{IS}: Volume of internal standard in mL

m: mass of sample in mg

Prior to this step, a FAME mixture (C8-C24) obtained from Agilent Canada was run and the resulting retention times were used to aid identification.

3.4 Results and Discussion

All analysis was done in Minitab® 16.1.1.

1. A model was fitted to the data by inputting the yields for each run. The effects (contrasts) and corresponding sum of squares were calculated by the software. The total degrees of freedom and the T and P values for each factor were computed and displayed in the output results.
2. The active (important) effects were identified using an $\alpha = 0.05$ (level of significance). The P-values in the estimated effects and coefficients table were used to determine which effects were significant. All factors with P-values less than 0.05 were considered significant.
3. Effects plots (normal probability plots and a Pareto chart) were also generated and are interpreted as follows: the two charts are evaluated to see which factors influence the yield. On the Pareto chart, any effect that goes beyond the reference line is significant at the chosen level of significance (α=0.05). A reference value and subsequently, a reference line, was found at the T-value at α=0.05 and the degrees of freedom of the experiment. The normal probability plot was used to check for normality (assumption of zero mean and constant variance). Normality is required in order to apply the hypothesis tests.
4. Minitab outputs the errors in the coefficients as SE coeff. These give the variances of the coefficients. The error sum of squares (SS_E) gives the error of the equation between the best fit and the actual points. It is shown in the results as SS (residual error). SS_E is related to variance by the degree of freedom (n-p). Variance is shown as MS (residual error). To test the hypothesis (t-tests) about the slope and intercepts of the regression model, it was assumed that the errors are normally distributed and independently distributed with mean zero and variances σ^2. T and P give the T test statistic of the coefficients and the P values respectively. The T value was compared with the t value at the level of significance and

the degrees of freedom to determine if the coefficient is significant (test for significance of regression).

5. The adequacy of the model is determined using the coefficient of determination (R^2).

3.5 Results

The results (in % yield) for the Plackett-Burman design are presented below in *Table 4*. Six (6) factors were considered for a base run of 12 (36 runs in total, 3 replicates). The standard deviations and confidence intervals are also calculated for each run. The run sequence and factor distributions are as presented in *Table 1*.

Table 3-4: Results (% yield) from the screening experiment

RUN	1	2	3	AVERAGE	Standard deviation	Confidence Interval
1	77.586	75.007	77.524	76.706	1.472	1.665
2	80.151	76.410	79.189	78.583	1.943	2.198
3	38.608	39.009	36.653	38.090	1.261	1.427
4	94.211	93.325	93.092	93.543	0.590	0.668
5	0.968	0.567	0.939	0.824	0.224	0.253
6	59.222	61.651	62.376	61.083	1.652	1.869
7	94.736	99.085	99.252	97.691	2.560	2.897
8	0.183	0.133	0.148	0.155	0.026	0.029
9	2.064	2.413	2.323	2.267	0.182	0.205
10	2.500	2.770	2.703	2.658	0.141	0.159
11	56.680	59.992	62.917	59.863	3.120	3.531

12	59.835	60.105	62.660	60.866	1.559	1.764

The results as obtained from Minitab are presented in *Table 5* below.

The coefficient of determination values are also calculated to be R^2 = 93.70%, R^2 (predicted) as 90.30% and R^2 (adjusted) as 92.40%.

Table 3-5: Estimated Effects and coefficients for Yield

Term	Effect	Coef	SE Coef	T	P
Constant		47.69	1.678	28.430	0.000
Temp	9.08	4.54	1.678	2.710	0.011
Stir	16.66	8.33	1.678	4.960	0.000
Catalyst	27.03	13.52	1.678	8.060	0.000
MeOH	-4.37	-2.18	1.678	-1.300	0.203
FFA	-60.3	-30.18	1.678	-17.990	0.000
Time	10.31	5.16	1.678	3.070	0.005

The Analysis of Variance (ANOVA) table is also presented below;

Table 3-6: Analysis of Variance for YIELD

Source	**DF**	**Seq SS**	**Adj SS**	**Adj MS**	**F**	**P**
Main Effects	6	43737.8	43737.8	7289.6	71.93	0
Temp	1	741.6	741.6	741.6	7.32	0.011
Stir	1	2497	2497	2497	24.64	0
Catalyst	1	6577.7	6577.7	6577.7	64.9	0
MeOH	1	171.7	171.7	171.7	1.69	0.203
FFA	1	32792.6	32792.6	32792.6	323.57	0
Time	1	957.3	957.3	957.3	9.45	0.005
Residual Error	29	2939	2939	101.3		
Lack of fit	5	2880.1	2880.1	576	234.86	0
Pure Error	24	58.9	58.9	2.5		
Total	35	46676.9	46676.9			

3.6 Analysis

The assumption of normality was checked with the residual plots generated in Minitab. Normality requires that the data has zero mean and constant variance. This is necessary in order to apply the hypothesis tests. It is seen from *Figure 3-3* that the data meets this assumption. The only outlier in the data is the run 11 value of 56.68.

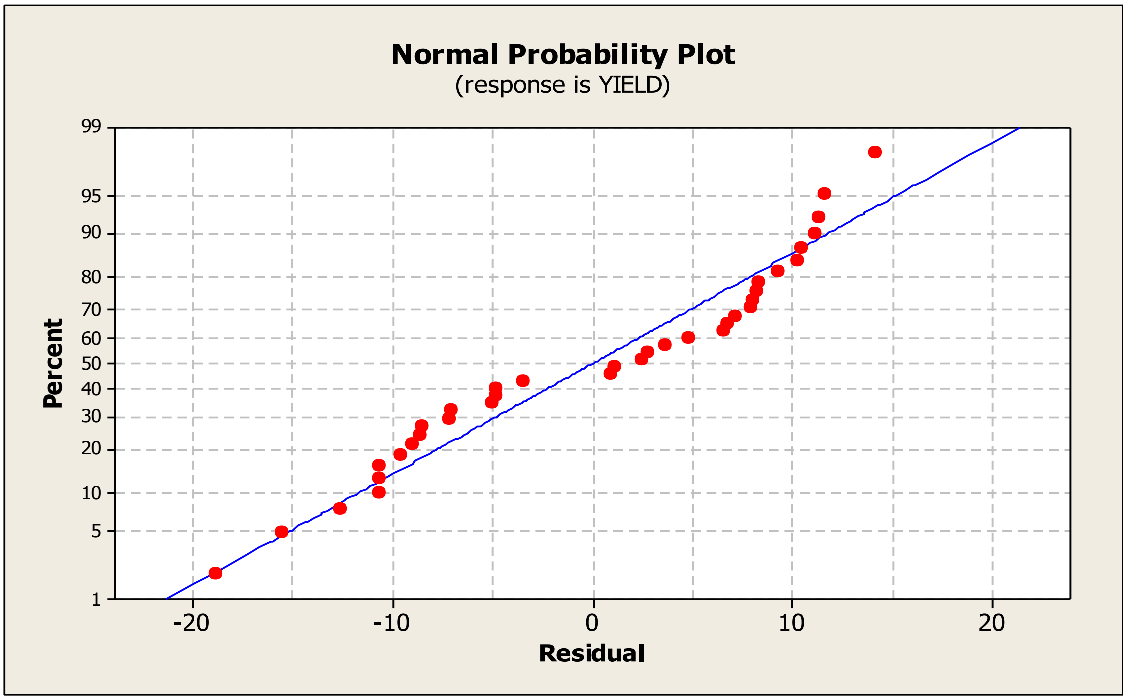

Figure 3-3: Normal Probability Plot for the Yield

The model equation obtained for the experiment is

$$Y = 47.69 - 30.18FFA + 13.52CATALYST + 8.33STIR + 5.16TIME + 4.54TEMP - 2.18MeOH$$ **…Equation 3-2**

Turck (2003) notes that increased FFAs react with the basic catalyst added for transesterification resulting in the formation of soap. As a consequence, one part of the catalyst is neutralised and is therefore not available for the transesterification reaction.

This clearly explains the very high negative effect of the FFA amounts on the yield of biodiesel. As the FFA amount is increased from 0.5 wt% to 6 wt % of the oil, there is increase in the saponification side reaction. The potassium carbonate reacts with the FFA to form soaps. This accounts for the drops in yield for reactions with high FFA amounts.

The catalyst amount is the second most important factor. The results show that increasing the catalyst amount from 1 wt% to 4 wt% oil greatly affects the yield of biodiesel. The importance of catalysis is well documented in literature (Feuge & Gros, 1949; Meher, et al., 2006; Freedman, et al., 1984). Base catalysis is particularly favoured and the results obtained truly reflect the importance of catalysis. Hartman (1956), compares the efficiency of several catalysts. This comparison was based on the amount of glycerol set free and the degree of soap formation. He mentioned that sodium methoxide and potassium carbonate set free 99-99.5% of the total glycerol and caused the least degree of saponification.

Potassium carbonate is not soluble in methanol (not at the temperatures studied). Stirring is employed to promote homogenisation of the reactants. Stirring facilitates the initiation of the reaction since it increases the reaction area between the oil and the catalyst-alcohol phase. Without stirring, the reaction would only occur at the interface of the different phases that may be present. This would make the transesterification process very slow and unfeasible. Ma, et al. (1999) note that the effect of stirring speed and time is only pronounced in the first 10 minutes. After a homogenous mixture is obtained, mixing does not affect the process that much. This could explain why increasing the rate of stirring from 400 rpm to 800 rpm does not affect the yield as much as the FFA and catalyst amounts do, even though stirring is very necessary to start the reaction. The importance of stirring is documented in Ma, et al. (1999) and Peterson et al. (1992).

Freedman, et al. (1984) studied the effect of methanol-oil molar ratio on yield from 1:1 to 6:1 molar ratios. It was found that the maximum conversion (98%) was obtained at 6:1 molar ratio, while 82% conversion was obtained at 3:1.. The amount of intermediates decreased as the molar ratios increased, indicating that conversion was complete. The methanol-oil ratio insignificance obtained in the present study suggests that the ratios investigated (3:1 and 6:1), exceeded the threshold requirement such that increasing the methanol-oil ratio did not have any effect on the yield.

It is only logical to assume that as the temperature increases, the rate of alcoholysis increases. Feuge and Gros (1949) and Freedman, et al. (1984) both studied the effect of temperature on the reaction yield. It was found that the initial stages of the reaction (0.1 hr) is highly affected by temperature but after 1 hr of reaction, the ester formation was identical for 60˚C and 45˚C and only slighly lower for 32˚C. This explains the low effect of temperature on the yield in changing it from 30˚C to 60˚C. The initial reaction rate is high for 60˚C but as the reaction approaches the hour mark, the yields obtained are not so different. Time and temperature have a strong relationship. Even though the reaction does not cease in 1 or 2 hours, it is very slow after the first hour (Feuge

& Gros, 1949). This explains why increasing the time of reaction from 1 to 3 hours has very little effect on the yield. The reaction nears completion in the first hour. After that, it proceeds slowly.

The Pareto chart below gives a graphical representation of the effects of the factors on the yield. It is also used to determine the active factors at the chosen 0.05 level of significance.

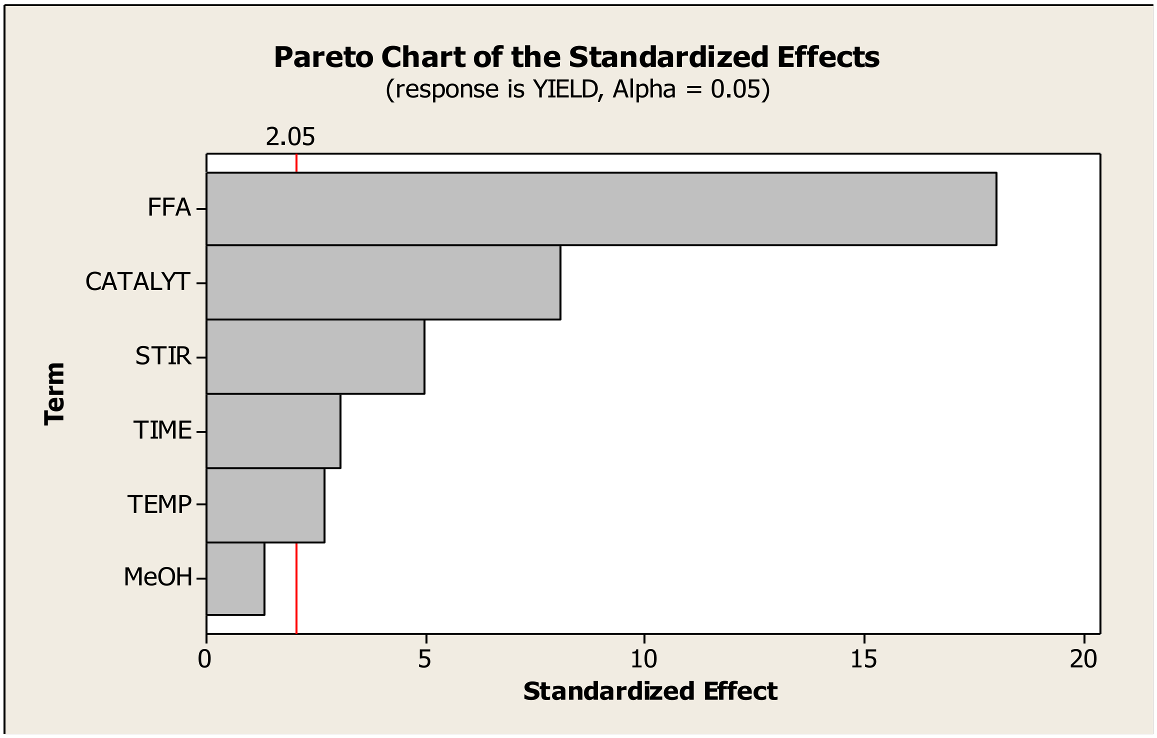

Figure 3-4: Pareto chart of Effects

At the chosen level of significance (α = 0.05) all the factors were found to be significant except the Methanol-Oil ratio. This means that changing the methanol-oil ratio from the low to high intervals used (3:1 to 6:1) did not affect the yield of biodiesel produced. It is realised above that FFA had the most significant effect.

The model obtained accounts for 93.70% of the total variability in the data as given by the R^2 value.

3.7 Conclusion

The Plackett-Burman methods is an effective screening method. The effects of each factor on the yield has been measured without having to do a full factorial design. The Pareto plot also affords a good way to tell which factors are active and need further consideration.

The amount of free fatty acid has the most negative effect on the yield of biodiesel. It is advised that where possible, the amount of FFA be reduced further before proceeding with base catalysis. Potassium carbonate is a very effective catalyst. Very high yields of biodiesel were obtained in an hour or so of reaction. It should however be mentioned that even though increasing the amount of catalyst increased the rate of the reaction and consequently the yield, a point is reached where there is an increase in the FFA catalyst side reaction. This could lead to the formation of soap.

It is also evident that the temperature and time of reaction has minimal effect on the yield on biodiesel obtained. Temperature only affects the initial stages of the reaction. The effects are mild afterwards. The transesterification reaction is also only rapid in the first hour of reaction. The rate of reaction proceeds slowly after that.

It is suggested that for maximum conversion of the ester, a 6:1 ratio be used. This is because even though the methanol-oil ratio doesn’t affect yield after the 3:1 ratio, it is always advised to have excess alcohol as this pushes the equilibrium position to the right, favouring the formation of products. Mixing is also very necessary, considering potassium carbonate is insoluble in methanol.

It is recommended that the effect of FFA, the weight of catalyst and the rate of stirring be further studied and optimised.

Chapter 4

4 Optimisation of biodiesel transesterification process variables: a Box-Behnken design application

4.1 Introduction

The production of biodiesel has seen tremendous growth in the last couple of years. Various researches have been conducted on finding the most favourable feedstock, feedstock catalyst combination and operating conditions. These parameters are also dependent on the availability of the feedstock, cost of production and the yield of biodiesel obtained.

While previous research has focused only on a few factors, the present study focussed on all key parameters that affect the yield of biodiesel (except pressure). Emphasis was not laid on the type of feedstock, therefore Canola oil was used as a base feedstock since it has been well studied in North America and makes a great choice for analysis. The oil used in the present study was particularly chosen to have very low FFA (<0.07%) so that the effect of FFA amounts on biodiesel yield could be studied.

In the transesterification reaction, triacylglycerol (TAG) is reacted with an alcohol (either methanol or ethanol), in the presence of a catalyst (base or acid) to produce glycerol and fatty acid alkyl esters. The entire biodiesel production process is summarized by this reaction and hence various reaction parameters are monitored to ensure that maximum yield (and/or conversion) and purity is achieved. These include:

- The alcohol to oil molar ratio
- Reaction temperature
- Catalyst concentration
- Reaction time

Various experiments have been conducted that propose the optimum values for the parameters stated above. These parameters (60°C reaction temperature and 6:1 methanol: oil molar ratio, 1wt% catalyst) have become a standard for methanol-based transesterification (Knothe, Gerpen, & Krahl, 2005).

Some reports also state that the transesterification reaction is more dependent on the alcohol to oil ratio, catalyst concentration and reaction time than on temperature (Joshi et al., 2009; Kuwornu & Ahiekpor, 2010)

From previous analysis done in our laboratory using the Plackett-Burman design, it was determined that within some specified intervals[4], the FFA amount, the rate of stirring and the amount of catalyst affect the yield of biodiesel more than the other factors do. Freedman et al. (1984) studied the effect of methanol-oil molar ratio on yields from 1:1 to 6:1 molar ratios. It was found that the maximum conversion (98%) was obtained at 6:1. They also observed that depending on the alcohol used, reactions at 60˚C to 100˚C resulted in 80-99% conversions in 2-60 minutes. Feuge & Gros (1949) and Freedman et al. (1984) also found that reaction is only highly affected by temperature in the initial stages of reaction. These observations are consistent with the findings of our previous work, hence the temperature, reaction time and methanol-oil ratio were kept constant at 60˚C, 1 hr and 6:1, respectively.

The Box-Behnken method was used for the present analysis. It is a 3-level spherical design with all the points lying on a sphere of radius $\sqrt{2}$. The Box-Behnken design does not contain any points at the vertices of the cubic region created by the upper and the lower limits of each variable (Montgomery, 2001). This design was preferred to the central composite design because the axial and corner points were thought to be extreme and that such high levels were not typical. This in effect reduced the number of runs for the Box-Behnken design.

4.2 Materials

Canola oil (certified organic) with FFA concentration of less than 0.10% was obtained from Sigma-Aldrich. Anhydrous potassium carbonate (min. 99 %) supplied by Caledon labs was obtained from the chemical store. Anhydrous grade methanol (99.8%) and technical grade linoleic

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[4] Refer to P.B notes

acid (about 65%) were also purchased from Sigma-Aldrich. Analytical grade methyl nonadecanoate (≥98.0%) from Sigma Aldrich and toluene were also purchased for the GC analysis.

4.3 Method

4.3.1 Experimental Set-Up

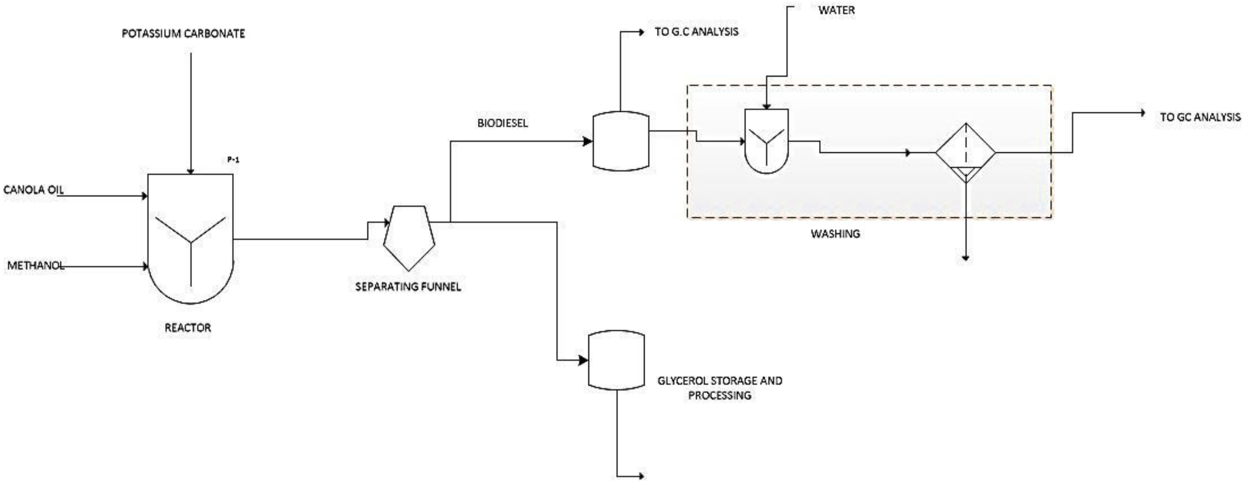

Figure 4-1: Process flow diagram; Transesterification stage

The reactor was a 250-mL Erlenmeyer flask. The opening was fitted with a Liebig condenser. To make the process water tight, the other opening of the condenser was fitted with a bent tube filled with (drierite) calcium sulphate and cotton. These materials were chosen to minimize any pressure build up that may accompany the sealing of the condenser.

This set up was mounted on a VWR 800 series advanced digital hot plate with a stirrer. The hot plate was also equipped with a temperature probe to ensure efficient measuring of temperature. To use the probe, an opening was made on the flask (reactor). This opening was made at a 60° angle to the surface of the flask. It was fitted with a rubber septum through which the probe was passed. The septum prevented airflow into the system. The stirrer also had a stop watch that measured the reaction time and automatically ended the reaction at the desired reaction time.

The reaction mixture was allowed to settle overnight by gravity in the separating funnel, and the two resulting phases were decanted into separate bottles. The glycerol was stored, tested for free fatty acids and later disposed of, while the FAME phase was taken for further testing (washing and methyl ester determination in the GC).

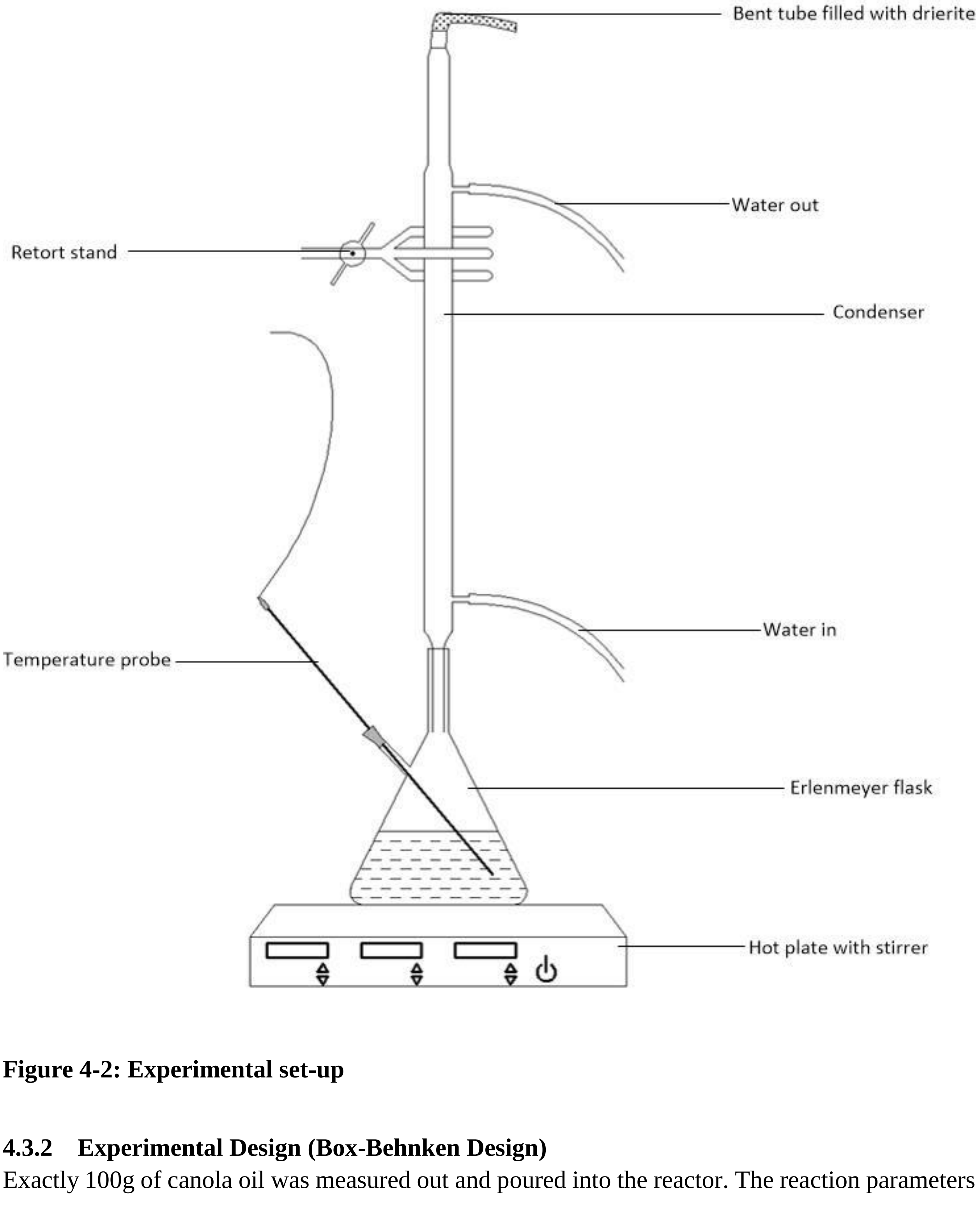

Figure 4-2: Experimental set-up

4.3.2 Experimental Design (Box-Behnken Design)

Exactly 100g of canola oil was measured out and poured into the reactor. The reaction parameters were modified for each run from the design. The design is as shown in table

Table 4-1: Box-Behnken Design

STANDARD ORDER	**FFA**	**STIR**	**CATALYST**
1	-1	-1	0
2	1	-1	0
3	-1	1	0
4	1	1	0
5	-1	0	-1
6	1	0	-1
7	-1	0	1
8	1	0	1
9	0	-1	-1
10	0	1	-1
11	0	-1	1
12	0	1	1
13	0	0	0
14	0	0	0

For a reaction time of 1hr, the temperature was kept constant at 60˚C and 6:1 methanol-oil ratio. The -1 (s), 0 (s) and 1 (s) are coded variables used to denote the high, center and low points of each variable. The actual values are given in *Table 7* below. The values used for each of the factors is based on findings from the Plackett-Burman design. Also, Yuan, et al., (2008) mentions that the transesterification would not occur if the FFA amount in the oil was over 2%. This explained the low yields of biodiesel that were obtained in the PB design with FFA amounts of 6% wt of oil. Hence, the FFA amount was decreased to 2% and used for the Box-Behnken design.

The amounts to use for each run was calculated (for a 100g of Oil) based on how the reaction proceeds. The reaction was reduced to as follows;

TAG + (x+y) MeOH = x FAME + GLYCEROL + y MeOH

The 6:1 Methanol-Oil ratio was calculated to be 21.762g.

Table 4-2: factor notations and amounts

NOTATION	FACTORS	LOW (-1)	CENTER (0)	HIGH (+1)
A	FFA amount (wt % oil)	0.5	1.25	2
B	Stirring Speed (rpm)	400	600	800
C	Catalyst Amount (wt % oil)	1	2.5	4

Two replicates of each run were done and the corresponding yield determined. The runs were also randomised to remove any correlations that may be present.

At the end of each run, the mixture was transferred into a separating funnel and the left to settle (by gravitation) overnight. The resulting layers are then decanted into separate bottles for analysis.

4.3.3 Gas Chromatography Analysis

The yield determination was done using gas chromatography. The method used is as outlined in EN 14103 (Determination of total FAME in B100 biodiesel).

Exactly 100 mg of each sample was measured using a high precision balance and put into a 12 mL vial. This was followed by addition of 100 mg of the internal standard (C19) to each sample. The masses in each case were recorded to the nearest 0.1 mg. The sample and standard were then dissolved in 10 mL of toluene. The resulting mixture was allowed to settle; it was then mixed thoroughly for 15 minutes after which three samples were drawn from each vial for GC analysis.

The yield of FAME is computed as:

$$C = \frac{\Sigma A - A_{IS}}{A_{IS}} x \frac{C_{IS} x V_{IS}}{m} x 100\ \%$$

Where ΣA: total peak area from C14 to C24

A_{IS} : Internal standard peak area

C_{IS}: Concentration of internal standard in mg/ml

V_{IS}: Volume of internal standard in ml

m: mass of sample in mg

Prior to this step, a FAME mixture (C8-C24) obtained from Agilent Canada was run and the resulting retention times used to aid in identification.

4.4 Results and Discussion

6. All the analysis was done in Minitab® 16.1.1.

- A model was fit to the data by inputting the yields for each run. The effects (contrasts) and corresponding sum of squares were calculated by the software. The total degrees of freedom and the T and P values for each factor are computed and displayed in the output results.

- The active (important) effects were identified using an $\alpha = 0.05$ (level of significance). The P-values in the estimated effects and coefficients table were used to determine which effects were significant. All factors with P-values less than 0.05 are significant.
- The normal probability plot was used to check for normality (assumption of zero mean and constant variance). Normality is required in order to apply the hypothesis tests.
- The errors in the coefficients are given as the SE coeff values. These give the variances of the coefficients. The error sum of squares (SS_E) gives the error of the equation between the best fit and the actual points. It is shown in the results as SS (residual error). SS_E is related to variance by the degree of freedom (n-p). Variance is shown as MS (residual error). To test hypothesis (t-tests) about the slope and intercepts of the regression model, it was assumed that the errors are normally distributed and independently distributed with mean zero and variances σ^2. T and P give the T test statistic of the coefficients and the P values respectively. The T value was compared with the t value at the level of significance and the degrees of freedom to determine if the coefficient is significant (test for significance of regression).
- The adequacy of the model was determined using the coefficient of determination (R^2).
- Response surface and contour plots were also used to graphically display the yields of biodiesel at different factor combinations.

4.4.1 Results

The results (in % yield) from the Box-Behnken designed is as summarised in Table 1. Three factors were analysed for a base run of 14. For two replicates of each run, 28 runs were considered in total (2 center points). The average values have been calculated for each yield and the corresponding standard deviation and confidence intervals also calculated.

Table 4-3: Results (in % yield) from the Box-Behnken design experiment

RUNS	1	2	AVERAGE	Standard Deviation	Confidence Interval
1	92.976	92.800	92.888	0.124	0.172
2	85.829	86.834	86.331	0.711	0.985
3	93.787	94.606	94.197	0.579	0.803
4	90.244	90.642	90.443	0.282	0.391
5	83.264	81.244	82.254	1.429	1.980
6	0.000	0.000	0.000	0.000	
7	97.405	97.556	97.481	0.106	0.147
8	93.189	93.157	93.173	0.023	0.031
9	1.552	1.456	1.504	0.068	0.094
10	69.876	73.664	71.770	2.679	3.713
11	95.543	93.591	94.567	1.380	1.913
12	95.814	94.753	95.283	0.751	1.040
13	87.173	89.622	88.398	1.731	2.400
14	87.955	88.731	88.343	0.549	0.760

4.4.2 Analysis

The assumption of normality was checked with the residual plots generated in Minitab. Normality requires that the data has zero mean and constant variance. This is necessary in order to apply the hypothesis tests. It is seen from *Figure 4-3* that the data meet this assumption.

The analysis of variance table, also generated in Minitab is shown below. At the chosen level of significance, the high F value (F_{model} = 20.01) and the very low probability value (P = 0.00) indicates the high significance of the fitted model. The same can be said for the linear, quadratic and interaction terms.

At 95% significance level, all the linear terms were significant but only the catalyst quadratic term was significant. It can also be seen that the FFA*Catalyst and the Stir*Catalyst interaction terms were significant while that between stirring and FFA wasn’t. All the terms are further discussed below.

The coefficient of determination (R^2) was found to be 90.91% (R-Sq.(adj) = 86.37%), indicating that the fitted model accounted for 86.37% (adjusted) of the total variation of the process and that only 13.63% was not explained by the model.

Table 4-4: Estimated coefficients and effects for yield

TERM	COEF	SE COEF	T	P

Constant	88.370	5.964	14.818	0.000
LINEAR				
FFA	-12.109	2.982	-4.061	0.001
STIR	9.550	2.982	3.203	0.005
CATALYST	28.122	2.982	9.431	0.000
QUADRATICS				
FFA	2.520	4.715	0.535	0.600
STIR	0.074	4.715	0.016	0.988
CATALYST	-22.664	4.715	-4.807	0.000
INTERACTIONS				
FFA*STIR	0.701	4.217	0.166	0.870
FFA*CATALYST	19.487	4.217	4.621	0.000
STIR*CATALYST	-17.387	4.217	-4.123	0.001

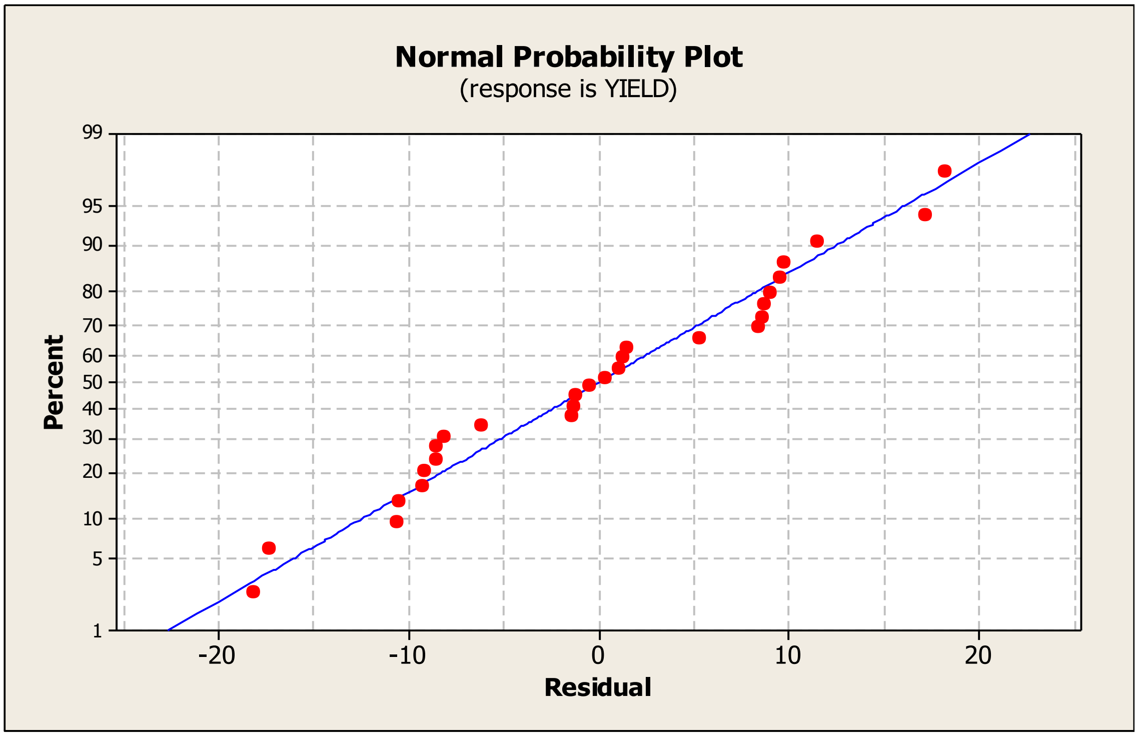

Figure 4-3: Normal Probability Yield

Table 4-5: Analysis of Variance for Yield

SOURCE	DF	SEQ SS	ADJ SS	ADJ MS	F	P
REGRESSION	9	25618.9	25618.9	2846.5	20.01	0.000
Linear	3	16458.9	16458.9	5486.3	38.56	0.000
FFA	1	2346.1	2346.1	2346.1	16.49	0.001
STIR	1	1459.3	1459.3	1459.3	10.26	0.005
CATALYST	1	12653.5	12653.5	12653.5	88.94	0.000
Square	3	3699.6	3699.6	1233.2	8.67	0.001
FFA*FFA	1	270.9	40.6	40.6	0.29	0.600
STIR*STIR	1	141.5	0.0	0.0	0.00	0.988

CATALYST*CATALYST	1	3287.3	3287.3	3287.3	23.11	0.000
Interaction	3	5460.3	5460.3	1820.1	12.79	0.000
FFA*STIR	1	3.9	3.9	3.9	0.03	0.870
FFA*CATALYST	1	3037.8	3037.8	3037.8	21.35	0.000
STIR*CATALYST	1	2418.5	2418.5	2418.5	17.00	0.001
Residual Error	18	2560.8	2560.8	142.3		
Lack-of-Fit	3	2544.8	2544.8	848.3	798.27	0.000
Pure Error	15	15.9	15.9	1.1		
Total	27	28179.7				

From the estimation of effects table, increasing the amount of FFA has a high negative effect on the yield of biodiesel obtained. From the ANOVA table, it can also be seen that there is a significant linear relationship between the yield and the FFA amount (F= 16.49, P = 0.01) but there is no quadratic relationship between the two (F=0.29, P= 0.60) at 95% significance.

The effect of FFA amounts on biodiesel yields is well documented and known. Turck (2003), mentions that increased FFAs react with the basic catalyst added for transesterification resulting in the formation of soap. As a consequence, one part of the catalyst is neutralised and is therefore not available for the transesterification reaction.

The results also show that increasing the catalyst amount from 1 wt% to 4 wt% oil greatly affects the yield of biodiesel. The catalyst has a significant linear (F = 88.94, P = 0.00) and quadratic term (F= 23.11, P= 0.00). It is realised that the quadratic term has a negative coefficient. This indicates that there is a possible point of inflexion after which increasing the amount of catalyst will have a rather negative effect on the yield. This is paricularly true since there will be an increase in the rate of the catalyst-FFA side reaction which leads to soap formation.

Stirring has a positive effect on the yield of biodiesel even though it is not as pronounced as that of the other factors. Ma, et al., (1999) mentions that the effect of stirring speed and time is only pronounced in the first 10 minutes. After a homogenous mixture is obtained, mixing does not affect the process that much. Stirring only has a linear relationship with the yield of biodiesel and a smaller coefficient compared to that of catalyst and FFA amounts. This could explain why increasing the rate of stirring from 400 rpm to 800 rpm doesn't affect the yield as much as the FFA and catalyst amounts do even though stirring is very necessary to start the reaction.

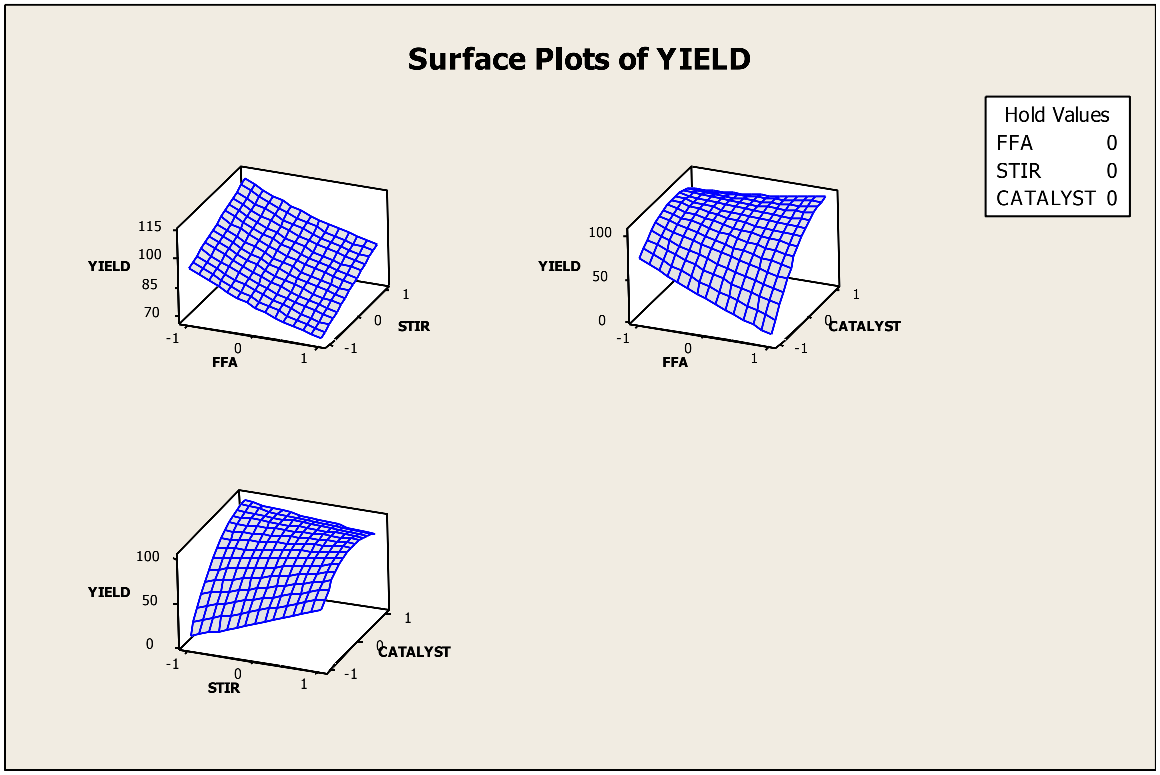

Figure 4-4: Surface Plot of Yield against factors

Interactions exist between the catalyst amounts and the rate of stirring and the amount of FFA. Interaction generally implies that the effect on the yield produced by one variable depends on the level of another variable. The FFA*Stir interaction term is insignificant (F = 0.03, P = 0.87). The surface plots make it easier to observe the interaction effects on the yield. In the FFA*Catalyst plot, it is noticed that if the FFA amount is changed from say 0 to 1, the change in yield at 1 level of catalyst isn't as pronounced as that at catalyst levels of -1. The similar analogy can be drawn for the Stir*Catalyst surface plot.

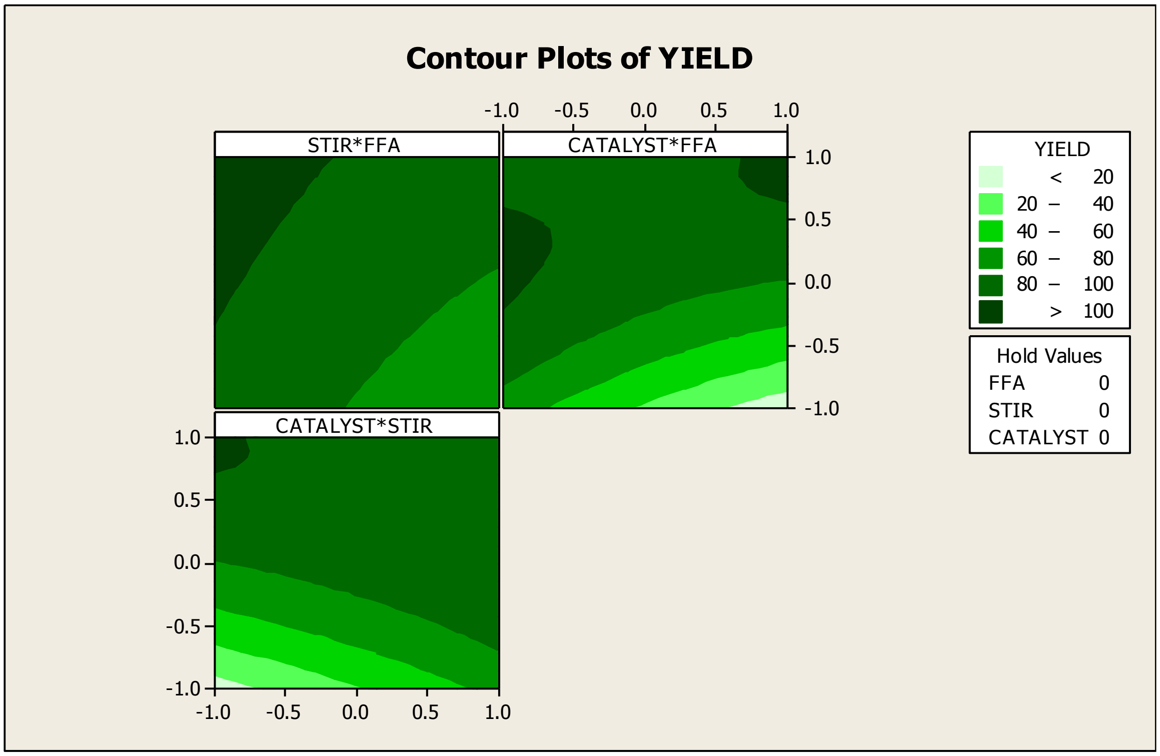

Figure 4-5: Contour plot of Yield

The contour plots below show the yield distributions for varying combinations of the factors. By holding one value constant at its middle value, the percentage yield is determined for two factor combinations. Realise from, say, the Catalyst*FFA plot, the yield increases with increasing catalyst amount for a given FFA amount. Similar deductions can be made from the other plots.

Using the surface optimiser in the Minitab® software package, it is found that the optimum factor combinations for a percentage yield greater than 98% is low (-1/ 0.5 g) FFA, low (-1/ 400 rpm) stirring rate and high catalyst amount (1/ 4 g).

4.5 Conclusion

7. The Box-Behnken method has effectively been used in determining the linear and quadratic relationship between the yield and the three factors considered for the study. It is also realised that the amount of FFA and catalyst amounts affect the yield greatly even though they have opposite effects.

8. The contour and surface plots give a graphical representation of the relationship between the factors and the yield. This helps in easily identifying optimum factor combinations for production. As per the results from the surface optimiser, it is advised that for optimum yield, the amount of FFA be reduced to the barest minimum; 0.5g in this case. Also, the stirring can be kept at 400 rpm for the process since it is only needed at the initial stages of the reaction. This also reduces cost that may accompany higher stirring speeds. The optimum catalyst amount is also found to be 4 g. It should however be remembered that increasing the catalyst amount also increased the rate of the saponification side reaction as was indicated by the quadratic relationship.

9. Using statistical methods, a process that could have involved optimising 6 individual factors has been done in the shortest time with very few runs. It is recommended that future experiments are designed and the appropriate statistical methods used. The Plackett-Burman design can always be used as a first step screening design before applying a surface response model.

4.6 References

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Chapter 5

5 Discussion and Conclusion

The advantages of designed experiments are well documented and known. Various designs have been proposed and have been used successfully in many fields. In the field of biofuels and particularly, biodiesel production, these methods are rarely used. The best guess and the one-factor-at-a-time approach have been used many a time. These methods, however, can produce very misleading results. It is advised that the factorial design be used. The Plackett-Burman and Box-Behnken methods were used effectively to determine and optimise the active factors at the transesterification stage of biodiesel respectively.

The Plackett-Burman method is a mathematical tool that is used to determine all the active factors in an experiment. In this experiment, the method was used to determine and rank all the 6 factors that were considered in the initial screening design. It was found that the amount of FFA had the most effect (negative) on the yield of biodiesel obtained. It was also found that increasing the methanol-oil ratio from 3:1 wt% to 6:1 wt% had an insignificant effect on the yield. The pareto plot was used to rank the factors in order of magnitude of effect on yield. Based on these findings, three factors were selected for further analysis.

The Box-Behnken method was then used to optimise the amount of FFA, the stirring speed and the amount of catalyst. The surface and contour plots were effectively used in determining the optimum factor combinations for the maximum yield.

It is realised that by using these designed experiments, the number of runs have been reduced. Fewer runs were used to determine the optimum conditions as opposed to the other methods used in experiments. These consequently reduced the cost of running the experiments, the time to run the experiments and also obtain the optimum conditions for production of biodiesel. It is suggested that where several factors affect a process, an initial screening experiment (using Plackett-Burman design) be used to identify the active factors before proceeding with the full experiment.

The results from this experiment can be used to model future experiments on the optimisation of biodiesel. The results of the screening experiment in particular can be used to decide what factors to consider for optimisation for a given experiment. The feedstock used is one that has been experimented on many times in Canada and hence its properties are very well known. This experiment, unlike others does not focus on the starting materials but on using mathematical methods to determine the optimum factor combinations for biodiesel production. The model equation obtained can be used as a base to predict the effects of the factors on different feedstock.

Chapter 6

6 Appendix

6.1 GC Conditions

1. Column temperature: 60˚C hold for 2 mins

   10˚C/min to 200˚C

   5˚C/min to 240˚C

   Hold 240˚C for 7mins

2. Injector and detector temperature: 250˚C
3. Carrier gas flow rate: 1-2 ml/min
4. Injected sample volume: 1 µl
5. Hydrogen pressure: 70 kPa
6. Split flow: 100 ml/min

6.2 Plackett-Burman Results

INITIAL 12 RUNS						
RUN	1	2	3	AVERAGE	S.D	C.I
1	77.363	75.448	79.948	77.586	2.258	2.555
2	80.717	79.005	80.730	80.151	0.992	1.123
3	41.884	36.151	37.790	38.608	2.953	3.341
4	94.211			94.211		
5	0.748	1.068	1.088	0.968	0.191	0.216
6	61.228	60.813	55.626	59.222	3.121	3.532
7	96.148	92.810	95.251	94.736	1.727	1.955
8	0.100	0.210	0.240	0.183	0.074	0.083
9	2.097	1.878	2.216	2.064	0.171	0.194
10	2.794	2.355	2.350	2.500	0.255	0.288
11	56.521	53.188	60.331	56.680	3.574	4.044
12	58.382	60.472	60.650	59.835	1.261	1.427

REPLICATE 1						
RUN	1	2	3	AVERAGE	S.D	C.I
1	71.265	74.180	79.575	75.007	4.216	4.771
2	83.233	73.374	72.622	76.410	5.921	6.700
3	39.205	38.460	39.361	39.009	0.482	0.545
4	92.835	95.191	91.948	93.325	1.676	1.897
5	0.550	0.530	0.620	0.567	0.047	0.053
6	63.718	63.102	58.134	61.651	3.062	3.465
7	99.372	98.709	99.173	99.085	0.340	0.385
8	0.131	0.117	0.152	0.133	0.018	0.020
9	3.250	2.260	1.730	2.413	0.772	0.873
10	2.210	3.340	2.760	2.770	0.565	0.639
11	53.840	62.035	64.100	59.992	5.427	6.141
12	60.144	60.065	48.200	60.105	0.056	0.077

REPLICATE 2						
RUN	1	2	3	AVERAGE	S.D	C.I
1	77.752	77.219	77.600	77.524	0.275	0.311
2	80.131	78.270	79.165	79.189	0.931	1.053
3	37.850	36.330	35.778	36.653	1.073	1.214
4	96.535	91.322	91.419	93.092	2.982	3.375
5	0.574	1.358	0.884	0.939	0.395	0.447
6	61.091	61.188	64.850	62.376	2.143	2.425
7	100.000	99.376	98.380	99.252	0.817	0.925
8	0.168	0.130	0.144	0.148	0.019	0.022
9	2.290	2.060	2.620	2.323	0.281	0.319
10	2.370	3.060	2.680	2.703	0.346	0.391
11	60.710	63.240	64.800	62.917	2.064	2.336
12	62.610	67.790	62.710	62.660	0.071	0.098

6.3 Box-Behnken Results

FIRST SET						
RUN	1	2	3	AVERAGE	S.D	C.I
1	91.988	93.964		92.976	1.397	1.936
2	84.686	83.177	89.623	85.829	3.371	3.815
3	92.003	94.253	95.106	93.787	1.603	1.814
4	90.349	90.138		90.244	0.149	0.207
5	82.385	83.709	83.699	83.264	0.762	0.862
6	0.000	0.000	0.000	0.000	0.000	
7	95.952	100.000	96.264	97.405	2.252	2.549
8	91.490	93.650	94.427	93.189	1.522	1.722
9	1.200	1.305	2.152	1.552	0.522	0.591
10	70.515	69.236		69.876	0.904	1.253
11	93.843	98.734	94.052	95.543	2.765	3.129
12	96.300	95.421	95.722	95.814	0.447	0.505
13	84.435	86.590	90.495	87.173	3.072	3.476
14	85.818	84.220	93.827	87.955	5.148	5.825

REPLICATE ONE						
RUN	1	2	3	AVERAGE	S.D	C.I
1	93.299	92.301		92.800	0.706	0.978
2	87.280	86.155	87.066	86.834	0.597	0.676
3	94.613	93.963	95.243	94.606	0.640	0.724
4	93.960	89.593	88.373	90.642	2.938	3.324
5		82.215	80.273	81.244	1.373	1.903
6	0.000	0.000	0.000	0.000	0.000	
7	96.795	97.827	98.045	97.556	0.668	0.756
8	93.852	92.462		93.157	0.983	1.362
9	1.387	1.525		1.456	0.098	0.135
10	74.210	72.558	74.224	73.664	0.958	1.084
11	94.051	93.131		93.591	0.651	0.902
12	89.659	94.599	100.000	94.753	5.172	5.853
13	87.556	90.543	90.767	89.622	1.793	2.029
14	86.912	88.650	90.631	88.731	1.861	2.106

6.4 Formulae and short notes

i. Effects = $\frac{contrasts}{number\ of\ runs}$

ii. Sum of squares = $\frac{contrasts^2}{number\ of\ runs}$

iii. contrasts refers to the sum of the quantities that correspond to the + and – in the design matrix

iv. Plackett-Burman design has the main effects partially confounded with all interactions that do not contain that main effect. i.e. A = A + $\frac{1}{3}[BC + \cdots]$ for A,B,C.

v. $S^2 = \frac{\Sigma(X-\chi)^2}{N-1}$ where (N-1) = Degrees of freedom, S^2 = Variance, (X-X) = Residual

vi. $SS_T = SS_E + SS_R$ where SS_T = Total sum of squares, SS_E = Error sum of squares, SS_R = Regression sum of squares

vii. $MS_T = \frac{SS_T}{n}$, $MS_E = \frac{SS_E}{n-k}$, $MS_R = \frac{SS_R}{k}$ where MS = mean square

viii. S_E is the standard deviation of the error term

ix. MS_E = Variance of the error term = S_E^2

x. R^2 = ratio of the variance in the regression model to the total regression = $\frac{SS_R}{SS_T}$. It is the proportion of the variability in the response explained by the model.

xi. F distribution, $F_o = \frac{MS_R}{MS_E}$, is an asymmetrical distribution that has a zero minimum value and no maximum value. It has two degrees of freedom corresponding to the SS_R and SS_E respectively.

xii. Predicted R^2 reflects how well the model will predict future data.

xiii. Adjusted R^2 is a modified R^2 that adjusts for the number of terms in the model. It is obtained by dividing SS_R and SS_T by their degrees of freedom.

xiv. SE Coef is the standard error of the coefficient. It is calculated from the variance of the error term (MS_E) and the covariant matrix.

xv. Seq. SS reports how much the model sum of squares increases when each group of terms is added a model that contains the terms listed above the group.

xvi. Adj. SS reports how much the model sum of squares increases when each group of terms is added to a model that contains all the other terms.

xvii. T-value = $\frac{coeff}{SE\ Coeff}$

Chapter 7

7 Curriculum Vitae

CAREER OBJECTIVES

- To have a challenging career in Process and Project Engineering where I will have the chance to share with and learn from others new ideas. These I hope I can implement in future operations

PROJECTS

- The destructive distillation of a local Bamboo species; Determination of the physicochemical properties of the charcoal and determination of the composition of the distillate
- Plant design to treat Acid Mine Drainage by physicochemical methods
- Production of biogas from waste bio-materials
- Optimisation of the biodiesel production process of Canola Oil and Potassium Carbonate using Plackett – Burman and Response Surface Designs

WORK EXPERIENCE

- Teaching and Research Assistant, Civil and Environmental Engineering Dept., UWO.
    - Help with Hydrology and Air Pollution classes and Matlab classes.
- Teaching Assistant, Chemical Engineering Department, KNUST
  (August 2010 – August 2011)

  - Help with Thermodynamics, Mechanical Separation and Engineering Drawing Classes.
- AngloGold Ashanti Ltd; Sulphide Treatment Plant – Vacation Internship
  (June - August 2008)
  - Trained in BIOX, CIL and CMF
  - Trained in laboratory work
- Teacher, St. Philip's School (September 2005 – July 2006)

ACTIVITIES

- Research group leader, Chemical Engineering projects, 3rd and 4th years, KNUST.
- Teaching and Research Assistant , Chemical Engineering Department, KNUST
- Teaching Assistant, Civil and Environmental Engineering Department, UWO
- Afren PLC Oil seminar
- Member, Chemical Engineering Students Association, Ghana
- Member, Ghana Engineering Students Association, Ghana
- Member, Brilliant Science and Maths Quiz Team, St. Augustine's College

HONOURS

- First class honours, Kwame Nkrumah University of Science and Technology
- Best core Mathematics student, St. Augustine's College
- Overall Best student, St. Philip's School
- COCOBOD Scholarship recipient, St Augustine's College
- Nominee for Presidential Award, Obuasi Municipality
- Research team leader – KNUST RPI biogas project

EDUCATION

- St Philip's School, Obuasi, Ashanti Region. Ghana (1999 – 2002)
- St Augustine's College, Cape Coast, Central Region. Ghana (2002 – 2005), Gen. Science
- Kwame Nkrumah University of Science and Technology, Kumasi, Ashanti Region. Ghana (2006 – 2010), BSc. Chemical Engineering
- University of Western Ontario, London, Ontario. Canada (2011 to date), Civil and Environmental Engineering

PERSONAL ATTRIBUTES

- I am a team player
- Disciplined and competent
- I am optimistic and ready to learn

COMPUTER SKILLS

I have competent knowledge in;

- Microsoft Office
- AutoCAD
- Minitab
- Matlab
- General use of the internet