BIODIESEL PROCESS OPIMIZATION USING HETEROGENOUS CATALYST

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Dehradun
May, 2008

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A thesis submitted in partial fulfilment of the requirements for the Degree of
Bachelor of Technology
(Applied Petroleum Engineering)

By

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(ISO 9001:2000 Certified)

CERTIFICATE

This is to certify that the work contained in this thesis titled “Biodiesel process optimization using heterogeneous catalyst” has been carried out by Ankur Mishra & Ram Kumar under my supervision and has not been submitted elsewhere for a degree.

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ABSTRACT

Biodiesel is a cleaner burning fuel than diesel and a suitable replacement. It is made from non-toxic, biodegradable, renewable resources, such as new and used cooking oil, and animal fats. Fats and oils are chemically reacted with alcohols (ethanol was used in this work) to produce chemical compounds known as fatty acid ethyl esters (biodiesel). Glycerol, used in the pharmaceuticals and cosmetics industry along with many other applications, is produced in this reaction as a by-product. The relative high cost of refined oils, fats and production methods makes biodiesel more expensive than petroleum-derived fuel. It was found that the high consumption of catalyst and low yields of ethyl esters in conventional processing limits the use of crude feed stocks. Preliminary studies with crude feed stocks, such as crude tallow and used oils and several different catalysts provided some kinetic data on the transesterification reaction. This was achieved by conducting the reactions at various temperatures and reactant molar ratios.

Although homogenous acid catalysed esterification is slower than alkali catalysed transesterification, at moderate temperatures, it is significantly increased at temperatures up to 240°C. Unlike current commercial processes, this reaction can make use of crude feedstocks and gives high yields, which have subsequently generated much interest. The data during this project was obtained in a pressurised batch reactor with the future intent of applying it to a continuous process with a heterogeneous catalysts and crude feed stocks. In order to meet the detailed requirements for biodiesel fuel, gas chromatography coupled with a simple sample preparation step was developed to handle quantitative analysis of the product mixture. Although, this method analyses the full spectrum of products and is accurate, reliable, but a slightly expensive; new technology like Near Infrared Spectroscopy may offer inexpensive online analysis.

ACKNOWLEDGEMENT

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1.0 INTRODUCTION

1.1 OBJECTIVES

Biodiesel presents a suitable renewable substitute for petroleum based diesel. The current production process for biodiesel is through a batchwise reaction, which disadvantages it because of high capital costs, labour intensity and difficult process and product quality control. An obvious method to avoid or minimise these difficulties is to use a continuous production process, to achieve this it is necessary to have a good knowledge of the chemical transformation reactions and their kinetics. Underlying this is the requirement to be able to analyse the conversion on a dynamic basis. This therefore permits the reaction conditions to be optimised. The primary objectives of this thesis are therefore to quantify the kinetics of the reaction with a batch reactor and develop a suitable analysis technique for this purpose. The literature review has shown that there are a variety of options for the production of biodiesel. These are all disadvantaged by raw materials that are high in free fatty acids and have a significant quantity of water present. There would be clear commercial advantages in being able to process low grade raw materials that are cost effective in a continuous process. These issues all arise due to the limitations associated with current catalysts. To take advantage of these further developments catalyst development needs to be achieved. This work addresses these as specific objectives;

a) test potential catalysts for their suitability and
b) collect kinetic data on their subsequent reaction rates

This information will then be used for the development of a continuous process. A key requirement for a continuous process is a suitable heterogeneous catalyst that not only fulfils the high reaction rate requirements but also has features such as; insolubility in the reaction mixture, long working life, suitable particle size, high temperature resistance and a large surface area.

1.1.1 Implementation

An analytical procedure that correctly quantified the products and extent of conversion represents the single most important requirement of this project. This was therefore accorded a very high priority. Nevertheless, developing an analytical procedure that routinely provided trustworthy and reproducible results, presented a significant hurdle which consumed the major part of the project program. A plug flow continuous reactor is correctly simulated by a batch reactor, and this provides a convenient means for screening reactions for preparation of their use in a plug flow tubular reactor. Batch experiments typically took two hours to conduct; analytical preparations took approximately five hours. This limited the total number of experiments that could feasibly be conducted in the period available.

2.0 LITERATURE REVIEW

2.1 SCOPE

This literature survey discusses the benefits of using biodiesel as a suitable diesel substitute, whilst briefly touching on the history behind alternative compression engine fuels. It discusses some of the more current manufacturing techniques for the production of biodiesel as well as some new technology that is being researched. This is primarily focusing on developments in catalyst application, problems associated with different catalysts and the benefits of various catalyst systems. The area of downstream processing is briefly discussed, however separation is outside the focus of this work. Some critical analysis is discussed on the pros and cons of different systems and details of the analysis methods available and why and why not they are implemented in this work. Finally there is a discussion section and recommendation for further research section that highlights the areas in this research that are in need of further development.

2.2 INTRODUCTION

With the exception of hydroelectricity and nuclear energy, the majority of the worlds energy needs are supplied through petrochemical sources, coal and natural gas. All of these sources are finite and at current usage rates will be consumed by the end of the next century (Aksoy, 1990). The depletion of world petroleum reserves and increased environmental concerns has stimulated recent interest in alternative sources for petroleum-based fuels. Biodiesel has arisen as a potential candidate for a diesel substitute due to the similarities it has with petroleum-based diesel.

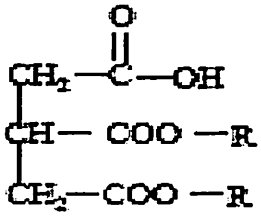
2.3 BACKGROUND

2.3.1 Fats and Oils

The use of vegetable oils as alternative fuels has been around since 1900 when the inventor of the diesel engine Rudolph Diesel first tested them, in his compression engine (Foglia, Jones, Haas, & Scott, 2000). To date there have been many problems found with using vegetable oils directly in diesel engines (especially in direct injection engines). These include (Ma, 1999):

1. Coking and trumpet formation on the injectors to such an extent that fuel atomisation does not occur properly or is even prevented as a result of plugged orifices,
2. Carbon deposits,
3. Oil ring sticking,
4. Thickening and gelling of the lubricating oil as a result of contamination by vegetable oils, and
5. Lubricating problems.

Other disadvantages to the use of vegetable oils and especially animal fats, are the high viscosity (about 11 to 17 times higher than diesel fuel), lower volatilities content which causes the formation of deposits in engines due to incomplete combustion and incorrect vaporisation characteristics. Table 1 shows the percentages of unsaturated fatty acids in some typical oils, the degree of saturation is dictated by the number of double bonds in the fatty acids e.g. 18:01 denotes a carbon length of 18 with on double bond. At high temperatures there can be some problems with polymerization of unsaturated fatty acids, this is where cross linking starts to occur between other molecules, causing very large agglomerations to be formed and consequently guming occurs (Pryde, 1983). This problem does not occur with fats as they have a very low concentration of unsaturated fatty acids as can be seen in table 2. Ethanol can be used as an additive to improve these properties, but pure vegetable oils are rarely used for a straight diesel fuel substitute. Ethanol as an additive or a reactant is often preferred in place of other simple alcohols, such as methanol because it is less toxic and because it is easily produced from renewable sources such as biomass or grains (Foglia et al., 2000). Fats, due to their high melting point and viscosity, can not be used directly in diesel engines or mixed with diesel fuels. The degree of saturation of the fatty acids attached to the glycerol backbone determines the boiling point of the triglyceride. As such, compared with oils, little research has been done on their potential as diesel fuel. Some typical composition of fats and oils can be found in tables 1& 2 (Ma, 1999). Fats and oils are primarily composed of triglycerides, esters of glycerol (mono- & diglycerides) and fatty acids (carboxylic acids). The term monoglyceride or diglyceride refers to the number of fatty acids that are attached to the glycerol backbone i.e. a diglyceride would have one hydroxyl group and two fatty acid groups attached to the glycerol backbone as in figure 1.



Diglyceride

Fig. 1. Diglyceride with two fatty acid groups

Table 1. Typical chemical properties of vegetable oil (Groaring et al., 1982)*

Vegetable oil	Fatty acid composition, % by weight						
	Palmitic	Stearic	Oleic	Linoleic	Linolenic	arachidic	
	16:00	18:00	18:01	18:02	18:03	20:00	Acid*Value
Corn	11.67	1.85	25.16	60.6	0.48	0.24	0.11
Cottonseed	28.33	0.89	13.27	57.51	0	0	0.07
Crambe	2.07	0.7	18.86	9	6.85	2.09	0.36
Peanut	11.38	2.39	48.28	31.95	0.93	1.32	0.2
Rapeseed	3.49	0.85	64.4	22.3	8.23	0	1.14
Soybean	11.75	3.15	23.26	55.53	6.31	0	0.3
Sunflower	6.08	3.26	16.93	73.73	0	0	0.15

Table 2. Typical fatty acid composition - of common oil source (Kincs, 1985)

Lipid	Fatty acid composition, % by weight						
	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic
	12:00	14:00	16:00	18:00	18:01	18:02	18:03
Soybean	0.1	0.1	10.3	3.7	22.8	53.7	8.6
Cottonseed	0.1	0.7	20.1	2.6	19.2	55.2	0.6
Palm	0.1	1	42.8	4.5	40.5	10.1	0.2
Lard	0.1	1.4	23.6	14.2	44.2	10.7	0.4
Tallow	0.1	2.8	23.3	19.4	42.4	2.9	0.9
Coconut	46.5	19.2	9.8	3	6.9	2.2	0

2.3.2 Biodiesel

Subsequent research found that triglycerides could be converted into simple alkyl fatty acid esters (Biodiesel) which has similar properties to diesel see table 3 & 4. The first documented commercial production of rapeseed oil methyl esters is reported to be in 1988 (Korbitz 2001). To date biodiesel production can be found in over 28 countries of which Germany and France are the world's largest [Kusdiana, 2002].

Table 3. Comparison of typical properties of diesel, canola oil and biodiesel

	Diesel	Canola	Biodiesel
Density (kg/L)	0.835	0.922	0.88
Gross calorific value (MJ/L)	38.3	36.9	33.3
Viscosity (mm^2/s @ 37.8°C)	3.86	37	4.7
C:H:O (ratio)	3.59	3.26	2.38
Sulphur (%)	0.15	0.0012	<0.01

Source: Adapted from Table 6.1 of BTCE (1994) and from www.afdc.doe.gov . The C:H:O ratio for biodiesel is taken from http://www.biodiesel.org/fleets/summary.shtml#attributes

*Table 4. Properties of ethyl ester and diesel control fuel**

	REE (Rapeseed Ethyl Ester).	Diesel
Gross heat of combustion (MJ/kg)	40.5	45.2
Flash Point °C	124	82
Cloud Point °C	-2	-14
Pour Point °C	-10	-21
Viscosity cs @ 40°C	6.17	2.98
Cetane Number	59.7	49.2

*Based on analysis by Phoenix Chemical Lab, Inc. and the Agricultural Engineering Analytical Laboratory, University of Idaho. REE

Biodiesel has many benefits such as it is biodegradable, non-toxic, has a low emission profile (including potential carcinogens) and is a renewable resource (Ma, 1999). European biodiesel is typically made from rapeseed oil and methanol, whereas in the US it is predominately made from soybean oil. This reflects the agricultural practices of the two regions.

2.3.3 Production Costs

The greatest hurdle in commercialisation of biodiesel is the cost of production. Currently, raw material costs and the cost of production are keeping the retail price of biodiesel too high for it to be an option for many users. The current method of production is with large batch reactors. Raw materials generally consist of methanol mm_2 / s and high-quality vegetable oils. Only approximately 55% of the US biodiesel industry can use any fat or oil feedstock, the remainder is limited to refined vegetable oils, the least expensive of which is soy bean oil. Although the production of biodiesel is now conducted on a large scale, there are still many problems with using crude feed stock (Ma, 1999). Until these problems are resolved with measures such as a continuous process and the use of crude oils waste fats, such as used cooking oils and abattoir fats, the cost of production will remain relatively high. The recovery of high quality glycerol, a by-product which is required for many other processes, would also contribute to substantially reducing production costs.The European Union has set an objective to secure for motor biofuels a market share of 5% of total motor fuel consumption by 2005 (a significant amount of this will be biodiesel). The US Department of Energy estimates that up to 50% of the total diesel fuel consumption could be replaced with biodiesel. US production of biodiesel, from both fats and oils is currently approximately 7.12 billion litres (Alcantara 2000).

2.4 PROCESS OVERVIEW

There are several generally accepted ways to make biodiesel some more common than others, e.g. blending and transesterification, and several others that are more recent developments .e.g. reaction with supercritical methanol. An overview of these processes is as follows;

1. *Direct use and Blending*, which is the use of pure vegetable oils or the blending with diesel fuel in various ratios,
2. *Microemulsions* with simple alcohols,
3. *Thermal Cracking* (pyrolysis) to alkanes, alkenes, alkadienes etc

4. *Transesterification* (alcoholysis) which consists of several sub categories;
    i. esterification ,
    ii. saponification,
    iii. hydrolysis (reaction with water) and
    iv. aminolysis (reaction with amines)
5. *Other forms of catalysis*
    i. biocatalysts
    ii. reaction with supercritical methanol
    iii. catalyst free

2.4.1 Direct use and blending

The direct use of vegetable oils in diesel engines is problematic and has many inherent failings. It has only been researched extensively for the past couple of decades, but has been experimented with for almost a hundred years. Although some diesel engines can run pure vegetable oils engines, turbocharged direct injection engines such as trucks are prone to many problems (BTCE, 1994). Energy consumption, with the use of pure vegetable oils, was found to be similar to that of diesel fuel (Hemmerlein et al. 1991). For short term use ratios of 1:10 to 2:10 oil to diesel have been found to be successful (Ma, 1999). The difficulties may be grouped into three key areas:

2.4.2 Viscosity

As can be seen from table 3 the properties of canola oil and diesel are very similar, except a significant difference in viscosity, with canola oil having twelve times the viscosity of diesel. Even after heating to around 80°C it is still six times as viscous as diesel. This leads to problems with flow of oils from the fuel tank to the engine, blockages in filters and subsequent engine power losses. Even if preheating is used to lower the viscosity, difficulties may still be encountered with starting due to the temperatures required for oils to give off ignitable vapours. Further, engines can suffer coking and gumming which leads to sticking of piston rings due to multibonded compounds undergoing pyrolyses. Polyunsaturated fatty acids also undergo oxidation in storage causing gum formation and at high temperatures where complex oxidative and thermal polymerisation can occur (Ma 1999).

2.4.3 Microemulsions

Microemulsions are defined as a colloidal equilibrium dispersions of optically isotropic fluid microstructures, with dimensions generally in the 1-150 nm range. These are formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphophiles (Schwab et al., 1987). A microemulsion is designed to tackle the problem of the high viscosity of pure vegetable oils by reducing the viscosity of oils with solvents such as simple alcohols. The performances of ionic and non-ionic microemulsions where found to be similar to diesel fuel, over short term testing. They also achieved good spray characteristics, with explosive vaporisation which improved the combustion characteristics (Ma, 1999). In longer term testing no significant deterioration in performance was observed, however significant injector needle sticking, carbon deposits, incomplete combustion and increasing viscosity of lubricating oils where reported (Ma, 1999).

2.4.5 Thermal Cracking

Pyrolysis is the conversion of one substance into another by means of applying heat i.e. heating in the absence of air or oxygen with temperatures ranging from 450°C – 850°C (Sonntag, 1979b). In some situations this is with the aid of a catalyst leading to the cleavage of chemical bonds to yield smaller molecules (Weisz et al., 1979). Unlike direct blending, fats can be pyrolyised successfully to produce many smaller chain compounds. The pyrolysis of fats has been investigated for over a hundred years, especially in countries where there is a shortage of petroleum deposits. Typical catalyst that can be employed in pyrolysis are SiO_2 and ${}_{2\,3}Al\ O$. The ratios of light to heavy compounds are temperature and time dependent. Typical breakdown of compounds found from pyrolyisis of safflower and soybean oil, are listed in table 5.

Table 5. Compositional data of pyrolysis of oils (Ma 1999)

	Percent by weight	
	*HO Safflower	Soybean
Alkanes	40.9	29.9
Alkenes	22	24.9
Alkadienes	13	10.9
Aromatics	2.2	1.9
Unresolved unsaturates	10.1	5.1
Carboxylic acids	16.1	9.6
Unidentified	12.7	12.6

*HO High Oleic Safflower oil

The equipment for pyrolysis or thermal cracking is expensive for modest throughputs. Although, the products are chemically similar to pyrochemically based diesel, oxygen removal from the process decreases the products benefits of being an oxygenated fuel. This decreases its environmental benefits and generally produces more fuel similar in properties of gasoline than diesel, with the addition of some low value materials.

2.4.6 Transesterification

Transesterification is the reaction of a lipid with an alcohol to form esters and a byproduct, glycerol. It is in principle the action of one alcohol displacing another from an ester, the term alcoholysis (cleavage by an alcohol).The reaction, as shown in figure 2 is reversible and thus an excess of alcohol is usually used to force the equilibrium to the product side. The stoichiometry for the reaction is 3:1 alcohol to lipids; however in practice this is usually increased to 6:1 to increase product yield. A catalyst is usually used to speed up the reaction and may be basic, acid or enzymatic in nature (Ma, 1999). The alkalis that are generally used include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodiummethoxide, ethoxide, propoxide and butoxide. Sodium hydroxide is the most commonalkali catalyst that is used, due to economical reasons and availability. Alkali catalysed reactions are used more often commercially than acid catalysts, as the reactions are faster. Only simple alcohols can be used in transesterification such as, methanol, ethanol,propanol, butanol and amyl alcohol. Methanol is most often used for commercial and process reasons related to its physical and chemical nature (shortest chain alcohol and is polar). However ethanol is becoming more popular as it is a renewable resource and does not raise the same toxicity concerns as methanol (Ma, 1999). The type of catalyst, the reaction conditions and the concentration of impurities in a transesterification reaction determine the path that the reaction follows. For alkali catalysed transesterification, water and FFA are not favourable to the reaction, so anhydrous triglycerides and alcohol are necessary to minimise the production of soap. Soap production decreases the amount of esters and renders the separation of glycerol and esters difficult. In current commercial processes usingcrude feed stock, excess alkali is added to remove all the FFAs.

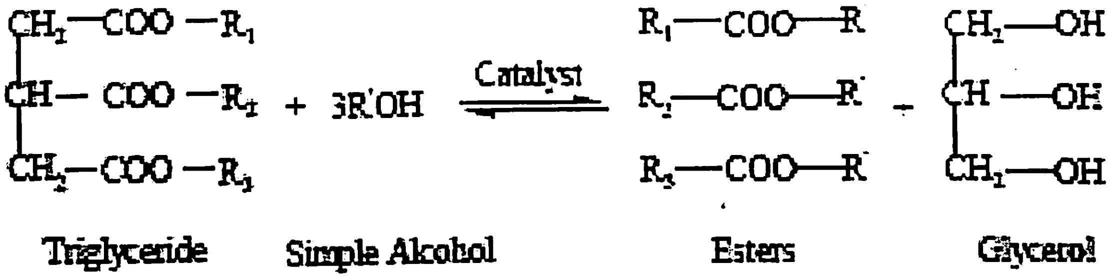
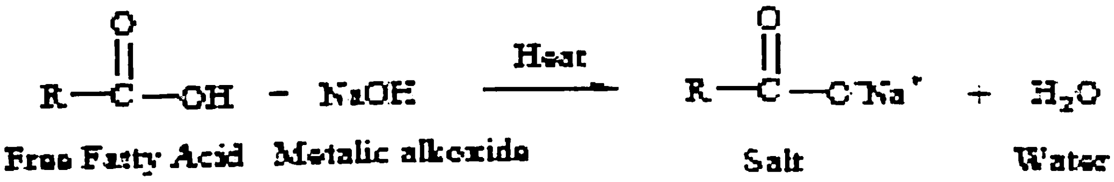


Fig. 2. Transesterification of triglycerides with alcohol

2.4.7 Saponification

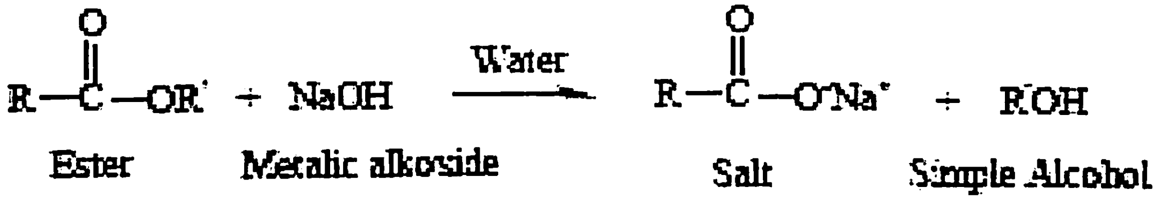
The production of soap sometimes called alkaline hydrolysis, converts triacylglycerols to glycerol and a mixture of salts of long-chain carboxylic acids. As can be seen from figures 3 & 4, the reaction can be carried out with an ester (i.e. triglycerides) or with carboxylic acids (i.e. free fatty acids). However, the production of fatty acids is an intermediate step when triglycerides are directly used for saponification. The commercial production of soap is usually conducted in two phases. The first phase is the conversion of lipids into FFAs by boiling with aqueous sodium hydroxide until hydrolysis is complete and then adding sodium chloride to precipitate the soap (Solomon, 1996).



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NaOH \xrightarrow{Heat} R-\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+ + H_2O$$

Fig. 3. Saponification from free fatty acid

or

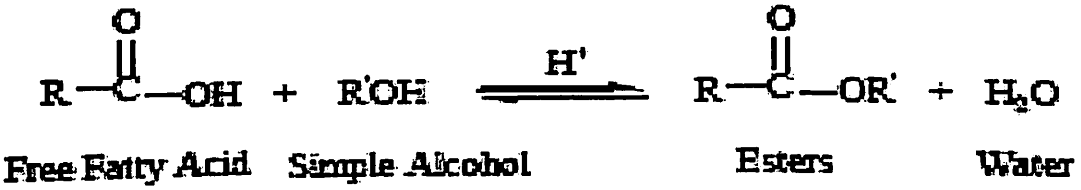


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + NaOH \xrightarrow{Water} R-\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+ + R'OH$$

Fig. 4. Saponification from ester

2.4.8 Esterification

The formation of esters occurs through a condensation reaction known as esterification. This requires two reactants, carboxylic acids (fatty acids) and alcohols. (Solomon, 1996). Esterification reactions are acid catalysed and proceed slowly in the absence of strong acids such as sulphuric acid, phosphoric acid, organic sulfonic acids and hydrochloric acid. The equation for and esterification reaction can be seen in figure 5.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R'OH \xrightleftharpoons{H^+} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + H_2O$$

Fig. 5. Esterification

2.4.9 Hydrolysis

The hydrolysis of lipids forms a heterogeneous reaction system made up of two liquid phases. The disperse aqueous phase consists of water and glycerol; the homogenous lipid phase consists of fatty acids and glycerides. The hydrolysis of glycerides takes place in the lipid phase in several stages via partial glycerides (diglycerides and monoglycerides) (*Ullmann's, 1987*). Acid catalysts are very effective at accelerating the hydrolysis reaction. However, at high temperatures substantial material corrosion occurs. Diabasic metal oxides have a higher activity than more strongly alkaline monobasic metal oxides. Zinc oxide in its soap form has been suggested to be the most active catalyst for hydrolysis reactions (*Ullmann's, 1987*). Reaction without a catalyst is not economical below 210°C, thus requiring the implication of high temperature, pressure techniques. Modern continuous plants operate at pressures between 0.6-1.2 MPa at 210-260°C without a catalyst. This increased pressure allows the mutual solubility of the two phases to increases to a point where the formation of continuous phase occurs.

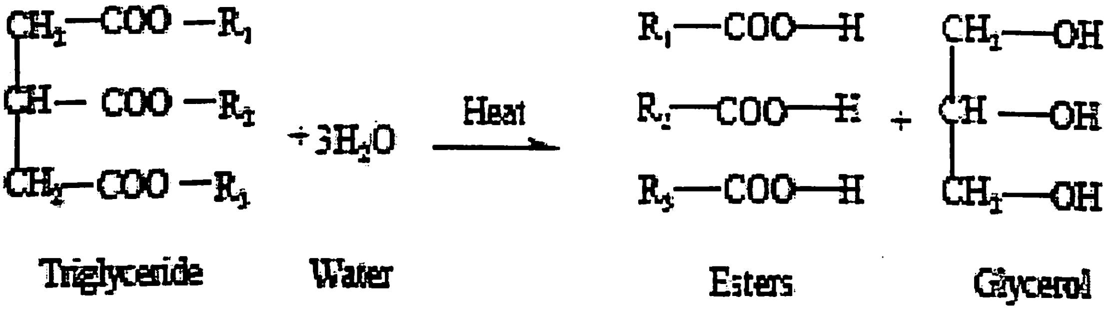


Fig. 6. Hydrolysis of triglycerides

2.4.10 Aminolysis

Esters undergo nucleophilic substitution at their acyl carbon atoms when they are treated with primary or secondary amines. These reactions are slow but are synthetically useful (Solomon, 1996).

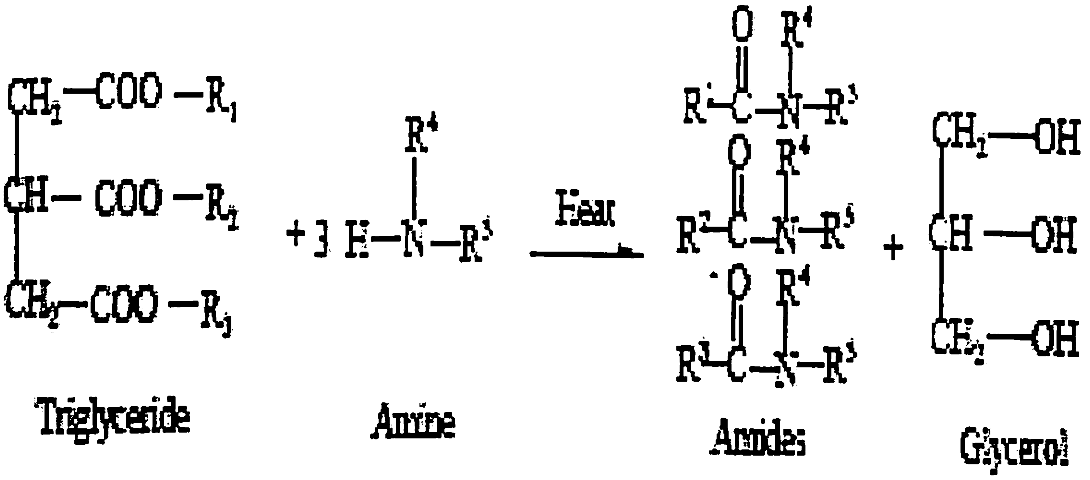


Fig.7. Aminolysis of triglycerides

2.4.11 Biocatalysts

Biocatalysts are usually lipases; however conditions need to be well controlled to maintain the activity of the catalyst. Hydrolytic enzymes are generally used as biocatalysts as they are ready available and are easily handled. They are stable, do not require co-enzymes and will often tolerate organic solvents. "Their potential for regioselective and especially for enantioseletive synthesis makes them valuable tools" [Schuchardt, 1998]. Recent patents and articles have shown that reaction yields and times are still unfavourable compared to base-catalysed transesterification for commercial application.

2.4.12 Catalyst Free

Transesterification will occur without the aid of a catalyst, however at temperatures below 300°C the rate is very low. It has been said that there are, from a broad perspective, two methods to producing biodiesel and that is with and without a catalyst.

2.4.13 Supercritical Methanol

The study of the transesterification of rapeseed oil with supercritical methanol was found to be very effect and gave a conversion of >95% within 4min. A reaction temperature of 350°C, pressure of 30MPa and a ratio of 42:1 of methanol to rapeseed oil for 240s were found to be the best reaction conditions. The rate was substantially high from 300 to 500°C but at temperatures above 400°C it was found that thermal degradation takes place. Supercritical treatment of lipids with a suitable solvent such as methanol relies on the relationship between temperature, pressure and the thermophysical properties such as dielectric constant, viscosity, specific weight and polarity (Kusdiana, 2000). A comparison of supercritical methanol production and alcoholysis can be seen in table 6.

2.5 COMPARATIVE ANALYSIS OF PROCESSES

There are several problems associated with the production of biodiesel with alkali homogenous catalysts. The batch process is time consuming, as purification of the product for catalyst and saponified products is necessary. There is also the problem of immiscible phases of the lipid and alcohol, which requires vigorous stirring to enable good contact of reactants for the reaction to occur (Kusdiana, 2000). In the base-catalysed transesterification method use of crude lipids that contain largequantities of FFA leads to catalyst destruction. It is suggested that the concentration of FFA be as low as possible, not exceeding 0.5%.

Table 6.Comparison between production of biodiesel

	Common Method	*SC MeOH method
Reaction Time	1-6h	0.067h
Reaction Condition	0.1MPa, 30-65°C	35MPa, 350°C
Catalyst	acid or alkali	none
Free Fatty Acids	Saponified products	methyl esters
Yield	97% (normal)	98.50%
Removal for Purification	methanol, catalyst and saponified products	methanol
Process	Detailed	Simple

*SC MeOH method - Supercritical Methanol

2.6 PROCESS OVERVIEW OF SEPARATION

Although not within the scope of this report, separation is an integral part of the production of biodiesel and therefore some basic concepts will here within be covered. The refining of the products from the production of biodiesel can be technically difficult and can substantially increase the cost of production. The purity of biodiesel must be high and generally conform to international standards such as the European Union (EU) standards for alternative fuels. Under the EU standards for alternative diesel fuels free fatty acids, alcohol, free and bound glycerin and water content must be kept to a minimum and the fuel must be at least greater than 96.5% pure (Karaosmanoglu, 1996). The typical product mixture of a transesterification reaction contains fatty acid esters (biodiesel), monoglycerides, diglycerides, glycerol, alcohol and catalyst, in varying concentrations. The primary goal is the removal of the esters from the mixture, maintaining low costs and ensuring a high purity product. Glycerol in its pure form is seen to be a secondary product of the reaction as it can be sold to various industries. To keep the cost of production competitive, the removal and resale of glycerol is essential. The remaining mixture contains by-products and alcohol that should have minimal contaminants if the conversion is high, except for the alcohol which would be distilled off.

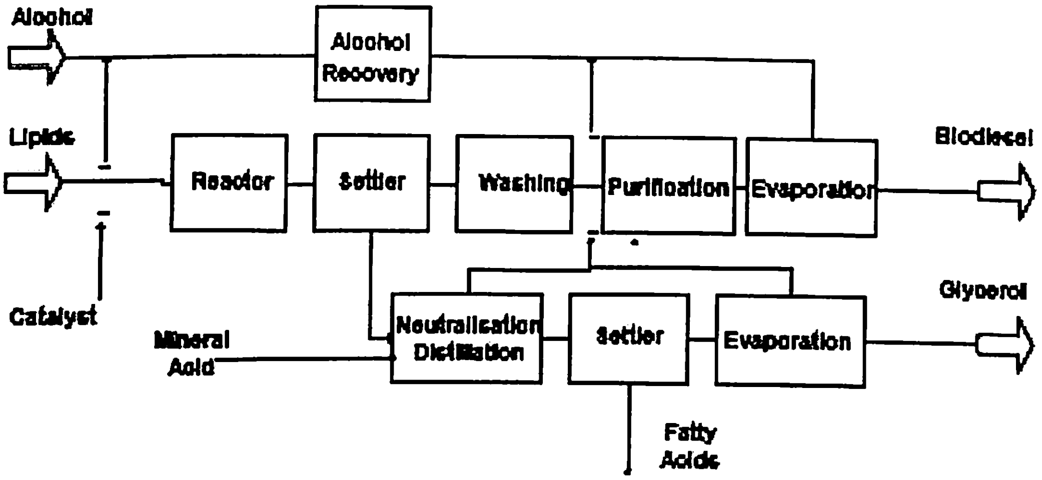


Fig.8. Typical flow chart of the process of esterification of lipids to biodiesel

If the reaction has reached a high level of conversion the product mixture will form two liquid phases, with a solid phase if a solid catalyst has been used. The bottom phase of the mixture would consist of glycerol and the top phase alcohol and esters. In a reaction that did not reach full conversion the unreacted lipids and bound glycerol would solidify in the bottom layer, as can be seen in figure 12. For molar ratios greater than 5.67 of MeOH it was reported that there are some difficulties in separating glycerin from methanol (Kusdiana, 2000).

2.6.1 Critical Analysis of the Literature

There where only two papers found that made mention of heterogenous catalysts. Of these there were 3 potential catalysts of which only one showed any promise. There is a distinct lack of information or research conducted on heterogenous catalysts. There are several references to co-solvents, however none make mention of biodiesel itself. The references to THF reported that it was suitable as a co solvent claiming it to be a low toxic compound, when the MSDS from Chemwatch showed it to have a high level of toxicity. There was little mention of the thermal degradation of products such as glycerol and triglycerides, particularly as glycerol degrades to a highly toxic compound, acrolein. Generally analysis techniques focused on glycerol and unconverted triglycerides, there was no mention of any residual components such as alcohol. This seems to be due to the currently accepted practice of extensily washing the product before analysis. Testing and quality control seems to focus on downstream fuel that is ready for retail sales, not necessarily testing for optimisation purposes. There is conflicting information on the impact of contaminants such as FFA and water. Some papers have said that water has a negative effect on the reaction and others have implied that acid catalysed reactions are not effected.

2.6.2 Heterogeneously Catalysed Process

The use of hydrogenized guanidine's on organic polymers as a catalyst for the transesterification of vegetable oils has been tested by Schuchard et al (1997). Principle tests conducted in a continuous reactor were promising and resulted in a patent (P93246, 1984). However there still appear to be some problems with this technique. For example, catalyst activity seems to deteriorate after an hour of operation (Schuchardt, 1998). This resulted in incomplete reaction and subsequent difficulties in phase separation. Irreversible protonation of the catalyst or catalyst leaching are a possible cause, however no definite test to confirm this had been conducted (Schuchardt, 1998). Experiments conducted by Suppes et al (2000) indicate that $CaCO_3$ may be suitable for use as a heterogeneous alcoholysis catalyst. Preliminary batch experiments used beef tallow or soybean oil as the triglyceride source and diethylene glycol (DEG) as the alcohol. Subsequent attempts to verify these results where conducted using a similar batch apparatus but as yet have failed to replicate those results obtained by Suppes et al. There is only one difference in the experimental procedure used to replicate Suppes's work which was the source of the$CaCO_3$, which was not sourced from Lancaster (Windham, NH). Trials conducted using CaO and ${}_2$ $Ca(OH)$ as the catalyst also appear to have failed to achieve significant conversion. Although, this has not been confirmed with GC analyses, the physical appearance of the samples very much favours a high content of lipids thus subsequent low conversion. CaO is documented as being an effective heterogeneous alcoholysis catalyst and is in common use for monoglycerides(which would be solids at room temperature) production at temperatures ranging from 200$_o$C to 220$_o$C with reaction times of 1 to 4 hours (Suppes, 2001). The apparent failure $CaCO_3$ as an alcoholysis catalyst may have been due to thermal degradation considering the high temperatures that the experiments were conducted under (>220$_o$C). Other factors that require investigation include the role of glycerolises, polymerisation and hydrolysis and the effect of high concentrations of free fatty acids. Certain carbonate systems are also known to promote glycerolisis however the overall effect this would have under these reaction conditions is not yet known. Glycerolisis is the reaction of glycerol with triglycerides to form monoglycerides. The calcium carbonate catalyst could function as a simple Bronsted base catalyst. The double bond migration, observed in the Na_2CO_3 and K_2CO_3 catalysed reactions, indicated that at these reaction temperatures the carbonate anion is an extremely strong base, however this has not been proven.

2.7 PRODUCT ANALYSIS

Biodiesel can be significantly contaminated with both free and bound glycerol, triglycerides and alcohol due to incomplete transesterification and or insufficient purification. As noted in literature, the presence of these minor contaminates can be

Table 7. List of potential catalysts

$Ti(OR)_4$	- Titanium IV alkoxides
$(C_{12}H_{27}Sn)_2O$	- bis(tri-n-butyltin)oxide - Organometallic tin complexes
Na_2CO_3	- (Solubility of some of these?)
K_2CO_3	
$ZnCO_3$	
$MgCO_3$	
$CaCO_3$	
ZnO	- supported on alumina
CH_3COOCa	- acetates of calcium and barium
CH_3COOBa	(Salts or esters of ethanoic acid)

Lancaster (Windham, NH)
Iowa Limestone Co. (Des Moines, IA)

detrimental to both engines and the environment through pollution. There are currently limits on the levels of these compounds in biodiesel that are set out in guidelines such as American Society for Testing and Materials (ASTM) which can be found in table 8. Over the past ten years there have been various investigations into methods to investigate the analysis of biodiesel, its impurities and by-products. The list includes Gas Chromatography (GC) distillation, solid phase separation, thin film liquid chromatography (TLC), High Precision Liquid Chromatography (HPLC), Refractometry, Near Infrared Spectroscopy with a Fibre-Optic probe (NIR) and Thin layer chromatography/flame-ionisation detection (TLC/FID) with an Iactroscan instrument [Plank, 1995, Freedman et al 1984]. The analysis technique needs to be accurate, reliable, reproducible, relatively quick and simple, and require equipment that is readily available. Formally HPLC, but more commonly now GC analysis is by far the most accepted methods for the analysis of biodiesel fuels (Knothe, 1998). The reasons behind this are simplicity, (once the system has been set up) and the high level of accuracy with which the results can be obtained (Plank, 1995).

*Table 8. Detailed requirements for biodiesel fuel**

Property	Test Method	Limits	Units
Flash Point (closed cup)	D93	100 min	°C
Water sediment	D2709	0.05 max	%Vol
Kinematic Viscosity	D445	1.9-1.6	mm^2/s
Sulphated ash	D874	0.02 max	% mass
Sulphur	D2622	0.05 max	% mass
Copper strip corrosion	D130	No. 3 max	
Cetane number	D613	40 min	
Cloud Point	D2500	RTC	°C
Carbon residue	D4530	0.05 max	% mass
Acid number	D664	0.8 max	mg KOH/g
Free glycerol	F	0.02	% mass
Total glycerine	F	0.24	% mass

*As out lined in ASTM PS-121 99

2.7.1 High Precision Liquid Chromatography

Mittelbach & Trathnigg detailed a method that is similar to GC in that the samples require derivatisation. This was using HPLC coupled with isocratic separation, such as differential refractometry or density detection. There where some problems associated with separation according to molecular mass and hydroxyl content, but where over come by using a combination of a GPC-column set and a polar column in series [Trathnigg, 1990]. Free fatty acids and glycerol where separated from the mixture before the analysis was carried out and it was said that the analysis time was approximately 20 minutes.

2.7.2 Gas Chromatography

The method proposed by Plank and Lorbeer using capillary gas chromatography, can provide qualitative and quantitative information about the concentrations of contaminants in biodiesel. The method is appropriate for measuring minor and major components in a sample, gives a high reliability of results, has simple instrumentation, requires a small amount of sample preparation and has a short analysis time (Plank,1995).

2.7.3 Near Infrared Spectroscopy

Near Infrared Spectroscopy (NIR) is becoming a preferred method for quality control of biodiesel fuel. Due to its operational ease, rapidity of measurement and non destructiveness it can be implemented as an online assessment of conversion in the transesterification reaction. The NIR method is less sensitive than GC for quantifying minor components, but can be used in combination with GC analysis for a higher level of analysis. However, that being said it is accurate to the point that it can be used in qualifying online conversion rates and major component concentrations. Standards' testing for biodiesel is time consuming and costly, but can be superseded by NIR which would significantly reduce both the cost and the time of testing (Knothe, 1998). The determination of glycerol after water extraction was described by Bondioli et al (Plank, 1995). This would involve the extraction of glycerol from biodiesel into an aqueous phase which has been shown to be highly effective. Glycerol has a high affinity for water, very low for methyl esters, moderate for monoglycerides and small for diglycerides. Solubility of glycerol in methyl esters is low in the order of 0.15% and in the presence of a large amount of water is negligible (Van Gerpen, 1996). The glycerol free mixture would then be analysed via GC or HPLC. Another method is the Conradson carbon residue, sulphate ash and phosphorous content. This involves the combustion of a sample and subsequently weighed to reveal the mass of carbon, although quit crude it is accepted as a quick estimate of the conversion in transesterification (Hodl, 1994).

2.8 LITERATURE REVIEW CONCLUSION

To date there has been extensive research into the area of the derivitisation of triglycerides for utilization in diesel engines. The development of a continuous reactor would greatly improve the economic viability of biodiesel as an alternative fuel source to petrochemical derived products.
As a result of recent changes in eating patterns, there is an increasing surplus of animal fats that cannot be consumed by the soap industry. Companies are increasingly interested in this as an energy source to be combusted in furnaces for grid energy production. Large-scale production (i.e. continuous reactor) would be required for this to be viable. The development of such a facility would require extensive research into the kinetics of tallow derived biodiesel production as opposed to the well-documented kinetics of vegetable oil derived biodiesel.

3.0 EXPERIMENTAL

3.1 PROPERTIES OF JATROPHA OIL

3.1.1 Viscosity

This experiment is perfomed in the biodiesel lab of University of Petroleum and Energy Studies Dehradun using the viscometer shown in the fig below.

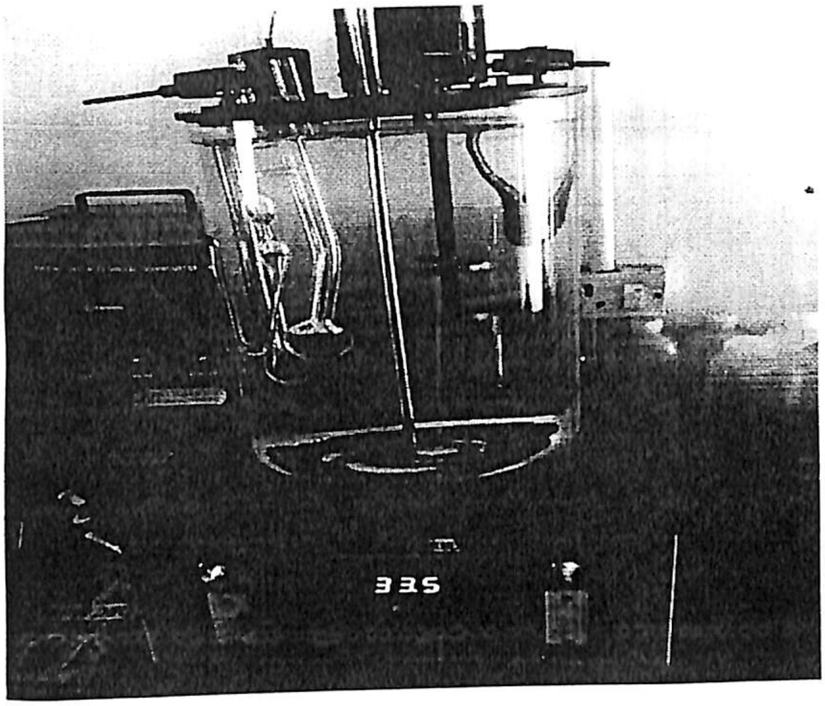


Fig.9 Viscometer

Observations and calculation

Kinetic viscometer water bath error- 2° C

We have to set the temperature- 40° C

Here viscosity, v= c x t

V= Kinematic viscosity, Centipoise

C= 0.02666, Calibration constant of the viscometer,

T= flow time, seconds

Observation, t_1= 26.03 min,   so, v_1 = 41.437588 cp

t_2= 26.54 min v_2 = 42.453384 cp

Average Viscosity, V= $(v_1 + v_2) / 2$ = 41.945486 cp

So the obtained average viscosity of jatropha oil sample is **41.95 cp**

3.1.2 Density

This experiment is performed to calculate the density of jatropha oil.

Weight of empty R & D bottle, W= 20.96g

Weight of bottle + Weight of distil water, W1= 45.86

Weight of water = (45.86- 20.96)g = 24.90g

Weight of bottle + Weight of oil = 43.66g

Weight of oil = 43.66- 20.91 = 22.75

Density,

d2/d1 =(W2- W)/ (W1-W)= (Weight of Oil/ Weight of water)

d2= density of oil

d1= density of distill water, g/cc.

d2/1 = (43.66- 20.96)- (45.86- 20.96) = 0.911g/cc**0.911 g/cm^3**

So density of jatropha oil is found to be

3.1.3 Clod Point and Pour Point

The cloud and pour point is calculated using the fig below

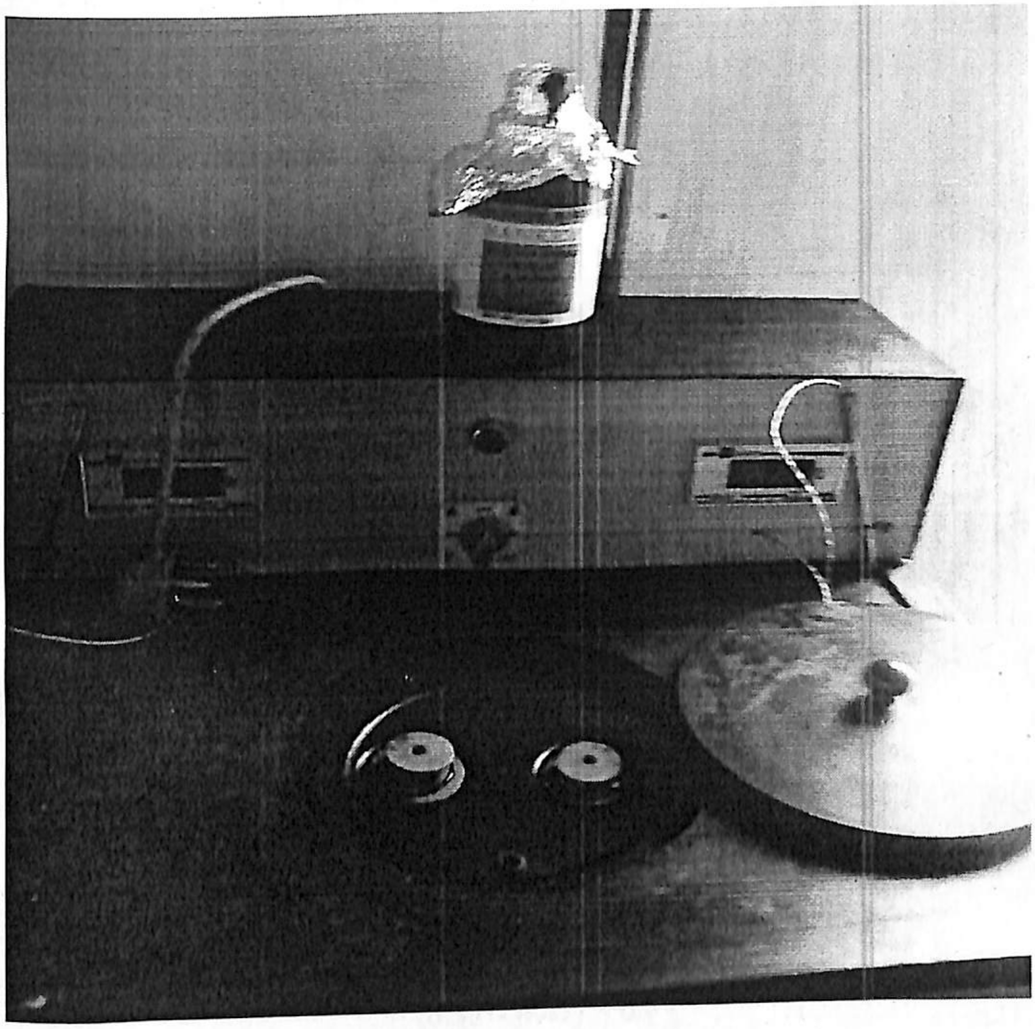


Fig. 10. Cloud and pour point apparatus

Observations and calculations

Temperatures for cloud point,

T1= 19.6° C, T2 = 19.0° C

Average cloud point Temperatures is **19.3° C**

Temperature for pour point

T1= -15.3° C, T2= -15.1° C

Average pour point temperature is **15.2° C**

3.1.4 Biodiesel production using heterogeneous catalyst

Feed required

Initial wt of jatropha oil – 150 ml = 110.50g

Weight of the catalyst – 0.5% of the jatropha = 0.55g

Methanol used- ratio- 1:6

Set temperature – 50°C

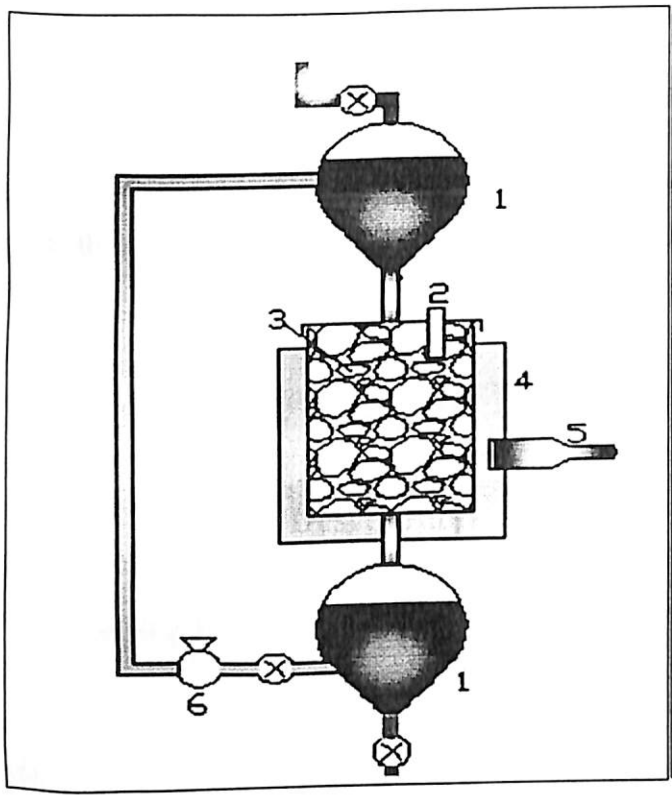
The feed is stirred for 2 hours and biodiesel is obtained.

Catalyst used in the reaction, initial wt – final wt

$$= (0.55 - 0.47) = 0.9 \text{ g}$$

3.2 PRODUCTION OF BIODIESEL

3.2.1 Apparatus Description



Item no.	Name
1	**Separating funnel**
2	**Temperature indicator and Thermocouple**
3	**Fixed bed reactor**
4	**Oil bath**
5	**Resistant heater with controller**
6	**Centrifugal monoblock pump**

The feed is entered to from separating funnel 1. The feed mainly consist of Jatropha oil and methanol. The feed is then entered to fixed bed reactor by gravity flow, where it will react with the heterogeneous catalyst. Fixed bed reactor is covered by an oil bath to maintain temperature. The products are obtained from the bottom and again circulated by a pump, so that the reaction will again take place. This is a continuous batch process.

3.2.2 Safety

Safety issues are always paramount whilst handling chemicals and operating equipment such as pressure vessels. Although some chemicals in their natural form, such as glycerol are fairly innate, upon reaction or thermal change they can become toxic. It was found that glycerol, will thermally decompose at temperatures exceeding 290°C to acrolein, which is highly toxic. Care must be taken that this doesn't occur and subsequently the temperature was kept below 290°C. Throughout the project proper handling of all chemicals was conducted and there were no incidents during this time. An initial assessment was conducted on the equipment, to ensure that all safety measures where in place. No safety breaches were conducted or any injuries incurred over the duration of this project.

4.0 DISCUSSION

4.1 ANALYSIS

The development of an analysis technique required a considerable amount of time to establish. However, with this technique now proven to be reliable and effective, further research will not be hampered by this restriction. The complexity of the reactant mixture was one of the challenges in finding an appropriate method. Although, a combination of methods may have also been possible, it was not cost or time effective to have several methods of analysis, all requiring different preparation. However, NIR can determine the major constituents of the reaction mixture but if the product is to meet international standards, further testing will have to be conducted, such as flash point, cloud point and various other tests.

4.2 ANALYSIS ERROR

At this stage rigorous quantitative analysis has not been carried out as there are many components to consider if this is to be done correctly. In saying this, analysis was requested on some biodiesel samples that where supplied to a company for engine testing

4.3 REACTIONS

The reactions are relatively straightforward, as the equipment is simple and the reactants are very stable. The sampling method that was previously used was unacceptable and a new method was adapted to minimise the amount of sample taken and cover issues of contamination. There are some issues with getting the reaction to a desired temperature before the reaction reaches equilibrium. This is due to the time taken for the reactor to heat up, this can in some cases, and take up to 20min. Thus by the time the required temperature has been reached the reaction may have already reached equilibrium. A solution to this may be dynamic modelling which will generate some complex calculations but should give reasonable kinetic information.

4.3.1 Catalysts

Homogenous acid catalysts are very taxing on equipment and at elevated temperatures severely affect any metallic components. Although, acid catalysed reactions are slower than basic ones, they have potential if they can be immobilised. Problems with saponification are not present when esterification occurs and acid catalysts are not affected by FFA's. Heterogeneous catalysts are the key to new developments in the production of biodiesel, combined with their application in a continuous process and easy separation, they will substantially decrease the costs of production. Problems with water have not yet been fully addressed. There are some concerns over hydrolysis inhibiting the conversion in transesterification, this is yet to be tested and will need to be resolved in the near future.

5.0 CONCLUSIONS

The main issues with this project where finding an analysis method, a suitable catalyst and obtaining useful kinetic data . Gas chromatography provides an appropriate method of chemical analysis and it can be suitably calibrated for the products of this reaction. The preparation methods for the samples have been established and the method's reliability, precision and reproducibility have been demonstrated. The solid catalysts that were trialled do not appear to be effective. The results reported in the literature cannot be replicated and their veracity is doubtful. The homogenous acid catalysed reactions proved to be effective, but the nature of the catalyst may limit any future use.

The batch reactor provides a convenient and safe method for screening catalysts and obtaining kinetic data. It is easily scaled up to a continuous reactor and a sampling method allowing samples to be taken within short intervals of two minutes has been implemented. The greater project is in good shape for rigorous catalyst testing and the equipment and methods have proven that a high level of accuracy can be obtained.

6.0 FUTURE WORK AND RESEARCH

Preliminary catalyst trials are required to identify heterogeneous candidates. This is the most important requirement for the work at this stage. Catalysts such as organic titanium oxides may hold some potential as they are currently used in the plastics industry for transesterification reactions. Once a range of catalysts have been identified, rigorous experimentation needs to be conducted with varying conditions.

Kinetic data needs to be obtained for each catalyst in at least duplicate, preferably triplicate, to identify any discrepancies. The use of crude feed stocks is important if the cost of production is to be kept at a minimum, so catalysts would be tested with tallow and or used oils. Catalyst free reactions with supercritical methanol could potentially be a solution to many processing problems. There should be no reason why this reaction, carried out at pressures of up to 300atm, can not be conducted with supercritical ethanol. Further research into the conditions and equipment would be beneficial considering conversions are reported to be high, in the order of 98% in 3min. The information obtained from batch testing will be fundamental in the development of a continuous process. Once conditions and reaction system have been identified at the batch level, it will be necessary to run reactions in the continuous reactor at various conditions to optimise the process.

Alternative separation techniques have not yet been adequately developed. Washing and settling are well established for commercial batch processes, but may not be practical for continuous processes. Product separation needs to be extensively researched for alternatives methods of product separation for continuous production. There will be a large volume of excess ethanol that needs to be separated and this could add significant costs to production if all options are not explored.

Research into the method of near infrared spectroscopy and the equipment required needs to be further investigated as this may be a low cost online method to analyse the extent of conversion. Although the current method of analysis (gas chromatography) has proven to be the most effective method to analyze the full spectrum of the product mixture, it is not the most cost effective. There may be new technology still in its infancy that could offer a more cost effective and instantaneous analysis method.

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