2008

BIODIESEL PRODUCTION FROM JATROPHA CURCAS OIL

Chinmoy Baroi
Western University

BIODIESEL PRODUCTION FROM JATROPHA CURCAS OIL

(Thesis format: Monograph)

by

Chinmoy Baroi

Graduate Program in Engineering Science

Department of Civil and Environmental Engineering

A thesis submitted in partial fulfillment

of the requirements for the degree of

Master of Engineering Science

The School of Graduate and Postdoctoral Studies

The University of Western Ontario

London, Ontario, Canada

December, 2008

THE UNIVERSITY OF WESTERN ONTARIO

SCHOOL OF GRADUATE AND POSTDOCTORAL STUDIES

CERTIFICATE OF EXAMINATION

Supervisor

Dr. Ernest K. Yanful

Co-Supervisor

Dr. Maurice A Bergougnou

Examiners

Dr. Horia Hangan

Dr. Jonathon Southen

Dr. Shahzad Barghi

The thesis by

Chinmoy Baroi

entitled:

Biodiesel production from jatropha curcas oil

is accepted in partial fulfillment of the
requirements for the degree of
Master of Engineering Science.

Date

Dr. Denis M. O' Carroll
Chair of the Thesis Examination Board

ABSTRACT

In this work an effort has been made to produce an environment friendly and renewable fuel (biodiesel) from an inedible vegetable oil (*Jatropha curcas* oil), which can be a substitute feedstock of traditional food crops for biodiesel production. This is a bench scale feasibility study. Here, unsupported potassium carbonate was used as a catalyst. Researching the potential and the behavior of potassium carbonate is very important because every biomass contains this compound in a significant amount. It can be extracted by using classical extraction or leaching technologies. During the biodiesel production reaction, the formation of soap as a byproduct was also monitored using the FTIR-ATR method. After a series of experiments, 6 wt% unsupported catalyst, 6:1 methanol to oil molar ratio, 65°C and 600 rpm were selected to be the optimum reaction parameters, that are able to produce quality biodiesel.

Keywords: *Jatropha curcas* oil, Transesterification, Biodiesel, FTIR-ATR.

ACKNOWLEDGEMENTS

First and foremost I would like to thank my principal supervisor Dr. E. K. Yanful for suggesting the project, supporting me and my research work financially, for his endless care and patient supervision, and for his superb and creative suggestions and extensive criticism throughout my research.

I would like to thank my co-supervisor Dr. M. A. Bergougnou for his endless care and patient supervision, and for his superb and creative suggestions and extensive criticism throughout my research.

I would like to thank Dr. Jason I. Gerhard for allowing me to use his GC-MS.
I wish to express my gratitude to Mary Jane Walzak, Senior Research Scientist of Surface Science Western, University of Western Ontario, London, Ontario, Canada for analyzing the results using FTIR-ATR. I would also like to thank Mr. Brian Dennis, laboratory technician of the Department of Chemical and Biochemical Engineering, who helped me with the development of the experimental concepts of my research topic.

Special thanks to Mr. Tim Stephens, laboratory technician of the Department of Civil and Environmental Engineering for his assistance with the GC-MS analysis and general laboratory support. I would like to thank my fellow graduate students and friends who helped me with their constructive and beneficial discussions.

Finally, I would like to thank my parents for their endless support and kind encouragement throughout my academic career.

To the ultimate source of love, care and Inspiration

My mother Late Nomita Baroi

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS AND NOMENCLATURE

ATR-FTIR	Attenuated Total Reflectance – Fourier Transform Infrared
cP	Centri poise
DG	Di - Glyceride
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GC-MS	Gas Chromatograph – Mass Spectroscopy
JTC	Jatropha Curcas
MG	Mono - Glyceride
θc	Critical angle of incident radiation

Chapter 1

INTRODUCTION

1.1 Background of the research

In the United States, oil is the fuel of transportation. Coal, nuclear power, hydropower, and natural gas are primarily used for electric power generation. The United States, with 5% of the world's population, consumes 25% of the world's petroleum, 43% of the gasoline, and 25% of the natural gas. Worldwide reserves at the beginning of 2004 were 1.27 trillion barrels of oil and 6,100 trillion cubic feet of natural gas. At today's consumption level of about 85 million barrels of oil and 260 billion cubic feet per day of natural gas, the reserves represent 40 years of oil and 64 years of natural gas consumption (Vasudevan and Briggs, 2008).

The limited stock of fossil fuels and environmental pollution from the use of these fuels has intensified the need to investigate the production of biofuels. Any liquid or gaseous fuel that is produced predominantly from biomass is called biofuel. There are two global biomass based liquid fuels that might replace gasoline and diesel fuel. These are bioethanol/ biobutanol and biodiesel. It is assumed that biodiesel is used as a diesel fuel replacement and bioethanol/ biobutanol as gasoline replacement. Biobutanol is more advantageous than bioethanol, because it is less miscible in water and far less corrosive. Thus it can be shipped and distributed through existing infrastructure. Compared to ethanol, butanol has a higher octane number and higher viscosity (Capital, 2008). Diesel fuels have an important role in the industrial economy of a country. These fuels are used in heavy trucks, city transport buses, locomotives, electric generators, farm equipment and underground mine equipment. In that sense, biodiesel can play a significant role in a

country's economy. But neither biodiesel nor bioethanol/ biobutanol would probably be able to replace fossil fuels because of their traditional feedstock seeds and grains. These feedstocks are corn, beet, potato, wheat, sugarcane, sugar beet, wheat straw, woody crops for bioethanol/ biobutanol and rapeseed, soybean, sunflower, coconut and palm oil for biodiesel. Most of these feedstocks are foodcrops. In fact, it is now widely believed that the recent world food crisis is the result of the utilization of food crops in producing biofuels. Human rights activists have called for a ban on the production of biofuels from food crops for several years. Waste cooking oil and tallow from animal fats can be alternative feedstocks for biodiesel production, but large scale biodiesel production from these sources may not be possible because of lack of continuous and sufficient supply of these types of feedstock. There is thus a need for an alternative biodiesel feedstock that is inexpensive, inedible and which meets all the criteria for biodiesel feedstock.

Jatropha curcas oil, an inedible tropical plant seed oil, has tremendous potential for biodiesel production. The plant has been referred to as the second generation cropping solution for biofuel production (Gressel, 2008). Though the land requirement of third generation biofuel feedstock (i.e. algae) is much less, the production of biofuel from these third generation feedstocks is much more complex than from the second generation feedstock (*Jatropha curcas*). Moreover, *Jatropha curcas* grows in any type of soil, even in stony soil and in the presence of a small amount of water, which makes it a more attractive feedstock for biodiesel production. *Jatropha curcas* has an annual seed yield of 5 tons per hectare (Aderibigbe et al., 1997). One estimate shows that the jatropha seed contains 30-32% protein and 60-66% lipid (Augustus et al., 2002). The oil content of the seeds varies from 30 to 60% depending on the variety, place and the method of oil

extraction. The seed and/or the oil have been found to be toxic, so the oil cannot be used for cooking purposes. But the oil has an excellent fuel property. It can be used for lighting and as a fuel for cooking. It was used as diesel fuel substitute during the Second World War (Shah et al., 2004).

Biodiesel is a renewable diesel fuel, normally obtained by transesterification of vegetable oils, waste cooking oils and fats with lower alcohols (methanol, ethanol), in the presence of acid/base or enzyme catalysts at a lower temperature and pressure or in the absence of catalysts at a higher temperature and pressure. As the base catalyzed transesterification reaction is faster than the acid catalyzed reaction, most commercial processes use a homogeneous base i.e. NaOH, KOH, or related alkoxides for biodiesel production (Ataya et al., 2007). Generally methanol is used as it is cheaper than ethanol. One of the major problems with using basic catalysts is the formation of soap when oils with high free fatty acids are used as feedstock. This results in lower yields of biodiesel and subsequent washing of biodiesel is required to remove the soap from the biodiesel to maintain its quality. The main factor responsible for the overall biodiesel production cost is the price of the refined oil feedstock (free of fatty acids), which accounts for 88% of the total estimated production cost (Di Serio et al., 2007). Thus many commercial processes use cheaper feedstock i.e. waste cooking oil, waste fat and oils despite their high free fatty acids content.

Hartman showed that potassium carbonate, a salt of potassium hydroxide, is better than traditional base catalysts (KOH, NaOH, $NaOCH_3$ and $KOCH_3$) as it ensures practically complete alcoholysis and produced the least amount of soap (Hartman, 1956). He also showed that sodium methylate ($NaOCH_3$) is also a good base catalyst which

produces less soap than other traditional catalysts. However, it promotes other secondary reactions at the same time. Potassium carbonate is free of this problem (Hartman, 1956). But after his work, no one tried unsupported potassium carbonate as a catalyst for biodiesel production for a long time. One of the reasons is the current potassium carbonate production technology. Among traditional catalysts KOH and its methylate are the most expensive. At present KOH is produced by electrolysis of KCl solutions. Then K_2CO_3 is produced by reacting KOH with CO_2. Thus the price of potassium carbonate is higher than the one of KOH.

In 1985 a group of french scientists used ashes of coconut shell and palm kernel as a catalyst for biodiesel production from coconut oil and palm oil respectively and they obtained a good result. The main component of those ashes was potassium carbonate (Graille et al., 1985; Grallie, 1986). US patents 6890451 B2 (Sapienza et al,. 2005) and 7138071 B2 (Sapienza et al., 2006) show that glycerol containing potassium carbonate can be an excellent environmentally benign anti-icing or deicing fluid, which can be used on the wings, fuselage, and tail of aircrafts for de-icing, and in some instances on airport runways (Sapienza et al., 2005 and Sapienza et al., 2006).

Potassium is one of the major inorganic components of *Jatropha curcas* seedcake. It contains around 1% of potassium by weight (Openshaw, 2000). So, there is the necessity for research to use reagent grade potassium carbonate at first as a catalyst for biodiesel production using jatropha oil. Future research should also consider the possibility of extracting potassium carbonate from the ash of the jatropha seedcake and gasification of jatropha seedcake to obtain synthesis gas and means to recover potassium

carbonate from the residue of gasification. The synthesis gas can be converted to methanol which can be fed to the biodiesel production process.

1.2 Objectives of the research

The main objectives of the research were:

i) Evaluate the feasibility of using unsupported potassium carbonate as a catalyst to produce biodiesel using *Jatropha curcas* oil. This is known in Industrial R & D as a bench scale product and process feasibility study.

ii) Analyze the effect of the reaction parameters to produce biodiesel of reasonable quality.

The above objectives were achieved by performing the following:

i) Monitor the transesterification reaction.

ii) Monitor the by-product (soap) production.

iii) Monitor the phase purity of the biodiesel while using different reaction parameters.

1.3 Experimental strategy

- Start the experiments using a methanol to oil molar ratio of 6:1 and a reaction temperature of 60°C for reaction time sufficient to get a high conversion.
- Vary the catalyst amount as weight percent of the oil feedstock to obtain a preliminary optimum catalyst amount.
- Maintain the above catalyst amount, but vary the methanol to oil molar ratio at 60°C reactor temperature.
- Operate at different reaction temperatures, keeping the methanol to oil molar ratio at 6:1 and the optimum catalyst amount.
- Choose the best reaction parameter combination based on two criteria: highest oil conversion and best phase purity of the biodiesel.
- Determine biodiesel quality for the best reaction parameter combination.

1.4 Originality and contribution of the thesis

- In this research, unsupported potassium carbonate was used as a catalyst for the first time for transesterification of *Jatropha curcas* oil to produce biodiesel.
- The analytical FTIR – ATR method was used for the first time to determine the biodiesel conversion from *Jatropha curcas* oil.
- For the first time, the soap production during transesterification reaction from *Jatropha curcas* oil was also qualitatively determined by the FTIR – ATR method.
- The quality change of biodiesel during extended settling of the reactor contents was also monitored using FTIR – ATR for the first time for *Jatropha curcas* oil.

Chapter 2
LITERATURE REVIEW

Diesel fuels have an important role in the industrial economy of a country. These fuels are used in heavy trucks, city transport buses, locomotives, electric generators, farm equipment and underground mine equipment. These hydrocarbon based diesel fuels contain sulphur, which causes environmental pollution by creating sulphuric acid (Srivastava and Prasad, 2000). From the standpoint of preserving the global environment and the concern regarding long-term supplies of conventional hydrocarbon-based diesel fuels, it is logical to research alternative diesel fuels, which must be technically acceptable, economically competitive, environmentally friendly and easily available (Srivastava and Prasad, 2000).

Vegetable oils can be an excellent source of alternative diesel fuels. The sulphur content of vegetable oils is very low and these plant oils take away more carbon dioxide from the atmosphere during their production than is added to it later on by their combustion (Srivastava and Prasad, 2000). More than 100 years ago Dr. Rudolph Diesel, inventor of the compression – ignition diesel engine used peanut oil as fuel in his engine (Demirbas, 2002).

Vegetable oils have molecular weights in the range of 600 to 900, which are three or more times higher than petroleum diesel fuels. Vegetable oils have higher viscosity, flash points, cloud points and pour points due to their large molecular weight and chemical structure (Srivastava and Prasad, 2000).

2.1 Lipids, Fats and Oils

In general lipids are considered to be extractable compounds from plants and animal matter which are insoluble in water but soluble in "fat solvents" for example, ether, chloroform and benzene. Lipids are divided into several groups: fats, waxes, phospholipids and other components (Gunstone, 1958; Eckey and Miller, 1954).

Fats are one of the three main organic building materials of living organisms. "Fat" refers to material that is insoluble in water which has a characteristic oily or greasy feel and consistency and which can be separated from plant and animal tissues. The word "Oil" refers to the same kind of material as fat, except that it is completely liquid instead of being partly solid at ordinary temperatures (Eckey and Miller, 1954).

Oils consist of mainly esters. These esters are nonvolatile and odorless but possess all the properties that are general characteristic of esters. Basically they are remarkably simple in composition. That is, they are composed of trihedral alcohol-glycerol molecules combined with organic fatty acids which belong to the aliphatic straight-chain type, with few exceptions. These organic acids always have an even number of carbon atoms per molecule, usually in the range between 8 and 24. In addition to these esters, there are some minor constituents which are phospholipids, sterols, vitamins, antioxidants, pigments, free fatty acids and in some fats hydrocarbons and other materials (Eckey and Miller, 1954). The other name of these oils or fats is triglyceride, because in the fat or oil, glycerol is esterified with three equivalents of fatty acids. These fatty acids may be the same acid or different acids attached with the same molecule of glycerol. In the fats or oils, glycerol may also be esterified with one or two equivalents of fatty acids to form mono or di-glycerides (Eckey and Miller, 1954).

The fatty acid present in the triglyceride may be of different types. These naturally occurring fatty acids may be saturated or unsaturated. In saturated fatty acids carbon atoms are joined by single bonds. Fatty acids having one or more double bonds in their structure are called unsaturated fatty acids. In most cases these fatty acids are expressed in terms of shorthand notation (x:y system), where x represents the number of carbon atoms present in the acid chain and y represents the number of double bonds present in the chain (Hoffmann, 1989).

The double bonds of unsaturated fatty acids are easily (auto)oxidized, isomerized, and polymerized (Eckey and Miller, 1954; Markley, 1947). Autoxidation refers to the spontaneous nature of the reaction between atmospheric oxygen and unsaturated fats and fatty acids. Light, heat, concentration of oxygen, the presence of catalysts or inhibitors and moisture affect the (auto) oxidation reaction and different products can be produced (Markley, 1947). Depending up on the nature of the oxidation, the products formed are: peroxides, aldehydes, ketones, acids, water, carbon dioxide, hydroxy acids and polymerized fats (Eckey and Miller, 1954).

Vegetable oils contain 90 to 98% triglycerides and small amounts of mono and diglycerides.These oils contain substantial amounts of oxygen in their structure. Generally these oils contain 1 to 5% free fatty acids (Srivastava and Prasad, 2000).

2.2 *Jatropha curcas*: The plant of oil and energy

Karl von Linne first classified the jatropha plant in 1753 and gave it the botanical name *Jatropha curcas.* A fossil discovered in Belem, Peru, places the existence of jatropha around 70 million years ago. The genus name *Jatropha* is derived from the

Greek *iatros* (doctor) and *trophe* (food), which means medicinal use (Becker and Makkar, 2008; Kumar and Sharma, 2008). The *Jatropha curcas* is a drought – resistant oil bearing multipurpose shrub/small tree which belongs to the family of Euphorbiaceae (Ackom and Ertel, 2005; Achten et al.; Staubmann et al., 1999). It originates from Central America and was distributed by Portuguese seafarers via the Cape Verde Islands to countries in Africa and Asia (Henning, 2000). These days jatropha is widely grown in Mexico, China, north-east Thailand, India, Nepal, Brazil, Ghana, Mali, Foso, Zimbabwe, Nigeria, Malawi, Zambia and some other countries (Ackom and Ertel, 2005; Openshaw, 2000). There are 175 species of jatropha around the world (Becker and Makkar, 2008). Jatropha grows in arid and semi arid climates and in a wide range of rainfall regimes, from 200 to 1500 mm per annum (Achten et al.). It can survive in poor stony soils (Aderibigbe et al., 1997). The plant grows quickly forming a thick bushy fence in a period of time of 6-9 months, and growing up to a height of 4 m with thick branches in 2-3 years and the branches contain latex (Henning, 2000; Augustus et al., 2002). The life span of the *Jatropha curcas* plant is more than 50 years (Henning, 2000). Almost all parts of the plant have a medicinal value (Staubmann et al., 1999). The bark is rich in tannin and also yields a dark blue dye. The tender green leaves are fed to silk worms, for small scale silk production (Augustus et al., 2002). In many countries jatropha is planted in the form of hedges to protect gardens and field crops from roaming animals. Since jatropha plants have lateral roots near the surface, they can be used to fix small earth dams which reduce the flow of run-off water (Henning, 2000). Its seeds resemble castor seeds in shape, but are smaller and brown (Augustus et al., 2002) and have an annual seed yield of 5 tons per hectare (Aderibigbe et al., 1997). One estimation shows that seeds contain 30-

32% protein and 60-66% lipid (Augustus et al., 2002). The oil content of the seeds vary from 30 to 60% depending on the variety, place and the method of oil extraction. The seed and /or the oil have been found to be toxic, so the oil cannot be used for cooking purposes and the cake after extracting oil from the seed cannot be used as cattle feed or for any edible purpose. The cake contains about 6% N, 3% P, and 1% K. But the oil has an excellent fuel property. This oil can be used for lighting and as fuel for cooking. It was used as diesel fuel substitute during World War II (Shah et al., 2004). A comparison of jatropha oil and petrodiesel is given in the table below (Ackom and Ertel, 2005):

Table 2.1 Comparison of properties of raw Jatropha oil and Petrodiesel

Parameter	Diesel	Jatropha oil
Energy Content (MJ/Kg)	42.6 - 45.0	39.6 – 41.8
Specific Weight (15/40°C)	0.84 – 0.85	0.91 – 0.92
Solidifying point (°C)	-14.0	2.0
Flash point (°C)	80	110-240
Cetane value	47.8	51.0
Sulphur (%)	1.0 – 1.2	0.13

2.3 Processes for preparing alternative diesel fuels

Raw vegetable oils cannot be used as a diesel substitute because of their higher viscosity, which cause inadequate atomization and incomplete combustion. Another problem with using raw vegetable oil is the reactivity of the unburned fuel, which causes fouling of the injector nozzles and cylinder deposition (Forson, 2004).

The American Society for Testing and Materials (ASTM) defines methods for testing some important diesel fuel properties and their limits in order to be used safely in engines, which are given in the table below (Dunn, 2005):

Table 2.2 ASTM specifications for Petrodiesel

Property	Unit	ASTM method	Limits
Kinematic viscosity (ν) at 40°C	mm^2/s	D 445	1.9 – 4.1
Distillation temperature at 90 vol% recovered	°C	D 86	282 – 338
Cloud point (cP)	°C	D 2500	-
Pour point (PP)	°C	D 97	-
Flash point (FP)	°C	D 93	≥ 52
Water and sediment	vol%	D 2709	≤ 0.05
Carbon residue at 10% residue	wt%	D 524	≤ 0.35
Ash	wt%	D 482	≤ 0.01
Sulfur	wt%	D 2622	≤ 0.05
Copper strip corrosion rating, 3 h at 50°C	-	D 130	No. 3 (max)
Cetane number	-	D 613	≥ 40

In order to be used as an alternative to diesel fuel, the properties of alternative diesel fuel should be similar to the ones of hydrocarbon fuels. There are several processes for producing alternative diesel fuels, which are:

Dilution

Dilution of vegetable oils can be accomplished by traditional diesel fuels or in a solvent. Several experiments have been run on the dilution of vegetable oils with petrodiesel. Most studies concluded that blending of vegetable oil with petrodiesel is not suitable for long term fueling of direct injection diesel engines (Dunn, 2005). Because the more unsaturated vegetable oil will be used in the blend, the greater will be the tendency of the blend to oxidize and polymerize and cause thickening of the blend. Different tests show that blending may cause injector coking, carbon deposition in the combustion chamber of the engine. A study showed that *Jatropha curcas* oil/petrodiesel blends increased fuel consumption and decreased thermal efficiency and exhaust temperature relative to straight petrodiesel (Dunn, 2005). However, another study shows that a blend of 97.4% diesel and 2.6% jatropha oil (by volume) gave the highest cetane number and even better engine performance with less fuel consumption than the diesel fuel (Forson, 2004).

Microemulsification

Microemulsions are usually called hybrid fuels. It is a clear or translucent stable dispersion of oil, alcohol or ester and amphiphilic molecule(s). Micro emulsions do not require agitation to remain in single-phase at constant temperature and pressure (Srivastava and Prasad, 2000; Dunn, 2005). Alcohols such as methanol or ethanol have limited solubility in nonpolar vegetable oils. Therefore amphiphilic molecules, which have one polar hydrophilic end and one non polar hydrophobic end in their structure, can bring them into one phase. Medium chain (C_4- C_{12}) *n* – alcohol/long chain unsaturated fatty alcohols behave as amphiphile compounds and can be used to prepare microemulsion using lower alcohols (C_1- C_3) and vegetable oils (Srivastava and Prasad, 2000; Dunn, 2005). A microemulsion of methanol with vegetable oils can perform nearly as well as diesel fuels (Srivastava and Prasad, 2000). Like blending of vegetable oils, micro emulsion also has problems of long term use in engines.

Pyrolysis

Pyrolysis or cracking involves the cleavage of chemical bonds to form smaller molecules by the application of thermal energy in the absence of air or in the presence of nitrogen. A study on the pyrolysis of vegetable oils shows that with increase in the temperature, the liquid fraction products are decreased and the gaseous fraction products increase and the aromatics are increased in the liquid fraction products (Baroi et al., 2007). Cracking or thermal decomposition of triglycerides or vegetable oils produces a class of compounds that includes alkanes, alkenes, alkadienes, aromatics and carboxylic acids. Different types of vegetable oils produce large differences in the composition of

the thermally decomposed oil. The pyrolysed vegetable oils possess acceptable amounts of sulphur, water and sediment and give acceptable copper corrosion values but unacceptable ash, carbon residue amounts and pour point (Srivastava and Prasad, 2000). Carboxylic acids present in the pyrolized vegetable oils are undesirable because they contain oxygen and are corrosive to metals. To reduce these undesirable carboxylic acids and increase the saturated alkanes in the product oil, catalytic cracking (cracking in presence of catalyst) and catalytic hydrocracking (cracking in presence of catalyst and hydrogen) are the suitable processes. Of these two processes catalytic hydrocracking is the most suitable process because it can produce a higher alkane content liquid fraction fuel than catalytic cracking with lower cyclic compounds (aromatics) and carboxylic acid content (Baroi et al., 2007).

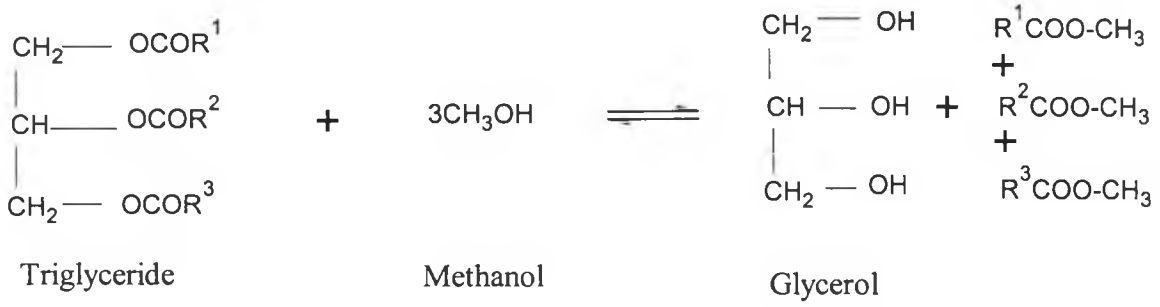
Transesterification

The other name of transesterification is alcoholysis because in this process one alcohol is replaced by another i.e. the higher alcohol (glycerol) present in the triglyceride is replaced by a lower alcohol (i.e. methanol, ethanol) and the resultant monoalkyl esters of long chain fatty acids are called biodiesel. This process is widely used to reduce the viscosity of triglycerides. When methanol is used as the lower alcohol to replace the glycerol of the triglycerides then the process is called methanolysis and the fatty acid methyl esters (FAME) are formed (Meher et al., 2006a). The properties of biodiesel are close to those of diesel fuels. The conversion of triglycerides into biodiesel through transesterification reduces the molecular weight to one-third that of the triglyceride, and the viscosity is reduced by a factor of eight compared to the triglycerides. Biodiesel

contains 10 to 11% oxygen by weight, which may improve combustion compared to hydrocarbon-based diesel fuels. Biodiesel has a lower heating value and higher cetane number and flash point. The cloud point and pour points of biodiesel are also 15 to 25°C higher than those of petrodiesel fuel (Srivastava and Prasad, 2000). These properties of biodiesel make it relatively easy to handle and to store it more safely compared to diesels. That's why biodiesel becomes a strong candidate to replace the diesel fuels as an alternative fuel.

In the transesterification reaction polar alcohols (methanol, ethanol, propanol and other alcohols) and non polar oils and fats (edible and non edible) are used as reactants. Transesterification of triglycerides produce fatty acid alkyl esters and glycerol. The glycerol phase settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. The general equation of transesterification is given below:

Fig. 2.1 General overall reaction of transesterification



Triglyceride Methanol Glycerol

Fig. 2.2 Overall transesterification reaction using methanol (Methanolysis)

There are three consecutive and reversible reaction steps which are believed to occur. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and of monoglycerides to glycerol, yielding one methyl ester from each glyceride at each step. The detailed reaction is given in Figure 2.3.

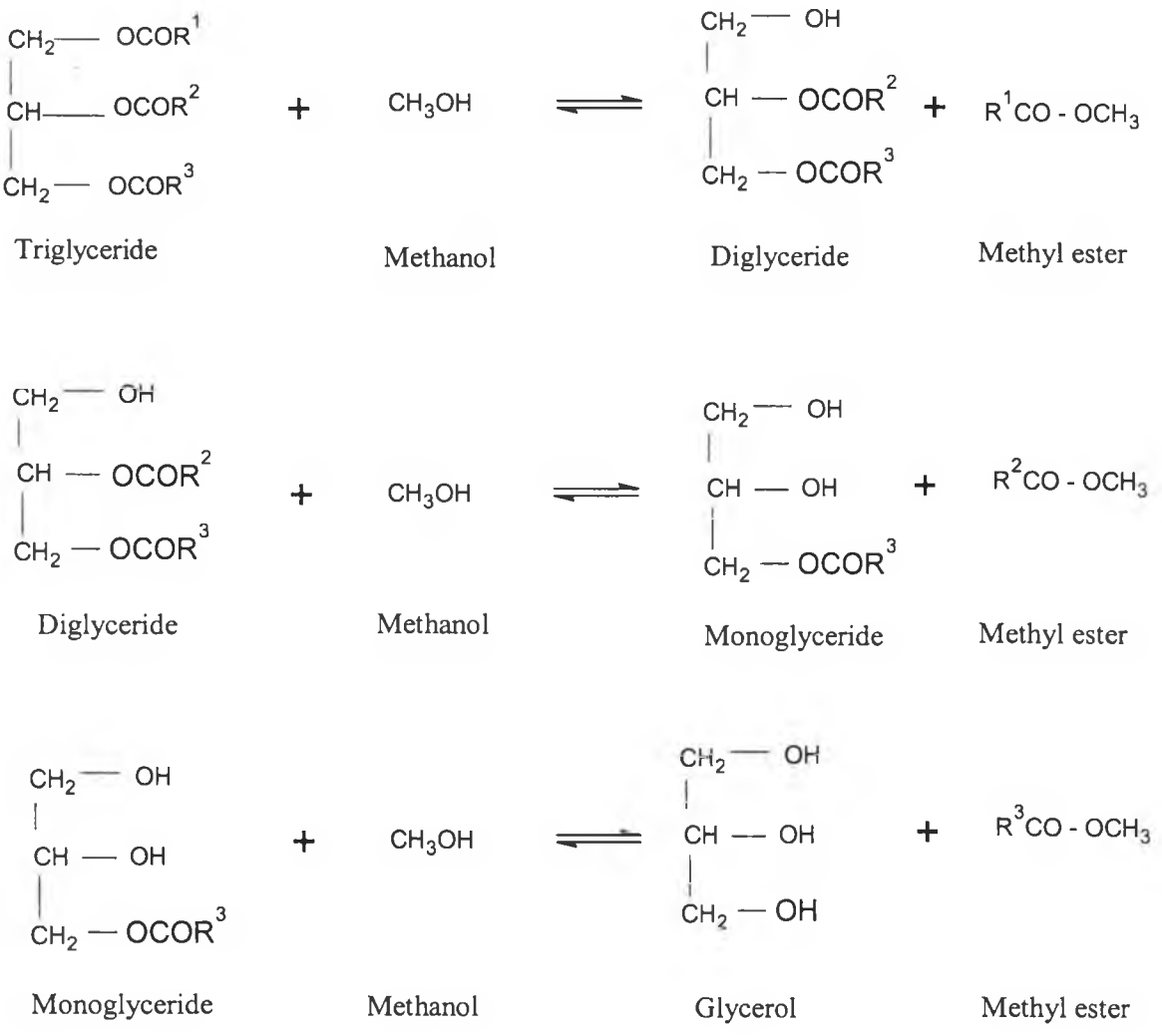


Fig. 2.3 Detailed steps of the transesterification reaction

As the step wise reaction steps are reversible a molar excess of alcohol is used to shift the equilibrium towards the formation of esters according to Le Chatellier's principle. In presence of a large molar excess (30:1) of alcohol the forward reaction is pseudo-first order; in presence of a smaller molar excess (6:1) of alcohol the reaction is second-order and the reverse reaction is found to be second order (Meher et al., 2006a;

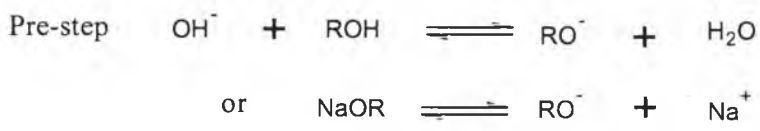
Gerpen and Knothe, 2005). Although transesterification is a reversible reaction, in the final step when mono alky ester is formed, the back reaction does not take place or is very negligible because the glycerol formed is not miscible with the product, leading to a two-phase system (Gerpen and Knothe, 2005).

The transesterification reaction can occur without any catalyst using a large excess of alcohol in such a temperature and pressure that the alcohol reaches its supercritical state. In case of methanolysis the minimum reaction temperature and pressure should be above 512.2 K and 8.1 MPa, because these are the critical temperature and pressure of methanol (Demirbas, 2007). In this method a very high conversion can be obtained at the price of high temperature and pressure. This process solves the problems associated with the two-phase nature of normal methanol/oil mixtures by forming a single phase as a result of the lower value of the dielectric constant of alcohol in the super critical state (Demirbas, 2007).

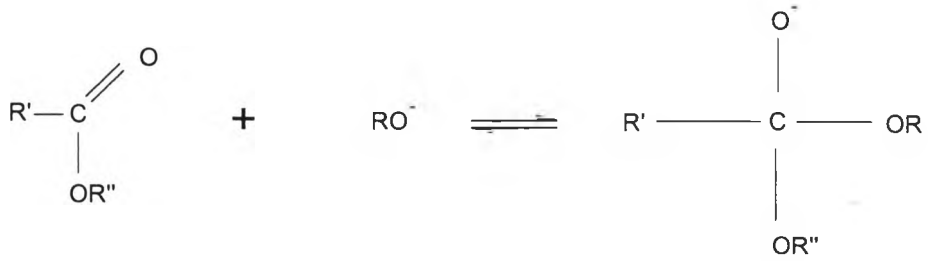
The transesterification reaction can take place using catalysts at lower temperatures, atmospheric pressure and lower molar excess of alcohol. For methanol based transesterification the most commonly used temperature is 60°C and the methanol to oil molar ratio is 6:1 (Gerpen and Knothe, 2005).

The catalysts used for the reaction may be homogeneous base or acid or heterogeneous base, acid or enzymes. Homogeneous alkali metal alkoxides are the most effective transesterification catalyst compared to acidic catalysts. Sodium alkoxides are among the most efficient catalysts used for the purpose and sodium methoxide is widely used for commercial scale biodiesel production. Potassium hydroxide, sodium hydroxide, potassium methoxide are also used as catalysts. The base catalyzed transesterification

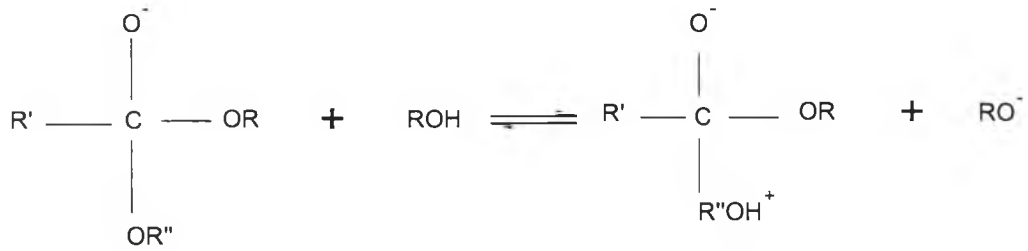
reaction is 4000 times faster than the acid catalyzed reaction. Partly for this reason and partly because base catalysts are less corrosive to industrial equipments compared to acidic catalysts, most commercial transesterifications are conducted with alkaline catalysts (Srivastava and Prasad, 2000). In the base catalyzed reaction mechanism the first step involves the attack of the alkoxide ion on the carbonyl carbon of the triglyceride molecule, which results in the formation of a tetrahedral intermediate. The reaction of this intermediate with an alcohol produces the alkoxide ion in the second step. In the last step the rearrangement of the tetrahedral intermediate gives rise to an ester and a diglyceride (Meher et al., 2006a). This mechanism is shown in Figure 2.4. One of the major problems associated with base catalyzed reaction is formation of soap as an undesired reaction between free fatty acids (FFA) and bases, which consumes some of the base. Thus the base available for catalyzing the reaction is reduced. FFA content up to 3% in the oil or the feedstock doesn't affect the process significantly but if the oil contains more than 5% FFA the soap inhibits separation of glycerol from the methyl esters (Gerpen and Knothe, 2005). When potassium or sodium hydroxide is used as the catalyst, the hydroxide ion of these catalysts reacts with alcohol (i.e. methanol, ethanol), irrespective of whether the alcohol is anhydrous or not, and water is formed. Then this water reacts with triglycerides and as a result of a hydrolysis reaction, diglycerides and free fatty acids are formed. This FFA reacts with potassium or sodium ions and as a result soap is formed. This saponification increases with the reaction temperature (Bondioli, 2004).



Step.1.

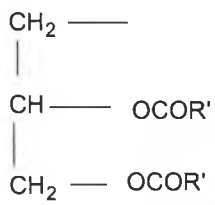


Step.2.



Step.3.

Where R" =

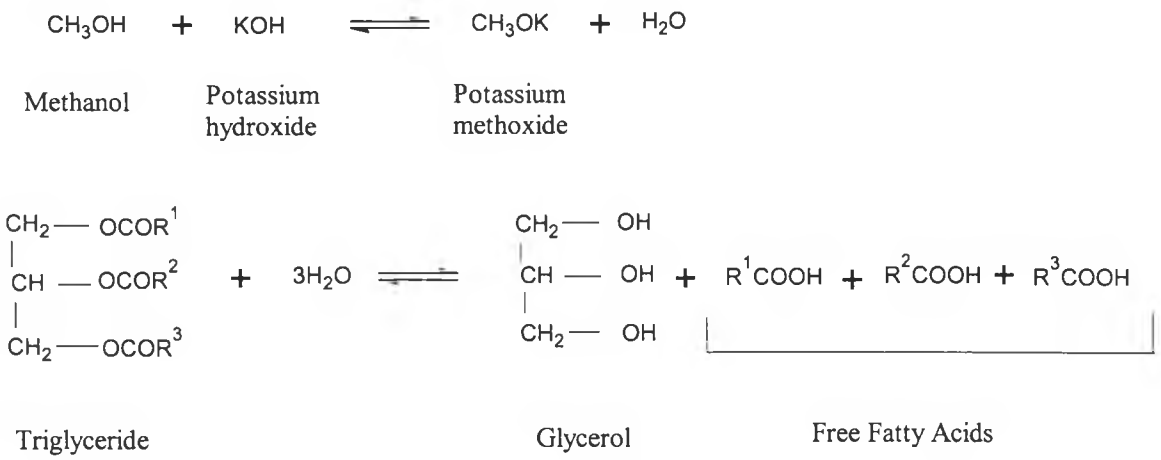


R' = Carbon chain of fatty acid

R = Alkyl group of alcohol

Fig. 2.4 Mechanism of base catalyzed transesterification (Meher et al., 2006a)

As the hydrolysis reaction creates FFA, this FFA not only consumes some amount of potassium or sodium ion, it also reduces the formation of mono alkyl esters. If sodium or potassium alkoxide or methylate is used as a catalyst, the soap formation can be reduced to a large extent because of the absence of the hydroxide ion, which favors formation of water. The reaction scheme is shown in Figure 2.5.



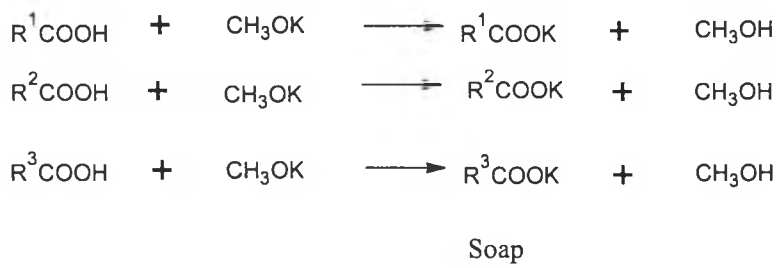


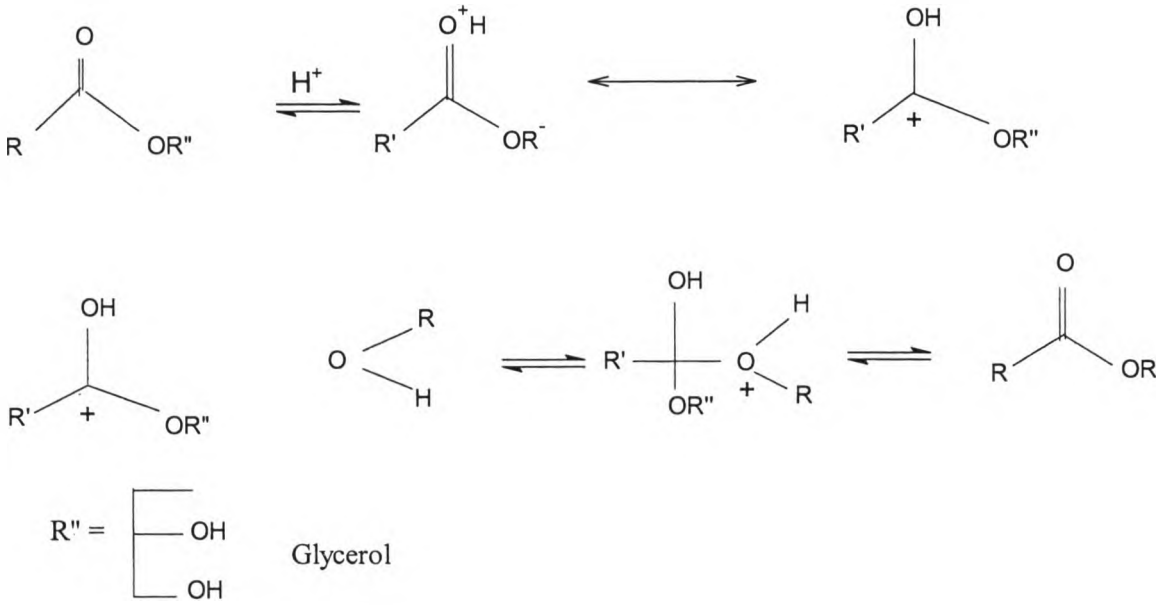
Fig. 2.5 Formation of soap

In a study using sodium hydroxide, sodium methoxide, calcium oxide, barium oxide, strontium oxide and potassium carbonate, it was found that potassium carbonate formed the least amount of soap when oxidized fat was used as the feedstock. The reason may be lack of formation of water by the reaction when potassium carbonate was used.

The little soap formed might be due to the presence of moisture in the alcohol, air and in the triglyceride (Bondioli, 2004).

When the FFA content in the oils or feedstock is higher, then the acid catalyzed transesterification reaction is preferred at the expense of longer reaction times. Acid catalysts can catalyze simultaneously the esterification and transesterification reactions. Thus the FFA present in the oil in presence of acid catalysts, go through esterification reaction to form FAME. The acid catalyzed esterification reaction is faster than the transesterification reaction (Ataya et al., 2007). Because FFA, alcohol and the acid catalysts are polar in nature, there is no phase difference in the reaction. In the acid catalyzed transesterification reaction mechanism at first the carbonyl group is protonated by the acid catalyst; the compound formed in the intermediate steps by the nucleophilic attack of the alcohol produces a tetrahedral intermediate. The last step is the proton migration and breakdown of the intermediate. This mechanism is shown in the Figure 2.6. The acid catalyzed protonation of the carbonyl oxygen increases the electrophilicity of the adjoining carbon atom, making it more susceptible to nucleophilic attack. On the other hand, base catalysis takes on a more straight-forward route. It creates first an alkoxide ion, which directly acts as a strong neucleophile, giving rise to a different chemical pathway for the reaction. This difference, i.e. the formation of a more electrophilic species (acid catalysis) versus that of a stronger nucleophile (base catalysis) is responsible for the different reaction rates (Loreto et al., 2005). In acid catalyzed transesterification, the presence of water or the formation of water during the esterification reaction (Fig. 2.7) of FFA affect the accessibility of the catalyst to the triglyceride molecules and inhibit the transesterification reaction (Ataya et al., 2007).

H_2SO_4 is the most widely used acid for the acid catalyzed transesterification. Other acids used for this purpose are HCl, BF_3, H_3PO_4 and organic sulfonic acids (Loreto et al., 2005).



R' = Carbon chain of fatty acid

R= Alkyl group of the alcohol

Fig. 2.6 Acid catalyzed transesterification reaction (Meher et al., 2006a)

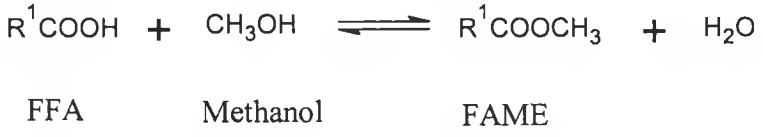


Fig. 2.7 Esterification reaction

An immobilized enzyme (lipase) is also used as the catalyst for the transesterification reaction. According to the proposed mechanism, the enzyme at first catalyzes the hydrolysis reaction in which FFA are liberated and then these FFA go through enzyme catalyzed esterification reaction in which fatty acid alkyl ester/biodiesel

are formed (Al-Zuhair, 2006). Low temperature requirements of the reaction, easy separation of the enzymes and obtaining relatively pure glycerol without any treatment are the advantages of using these biocatalysts. But immobilized enzymes are costly and another drawback of these enzymes is that they cannot be reused because they become deactivated in presence of short chain alcohols (i.e. methanol, ethanol) conventionally used in the biodiesel production process. This deactivation can be avoided using an organic solvent (e.g. n-hexane) in the reaction as a diluent and higher conversion can be obtained in its presence. But using a diluent decreases the reaction rate because of a lower concentration of methanol in the reaction mixture (Modi et al., 2006). Without using an organic solvent the alternative approaches are either using longer chain alcohols as miscibility of triglycerides increase with the increase of the chain length of the alcohols or step by step addition of short chain alcohols (Modi et al., 2006; Shimada, 2002). Glycerol, one of the products of transesterification, also negatively affects the rate and extent of the conversion, because it is easily absorbed on the surface of the enzyme (Xu et al., 2003; Belafi-Bako et al., 2002). Removal of glycerol from the reaction mixture is also necessary to obtain a high conversion and a rate of the reaction.

For easy separation of reaction products and for minimizing waste formation due to neutralization of homogeneous base/acid catalysts, heterogeneous base/acid catalysts are thought to be very attractive for biodiesel production. Heterogeneous base/acid catalysts could be classified as Bronsted or Lewis catalysts, though in many cases both types of sites could be present and it is difficult to evaluate the relative importance of the two types of the sites in the reaction. The reaction mechanisms of both Bronsted and Lewis catalysts are similar to homogeneous Bronsted basic homogenous catalysts (i.e.

NaOH, KOH) (Di Serio et al., 2008). This is different in the case of acid catalysts. Both homogeneous (i.e. H_2SO_4, *p*-toluensulfonic acid) and heterogeneous Bronsted acid catalysts are active mainly in the esterification reaction whereas both homogeneous (i.e. metal acetate, metal complex) and heterogeneous Lewis acid catalysts are more active in the transesterification reaction. These Lewis catalysts can be deactivated due to the formation of water in the esterification reaction (Di Serio et al., 2008). The activity of the acid catalysts in the transesterification reaction is normally quite low, so that to obtain a sufficient reaction rate, increase of the reaction temperature is necessary (Di Serio et al., 2008).

Although it is claimed that the heterogeneous catalysts are insoluble, in many experiments, leaching of catalysts was observed (Di Serio et al., 2008; D'cruz et al. 2007). One of the reasons may be presence of glycerol in the reaction. Because glycerol has remarkable solvent properties, it will dissolve deliquescent salts, such as compounds of lithium and calcium, as well as take up large quantities of the halogen salts of common metals, including even those that dissolve with difficulty in water, as well as many sulphates and nitrates (Schmidt, 1913).

Both basic (anion exchange) and acidic (cation exchange) ion exchange resins have been tried as heterogeneous catalysts. In case of basic ion exchange resins (i.e. PA308, PA 306, PA 306s, HPA 25) the catalytic activity diminishes during the reactions because of the resin's hydroxyl ion exchange reactions with triglycerides and as a result of the formation of fatty acids. In case of acidic resins (i.e. Amberlyst -15) the catalytic deactivation is due to the blockage of the sites by adsorbed intermediates or product species (Di Serio et al., 2008).

In the transesterification reaction the reactants are two phasic i.e. polar alcohol and non polar triglycerides. When homogenous base or acid catalysts are used in the reaction, they are dissolved in the alcohol phase and the reaction interaction takes place in the alcohol phase. It is one of the reasons why to get a higher reaction rate and a higher conversion one uses a higher molar ratio of alcohol to triglycerides. But a higher molar ratio of alcohol to triglycerides interferes in the separation of glycerol (Srivastava and Prasad, 2000). When using heterogeneous catalysts, they don't dissolve in either phase. Therefore the reaction starts with three phases. Thus in most cases it is observed that for getting higher reaction rates and conversions, one needs higher temperature, pressure, higher molar ratio of alcohol to triglycerides or other means to overcome the mass transfer limitations (Di Serio et al., 2008).

Initially the transesterification reaction is diffusion-controlled and poor diffusion between the phases results in a slow rate. As alkyl esters are formed, they act as a mutual solvent for the reactants and a single phase system is formed (Srivastava and Prasad, 2000). The interaction between the two phase reactants before alkyl ester formation is very important. The interaction by stirring or mixing using impellers is significant up to a certain range of speed; beyond that speed the reaction rate may be independent of the impeller speed (Vicente et al., 2005). In place of mechanical stirring one can use ultrasonic cavitations or hydrodynamic cavitations. Among mechanical stirring, ultrasonic cavitations and hydrodynamic cavitations, ultrasonic cavitations give the highest conversion within the shortest time. On the other hand hydrodynamic cavitations are the most cost effective on the basis of the power consumption though they give a little slower conversion than ultrasonic cavitations. Mechanical stirring performance is the

worst among these three methods both in cost and conversions (Ji, et al., 2006). Temperature has a positive impact on the increasing miscibility of the alcohol and of the oil phase. Use of co-solvent can improve the mass transfer limitation arising from phase difference. Cyclic ethers especially THF are preferred to use as the co-solvent as they can dissolve both alcohol and the oil phase. The boiling point of THF is close to the one of methanol (most commonly used in biodiesel production), so it can be easily removed and recovered along with excess methanol (Boocock et al., 1996).

2.4 Biodiesel quality and specifications

The ASTM defined specification for 100% biodiesel is given below (http://biodiesel.org/pdf_files/fuelfactsheets/BDSpec.PDF visited 22.02 hours, 13 January, 2008.):

Table 2.3 ASTM specifications of Biodiesel

Property	ASTM Method	Limits	Units
Calcium & Magnesium, combined	EN 14538	5 max	ppm (ug/g)
Flash Point (closed cup)	**D 93**	**93 min.**	**Degrees C**
Alcohol Control (One of the following must be met)			
1. Methanol Content	EN14110	0.2 Max	% volume
2. Flash Point	D93	130 Min	Degrees C
Water & Sediment	**D 2709**	**0.05 max.**	**% vol.**
Kinematic Viscosity, 40 C	D 445	1.9 - 6.0	mm^2/sec
Sulfated Ash	D 874	0.02 max.	% mass
Sulfur			
S 15 Grade	**D 5453**	**0.0015 max. (15)**	**% mass (ppm)**
S 500 Grade	**D 5453**	**0.05 max. (500)**	**% mass (ppm)**
Copper Strip Corrosion	D 130	No. 3 max.	
Cetane	D 613	47 min.	
Cloud Point	**D 2500**	**Report**	**Degrees C**
Carbon Residue 100% sample	D 4530*	0.05 max.	% mass
Acid Number	**D 664**	**0.50 max.**	**mg KOH/g**
Free Glycerin	**D 6584**	**0.020 max.**	**% mass**
Total Glycerin	**D 6584**	**0.240 max.**	**% mass**
Phosphorus Content	D 4951	0.001 max.	% mass
Distillation, T90 AET	D 1160	360 max.	Degrees C
Sodium/Potassium, combined	EN 14538	5 max	ppm
Oxidation Stability	**EN 14112**	**3 min**	**hours**

The above overall ASTM specification for biodiesel is known as ASTM 6751-07b.

The viscosity of biodiesel is an important factor as viscosity controls the characteristics of the injection from the diesel injector. The viscosity of fatty acid methyl esters can go to very high levels and hence it is important to control the viscosity within an acceptable limit to avoid negative impacts on the fuel injector system performance (Meher et al., 2006a).

In the specification maximum calcium, magnesium, sodium, potassium, phosphorus contents are specified because these have a negative effect on fuel property and corrosion. The copper strip corrosion of biodiesel is specified to ensure the acceptable corrosiveness of the biodiesel to the engine. Neutralization number or acid number is specified to ensure proper aging of the fuel and /or a good manufacturing process. It reflects the presence of free fatty acids and the degradation of biodiesel due to thermal effects (Meher et al., 2006a). Carbon residue of the fuel is indicative of carbon depositing tendencies of the fuel. Carbon residue of biodiesel is more important for biodiesel because it shows a high correlation with presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids and inorganic impurities (Meher et al., 2006a). The presence of high alcohol concentrations in biodiesel cause accelerated deterioration of natural rubber seals and gaskets. Thus the presence of alcohol in the biodiesel is specified. The presence of water in the biodiesel causes a hydrolytic degradation of biodiesel through a hydrolysis reaction, which has an inhibiting effect on long-term storage. The presence of free glycerol and bound glycerol (mono-, di-, and triglycerides) cause engine problems like fuel filter plugging. Mono- and diglycerides have a tendency to absorb water, which causes the hydrolytic degradation of biodiesel (Srivastava and Prasad, 2000; Meher et al., 2006a). Oxidation stability is the measure of

the oxidative degradation which also inhibits long term storage of biodiesel. Oxidative degradation develops when unsaturated molecules (higher iodine value is an indication of higher degree of unsaturation and vice versa) present in the biodiesel react with atmospheric oxygen and are converted to peroxides. Cross-linking at the unsaturation site can occur and the material may get polymerized into a plastic-like body. At high temperature, commonly found in an internal combustion engine, the process can get accelerated and the engine can quickly become gummed up or clogged with the polymerized biodiesel (Azam et al., 2005). The flash point of a fuel is the temperature at which it will ignite when exposed to a flame or a spark. The flash point of biodiesel is higher than that of petro diesel. This makes it safe for transport purposes. The Pour point is the lowest temperature at which the oil specimen can still flow (Baroi et al., 2007). The cloud point is the temperature at which waxy solid first appear during the cooling of fuels. The cetane number of a fuel is an indication of its ignition characteristics. The cetane number measures how easily ignition occurs and the smoothness of combustion. The higher the cetane value the better the ignition properties. The cetane number affects a number of engine performance parameters like combustion, stability, white smoke, noise and emissions of CO and Hydrocarbons. Biodiesel has higher cetane value than conventional diesel fuel, which results in higher combustion efficiency (Meher et al., 2006a). But with the increase of cetane number the iodine value decreases which means the degree of unsaturation decreases. This situation leads to solidification at higher temperature. It means that biodiesel with a very high cetane number may have higher melting point, cloud point and pour point and that it can solidify at or above 0°C depending on the value of the cetane number or the iodine number of the biodiesel. For

this reason in the US biodiesel standards the upper limit of cetane numer has been specified at 65 (Azam et al., 2005). This upper limit of the cetane number/value is very important especially for cold climate countries where the Cold Filter Plugging Point (CFPP) of the fuel is very important. The CFPP of a fuel reflects its cold weather characteristics (Meher et al., 2006a). At low temperatures below 0°C biodiesel (commonly fatty acid methyl esters) will crystalline. Such crystals can plug fuel lines and filters, causing problems in fuel pumping and engine operation (Azam et al., 2005). CFPP defines the fuels limit of filterability. Normally either pour point or CFPP are specified (Meher, et al., 2006). One of the solutions for this problem is using branched chain alcohols to prepare fatty acid branched chain alcohol esters (Srivastava and Prasad, 2000). Crystallization involves the arrangement of molecules in an orderly pattern. When branches are introduced into linear long-chain ester structures, intramolecular associations should be attenuated and the crystallization temperature reduced. But highly branched and heavy molecular weight alcohols are not as effective for the transesterification reaction for biodiesel production. In this method, so far, use of isopropanol as a branched chain alcohol is feasible though isopropanol is more expensive than methanol or ethanol. Other higher branched chain alcohols are very expensive and their transesterification give lower yield and more impurities than isopropanol (Lee et al., 1995). Thus the use of other branched alcohols is not economically feasible. Another method to improve the cold flow properties of biodiesel is to remove high-melting saturated esters by inducing crystallization with cooling. This method is known as winterization. This process depresses the cloud point of esters by equilibrating them at temperatures below their cloud point and above their pour point over an extended period

of time, then filtering away the solids and as a result the cloud point of the biodiesel is reduced to a lower temperature. The other method is to use a cold flow additive in the biodiesel, which can improve the pour point but doesn't greatly affect the cloud point, whereas both CFPP and low temperature flow tests are nearly a linear function of cloud point (Srivastava and Prasad, 2000). As a consequence the use of a cold flow additive is not a very good option to improve the cold flow properties of biodiesel.

In biodiesel the lower limit of fatty acid alkyl ester should be 98.5% by mass and the upper limit preferably 99.9% by mass (Oku et al., 2007).

Chapter 3

MATERIALS AND METHODS

3.1 Materials

Anhydrous grade (99.9%) methanol was purchased from Alfa Aesar (Oakville, Ontario, Canada) and ACS grade (99%) K_2CO_3 was obtained from common chemical storage. Triolein (≈99%), methyl oleate (≈99%) and n-heptane were bought from Sigma Aldrich (Oakville, Ontario, Canada). MSTFA (N-Methyl- N- Trimethylsilyl Trifluroacetamide) was brought from Chromatographic Specialties Inc. (Brockville, Ontario, Canada). Double press virgin *Jatropha curcas* oil was purchased from Medors Biotech Pvt Ltd, New Delhi, India. The properties of the oil as specified by the vendor were (Appendix A.1):

Table 3.1 Composition and properties of the JTC oil given by the vendor

Parameters	Analytical Results
Acid value	2.51 mg KOH/gm
Free fatty acid	1.47% w/w (as oleic acid)
Iodine value	110
Saponification value	180
Viscosity (at 31°C)	70 cPs
Flash point	152°C
Fatty acid Composition Palmitic acid (C16:0) Stearic acid (C18:0) Oleic acid (C18:1) Linoleic acid (C18:2) Other acids	 12.25% 3.5% 24.32% 24.72% 32.67%
Density	0.920
Average Molecular Weight	832

The composition and properties of the *Jatropha curcas* oil feedstock were checked by Intertek Caleb Brett, Hamilton, Ontario. (Appendix A.2).

Table 3.2 Composition and properties of the JTC oil feedstock given by the Intertek Caleb Brett Laboratory, Hamilton, Ontario.

Fatty acid Composition	
Palmitic acid (C16:0)	14.45%
Palmitoleic acid (C16:1)	0.45%
Stearic acid (C18:0)	4.69%
Oleic acid (C18:1)	26.51%
Linoleic acid (C18:2)	31.9%
Linolenic acid (C18:3)	3.34%
Arachidic acid (C20:0)	0.81%
Eicosenic acid (C20:1)	2.28%
Behenic acid (C22:0)	13.62%
Erucic acid (C22:1)	0.62%
Lignoceric acid (C24:0)	0.59%
Others	0.74%
Iodine value	97.9

The composition of the *Jatropha curcas* oil feedstock was again checked by GC-MS in one of our own laboratory at the end of all experiments. The properties were (Appendix A.3):

Table 3.3 Composition of the JTC feedstock given by own laboratory GC-MS at the end of the all experiments (see Appendix A.3)

Fatty acid Composition	
Palmitic acid (C16:0)	20.67%
Stearic acid (C18:0)	11.31%
Oleic acid (C 18:1) + Linoleic acid (C18:2)	58.25%
Propanoic acid	1.3342%
Other components	8.436%

3.2 Experimental set up

A 250 mL Erlenmeyer flask was modified to use as the reactor. The top of the flask was made narrower to fit into the bottom part of the 24/40 size Liebig condenser. The flask was modified to have two more openings (Fig. 3.1). One opening was to fit the temperature sensing probe inside the reactor. This opening was made by connecting 2.5 inch length 14/23 glass tubing with the flask. This connection was made at 3 inch height from the bottom of the flask and the extended opening made an angle of 60° with the horizontal. A rubber septum was used to close this opening during the reaction and the temperature sensing probe was inserted through the septum. The second opening was made at a height of 1.75 inch from the bottom of the flask. This opening consisted in connecting 1.5 inch length glass tubing with the flask. This extended opening also made an angle of 60° with the horizontal. This opening was also blocked by a rubber septum during the reaction and samples were collected with the help of an injection syringe through the septum. The condenser was used to condense the methanol vapor. Normal tap water entered at the bottom side of the condenser and left from the top side of the condenser. The top of the condenser was fitted with a 19/26 size glass bent tube (Fig.3.2).

The bent tube was filled up with anhydrous calcium sulfate blocked by cotton on both sides of the tube to ensure entrance of moisture free air into the system. A VWR 800 series advanced digital hot plate with stirrer (VWR, Oakville, Ontario, Canada) was used to provide controlled heat at a desired temperature and controlled stirring. This advanced hot plate and stirrer had a stop watch integrated with it. This watch ensured automatic shutdown of stirring and heating after the desired reaction time.

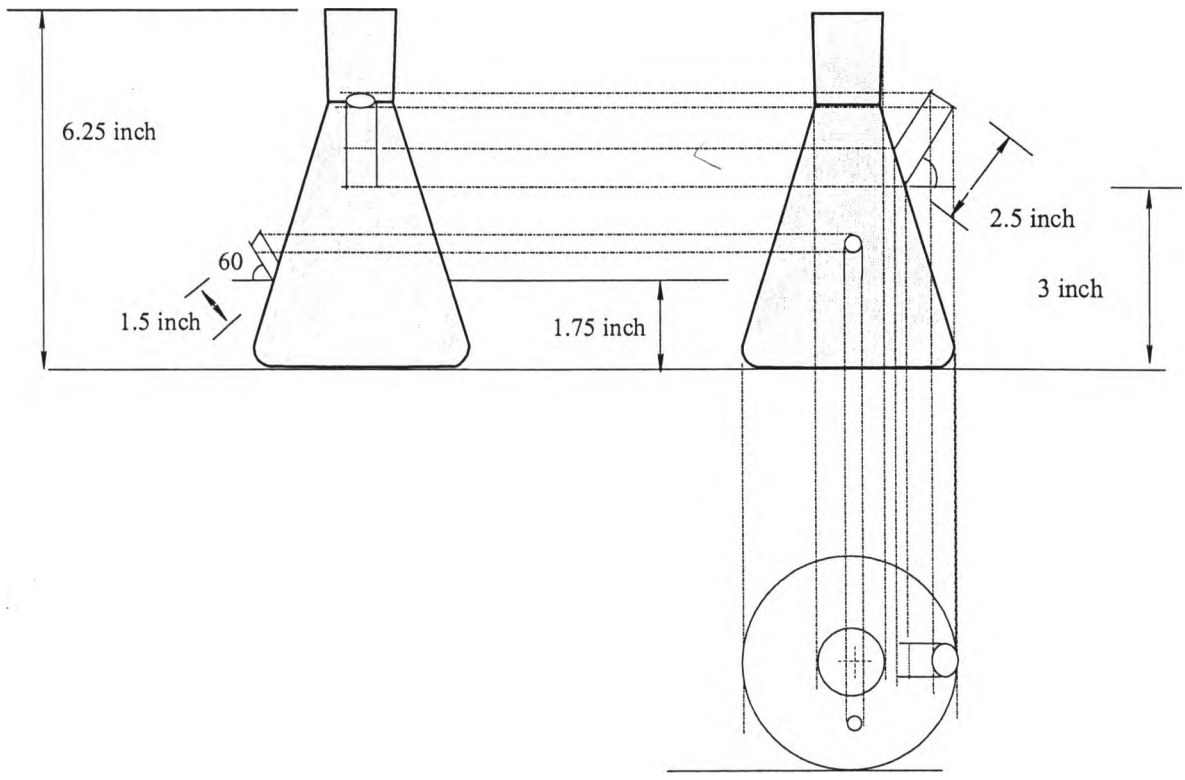


Fig. 3.1 Dimensions of the reactor

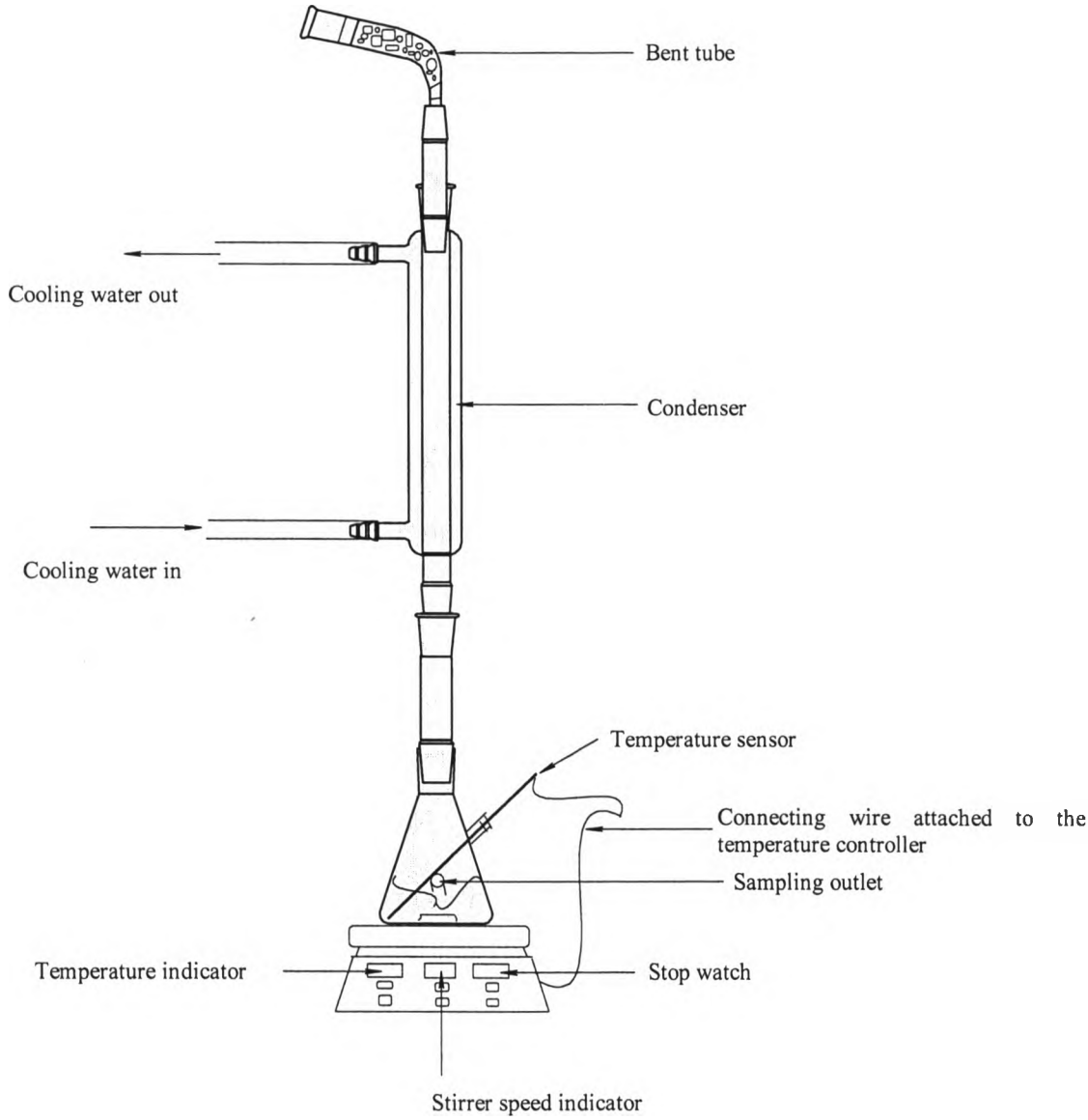


Fig. 3.2 Experimental set up

3.3 Equipment calibration

The sensitivity of the temperature sensing probe of the digital controller of the hot plate was checked using a traceable ISO 17025 calibrated lollipop digital thermometer (VWR, Oakville, Ontario, Canada) and the difference in temperature was ± 0.2 °C. A vendor specified magnetic stirrer bar especially designed for this digital hot plate and stirrer was used. The stirring sensitivity with respect to the rpm was ± 2% as defined by the vendor. A 5 - digit precision electronic balance was used to weigh the catalyst (K_2CO_3). The sensitivity of the balance was verified with reference weights. The weight indication was accurate up to 4 digits.

3.4 Procedure

The jatropha oil was stored in a cold and dark room at 5°C under argon to prevent oxidation. The oil containers were flushed with argon after each opening. One hundred grams (110 mL) of jatropha oil were introduced into the reactor. Then 30 mL of methanol (6:1 methanol to oil molar ratio) and different amounts of catalyst were added into the reactor. This procedure was followed to obtain an optimum catalyst amount. Once this optimum catalyst amount was obtained, then in the second part this parameter was kept fixed and the methanol to oil molar ratio was varied keeping the temperature of the reaction constant. In the experiments where the reaction temperature was varied, the methanol to oil molar ratio was 6:1 and the optimum catalyst amount was used. All the reactor contents were preheated to the desired temperature. Stirring was then started and this point was counted as the starting of the reaction. The reaction was allowed to run for 10 hours, at which time heating and stirring were stopped by the control system. This 10

hour reaction time was selected based on the preliminary rough experimental runs (Appendix A.4).

3.5 Analysis of the results

Off-line FTIR - ATR (Fourier Transform Infrared spectroscopy - Attenuated Total Reflectance) has been used as a primary method for detecting biodiesel conversion because of its easy and fast detection techniques. In FTIR - ATR spectroscopy, IR radiation is passed through an IR transmitting crystal of a high refractive index thereby allowing the radiation to penetrate the sample in contact with the ATR sampling surface for a very short distance (micrometer) and reflect back to the IR spectrometer. Since the sample path length is very short and the IR absorption features become clear, the sample can be directly analyzed without dilution (Tseng and Wang, 2007). For ATR, the angle of incidence of the IR radiation must exceed the critical angle (θ_c) (Fig. 3.3). By using a crystal of higher refractive index, the critical angle and the penetration depth into the sample can be decreased. The penetration depth into the sample can also be increased by increasing the angle of incidence or by increasing the wave number of the incident IR radiation (Smith, 1996). During the analysis precaution was taken to ensure that the spectra were not saturated when performing the analysis. Saturated spectra occur when none of the IR light is transmitted at a particular wavelength and all the light is absorbed. Under this circumstance, it is impossible to make a quantitative analysis based on the peak. In saturated spectra, the peaks either have the same height or appear to be "grassy".

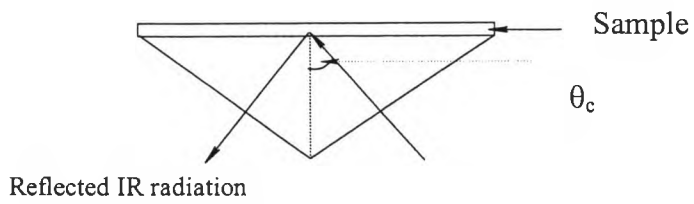


Fig. 3.3 ATR principle

The possibility of spectral saturation can be reduced by probing fewer microns into the sample. This can be done by changing the angle to 60° or changing the crystal material to one with a higher refractive index, such as germanium. In the present study, the use of germanium was not deemed necessary as spectral saturation was nonexistent using ZnSe crystal cell (Fig. 3.4).

The raw oils and the methyl esters are fairly strong absorbers in the infrared region. From a cursory examination of the literature, there are commercial units that use an integration of the side (1750 – 1760 cm^{-1}) of the carbonyl peak (~ 1744 cm^{-1}) to monitor the progress of the reaction. This method can be effective in a known system but is limited because it is not specific for the end product. There could be a number of interferences. The reason that the commercial units use this method is that they do not have to have spectral resolution to do more specific analysis. The peak typical of the methyl ester (O-CH_3) at 1436 cm^{-1} is very narrow and rides on the side of another peak (oil). Both of these characteristics make this peak unattractive to the commercial units for monitoring the biodiesel reaction progress. But this peak measurement gives a direct indication of the attachment of the alkyl group of the alcohol with the fatty acids of the triglycerides and this peak is free of the influence of the alkyl group (-CH_3) present in the alcohol (see Appendix A.5). Other FTIR - ATR analytical methods rely on the formation

of glycerol as a side product rather than on the direct measurement of the formation of the methyl ester (monitoring methyl peak). Another advantage of using FTIR -ATR is the ability to detect the presence of soap in the biodiesel. Soaps are the sodium, potassium or other metal salts of the carboxylic (fatty) acids. In soap formation when the carboxyl groups (COO-) of fatty acids are attached to the metal ions, the CO_2 stretch band is usually seen at 1650-1540 cm^{-1} (Lin-vien et al., 1991). This single peak is an indication of the presence of soap.

Bruker IFS 55 FTIR was used for analysis and ZnSe through cell was used as the ATR (Attenuated Total Reflectance) cell. Air was taken as the background of the FTIR spectra. A 100 μL sample was placed on the ZnSe crystal plate. The IR light incident on the ZnSe crystal was at a 45° angle, reflected off the crystal several times before leaving the crystal (Fig. 3.5). All spectra were scanned 100 times and recorded at a resolution of 4 cm^{-1}. OPUS version 4.0 software was used to analyze the spectra in terms of absorbance mode as quantitative analysis (area integration) is possible in this mode. Integration method B (baseline to base line) within that software was used to calculate the peak area. The progress of the transesterification reaction was monitored by measuring the FTIR area (1446 – 1428 cm^{-1}) under the methyl ($O\text{-}CH_3$) peak (1436 cm^{-1}), which accounts for the methyl esters of all types of fatty acids in the biodiesel (Fig. 3.4). The presence of soap was qualitatively assessed by measuring the area of a single FTIR peak in the 1597 – 1544 cm^{-1} range of the "unwashed sample" spectrum.

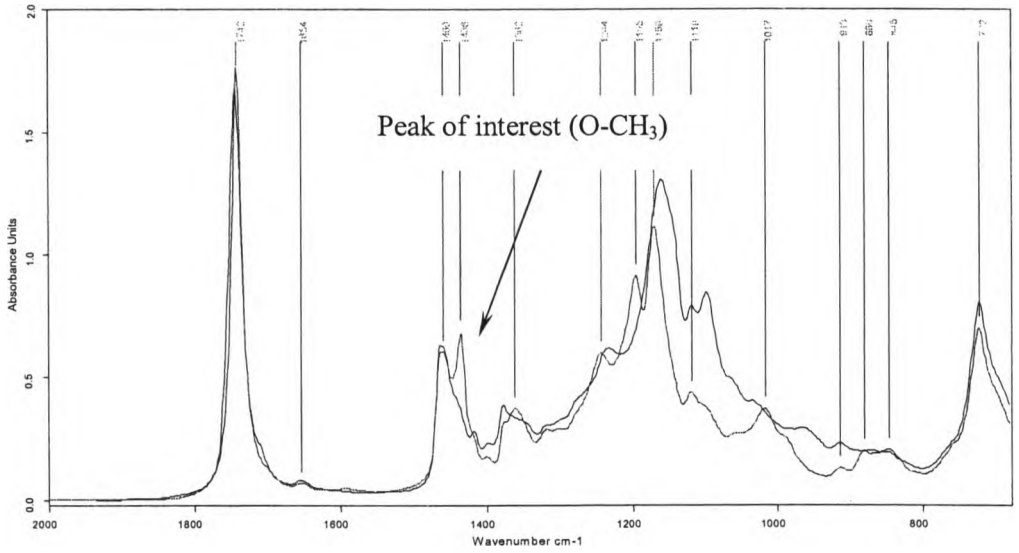


Fig. 3.4 FTIR - ATR Spectra of raw jatropha oil and washed biodiesel produced from jatropha (JTC) oil.

See Appendix A.6 for details of Figure 3.4

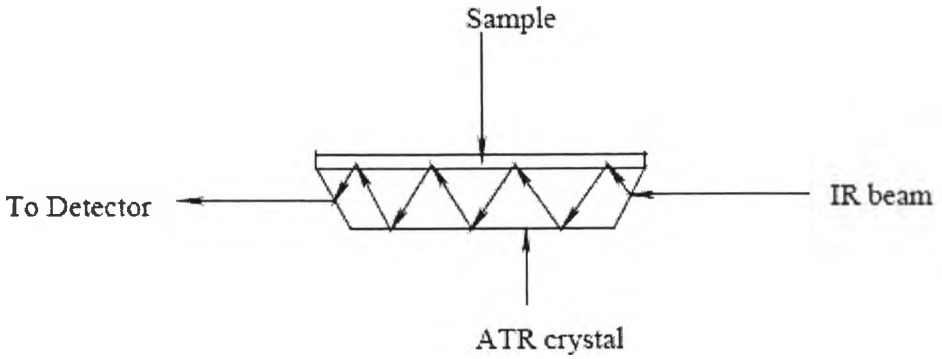


Fig. 3.5 A schematic diagram of an attenuated total reflectance accessory

For quantitative measurements of the reaction progress, different biodiesel standard solutions were prepared using triolein and methyl oleate by mixing them in different molar concentrations. The raw oil was assimilated to the glycerol ester of oleic acid (triolein) and the biodiesel was assimilated to the methyl oleate. These standard solutions were used to prepare a calibration curve which followed a second order polynomial form (See Appendix A.7).

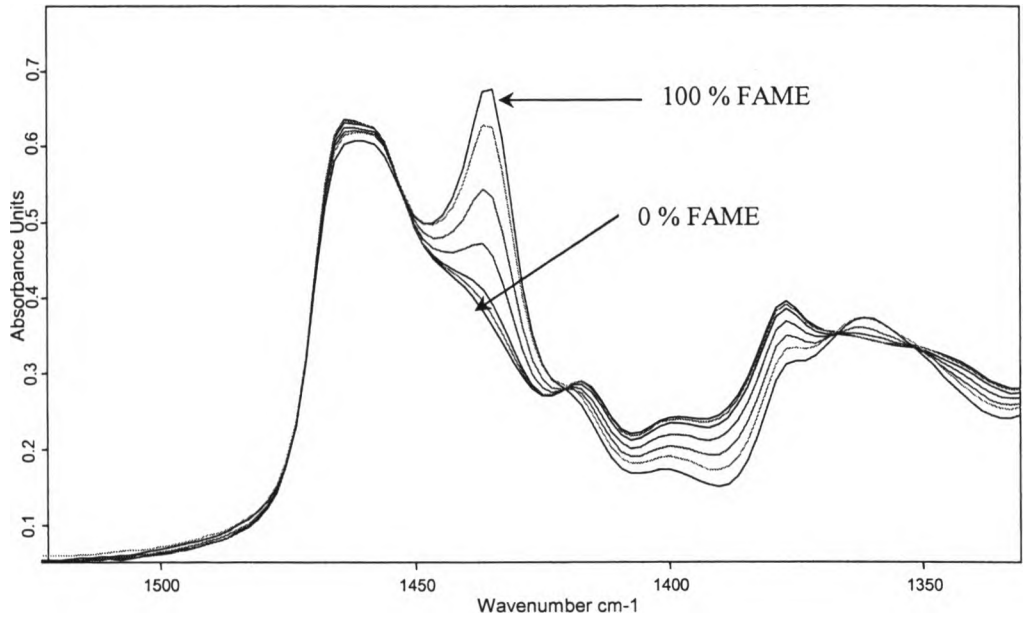


Fig. 3.6 Change in methyl peak (O-CH_3) with molar concentration of FAME in the standard solution

The probe depth of the ATR crystal is dependent on the refractive index of the sample which is dependent on the viscosity of the sample. The viscosities of the beginning material and of the end product are not the same. Moreover, the FTIR response is also dependent on the extinction coefficients of the material in the sample and the coefficients are probably not the same for the raw oil and the biodiesel product. These variations could introduce the curvature in the calibration curve. A similar shape calibration curve was also observed in a commercial portable IR spectrometer for biodiesel analysis (http://www.wilksir.com/pdf/App-note_Biofuel-InfraSpec.pdf.).

The mole concentration (mole percent or mole fraction) of FAME (fatty acid methyl ester) in the reaction sample obtained using the calibration curve (see appendix A.6) was used to calculate the percent mole conversion in the following way. If "X" is the mole fraction of FAME (biodiesel) present in each sample (t = t) then,

$$\% \text{ mole conversion} = [(X/3)/ \{(X/3) + (1-X)\}] \times 100\% \quad (1)$$

The factor 1/3 in Equation (1) arises from the stoichiometry of the transesterification reaction.

The composition of the jatropha oil and biodiesel were analyzed with an Agilent 7890A GC-MS. The compositions were reported as a relative percentage of the total area. The instrument was equipped with a FID detector (flame ionization detector) and was fitted with a DB-5 column (30 m × 0.25 mm I.D. and film thickness of 0.25μm). The initial oven temperature was 50°C. Then the oven was heated : 50°C for 1 min, 15°C/min to 180°C: hold for 0 min, 7°C/min to 230°C: hold for 0 min, 30°C/min to 325°C: hold for 40 min. Total run time was 1 hour. Helium served as detector make up gas at an inlet pressure of 26.708 psi. Hydrogen was used as a carrier gas for the FID detector. FID detector temperature was 380°C.

The Brookfield DV-II + pro was used to estimate the viscosity of the biodiesel in terms of cP at room temperature (25°C).

The acid number of the biodiesel was determined in the following way:

One gram of biodiesel was taken into a 40 mL beaker. Then 10 mL iso-propanol was mixed with it. Five drops of 1% alcoholic phenolphthalein were added as an indicator. Then the whole mixture was titrated with 0.1N potassium hydroxide solution. The acid number/value was calculated according to the following way (AOCS Cd 3d – 63):

Acid value, mg KOH/g of sample = [(A-B) × N × 56.1]/W

Where,

A = volume, mL of the potassium hydroxide solution used in the titration

B = volume, mL of the potassium hydroxide solution used in the titrating the blank.

N = 0.1 N

W= 1 g

The procedure was repeated 3 times to check the repeatability of the results.

3.6 Sample preparation

After 10 hours of reaction time, 10 mL of the reactor content were withdrawn and 20 mL of deionized water were used to stop the reaction and to wash out glycerol, methanol, catalyst and soap. This method was found to be effective and less expensive as shown in Table 3.1.

Experimental parameters: 6 wt% catalysts, 100 gm of jatropha oil, methanol to oil molar ratio is 6:1, stirring rate 600 rpm, 60°C temperature, 10 hours reaction time.

Table 3.4 Sample preparation method comparisons (analytical samples) (see Appendix A.8 for details)

Run No.	Mole conversion %		
	Method A	Method B	Method C
1	98.272	97.960	97.988
2	98.189	98.440	98.400
3	98.181	98.210	98.031

Method A = 20 mL deionized water was used to wash out the catalyst, methanol and glycerol from the biodiesel phase. The washed biodiesel phase was allowed to settle over the wash water for 2 hours and then dried over anhydrous sodium sulphate **(pH in the wash water is 10).**

Method B = 20 mL deionized water was used to wash out the catalyst, methanol and glycerol from the biodiesel phase. Then 6 mL 0.1 N HCl solution was used to wash the biodiesel phase again. The washed biodiesel phase was allowed to settle over the wash water for 2 hours and then dried over anhydrous sodium sulphate **(pH in the wash water is 8).**

Method C = 10 mL deionized water was used to wash out the catalyst, methanol and glycerol from the biodiesel phase. Then 10 mL 0.1 N HCl solution was used to wash the biodiesel phase again. The washed biodiesel phase was allowed to settle over the wash water for 2 hours and then dried over anhydrous sodium sulphate **(pH in the wash water is 7).**

Thus method A was used for sample preparation.

In the experiments (part B-chapter 4) where methanol to oil molar ratio and temperature were varied keeping the catalyst concentration at the optimum value (6 wt% of the oil), 60 mL deionized water were needed to use in place of 20 mL water. Because with the increase of the methanol to oil molar ratio it was necessary to use excess amount of water to remove excess methanol and other undesired compounds from the sample, which could introduce error in the results as shown in Table 3.2 and 3.3.

Table 3.5 Percent mole conversion in samples using 20 mL and 60 mL wash water, when 6:1 methanol to oil molar ratio, 60°C, 6 wt% catalyst was used (run ID 9) (see Appendix A.8 for details)

Replicate No.	Mole conversion%	
	Using 20 mL wash water	Using 60 mL wash water
1	98.328	98.682
2	98.308	98.482
3	98.432	98.455

Table 3.6 Percent mole conversion in samples using 20 mL and 60 mL wash water, when 9:1 methanol to oil molar ratio, 60°C, 6 wt% catalyst was used in two different runs (see Appendix A.8 for details)

Run	Avg. mole % conversion	Error% at 95% confidence level
X (sample prepared using 20 mL wash water)	97.27	0.313
Y(sample prepared using 60 mL wash water)	98.52	0.112

The mixture was then allowed to settle (2 hrs). Then a 2.5 mL of sample from the upper biodiesel phase were taken out and dried with anhydrous Na_2SO_4. One mL of this sample was stored at - 18 °C before analysis. This sample was referred to as "Washed Sample". The rest of the reaction mixture in the reactor was poured into a separatory flask and the flask was then capped. After 14 hrs of settling a 2.5 mL sample of the upper phase (biodiesel) was taken out for analysis. The sample collected from the upper phase

(biodiesel) was called "Unwashed sample". The analysis of the latter is important to understand the presence of soap in the actual biodiesel to assess its quality and the degree of washing needed to purify it. An additional 10 mL of the unwashed sample was taken (during effect of catalyst amount experiments – part A) and washed with twice its volume of deionized water. After settling for 2 hrs, this sample was dried with anhydrous Na_2SO_4 and the dried sample was called "Washed sample after extended time (14 hours settling time)". This sample was analyzed to check the change in conversion of jatropha oil into biodiesel after settling.

In the case of experiments where samples were withdrawn from time to time, 1.5 mL reactor content was withdrawn for each test and 9 mL of deionized water were used to stop the reaction and to wash out glycerol, methanol, catalyst and soap. The mixture was then allowed to settle (2 hrs). Next a 500 μL sample from the upper biodiesel phase was taken out and dried with anhydrous Na_2SO_4. Around of 300 μL this sample was stored at - 18 °C before analysis.

For GC-MS analysis, a 100 μL sample was silylated with 100 μL MSTFA (N-Methyl- N- Trimethylsilyl Trifluroacetamide). After 15 min at room temperature, the silylated mixture was diluted with 8 mL n-heptane and 1 μL of this mixture was injected into the GC-MS.

3.7 Statistical analysis

The average of the percent mole conversions for the three repetitive reaction experiments has been counted as the percent mole conversion of the reaction. The errors were calculated on the basis of the 95% confidence level. At the 95% confidence level a *t*-significance test was performed for important data sets.

Chapter 4

RESULTS AND DISCUSSIONS

The results were obtained after performing the experiments in the following way:

Table 4.1 Experiment format

Experiment name	Catalyst amount (wt% of oil)	Methanol to oil molar ratio	Reaction temperature	Reaction time (hr)	Stirring speed (rpm)
Effect of catalyst amount (wt% of oil)	Variable	6:1	60°C	10	600
Effect of methanol to oil molar ratio	6	Variable	60°C	10	600
Effect of reaction temperature	6	6:1	Variable	10	600

Part A – Effect of the catalyst amount

4.1 Effect of catalyst amount

The results of the experiments indicated that 6 percent potassium carbonate (wt% of jatropha oil) gave the highest mole conversion (98.214%), when 100 g of jatropha oil was reacted with methanol at a 1:6 molar ratio at a temperature of 60°C with stirring at 600 rpm for 10 hours. Table 4.2 presents the experimental data. The percent mole conversion increased with the amount of catalyst up to 6 wt% and then decreased after that amount. Therefore, it is considered that the optimum amount of catalyst for biodiesel production from *Jatropha curcas* oil at the reaction conditions stated above is 6% of the weight of the oil.

Table 4.2 Effect of catalyst amount on percent mole conversion of the reaction (washed sample) (details in Appendix B.1)

Run ID no.	Catalyst amount (wt% of jatropha oil)	Washed sample	
		Average % mole conversion of the raw oil	Error% at 95% confidence level
1	1	2.51	1.63
2	2	92.79	0.37
3	3	94.95	1.08
4	4	96.84	0.28
5	5	97.85	0.64
6	6	98.21	0.12
7	7	97.48	0.39

The change in percent mole conversion was further checked by determining the conversion for the unwashed sample. It was found that the difference in percent mole conversion between washed and unwashed samples increased with an increase in the catalyst wt% (Table 4.3 and Appendix B.1). The amount of soap was estimated in the unwashed sample by measuring the area of the peak in the wave number range 1597 – 1544 cm^{-1}. The results showed that the amount of soap formed was almost the same for 2-3 wt% catalyst but increased from 3% catalyst (wt% of jatropha oil) (Fig. 4.1). Figure 4.1 shows further that the amount of soap was almost the same again for 5 – 6 wt % catalyst. The amount of soap increased dramatically when 7 wt% catalyst was used. This was an indication of saponification of triglycerides as a secondary reaction with respect to transesterification. Previous studies showed that excess alkali catalyst caused the saponification of triglycerides resulting in the formation of soap and in an increase of the viscosity for the reactants. It caused lower ester formation (Dorado et al., 2004; Rashid and Anwar, 2008). Thus secondary saponification might be responsible for significantly

lower conversion of jatropha oil to biodiesel (FAME) when 7 wt% potassium carbonate catalysts were used instead of 6 wt% (see Table B.1.1 and B.1.2).

Table 4.3 Effect of catalyst amount on percent mole conversion of the reaction (unwashed sample) (details in Appendix B.1)

Run ID no.	Catalyst amount (wt% of jatropha oil)	Unwashed sample	
		Average % mole conversion of the raw oil	Error% at 95% confidence level
1	1	-	-
2	2	91.34	1.57
3	3	94.75	0.57
4	4	92.50	1.79
5	5	90.08	2.85
6	6	89.29	1.18
7	7	65.87	5.80

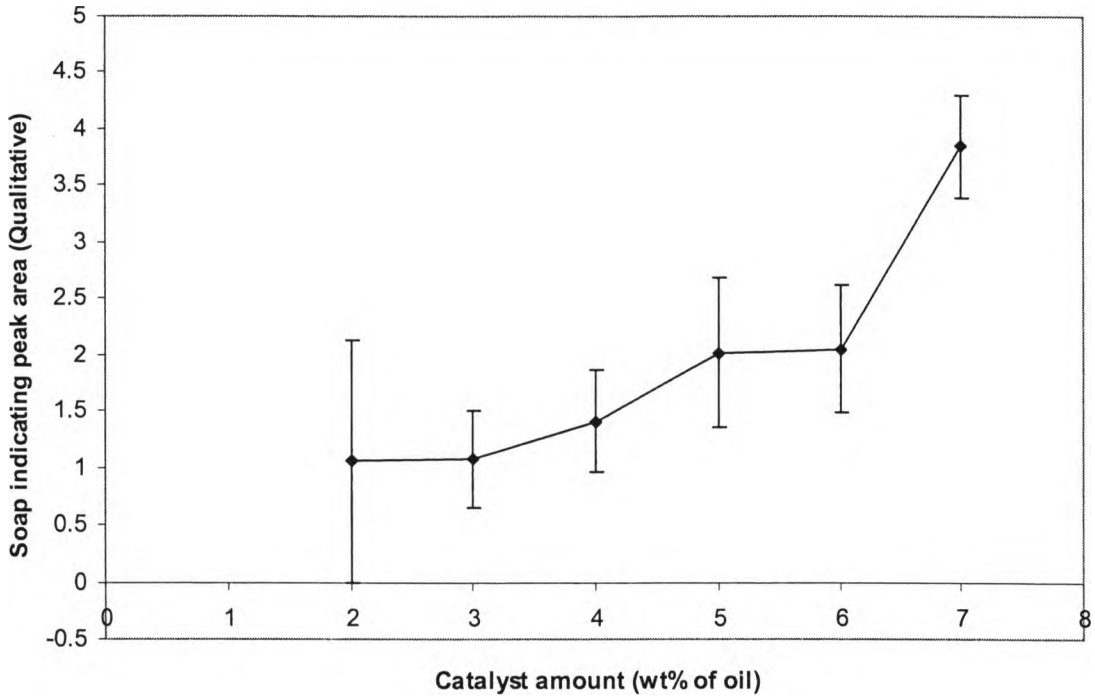


Fig. 4.1 Qualitative amount of soap in the biodiesel phase (detected by FTIR - ATR) versus % catalyst (wt% of jatropha oil) using oil to methanol molar ratio 1:6 for 10 hours at 60°C, stirring at 600 rpm (unwashed sample)

When 1 wt% catalyst was used, the reaction intermediate formed was highly unstable in the presence of air and it was difficult to get repeatable results using FTIR-ATR. This was an indication that 1 wt% catalyst was not enough to catalyze the reaction to produce FAME.

The decrease in percent mole conversion for the unwashed sample was not due to any FAME (biodiesel) degradation (see section 3.5 for definitions of washed and unwashed samples). This was confirmed by checking the percent molar conversion of the washed sample after an extended time (14 hours settling time of the reactor contents). For 2 and 7 wt% catalyst, the percent molar conversion of the washed sample (before

settling) and of the washed sample after extended time (14 hours settling time of the reactor contents) was almost the same (Tables 4.1, 4.3 and Appendix B.1.6).

The decrease in percent molar conversion at high catalyst amount was due to the reduction in the molar concentration of FAME in the biodiesel phase which resulted probably from the increased solubility of soap and other components into the biodiesel phase. The qualitative soap presence (Fig. 4.1) also agreed with this conclusion. These results confirmed that the saponification reaction occurred during the transesterifcation reaction and that there were no side reactions during the settling of the biodiesel.

Table 4.4 Effect of catalyst amount on percent mole conversion of the reaction (washed sample after extended time: 14 hours of settling) (details in Appendix B.1)

Run ID no.	Catalyst amount (wt% of jatropha oil)	Washed sample after extended time (14 hours of settling)	
		Average % mole conversion of the raw oil	Error% at 95% confidence level
2	2	93.12	0.78
7	7	97.60	0.15

A previous study on the solubility of anhydrous potassium carbonate in methanol showed that potassium carbonate and methanol undergo a reversible reaction in the following way (Platonov et al., 2002):

$$CH_3OH + K_2CO_3 \rightleftharpoons CH_3OK + KHCO_3 \qquad (A)$$

That study showed that more than 99% of the total quantity of $KHCO_3$ generated according to the above reaction remained in the solid phase along with potassium carbonate at room temperature (25°C). The phase distribution of $KHCO_3$ between solid and liquid phase promoted the shifting of the equilibrium of the reaction towards product

formation according to Le Chatellier's principle. Increasing the temperature caused more $KHCO_3$ to dissolve into the liquid phase from the solid phase. This increased the rate of the reverse reaction. As a result the concentration of CH_3OK decreased and at the same time the concentration of K_2CO_3 increased (Platonov et al., 2002). However, $KHCO_3$ was found to be a poor catalyst with negligible catalytic activity when compared to that of K_2CO_3 (Arzamendi et al., 2008). This indicates that CH_3OK formed from the reaction between K_2CO_3 and CH_3OH is the main catalyst compound. Thus the result of the transesterification reaction is largely dependent on the CH_3OK concentration hence on the reaction (A).

Part B –Effect of reaction parameters other than catalyst amount

Before starting this part, the optimum catalyst amount was checked and verified.

Table 4.5 Experimental data: washed sample for runs 8, 9 and 10 (see appendix B.2 for details)

Run ID no.	Catalyst amount (wt% of jatropha oil)	Washed sample	
		Average % mole conversion of the raw oil	Error% at 95% confidence level
8	5	97.43	0.45
9	6	98.54	0.31
10	7	97.55	0.08

Table 4.6 Experimental data: unwashed sample for runs 8, 9 and 10 (see appendix B.2 for details)

Run ID no.	Catalyst amount (wt% of jatropha oil)	Unwashed sample	
		Average % mole conversion of the raw oil	Error% at 95% confidence level
8	5	83.51	2.15
9	6	80.22	3.11
10	7	61.82	3.74

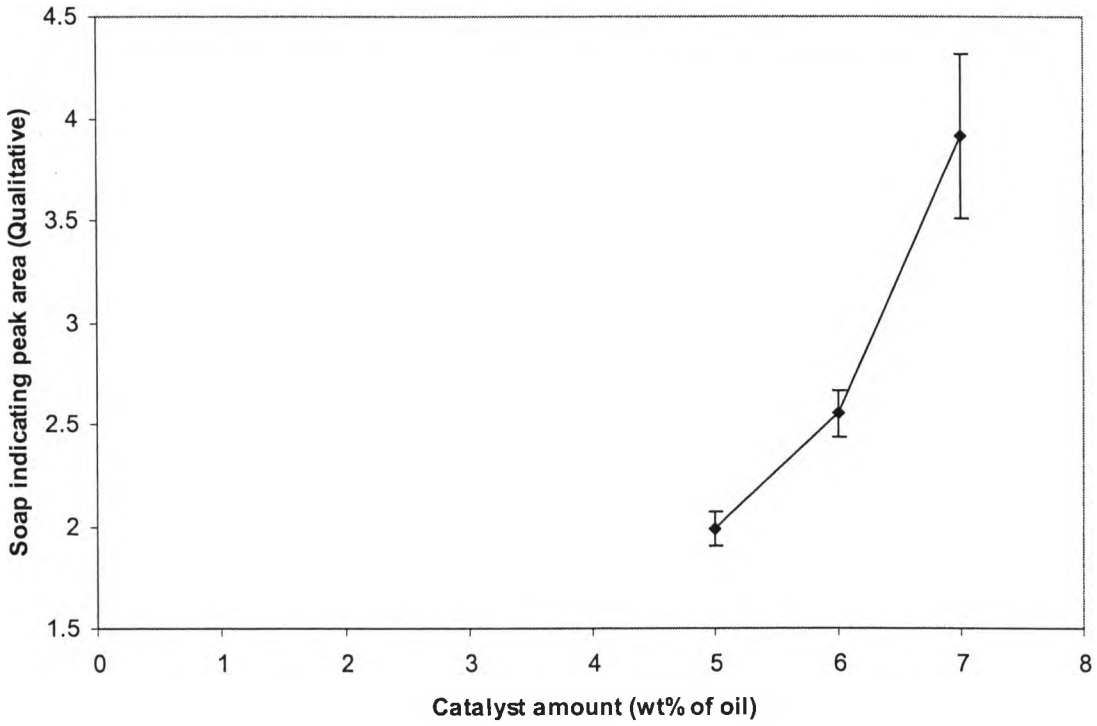


Fig. 4.2 Qualitative amount of soap in the biodiesel phase (detected by FTIR) versus % catalyst (wt% of jatropha oil) using oil to methanol molar ratio 1:6 for 10 hours at 60°C, stirring at 600 rpm (unwashed sample)

4.2 Effect of methanol to oil molar ratio

The results of the experiments indicated that 10:1 methanol to oil molar ratio gave the highest conversion (98.79%), when 100 g of jatropha oil was reacted with methanol at a temperature of 60°C with stirring at 600 rpm for 10 hours in the presence of 6 g potassium carbonate as a catalyst. Table 4.6 presents the experimental data. The percent mole conversion increased with the methanol to oil molar ratio from 4:1 to 6:1, then decreased for 7:1 and then started increasing again from 8:1 to 10:1. Beyond this methanol to oil molar ratio, change in percent mole conversion was not significant (see Table B.3.7).

Table 4.7 Effect of methanol to oil molar ratio on percent mole conversion of the reaction (washed sample) (details in Appendix B.3)

Run ID no.	Methanol to oil molar ratio	Washed sample	
		Average % mole conversion of the raw oil	Error% at 95% confidence level
11	4:1	98.13	0.07
12	5:1	98.51	0.19
9	6:1	98.54	0.31
13	7:1	97.65	0.39
14	8:1	98.18	0.07
15	9:1	98.52	0.11
16	10:1	98.79	0.13
17	11:1	98.77	0.03

The change in percent mole conversion was further checked by determining the conversion for the unwashed sample. It was found that the percent mole conversion started to decrease with the increase in methanol to oil molar ratio from 4:1 to 6:1, then increased for 7:1 and again started to decrease from molar ratio 8:1 and continued to

decrease (Table 4.7). Previously it was found that the decrease in percent mole conversion in the unwashed sample was due to the reduction in the molar concentration of FAME in the biodiesel phase, which resulted probably from the increased solubility of soap and other components into the biodiesel phase. The qualitative soap presence (Fig. 4.3) also agreed with this conclusion.

Table 4.8 Effect of methanol to oil molar ratio on percent mole conversion of the reaction (unwashed sample) (details in Appendix B.3)

Run ID no.	Methanol to oil molar ratio	Unwashed sample	
		Average % mole conversion of the raw oil	Error% at 95% confidence level
11	4:1	89.17	1.22
12	5:1	76.81	0.78
9	6:1	80.22	3.11
13	7:1	82.87	1.65
14	8:1	81.99	1.31
15	9:1	80.98	2.44
16	10:1	76.83	7.54
17	11:1	76.37	2.31

The reaction rate was fast when 7:1 methanol to oil molar ratio was used compared to that of 6:1 (Table 4.8). This reaction rate was almost the same at first, when 8:1 methanol to oil molar ratio was used (Table 4.8). But this reaction rate decreased and became the lowest compared to that of 6:1 and 8:1 starting after 10 mins (Table 4.8). This indicates that after 10 minutes the reaction (A) proceeded to the backward direction and as a result the concentration of the catalytically active CH_3OK decreased. Thus both the transesterification reaction conversion and the by-product soap formation were minimum compared to those of 6:1 and 8:1 methanol to oil molar ratio (Table 4.6, Table 4.7 and

Fig. 4.3). It was found in previous study that the excess molar ratio favored conversion of di- to monoglycerides but there were also recombination of esters and glycerol to monoglycerides because their concentration keeps increasing during the course of the reaction (Fillieres et al., 1995).

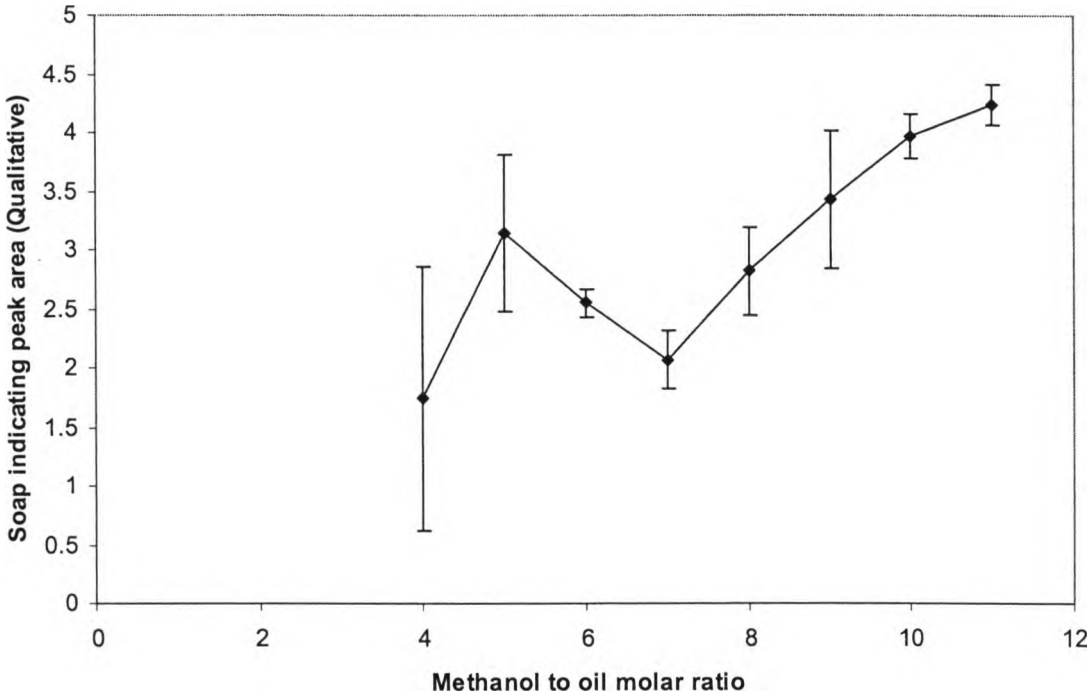


Fig. 4.3 Qualitative amount of soap in the biodiesel phase (detected by FTIR - ATR) versus methanol to oil molar ratio using 6 g catalyst for 10 hours at 60°C, stirring at 600 rpm (unwashed sample)

The fast transesterification reaction produces fast formation of monoglycerides and glycerol in the reaction as found in a previous study (Fillieres, et. al., 1995). In other previous studies it was observed that when glycerol remained in the reaction solution, it inhibits the forward direction of the transesterification reaction. (Krisnamgkura and Simamaharnnop, 1992; Meher et al., 2006a). These facts and the concentration of the methanol might be responsible for the backward direction of the reaction (A). When 8:1 methanol to oil molar ratio was used, probably the concentration of CH_3OK was higher

than the one for 7:1 methanol to oil molar ratio. As a result the reaction rate was faster than the one for 7:1 methanol to oil molar ratio and percent mole conversion increased and also did the soap formation.

Table 4.9 Reaction rate (mole/sec) using different methanol to oil molar ratios, keeping other parameters constant (60°C, 6g K_2CO_3, 600 rpm) (details in Appendix B.4)

Time (min)	Methanol to oil molar ratio		
	6:1 (run x)	7:1 (run y)	8:1 (run z)
1	0.071678	0.100502	0.103807
5	0.113256	0.111968	0.111005
10	0.003906	0.00071	0.00088
15	0.001567	1.7E-05	3.12E-05
30	2.52E-05	2.48E-06	6.68E-06
45	1.35E-05	1.18E-06	1.43E-06

4.3 Effect of reaction temperature

From the experiments it was observed that the percent molar conversion for the washed sample increased with an increase in the reaction temperature to 65°C, whereas the soap formation was higher at 65°C compared to the ones at 55°C and 60°C (Tables 4.9, 4.10 and Figure 4.4). It was reported previously (sec. 4.1) that the lower conversion in the unwashed sample was due to the presence of the soap, glycerol, methanol and catalyst in the biodiesel phase. This indicates that an increase in the reaction temperature tends to enhance the solubility of soap, glycerol, methanol and catalyst into the biodiesel phase.

Table 4.10 Effect of reaction temperature on percent mole conversion of the reaction (washed sample) (details in Appendix B.5)

Run ID no.	Reaction temperature °C	Washed sample	
		Average % mole conversion of the raw oil	Error% at 95% confidence level
18	55	98.15	0.48
9	60	98.54	0.31
19	65	98.77	0.03

Table 4.11 Effect of reaction temperature on mole percent mole conversion of the reaction (unwashed sample) (details in Appendix B.5)

Run ID no.	Reaction temperature °C	Unwashed sample	
		Average % mole conversion of the raw oil	Error% at 95% confidence level
18	55	78.99	3.26
9	60	80.22	3.1
19	65	76.39	2.74

Experiments at higher reaction temperature were avoided due to safety concerns with the experimental set up. Previous studies have also shown that higher reaction temperature enhances saponification of triglycerides by base catalysts before the completion of the transesterification reaction (Rashid and Anwar, 2008; Meher et al., 2006b).

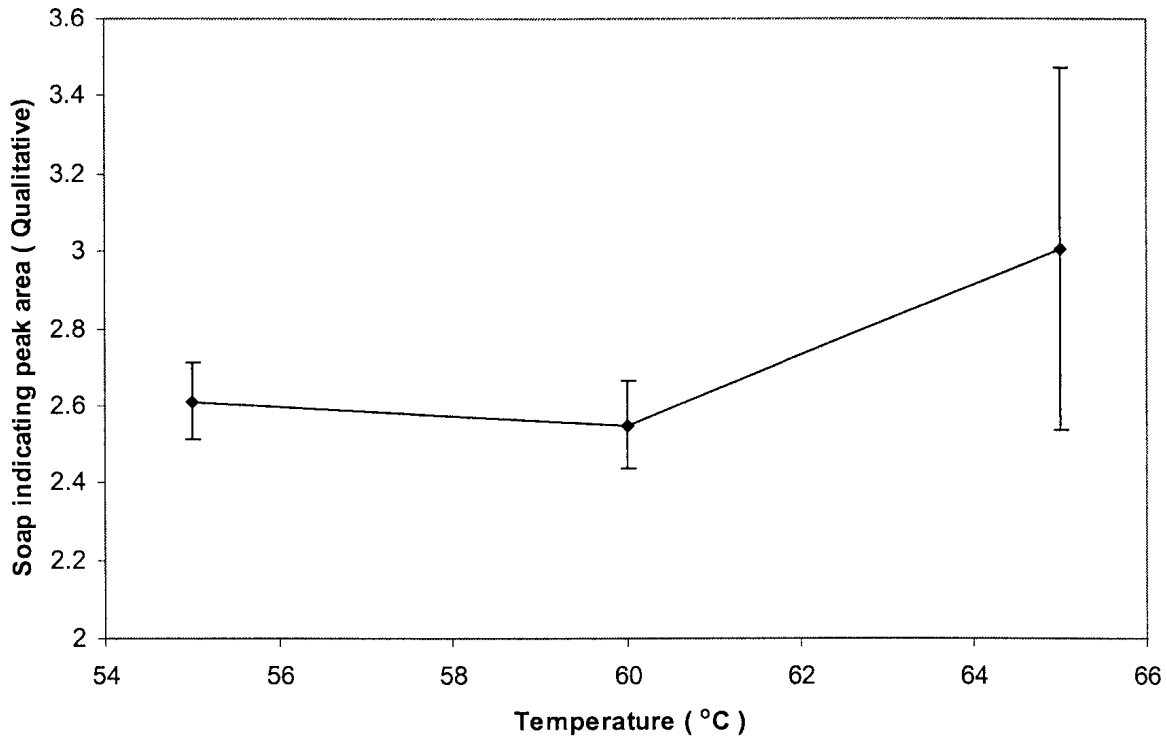


Fig. 4.4 Qualitative amount of soap in the biodiesel phase (detected by FTIR-ATR) versus reaction temperature using 6 wt% catalyst, 6:1 methanol to oil molar ratio for 10 hours, stirring at 600 rpm (unwashed sample)

4.4 Effect of different parameter combinations

Previously 6 wt% potassium carbonate was found to be the optimum amount of catalyst, when 6:1 methanol to oil molar ratio was used in the reaction at 60°C and stirring at 600 rpm. Thus keeping this 6 g of catalyst as a constant, a number of reaction parameters were investigated experimentally to identify optimum conditions in a preliminary way for the conversion of jatropha oil to biodiesel. The results are shown in the Table 4.12.

Table 4.12 Results for different parameter combinations

Combination	Catalyst amount (wt% of jatropha) oil	Temp °C	Methanol to oil molar ratio	Stirrer speed rpm	Avg. % mole conversion	
					Washed sample	Unwashed sample
A	6	60	6:1	600	98.54	80.22
B	6	65	6:1	600	98.77	76.39
C	6	60	10:1	600	98.79	76.83
D	6	65	10:1	600	98.19	68.02

Table 4.12 shows that parameter combination D gave lower conversion. It enhanced the undesired saponification reaction and increased the solubility of soap, glycerol, methanol and catalysts into the biodiesel phase. Therefore, this parameter combination was unacceptable.

It is clear from Table 4.12 that the most desired reaction parameter combinations would be either B - 6:1 methanol to oil molar ratio, 6 wt% catalyst, 65°C and 600 rpm or C - 10:1 methanol to oil molar ratio, 6 wt% catalyst, 60°C and 600 rpm because of higher conversion. The soap production from reaction parameter combination C was higher than the one for parameter combination B (Tables B.3.8 and B.5.5) and for the unwashed samples percent mole conversions were more consistent in parameter combination B (see Tables 4.7 and 4.10). Moreover, it was found, due to the presence of extra methanol in combination C, that a longer time was required for the subsequent stage of the separation of the biodiesel phase from the glycerol phase. This was due to the fact that methanol, with one polar hydroxyl group, can function as an emulsifier (Rashid and Anwar, 2008; Enciner et. al., 2005). Thus combination C may increase the separation cost and the purification cost of the biodiesel. In the case of parameter combination B, an easy and

rapid phase separation was observed. Therefore, parameter combination B was chosen as the optimum parameter combination for biodiesel production from jatropha oil.

4.5 Quality of the Biodiesel

The acid number of the produced biodiesel using optimized reaction parameters combination B was 0.54 mg KOH/g, whereas ASTM specified acid number should be 50 mg KOH/g.The viscosity at room temperature (25°C) was 5.97 cP. The composition (wt%) of the biodiesel was: Palmitic acid methyl ester 16.6825%, Oleic acid methyl ester 51.81%, Stearic acid methyl ester 6.4%, Erucic acid methyl ester 14.00%, other fatty acid methyl esters 3.9%, free glycerol 0.034%, monoglyceride 0.0762%, other organic compounds 7.09% (see Appendix B.7). This fatty acid methyl ester composition was used to predict the cetane number of the produced biodiesel using different correlations (Bamgboye and Hansen, 2008; Gerpen, 1996) as the conditions of these correlations were similar to the one here. The predicted cetane numbers using different correlations were 50.4, 50.61 and 53.19 (see Appendix B.8), which were very close. The total glycerin (free glycerin + monoglycerides) found in the biodiesel composition was also in the tolerable limit (0.24 wt% max).

In the oil composition, analyzed by our own lab GC-MS, Linoleic acid was absent. The reason was that the GC spectra failed to separate the two peaks of Oleic acid and Linoleic acid. They showed as a single peak. Also, the molecular weight difference (282.46 for Oleic acid and 280.45 for Linoleic acid) is very negligible. In the MS, the compound detecting and reporting software works on the probable structure based on the

peak, it thus failed to identify Linoleic acid (see Appendix B.9). Therefore in Table 3.3 the Oleic acid 58.25 wt% is actually (Oleic acid + Linoleic acid) wt%.

Other fatty acid compositions were also higher in Table 3.3 compared to the ones of Tables 3.1 and 3.2. The reason is that as the oil was unrefined, there were impurities in the oil, which settled with time. This is evident by analyzing the residual oil of an almost empty jatropha oil feedstock container (see Appendix B.10). The composition shows that the oil contained 33.1 wt% straight heavy chain hydrocarbon compounds. These compounds usually present in the plant as wax. Their presence in the oil reduced the (Linoleic + Oleic) acid composition to 41.33%.

The percent mole conversion difference between run ID no. 6 and run ID no. 9 was mainly due to using different amount of wash water for sample preparation. The conversion in run ID 9 was significantly different from the one of run ID 6 when the same amount of wash water (20 mL) was used (see Table 4.13 and Appendix B.11).

Table 4.13 Percent mole conversion obtained in run 9 from samples prepared using 20 mL wash water

Run No.	Average % mole conversion of the raw oil	Error% at 95% confidence level
6	98.21	0.125
9	98.36	0.166

The settling of the oil as mentioned above might contribute to this difference in percent mole conversion when 20 mL wash water was used for run ID 6 and run ID 9.

The overall material loss for parameter combination D (extreme parameter combination) was calculated and the loss was 0.293±0.065 wt% (see Appendix B.12). This indicates that the material loss was negligible and that the results from the experimental set up were reliable.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

Jatropha curcas oil can be an alternative feedstock for biodiesel production and can reduce the demand on food crops for renewable fuel production. The present research is a preliminary feasibility study using unsupported potassium carbonate as a catalyst to produce biodiesel from *Jatropha curcas* oil. Based on the study the following is concluded:

- A 6 wt% potassium carbonate (wt% of the oil) was the optimum catalyst amount when 6:1 methanol to oil molar ratio was used at a temperature of 60°C for 10 hours reaction time.
- With excess settling time, the presence of catalyst had no effect on either degradation or conversion of FAME (Biodiesel).
- A 7:1 methanol to oil molar ratio was the critical methanol to oil molar ratio. Below and beyond this molar ratio the percent mole conversion to FAME and soap formation were higher, when 6 wt% catalyst was used at 60°C for 10 hours reaction time.
- A 10:1 methanol to oil molar ratio gave the highest percent molar conversion when 6 wt% catalyst was used at 60°C for 10 hours reaction time.
- A 6 wt% potassium carbonate (wt% of the oil), 6:1 methanol to oil molar ratio, 65°C were selected to be the best optimum reaction parameters combination at 1 atm, stirring at 600 rpm.

- Using the selected best parameter combination mentioned above, the predicted cetane numbers (CN) of the biodiesel were 50.4, 50.61 and 53.19 depending on the literature correlations used.

Potassium carbonate is considered to be environment friendly, because after the catalyst is spent, the waste stream by-product can be used as a fertilizer. As well, this potassium carbonate can be extracted from the biomass plants. Thus the impact of using potassium carbonate on the environment is very low.

5.2 Recommendations

The present study identified some important areas that should be further studied in depth. Thus the following recommendations are made:

- The reaction time of 10 hours was chosen to allow sufficient reaction time to gain higher conversion. This was only for research purposes. However, research on the reaction using the best parameter combination should be conducted to obtain a shorter time as required for commercial operation.
- In this study taking out many samples from the reactor for analysis was not feasible due to the small volume of the reactor contents. Hence it is recommended that the study be conducted in a larger reactor in order to allow many samples to be taken from the reactor for the study of catalysis and reaction kinetics.

- The reaction and solubility behavior of potassium carbonate in methanol is not well known. Especially in the presence of the glycerol the effect of potassium carbonate on solubility and the reaction with methanol is unknown. Thus, there is a necessity to research the model study of the reaction and the solubility of potassium carbonate in methanol in the absence and presence of glycerol. Such study might identify the best catalytic activity of potassium carbonate with minimal loss of catalyst.
- When 7:1 methanol to oil molar ratio was used using 6 wt% potassium carbonate (based on the oil) at 60°C reaction temperature, the catalytic activity decreased and hence lower conversion was obtained. The exact reason for this reduced catalytic activity is unknown. Thus an in-depth study is required.
- The jatropha oil was preheated to the desired temperature before starting the reaction in the presence of potassium carbonate. This might involve the risk of saponification and loss of some oil as soap. One should find a better way to introduce potassium carbonate into the reactor just before starting the stirring.
- The study was conducted at atmospheric pressure. High pressure reaction might lower the catalyst amount requirements, the reaction temperature and the methanol to oil molar ratio. This might reduce the loss of oil by saponification. Thus it is recommended to conduct the study at a higher pressure.
- The biodiesel phase separation from glycerol is an important part of biodiesel production. Thus one should study such separation to minimize the phase separation time. It is also very important to obtain a biodiesel phase without entrained glycerol droplets.

- Potassium carbonate can be obtained from the ash of biomass. Thus it is recommended that a study be conducted on the efficient extraction of potassium carbonate from biomass.

BIBLIOGRAPHY

Achten, W.; Muys, B.; Mathijis, E.; Verchot, L. Biodiesel production from *Jatropha* in developing countries: Life cycle and relevant impact categories. Division Forest, Nature and Landscape Research. Belgium.

Ackom, E. K.; Ertel, J., 2005. An alternative energy approach to combating desertification and promotion of sustainable development in drought regions. Forum der Forschung, 18, 74 -78.

Aderibigbe, A.O.; Johnson, C.O.L.O; Makkar, H.P.S.; Becker, K.; Foidl, N., 1997. Chemical composition and effect of heat on organic matter – and nitrogen – degradability and some antinutrional components of jatropha oil. Animal Feed Science Technology, 67, 223 – 243.

Al-Zuhair, S., 2006. The effect of substrate concentrations on the production of biodiesel by lipase-catalyzed transesterification of vegetable oils. Journal of Chemical Technology and Biotechnology, 81, 299 – 305.

AOCS official method Cd 3d – 63. Official methods and Recommended practices of the AOCS. Fifth edition. 1998.

Arzamendi, G.; Arguinarena, E.; Campo, I.; Zabala, S.; Gandia, L.M., 2008. Alkaline and alkaline- earth metals compounds as catalysts for the methanolysis of sunflower oil. Catalysis Today, 305 -313.

Ataya, F.; Dube, M. A.; Ternan, M., 2007. Acid-catalyzed transesterification of canola oil to biodiesel under single and two phase reactions. Energy & Fuels, 21, 2450 – 2459.

Augustus, G.D.P.S.; Jayabalan, M.; Seiler, G.J., 2002. Evaluation and bioinduction of energy components of Jatropha curcas. Biomass and Bioenergy, 23, 161 – 164.

Azam, M. M.; Waris, A.; Nahar, N.M., 2005. Prospects and potential of fatty acid methyl esters of some non-traditional seeds oils for use as biodiesel in India. Biomass and Bioenergy, 29, 293 – 302.

Bamgboye, A.I.; Hansen, A.C., 2008. Prediction of cetane number of biodiesel fuel from the fatty acid methyl easter (FAME) composition. International Agro physics., 22, 21 – 29.

Baroi,C.; Yanful, E.K.; Rahman, F.; Bergougnou, M.A., 2007. Environment friendly bio-diesel from *Jatropha Curcas*: Possibilities and challenges. E 1.4. First International Conference on Environmental Research, Technology and Policy (ERTEP), July 17 – 19, Accra, Ghana-Africa.

Becker, K.; Makkar, H.P.S., 2008. Jatropha curcas: A potential source for tomorrow's oil and biodiesel. Lipid Technology, 20 (5), 104 -107.

Belafi-Bako, K.; Kovacs, F.; Gubicza, L.; Hancsok, J., 2002. Enzymatic biodiesel production from sunflower oil by *Candida antartica* Lipase in a Solvent – free System. Biocatalysis and Biotransformation, 20 (6), 437 – 439.

Biofuel Blend ratio and Total Glyceride Measurements. Application note. The Infraspec VFA-IR Spectrometer. Wilks Enterprise,Inc. http://www.wilksir.com/pdf/App-note_Biofuel-InfraSpec.pdf. Visited 02.10.2008 at 20.31 hours.

Bondioli, P., 2004. The preparation of fatty acid esters by means of catalytic reactions. Topics in catalysis, 27, 77 - 82.

Boocock, D. G. B.; Konar, S.K.; Mao, V.; Sidi, H., 1996. Fast one-phase oil-rich processes for the preparation of vegetable oil methyl esters. Biomass and Bioenergy, 11(1), 43 – 50.

Capital, G.W., 2008. Biofuels – Economic Aspects. Chem. Eng. Technol, 31 (5), 715 – 720.

D'Cruz, A.; Kulkarni, M. G.; Meher, L. C.; Dalai, A.K., 2007. Synthesis of biodiesel from canola oil using heterogeneous base catalyst. Journal of American Oil chemist's Society, 84, 937 – 943.

Demirbas, A., 2002. Biodiesel from vegetable oils via transesterification in supercritical methanol. Energy Conversion and Management, 43, 2349 – 2356.

Demirbas, A., 2007. Recent developments in biodiesel fuels. International Journal of Green Energy, 4, 15 – 26.

Di Serio, M.; Cozzolino, M.; Glordano, M.; Tesser, R.; Patrono, P.; Santacesaria,E., 2007. From Homogeneous to Heterogeneous Catalysts in Biodiesel Production. *Ind. Eng. Chem. Res.*, 46, 6379 – 6384.

Di Serio, M.; Tesser, R.; Pengmi, L.; Santacesaria, E., 2008. Heterogeneous catalysts for biodiesel production. Energy and Fuels, 22(1), 207 – 217.

Dorado, M.P.; Ballesteros, E.; Lopez, F.J.; Mittelbach, M., 2004. Optimization of Alkali-Catalyzed Transesterification of *Brassica Carinata* Oil for Biodiesel Production. Energy and Fuels, 18, 77 – 83.

Dunn, R.O., 2005. Chapter 10: Other Alternative Diesel Fuels from vegetable oils. Biodiesel Handbook. AOCS Press.

Eckey, E. W.; Miller, L. P., 1954. Vegetable fats and oils. Reinhold Publishing Corporation. New York, P. 1 – 40, 173 – 178.

Enciner, J.M.; Gonzalez, J.F.; Rodriguez-Reinares, A., 2005. Biodiesel production from Used Frying Oil. Variables Affecting the Yields and Characteristics of the Biodiesel. Industrial and Engineering Chemistry Research, 44 (15), 5491- 5499.

Fillieres, R.; Benjelloun-Mlayeh, B.; Delmas, M., 1995. Ethanolysis of rapeseed oil: quantitation of ethyl esters, mono-, di-, and triglycerides and glycerol by high-performance size-exclusion chromatography, *J.Am. Oil Chem. Soc.*, 72, 427.

Forson, F.K.; Oduro, E.K.; Donkoh, E.H., 2004. Performance of Jatropha oil blends in a diesel engine. Renewable Energy, 29, 1135-1145.

Gerpen, J.V., 1996. Cetane number testing of biodiesel. Liquid Fuel and Industrial Products from Renewable resources. Proceedings of the liquid Fuel conference, 3rd Nashville, sept 15 -17, 197 – 206.

Gerpen, J.V.; Knothe, G., 2005. Chapter 4: Biodiesel production. Biodiesel Handbook, AOCS Press.

Graille, J.; Lozano, P.; Pioch, D.; Geneste, P., 1985. Alcoholysis tests of vegetable oils with natural catalyzers for the production of diesel fuels. Oleagineux, 50(5), 271 – 276.

Grallie, J., 1986. Vegetable oil alcoholysis pilot trials using natural catalysis to produce diesel fuels. Oleagineux, 41(10), 457 – 464.

Gressel, J., 2008. Transgenics are imperative for biodiesel crops. Plant Science, 174, 246–63.

Gunstone, F. D., 1958. An Introduction to the chemistry of fats and fatty acids. John Willey & Sons Inc, New York, P. 38 – 39.

Hartman, L., 1956. Methanolysis of triglycerides. Journal of the American Oil Chemist's Society, 33, 129.

Henning, R., 2000. The Jatropha Booklet-A guide to the Jatropha System and its dissimination. GTZ-ASIP-Support-Project Southern Province, Choma.

Hoffmann, G., 1989. The chemistry and technology of edible oils and fats and their higher fat products. Academic Press, London.

http://biodiesel.org/pdf_files/fuelfactsheets/BDSpec.PDF visited 22.02 hours, 13 January, 2008.

Ji, J.; Wang, J.; Li, Y.; Yu, Y.; Xu, Z., 2006. Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation. Ultrasonics, 44, 411 – 414.

Krisnamgkura, K.; Simamaharnnop, R., 1992. Continuous transmethylation of palm oil in an organic solvent. *J. Am. Oil Chem. Soc.*, 69, 166.

Kumar, A.; Sharma, S., 2008. An evaluation of multipurpose oil seed crop for industrial uses (*Jatropha curcas* L.): A review. Industrial crops and products, 28, 1 – 10.

Lee, I.; Johnson, L.A.; Hammond, E.G., 1995. Use of branched-chain esters to reduce the crystallization temperature of biodiesel. Journal of American Oil Chemist's Society, 72 (10), 1155 – 1160.

Lin-Vien, D.; Colthup, N.B.; Fateley, W.G.; Grasselil, J.G., 1991. The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules. Academic Press, Inc., 1991.United Kingdom P. 141.

Loreto, E.; Liu, Y.; Lopez, D.E.; Suwannakarn, K.; Bruce, D.A.; Goodwin, J.G., 2005. Synthesis of biodiesel via acid catalysis. Ind. Eng. Chem. Res., 44 (14), 5353 – 5363.

Markley, K. S., 1947. Fatty Acids. Interscience Publishers, Inc. New York. P. 451 – 455.

Meher, L.C.; Sagar, D. Vidya; Naik, S.N., 2006a. Technical aspects of biodiesel production by transesterification- a review. Renewable and Sustainable Energy Reviews, 10, 248-268.

Meher, L.C.; Dharmagadda, V.S.S.; Naik, S.N., 2006b. Optimization of alkali-catalyzed transesterification of *Pongamia pinnata* oil for production of biodiesel. Bioresource Technology, 97(12), 1392 – 1397.

Modi, M.K.; Reddy, J.R.C.; Rao, B.V.S.K.; Prasad, R.B.N., 2006. Lipase-mediated transformation of vegetable oils into biodiesel using propan-2-ol as acyl acceptor. Biotechnology Letters, 28, 637 – 640.

Oku, T.; Nonoguchi, M.; Moriguchi, T., 2007. Method of production of fatty acid alkyl esters and/or glycerine and fatty acid alkyl ester – containing composition. US Patent 2007/0167642. Date issued: Jul. 19, 2007.

Openshaw, K., 2000. A review of Jatropha Curcas: an oil plant of unfulfilled promise. Biomass and Bioenergy, 19, 1-15.

Platonov, A. Y.; Evdokimov, A. N.; Kurzin, A. V.; Maiyorova, H. D.; 2002. Solubility of Potassium carbonate and Potassium Hydrocarbonate in Methanol. *J. Chem. Eng. Data.*, 47, 1175 – 1176.

Rashid, Umer; Anwar, Farooq., 2008. Production of Biodiesel through Base-Catalyzed Transesterification of Safflower Oil Using an Optimized Protocol. Energy and Fuels, 22, 1306 – 1312.

Sapienza, R.; Johnson, A.; Ricks, W., 2005. Environmentally benign anti – icing or deicing fluids employing triglyceride processing by-products. US Patent 6890451 B2.Date issued: 10 May, 2005.

Sapienza, R; Johnson, A; Ricks, W., 2006. Environmentally benign anti – icing or deicing fluids. US Patent 7138071 B2. Date issued: 21 Nov, 2006.

Schmidt, M. R., 1913. Work of M. R. Schmidt. The Freezing-point lowering, conductivity, and viscosity of solutions of certain electrolytes in water, methyl alcohol, ethyl alcohol, acetone, and glycerol and in mixtures of these solvents with one another. Published by Carnegie Institute of Washington, Washington. P. 133.

Shah, S.; Sharma, S; Gupta, M.N., 2004. Biodiesel preparation by lipase-catalysed transesterification of Jatropha oil. Energy & Fuels, 18, 154-159.

Shimada, Y.; Watanabe, Y.; Sugihara, A.; Tominaga, Y., 2002. Enzymatic alcoholysis for biodiesel fuel production and application of the reaction to oil processing. Journal of Molecular Catalysis B: Enzymatic, 17, 133 – 142.

Smith, B.C. 1996. Fundamentals of Fourier Transform Infrared Spectroscopy. CRC press Inc. USA, 117-125.

Srivastava, A.; Prasad, R., 2000. Triglycerides-based diesel fuels. Renewable and Sustainable Energy Reviews, 4, 111 – 133.

Staubmann, R.; Ncube, I.; Gubitz, G. M.; Steiner, W.; Read, J. S., 1999. Esterase and lipase activity in *Jatropha curcas* L. seeds. Journal of Biotechnology, 75, 117 - 126.

Tseng, C.; Wang, N., 2007. Fast analysis of fats, oils and Biodiesel by FT-IR. Lipid Technology, 19 (2), 39-40.

Vasudevan, P.T; Briggs, M., 2008. Biodiesel production – current state of the art and challenges. Journal of Industrial Microbilogy and Biotechnolgy, 35 (5), 421 – 430.

Vicente, G.; Martinez, M.; Aracil, J.; Esteban, A., 2005. Kinetics of sunflower oil methanolysis. Ind. Eng. Chem. Res., 44, 5447 - 5454.

Xu, Y.; Du, W.; Liu, D.; Zeng, J., 2003. A novel enzymatic route for biodiesel production from renewable oils in a solvent-free medium. Biotechnology Letters, 25, 1239 – 1241.

APPENDIX A: Supplementary material for chapter 3

A.1 Oil specifications supplied by the vendor, Medors Biotech Pvt. Ltd, India.

MEDORS BIOTECH PVT. LTD.

REPORT No.: MBPL/000321/2007/2008/08/00004

Medors Biotech P Ltd
D-1/3, Rana Pratap Bagh
New Delhi - 110007
Ph 91-11-27843109
Fax 91-11-27462731
E-mail info@medorsbiotech.com

REPORT OF INSPECTION

REF : IN/DEL/JAT/200700004 DATE : 31/08/2007 PAGE : 1 of 2

At the request of Chinmoy Baroi, we have inspected the consignment, as per instructions summarized as below.

- Sampling
- Quantity Verification
- Marking & Packing
- Analysis

Cargo described as	:	Indian Jatropha Oil (Double Filter Quality) 35 Litres (1 New Plastic Industrial Jerry Can x 35 Ltrs each)
Supplier [As declared]	:	Medors Biotech P. Ltd., D-1/3 Rana Pratap Bagh Delhi-110 007, India
Buyer [As declared]		Chinmoy Baroi The University Of Western Ontario Faculty Of Engineering Room No 14, Dock 17 Spencer Engineering Building London, Ontario,Canada, N6A5B9

Place & date of attendance : Medros Biotech P. Ltd, D-1/3 Rana Pratap Bagh, Delhi
On 28th August 2007

Sampling/Sealing

1 New Plastic Industrial Jerry Can x 35 Ltrs were selected and representative samples were drawn and filled in plastic jars. Jars were sealed with our monogram seal no. MBPL-0121 and distributed as under.

- One sealed sample was handed over to supplier
- One sealed sample was analyzed by us,

The record samples will be retained by us for a period of three months from the date of inspection until and unless definite instructions to the contrary are received in the meantime.

All Jerry Can were sealed with plier No. MEPL-AGRI-18

Weighment

Jerry Can check-weighed and the gross weight of Jerry Can found to be 34 Kgs. Tare weight as declared by the supplier 1 kg. Jerry Can, therefore the net would be 32. Jerry Can

915 gram = 1 liter ,therefore the net quantity of the oil in one Jerry Can would be 35 liter.

Packing

Material found filled in New Plastic Industrial Can with mouth closed with plastic cap

Soil to Oil

(R. C. SHARMA)

MEDORS BIOTECH PVT. LTD.

REPORT No.: MBPL/000321/2007/2008/08/00004

REF : IN/DEL/JAT/200700004 DATE : 31/08/2007 PAGE : 2 of 2

Marking (on sticker pasted on Jerry Can)

Jatropha Oil	
Quantity: 35 liter Net Net Weight: 32Kg. Gross Weight 34 Kg. Packed Date 28-07-2007 Double Filter Oil	Manufactured & Marketed By: Medors Biotech P Ltd. Correspondence Add:- Biotech House, D-1/3, Rana Pratap Bagh, New Delhi, India. Postal Code: 110007 Ph: 91-11-43805305 Fax: 91-11-27462731 Web Site: www.jatropohaplantation.com www.medorsbiotech.com E-mail: info@jatrophaplantatin.com info@medorsbiotech.com
	Not for Human Consumption

Analysis :

Sealed sample was analysed by our laboratory and the results are as under :

Parameters	Results	Protocol
Acid Value	2.51 mg KOH/gm	IS 548:PART 1:1996
Free Fatty Acid	1.47% w/w (as oleic acid)	IS 548:PART 1:1964(Reaff.2000)
Iodine Value	110.0	IS 548:PART 1: 1996
Saponification Value	180	IS 548:PART 1: 1996
Viscosity (at 31° C)	70 cps (Rv2 at 20rpm)	By Brookfield Viscometer
Flash Point	152° C	IS:1448: Part21:1992
Fattty Acid Composition		IS 548 (Part 3) / 1990 BY GC MS
Palmitic acid	12.25%	
Stearic acid	3.5%	
Oleic acid	24.32%	
Linoleic acid	24.72%	
Other acids	32.67%	
Density	0.920	At 15° C
Average Molecular Weight	832g	

This Report reflects our findings at the time, date and place of inspection only and does not refer to any other matter.

For MEDORS BIOTECH PRIVATE LIMITED

This report contains 2 (two) pages.

(R. C. SHARMA)

Soil to Oil

A.2 Analysis of the raw oil by Intertek Caleb Brett

Intertek

Report of Analysis

Client: UWO

Lab Report no.: **CA120-0003903**
Report date: November 27, 2007

Submitted on: November 19, 2007
Tested on: November 19 & 27, 2007
Customer Product Description: Feed stock
Sample identification: Jatropha Oil

Attention: Chinmoy Baroi

TESTS	UNITS	METHODS	SPECIFICATIONS	RESULTS
Iodine value	---	ASTM D 1959	---	97.9
FFA (C16 Palmitic Acid)	% mass	AOCS Ce-1c-89	---	14.45
C16-1 Palmitoleic Acid	% mass	AOCS Ce-1c-89	---	0.45
C18 Stearic Acid	% mass	AOCS Ce-1c-89	---	4.69
C18-1Oleic Acid	% mass	AOCS Ce-1c-89	---	26.51
C18-2 Lenoleic Acid	% mass	AOCS Ce-1c-89	---	31.9
FFA (C20 Arachidic Acid)	% mass	AOCS Ce-1c-89	---	0.81
C18-3 Lenolenic Acid	% mass	AOCS Ce-1c-89	---	3.34
C20-1 Eicosenoic Acid	% mass	AOCS Ce-1c-89	---	2.28
C22 Behenic Acid	% mass	AOCS Ce-1c-89	---	13.62
C22-1 Erucic Acid	% mass	AOCS Ce-1c-89	---	0.62
C24-0 Lignoceric Acid	% mass	AOCS Ce-1c-89	---	0.59
Others	% mass	AOCS Ce-1c-89	---	0.74

Megan Clarke

Iftikhar Chughtai, Laboratory Manager

Intertek Caleb Brett
651 Burlington Street East, Hamilton, Ontario, Canada L8L 4J5
Telephone 905-529-0090 Fax 905-529-5989 e-mail alison.gee@intertek.com

A.3

Table A.3.1 GC-MS analysis of the oil feedstock

[PBM Apex]

Time= Tue Sep 16 05:05:09 2008

Header=	PK	RT	Area Pct	Library/ID
1=	1	8.4168	2.3666	Trimethylsilyl ether of glycerol
2=	2	16.8241	20.6663	Hexadecanoic acid, trimethylsilyl ester
3=	3	18.4345	58.2485	Oleic acid, trimethylsilyl ester
4=	4	18.6228	11.307	Octadecanoic acid, trimethylsilyl ester
5=	5	20.6096	1.3342	Propanoic acid, 2-oxo-, trimethylsilyl ester
6=	6	20.9023	1.1402	1-Butanamine, N-methyl-
7=	7	24.9806	4.9372	.beta.-Sitosterol trimethylsilyl ether

A.4 Preliminary experimental runs

These experiments were run to make a preliminary guess of the reaction parameters. For these experiments the results were calculated using the material balance of the reaction. The assumptions for these calculations were:

1. After the transesterification reaction, if the reaction mixture was settled, all the catalyst, methanol and glycerol would be in the lower glycerol phase and the upper biodiesel (FAME) phase would be pure.
2. There would be no side reaction. Thus there would be no soap production.
3. Molecular weight of jatropha oil 832.
4. Molecular weight of glycerol 192.09
5. Molecular weight of methanol 32.04.

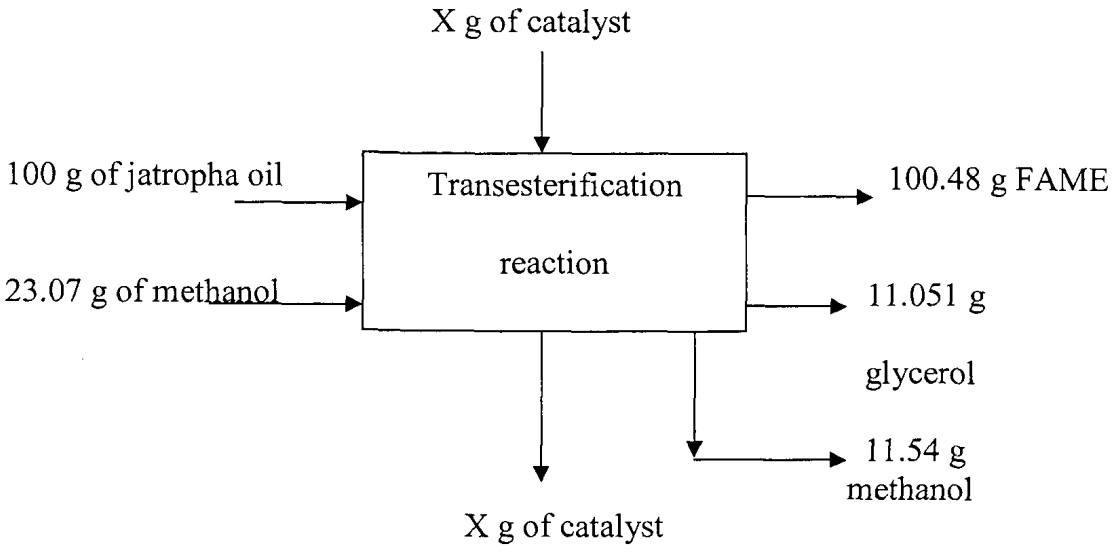
Example:

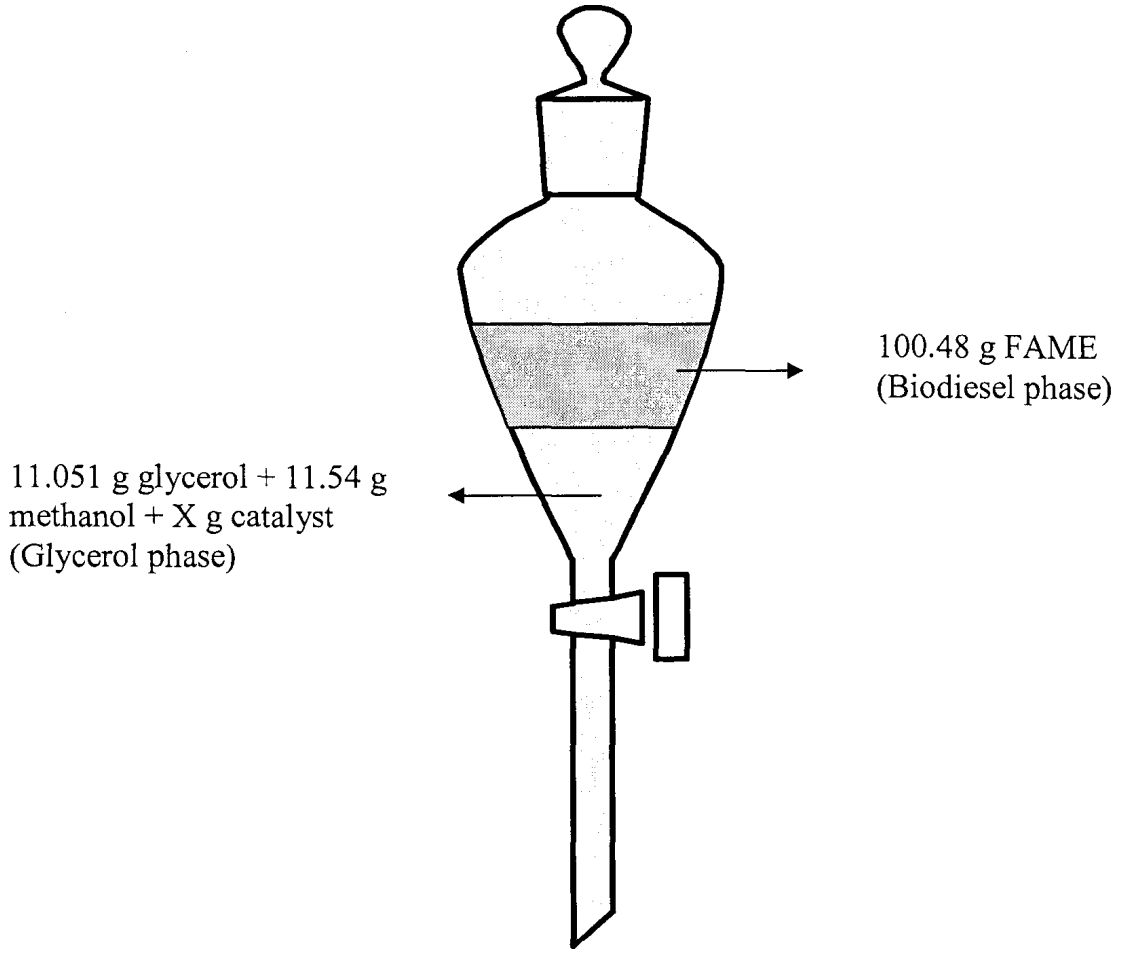
In a typical experiment if 100 g of jatropha oil and 6:1 methanol to oil molar ratio were used then,

100 g oil = 0.12 mole jatropha oil.

6:1 methanol to oil molar ratio = $6 \times 0.12 = 0.72$ mole methanol = 23.07 g methanol

According to the reaction stoichiometry 0.36 moles or 11.54 g methanol would be consumed and the rest would be left. If X g catalyst would be used, after the reaction this X g would be left in the glycerol phase. Graphically,


X g of catalyst
100 g of jatropha oil
23.07 g of methanol
Transesterification reaction
100.48 g FAME
11.051 g glycerol
11.54 g methanol
X g of catalyst


100.48 g FAME (Biodiesel phase)
11.051 g glycerol + 11.54 g methanol + X g catalyst (Glycerol phase)

Then

Theoretical weight of the glycerol phase = 11.051 g glycerol + 11.54 g methanol + X g catalyst

Yield% = [(Actual weight of the glycerol phase)/ (Theoretical weight of the glycerol phase)] ×100%

On the basis of the above calculation method, the obtained results are shown next page.

Table A.4 Preliminary experimental runs

Catalyst amount (wt% of jatropha oil)	Time (hr)	Temperature °C	Stirrer speed rpm	Yield%
2	12	25	N/C	41.65
2	12	25	N/C	33.1
2	12	25	N/C	36.12
3.5	4	50	400	68
3.5	4	60	400	69
5	6	60	400	68
5	6	50	400	57.8
5	8	50	400	72.6
5	6	50	500	72
6	6	50	800	55.4
6	6	60	600	80
7	6	60	600	60
6	8	60	600	82
7	8	60	600	86
7	10	60	600	94.7
6	10	60	600	81

In this method the percent error can be occurred upto ±10%. Thus the yield% of 82 and 81 are same when 6 wt% catalyst,6:1 methanol to oil molar ratio was used for 8 and 10 hours using a reaction temperature of 60°C and 600 rpm. Thus 7 wt% catalyst amount, 10 hour reaction time 60°C and 600 rpm gave 94.7% yield, which appeared to be higher compared to when the same reaction parameters were used for 8 hours.

So, 10 hour was chosen as the experimental reaction run time.

A.5

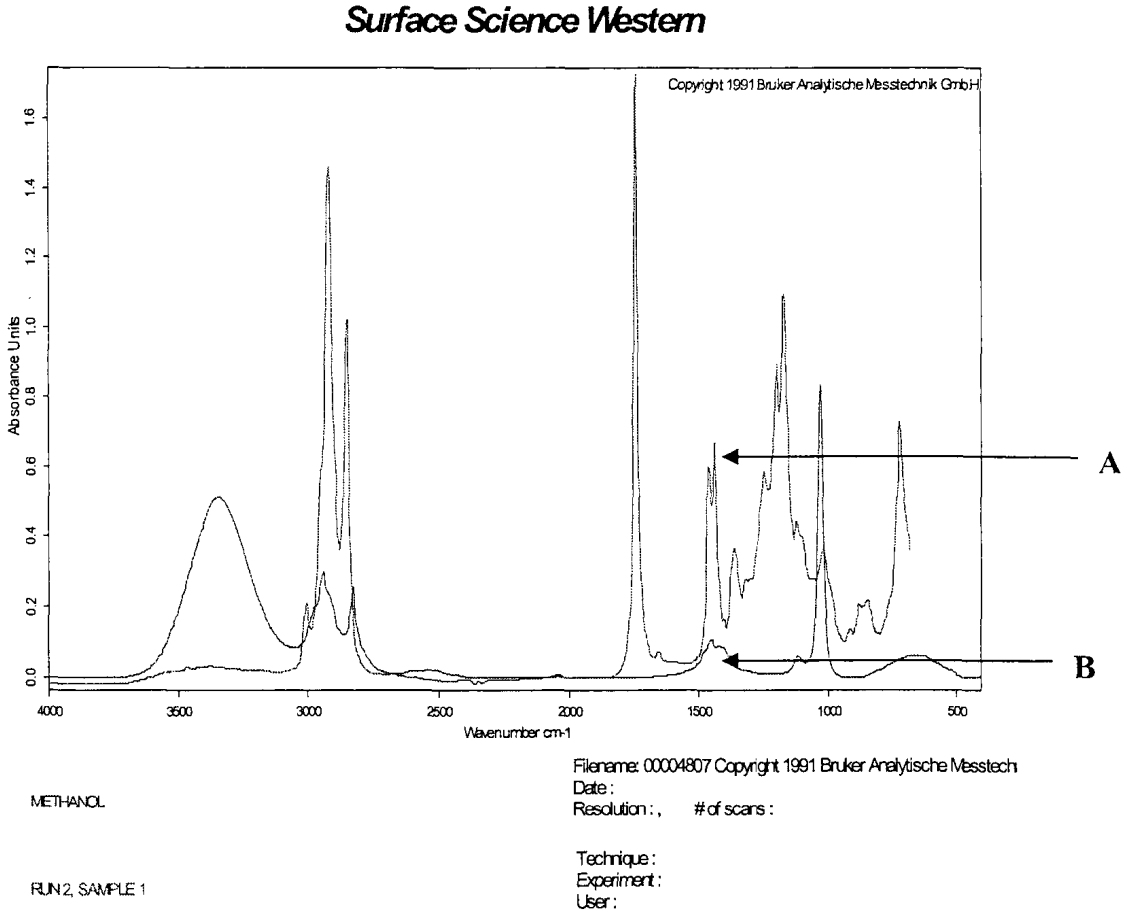
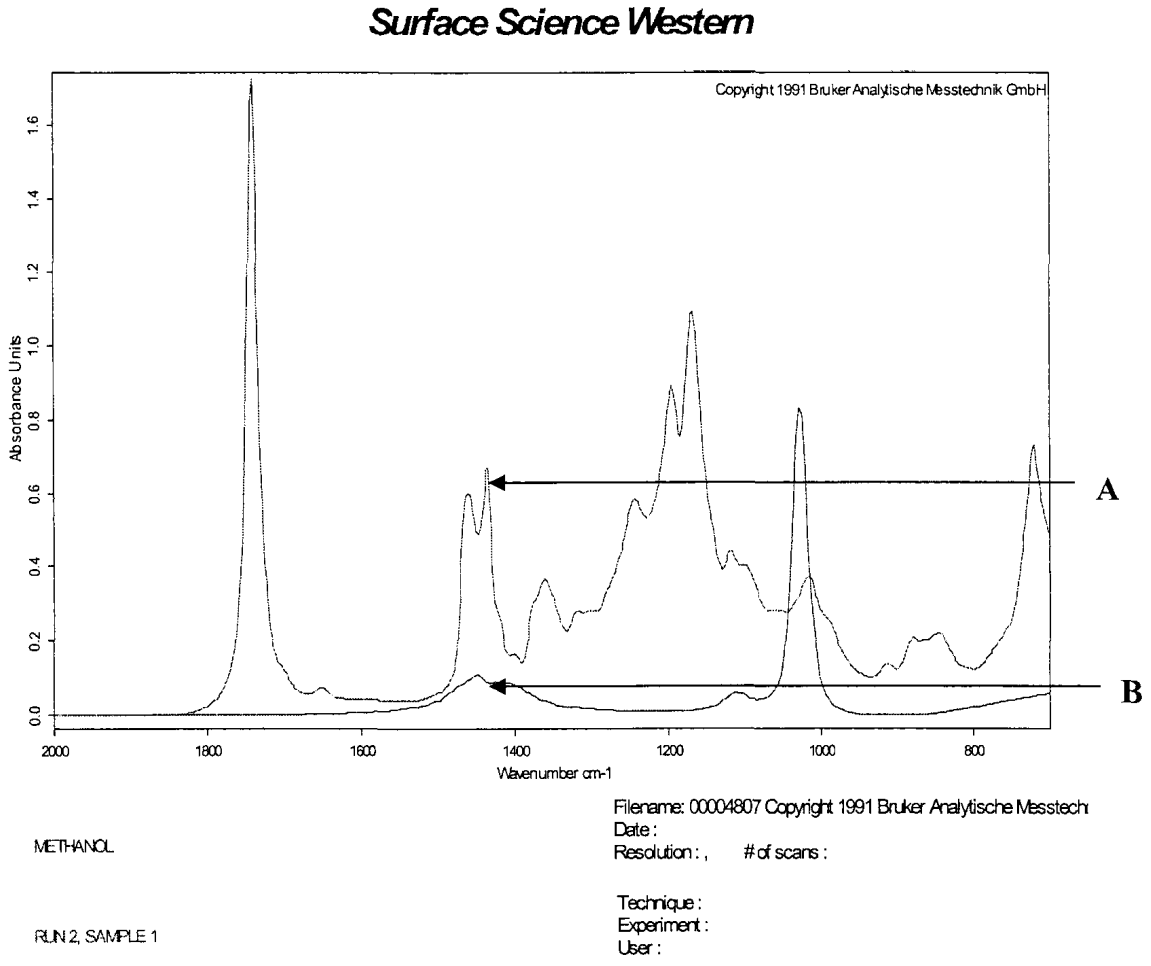


Fig. A.5.1 FTIR spectra of methanol and FAME



A = O-CH_3 peak for methyl ester

B = O-CH_3 peak for methanol

Fig. A.5.2 FTIR spectra of methanol and FAME

A.6

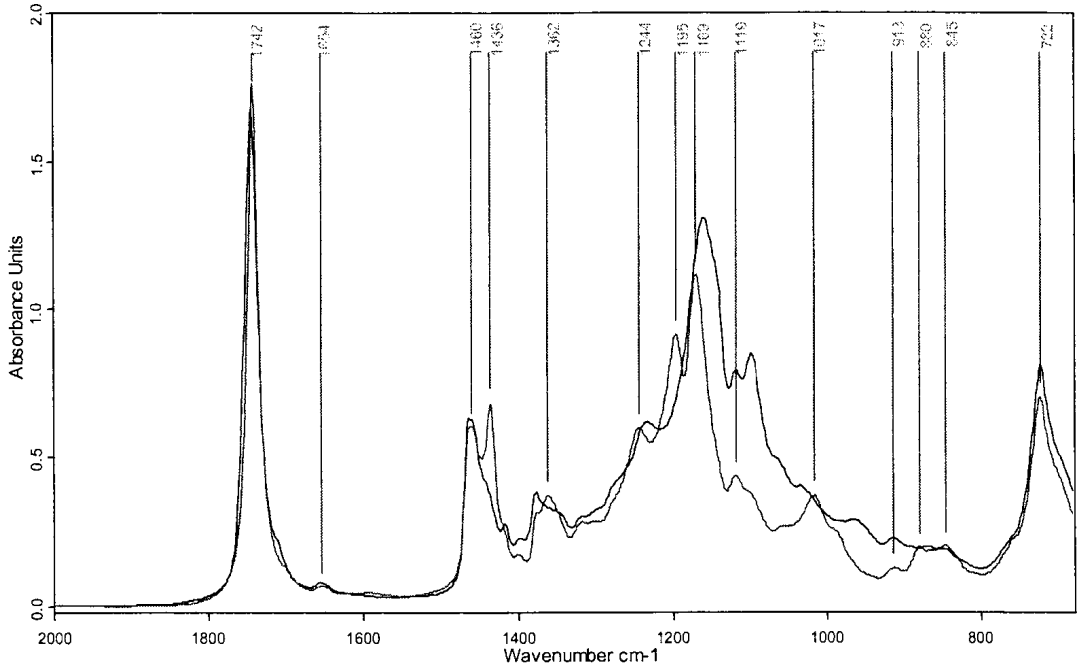


Fig. A.6 FTIR-ATR spectra of JTC oil and its biodiesel

A.7

Table A.7.1 FTIR-ATR calibration curve

Mole% of Methyl Oleate (representative of FAME)	Mole% of Triolein (representative of oil)	Area of peak ($O\text{-}CH_3$) FAME indication
0	100	0.307
25	75	0.601
50	50	1.012
75	25	1.541
90	10	1.997
100	0	2.697

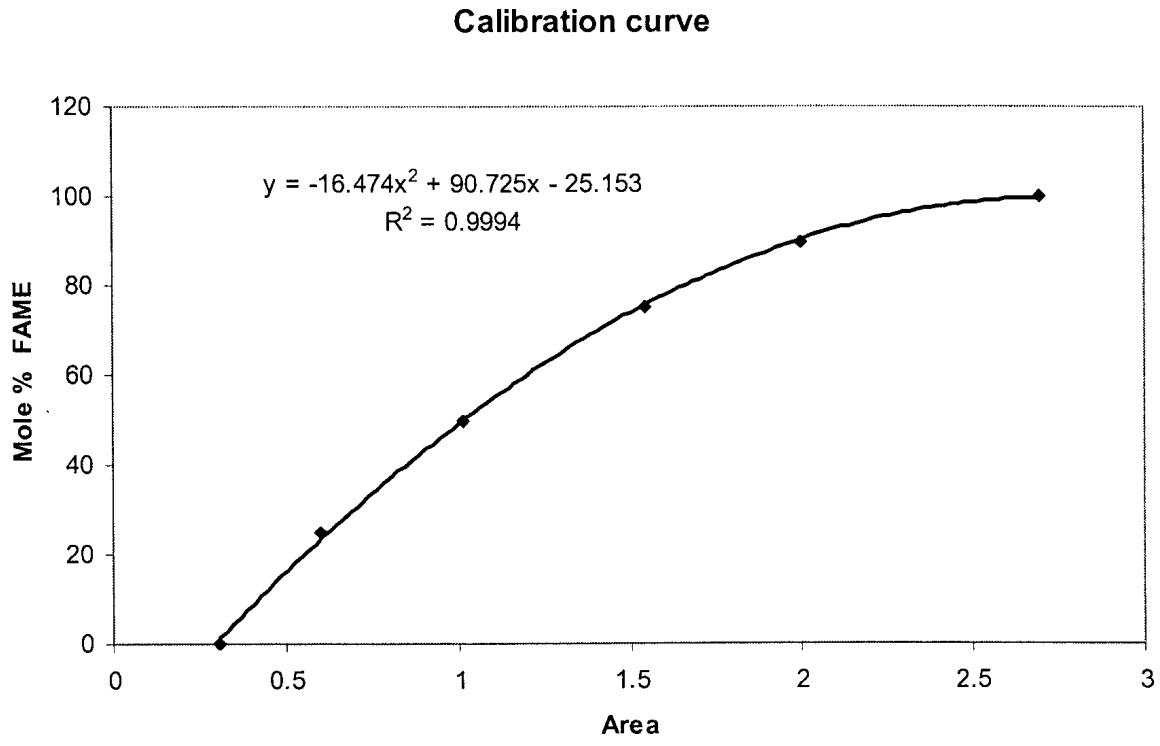


Fig. A.7 FTIR calibration curve

A.8 Comparison of sample preparation method

Error calculation:

Average conversion, $\bar{X} = \frac{x_1 + x_2 + x_3}{n}$

n = Sample size = 3

Degree of freedom, df = n-1 = 3-1 = 2

Standard Deviation, $\bar{S} = \sqrt{\frac{n\sum x_i^2 - \left(\sum x_i\right)^2}{n(n-1)}}$

Standard error = $\frac{\bar{S}}{\sqrt{n}}$

Value of t at 95% confidence level for degree of freedom 2 (df = 2) is 4.303

$\therefore$ Error at 95% confidence level = $\pm t \times \frac{\bar{S}}{\sqrt{n}}$

Interval at 95% confidence level = $\bar{X} \pm t \times \frac{\bar{S}}{\sqrt{n}}$

t- Significance test at 95% confidence level (Pair comparison)

n = Sample size = 3

Degree of freedom, df = n-1 = 3-1 = 2

Value of t at 95% confidence level for degree of freedom 2 (df = 2) is 4.303 (two tail)

Table A.8.1 Significance test method (t test)

Run No.	Method A (conversion)	Method B (conversion)	D = Method A - Method B	$(D-D_{mean})$	$(D-D_{mean})^2$
1	X_1	Y_1	$D_1=X_1 - Y_1$	$D_1 - D_{mean}$	$(D_1-D_{mean})^2$
2	X_2	Y_2	$D_2=X_2 - Y_2$	$D_2 - D_{mean}$	$(D_2-D_{mean})^2$
3	X_3	Y_3	$D_3=X_3 - Y_3$	$D_3 - D_{mean}$	$(D_3-D_{mean})^2$
			$D_{mean} = \Sigma D/n$		$\Sigma(D-D_{mean})^2$

$$\text{Variance } S^2 = \frac{\sum (D - D_{mean})^2}{n-1}$$

For significant difference between the Run A and Run B, t_{stat} must be greater than 4.303

Where,

$$t_{stat} = \frac{D_{mean}}{\sqrt{\frac{S^2}{n}}}$$

Table A.8.2 Significance test between methods A & B

	Washed sample
t obtained	0.043
t critical	4.303
Difference significant	**No**

Table A.8.3 Significance test between methods A & C

	Washed sample
t obtained	0.295
t critical	4.303
Difference significant	**No**

Table A.8.4 Significance test between samples using 20 mL and 60 mL wash water, when 6:1 methanol to oil molar ratio, 60°C, 6 wt% catalyst was used (run ID 9)

	Washed sample
t obtained	1.578
t critical	4.303
Difference significant	**No**

t- Significance test at 95% confidence level (non-pair comparison)

$n_1 = n_2 =$ Sample size = 3

Degree of freedom, df = $n_1 + n_2 - 2 = 3 + 3 - 2 = 4$

Value of t at 95% confidence level for degree of freedom 4 (df = 4) is 2.776 (two tail)

Replicate No.	Run A	Avg. $\bar{X}_A$		Run B	Avg. $\bar{Y}_B$	
1	X_1		$(X_1 - \bar{X}_A)^2$	Y_1		$(Y_1 - \bar{Y}_B)^2$
2	X_2		$(X_2 - \bar{X}_A)^2$	Y_2		$(Y_2 - \bar{Y}_B)^2$
3	X_3	$\bar{X}_A$	$(X_3 - \bar{X}_A)^2$	Y_3	$\bar{Y}_B$	$(Y_3 - \bar{Y}_B)^2$
			$\Sigma(X_i - \bar{X}_A)^2$			$\Sigma(Y_i - \bar{Y}_B)^2$

$$\text{Variance } s^2 = \frac{\sum (X_i - \bar{X}_A)^2 + \sum (Y_i - \bar{Y}_B)^2}{n_1 + n_2 - 2}$$

For significant difference between the Run A and Run B, t_{stat} must be greater than 2.776

Where,

$$t_{stat} = \frac{(\bar{X}_A - \bar{Y}_B)}{s\sqrt{\left(\frac{1}{n_1} + \frac{1}{n_2}\right)}}$$

Table A.8.5 Percent mole conversion in samples using 20 mL and 60 mL wash water, when 9:1 methanol to oil molar ratio, 60°C, 6 wt% catalyst was used in two different runs.

Run	Replicate No.	Mole conversion%	Avg. ± Error%
X (sample prepared using 20 mL wash water)	1	97.402	97.276±0.313
	2	97.151	
	3	97.277	
Y(sample prepared using 60 mL wash water)	1	98.471	98.52224±0.112
	2	98.562	
	3	98.534	

Table A.8.6 Significance test between samples using 20 mL and 60 mL wash water, when 9:1 methanol to oil molar ratio, 60°C, 6 wt% catalyst was used in two different runs.

	Washed sample
t obtained	16.079
t critical	2.776
Difference significant	**Yes**

APPENDIX B: Supplementary material for chapter 4

Error calculation:

Average conversion, $\bar{X} = \frac{x_1 + x_2 + x_3}{n}$

n = Sample size = 3

Degree of freedom, df = n-1 = 3-1 = 2

Standard Deviation, $\bar{S} = \sqrt{\frac{n\sum x_i^2 - \left(\sum x_i\right)^2}{n(n-1)}}$

Standard error = $\frac{\bar{S}}{\sqrt{n}}$

Value of t at 95% confidence level for degree of freedom 2 (df = 2) is 4.303

$\therefore$ Error at 95% confidence level = $\pm t \times \frac{\bar{S}}{\sqrt{n}}$

Interval at 95% confidence level = $\bar{X} \pm t \times \frac{\bar{S}}{\sqrt{n}}$

t - Significance test at 95% confidence level (non-pair comparison)

$n_1 = n_2 =$ Sample size = 3

Degree of freedom, df = $n_1 + n_2 - 2 = 3 + 3 - 2 = 4$

Value of t at 95% confidence level for degree of freedom 4 (df = 4) is 2.776 (two tail)

Replicate No.	Run A	Avg. $\bar{X}_A$		Run B	Avg. $\bar{Y}_B$	
1	X_1	$\bar{X}_A$	$(X_1 - \bar{X}_A)^2$	Y_1	$\bar{Y}_B$	$(Y_1 - \bar{Y}_B)^2$
2	X_2		$(X_2 - \bar{X}_A)^2$	Y_2		$(Y_2 - \bar{Y}_B)^2$
3	X_3		$(X_3 - \bar{X}_A)^2$	Y_3		$(Y_3 - \bar{Y}_B)^2$
			$\Sigma(X_i - \bar{X}_A)^2$			$\Sigma(Y_i - \bar{Y}_B)^2$

$$\text{Variance } s^2 = \frac{\sum (X_i - \bar{X}_A)^2 + \sum (Y_i - \bar{Y}_B)^2}{n_1 + n_2 - 2}$$

For significant difference between the Run A and Run B, t_{stat} must be greater than 2.776

Where,

$$t_{stat} = \frac{(\bar{X}_A - \bar{Y}_B)}{s\sqrt{\left(\frac{1}{n_1} + \frac{1}{n_2}\right)}}$$

B.1

Detailed data

Table B.1.1 Effect of catalyst amount on percent mole conversion of the reaction (washed sample) (Table 4.2)

Run ID No.	Catalyst amount (wt% of jatropha oil)	Replicate No.	Washed sample	
			Mole conversion%	Avg. ± Error%
1	1	1	1.762	2.515±1.635
		2	2.804	
		3	2.979	
2	2	1	92.897	92.794±0.366
		2	92.861	
		3	92.625	
3	3	1	94.532	94.950±1.079
		2	94.918	
		3	95.399	
4	4	1	96.797	96.840±0.283
		2	96.969	
		3	96.755	
5	5	1	97.892	97.854±0.643
		2	98.092	
		3	97.578	
6	6	1	98.272	98.214±0.125
		2	98.189	
		3	98.181	
7	7	1	97.641	97.476±0.390
		2	97.328	
		3	97.460	

Table B.1.2 Effects of catalyst amount on percent mole conversion of the reaction (unwashed sample) (Table 4.3)

Run ID No.	Catalysts amount (wt% of jatropha oil)	Replicate No.	Unwashed sample	
			Mole conversion%	Avg. ± Error%
1	1	1	-	-
		2	-	
		3	-	
2	2	1	90.948	91.344±1.572
		2	92.074	
		3	91.011	
3	3	1	94.707	94.755±0.572
		2	95.005	
		3	94.552	
4	4	1	91.698	92.497±1.789
		2	93.096	
		3	92.697	
5	5	1	89.145	90.079±2.849
		2	89.732	
		3	91.359	
6	6	1	89.746	89.287±1.1885
		2	88.791	
		3	89.326	
7	7	1	68.565	65.874±5.801
		2	64.674	
		3	64.382	

Table B.1.3 Significance test for runs 6 & 7 (Washed sample and unwashed sample)

	Washed sample	Unwashed sample
t value obtained (t_{stat})	7.744	40.660
Critical value of t(t_{crit})	2.776	2.776
Difference significant	**Yes**	**Yes**

Table B.1.4 Experimental data for Figure 4.1

Run ID no.	Catalyst amount (wt% of jatropha oil)	Replicate No.	Soap indicating peak area	Average area	Error at 95% confidence level
2	2	1	1.544	1.058	1.067
		2	0.901		
		3	0.729		
3	3	1	1.221	1.081	0.426
		2	0.890		
		3	1.131		
4	4	1	1.615	1.408	0.449
		2	1.324		
		3	1.284		
5	5	1	2.307	2.017	0.659
		2	1.786		
		3	1.959		
6	6	1	1.863	2.051	0.565
		2	1.985		
		3	2.304		
7	7	1	3.895	3.842	0.452
		2	3.993		
		3	3.640		

Table B.1.5 Effect of catalyst amount on percent mole conversion of the reaction (washed sample after extended time) (Table 4.4)

Run ID No.	Catalysts amount (wt% of jatropha oil)	Replicate No.	Washed sample after extended time	
			Mole conversion%	Avg. ± Error%
2	2	1	93.222	93.116±0.785
		2	93.365	
		3	92.761	
7	7	1	97.581	97.599±0.153
		2	97.548	
		3	97.668	

Table B.1.6 Significance test for washed sample and washed sample after extended time (Run 2 and Run 7)

	Run 2	Run 7
t value obtained (t_{stat})	1.597	0.927
Critical value of t(t_{crit})	2.776	2.776
Difference significant	**No**	**No**

B. 2

Table B.2.1 Experimental data: washed sample for runs 8, 9 and 10 (Table 4.5)

Run ID No.	. Catalysts amount (wt% of jatropha oil)	Replicate No.	Washed sample	
			Mole conversion%	Avg. ± Error%
8	5	1	97.565	97.434±0.454
		2	97.512	
		3	97.225	
9	6	1	98.682	98.539±0.308
		2	98.482	
		3	98.455	
10	7	1	97.593	97.556±0.079
		2	97.535	
		3	97.541	

Table B.2.2 Experimental data: unwashed sample for runs 8, 9 and 10 (Table 4.6)

Run ID No.	Catalysts amount (wt% of jatropha oil)	Replicate No.	Unwashed sample	
			Mole conversion%	Avg. ± Error%
8	5	1	84.232	83.509±2.150
		2	83.746	
		3	82.549	
9	6	1	80.207	80.223±3.109
		2	78.979	
		3	81.483	
10	7	1	60.598	61.818±3.743
		2	61.355	
		3	63.502	

Table B.2.3 Significance test for runs 8 & 9 (Washed sample and unwashed sample)

	Washed sample	Unwashed sample
t value obtained (t_{stat})	8.665	3.739
Critical value of t(t_{crit})	2.776	2.776
Difference significant	**Yes**	**Yes**

Table B.2.4 Significance test for runs 9 & 10 (Washed sample and unwashed sample)

	Washed sample	Unwashed sample
t value obtained (t_{stat})	13.306	16.274
Critical value of t(t_{crit})	2.776	2.776
Difference significant	**Yes**	**Yes**

B.3

Table B.3.1 Effect of methanol to oil molar ratio on percent mole conversion of the reaction (washed sample) (Table 4.7)

Run ID no.	Methanol to oil molar ratio	Replicate No.	Washed sample	
			Mole conversion%	Avg. ± Error%
11	4:1	1	98.141	98.127±0.067
		2	98.144	
		3	98.096	
12	5:1	1	98.572	98.508±0.189
		2	98.528	
		3	98.427	
9	6:1	1	98.682	98.539±0.308
		2	98.4817	
		3	98.4552	
13	7:1	1	97.474	97.654±0.387
		2	97.758	
		3	97.728	
14	8:1	1	98.154	98.184±0.074
		2	98.184	
		3	98.213	
15	9:1	1	98.471	98.522±0.115
		2	98.562	
		3	98.534	
16	10:1	1	98.736	98.795±0.126
		2	98.828	
		3	98.820	
17	11:1	1	98.782	98.775±0.027
		2	98.782	
		3	98.763	

Table B.3.2 Effect of methanol to oil molar ratio on percent mole conversion of the reaction (unwashed sample) (Table 4.8)

Run ID no.	Methanol to oil molar ratio	Replicate No.	Unwashed sample	
			Mole conversion%	Avg. ± Error%
11	4:1	1	88.882	89.176±1.223
		2	89.744	
		3	88.901	
12	5:1	1	76.449	76.808±0.785
		2	77.044	
		3	76.931	
9	6:1	1	80.207	80.223±3.109
		2	78.979	
		3	81.483	
13	7:1	1	82.553	82.870±1.655
		2	83.636	
		3	82.421	
14	8:1	1	82.595	81.987±1.308
		2	81.663	
		3	81.704	
15	9:1	1	80.281	80.982±2.442
		2	82.106	
		3	80.558	
16	10:1	1	79.852	76.834±7.545
		2	73.777	
		3	76.874	
17	11:1	1	75.363	76.370±2.307
		2	77.193	
		3	76.555	

Table B.3.3 Significance test for runs 12 & 9 (Washed sample and unwashed sample)

	Washed sample	Unwashed sample
t value obtained (t_{stat})	0.375	4.581
Critical value of t(t_{crit})	2.776	2.776
Difference significant	**No**	**Yes**

Table B.3.4 Significance test for runs 9 & 13 (Washed sample and unwashed sample)

	Washed sample	Unwashed sample
t value obtained (t_{stat})	7.702	3.233
Critical value of t(t_{crit})	2.776	2.776
Difference significant	**Yes**	**Yes**

Table B.3.5 Significance test for runs 13 & 14 (Washed sample and unwashed sample)

	Washed sample	Unwashed sample
t value obtained (t_{stat})	5.783	1.799
Critical value of t(t_{crit})	2.776	2.776
Difference significant	**Yes**	**No**

Table B.3.6 Significance test for runs 15 & 16 (Washed sample and unwashed sample)

	Washed sample	Unwashed sample
t value obtained (t_{stat})	6.836	2.250
Critical value of t(t_{crit})	2.776	2.776
Difference significant	**Yes**	**No**

Table B.3.7 Significance test for runs 16 & 17 (Washed sample and unwashed sample)

	Washed sample	Unwashed sample
t value obtained (t_{stat})	0.628	0.253
Critical value of t(t_{crit})	2.776	2.776
Difference significant	**No**	**No**

Table B.3.8 Experimental data for Figure 4.3

Run ID no.	Methanol to oil molar ratio	Replicate no.	Soap indicating peak area	Avg. ± Error% at 95% confidence level
11	4:1	1	2.255	1.740±1.113
		2	1.526	
		3	1.439	
12	5:1	1	3.159	3.141±0.664
		2	3.399	
		3	2.865	
9	6:1	1	2.498	2.551±0.114
		2	2.586	
		3	2.567	
13	7:1	1	1.968	2.070±0.242
		2	2.163	
		3	2.080	
14	8:1	1	2.783	2.819±0.368
		2	2.692	
		3	2.983	
15	9:1	1	3.209	3.424±0.586
		2	3.386	
		3	3.676	
16	10:1	1	3.636	3.971±0.815
		2	4.292	
		3	3.984	
17	11:1	1	4.573	4.236±0.748
		2	3.992	
		3	4.144	

B.4

Reaction rate (mole/sec) calculation

1 TG + 3 Methanol ⟷ 3 FAME + 1 Glycerol

Rate of this reaction (mole/sec) will be expressed:

r (mole/sec) = (1/3) * (Δ[C]/Δt) ; where [C] = [FAME]

Thus,

For table 4.6,

Table B.4.1 Parameter combination: 60°C, 6:1 methanol to oil molar ratio, 6g, 45 min, 600 rpm (run x)

Run time (min)	Time (sec)	dt	mole% conc.[C]	d[C]	d[C]/dt	r = 1/3* d[C]/dt
0	0		0			
1	60	60	12.9021	12.9021	0.215035	0.071678
5	300	240	94.44645	81.54436	0.339768	0.113256
10	600	300	97.9623	3.515848	0.011719	0.003906
15	900	300	99.3723	1.409998	0.0047	0.001567
30	1800	900	99.44041	0.068112	7.57E-05	2.52E-05
45	2700	900	99.4768	0.036392	4.04E-05	1.35E-05

Table B.4.2 Parameter combination: 60°C, 7:1 methanol to oil molar ratio, 6g, 45 min, 600 rpm (run y)

Run time (min)	Time (sec)	dt	mole% conc.[C]	d[C]	d[c]/dt	r = 1/3* d[C]/dt
0	0		0			
1	60	60	18.0903	18.0903	0.301505	0.100502
5	300	240	98.70742	80.61712	0.335905	0.111968
10	600	300	99.34611	0.638695	0.002129	0.00071
15	900	300	99.36141	0.015296	5.1E-05	1.7E-05
30	1800	900	99.36811	0.006705	7.45E-06	2.48E-06
45	2700	900	99.37129	0.00318	3.53E-06	1.18E-06

Table B.4.3 Parameter combination: 60°C, 8:1 methanol to oil molar ratio, 6g, 45 min, 600 rpm (run z)

Run time (min)	Time (sec)	dt	mole% conc.[C]	d[C]	d[C]/dt	r = 1/3* d[C]/dt
0	0		0			
1	60	60	18.68525	18.68525	0.311421	0.103807
5	300	240	98.6092	79.92395	0.333016	0.111005
10	600	300	99.40126	0.792067	0.00264	0.00088
15	900	300	99.42937	0.028105	9.37E-05	3.12E-05
30	1800	900	99.4474	0.018033	2E-05	6.68E-06
45	2700	900	99.45127	0.003868	4.3E-06	1.43E-06

B.5

Table B.5.1 Effect of reaction temperature on percent mole conversion of the reaction (Washed sample) (Table 4.10)

Run ID no.	Reaction temperature °C	Replicate No.	Washed sample	
			Mole conversion%	Avg. ± Error%
18	55	1	98.323	98.153±0.476
		2	98.190	
		3	97.945	
9	60	1	98.682	98.539±0.308
		2	98.482	
		3	98.455	
19	65	1	98.771	98.775±0.033
		2	98.764	
		3	98.790	

Table B.5.2 Effect of reaction temperature on percent mole conversion of the reaction (Unwashed sample) (Table 4.11)

Run ID no.	Reaction temperature °C	Replicate No.	Unwashed sample	
			Mole conversion%	Avg. ± Error%
18	55	1	78.697	78.999±3.262
		2	77.865	
		3	80.438	
9	60	1	80.207	80.223±3.109
		2	78.979	
		3	81.483	
19	65	1	77.634	76.393±2.739
		2	76.024	
		3	75.523	

Table B.5.3 Significance test for runs 9 & 18 (Washed sample and unwashed sample)

	Washed sample	Unwashed sample
t value obtained (t_{stat})	2.935	1.168
Critical value of t(t_{crit})	2.776	2.776
Difference significant	**Yes**	**No**

Table B.5.4 Significance test for runs 9 & 19 (Washed sample and unwashed sample)

	Washed sample	Unwashed sample
t value obtained (t_{stat})	3.272	3.976
Critical value of t(t_{crit})	2.776	2.776
Difference significant	**Yes**	**Yes**

Table B.5.5 Experimental data for Figure 4.4

Run ID no.	Reaction temperature	Replicate no.	Soap indicating peak area	Avg. ± Error% at 95% confidence level
18	55	1	2.567	2.612±0.098
		2	2.626	
		3	2.642	
9	60	1	2.498	2.551±0.114
		2	2.586	
		3	2.567	
19	65	1	2.962	3.006±0.466
		2	2.845	
		3	3.212	

B.6

Table B.6.1 Different parameter combination results (Table 4.12)

Parameter Combination	Run no.	Washed sample		Unwashed sample	
		Mole conversion%	Avg. conv. ±Error%	Mole conversion%	Avg. conv. ±Error%
D	1	98.174	98.192± 0.175	67.318	68.017± 4.536
	2	98.270		70.089	
	3	98.133		66.643	

Table B.6.2 Significance test for parameter combinations B & C

	Washed sample	Unwashed sample
t value obtained (t_{stat})	0.634	0.691
Critical value of t(t_{crit})	2.776	2.776
Difference significant	**No**	**No**

B.7

Table B.7.1 Composition of the biodiesel

Fri Sep 12 13:12:35 2008

PK	RT	Area Pct	Library/ID
1	4.4646	0.0077	Cyclopentane-1,2-diol
2	5.5959	0.011	2-Hexyne, 4-methyl-
3	6.2509	0.0129	Silane, (2-methoxyethoxy)trimethyl-
4	6.37	0.0176	3-Methylseleno-2-benzo[b]thiophenecarboxaldehyde
5	6.5486	0.021	1-tert-Butoxy-2-ethoxyethane
6	8.0173	0.017	1-(Ethoxycarbonylmethyl)pyridinium bromide
7	8.4341	0.034	Trimethylsilyl ether of glycerol
8	9.3073	0.3557	Butane, 1,2,4-tris(trimethylsiloxy)-
9	12.9195	0.156	Methyl tetradecanoate
10	14.0905	0.0108	Heneicosanoic acid, methyl ester
11	15.1027	0.7635	11-Hexadecenoic acid, methyl ester
12	15.4401	16.6825	Hexadecanoic acid, methyl ester
13	16.2935	0.0775	9-Octadecenoic acid (Z)-, methyl ester
14	16.4325	0.0511	Cyclopropaneoctanoic acid, 2-hexyl-, methyl ester
15	16.5714	0.0562	Heptadecanoic acid, methyl ester
16	17.1668	1.0259	Z,E-7,11-Hexadecadien-1-yl acetate
17	17.663	51.8056	9-Octadecenoic acid (Z)-, methyl ester
18	17.7821	6.3996	Octadecanoic acid, methyl ester
19	18.1195	0.3613	9,12-Octadecadien-1-ol, (Z,Z)-
20	18.318	0.0358	cis,cis-7,10,-Hexadecadienal
21	18.4172	0.5413	Cyclopropaneoctanoic acid, 2-octyl-, methyl ester
22	18.8538	0.5456	9-Eicosyne
23	19.0523	4.0136	2-Dimethyl(octyl)silyloxyoctane
24	19.1714	1.0015	Eicosanoic acid, methyl ester
25	19.3103	0.0643	Succinamic acid
26	19.4095	0.097	9-Eicosyne
27	19.6279	0.0491	7-Hexadecenoic acid, methyl ester, (Z)-
28	19.7271	0.0232	Heneicosanoic acid, methyl ester
29	20.1836	14.0062	13-Docosenoic acid, methyl ester, (Z)-
30	20.521	0.0914	3,6-Epoxy-2H,8H-pyrimido[6,1-b][1,3]oxazocine-8,10(9H)-dione, 3,4,5,6-tetrahydro-4,5-bis[(trimethylsilyl)oxy]-, [3R-(3.alpha.,4.beta.,5.beta.,6.alpha.)]-
31	20.6798	0.0541	Tricosanoic acid, methyl ester
32	20.8981	0.0366	Quinazolin-4(3H)-one, 2-[2-(4-methoxyphenyl)ethenyl]-
33	21.0172	0.6182	15-Tetracosenoic acid, methyl ester
34	21.0966	0.3623	Tetracosanoic acid, methyl ester
35	21.2553	0.0762	1-Monooleoylglycerol trimethylsilyl ether
36	21.9897	0.0217	Tetrasiloxane, decamethyl-
37	22.466	0.0149	Cyclotrisiloxane, hexamethyl-
38	24.292	0.04	Tetrasiloxane, decamethyl-
39	24.9668	0.1493	.beta.-Sitosterol trimethylsilyl ether
40	25.7011	0.291	Decanoic acid, 1,2,3-propanetriyl ester

B.8

According to the Bamgboye, 2008 correlation:

$$CN\ (Cetane\ number) = 61.1 + 0.088x_2 + 0.133x_3 + 0.152x_4 - 0.101x_5 - 0.039x_6 - 0.243x_7 - 0.395x_8$$

Where, x_1 .....x_8 are % composition of FAME

x_1 = Caprylic acid methyl ester (C 8:1)

x_2 = Lauric acid methyl ester (C 12:1)

x_3 = Myristic acid methyl ester (C 14:1)

x_4 = Palmitic acid methyl ester (C 16:0)

x_5 = Stearic acid methyl ester (C 18:0)

x_6 = Palmitoleic acid methyl ester (C 16:3)

x_7 = Oleic acid methyl ester (C 18:1)

x_8 = Linoleic acid methyl ester (C 18:2)

According to Gerpen, 1996 correlations:

CN (Cetane number) = 45.954 + 0.279* (% Methyl Palmitate)

CN (Cetane number) = 43.194 + 0.193* (% Methyl Oleate)

B.9

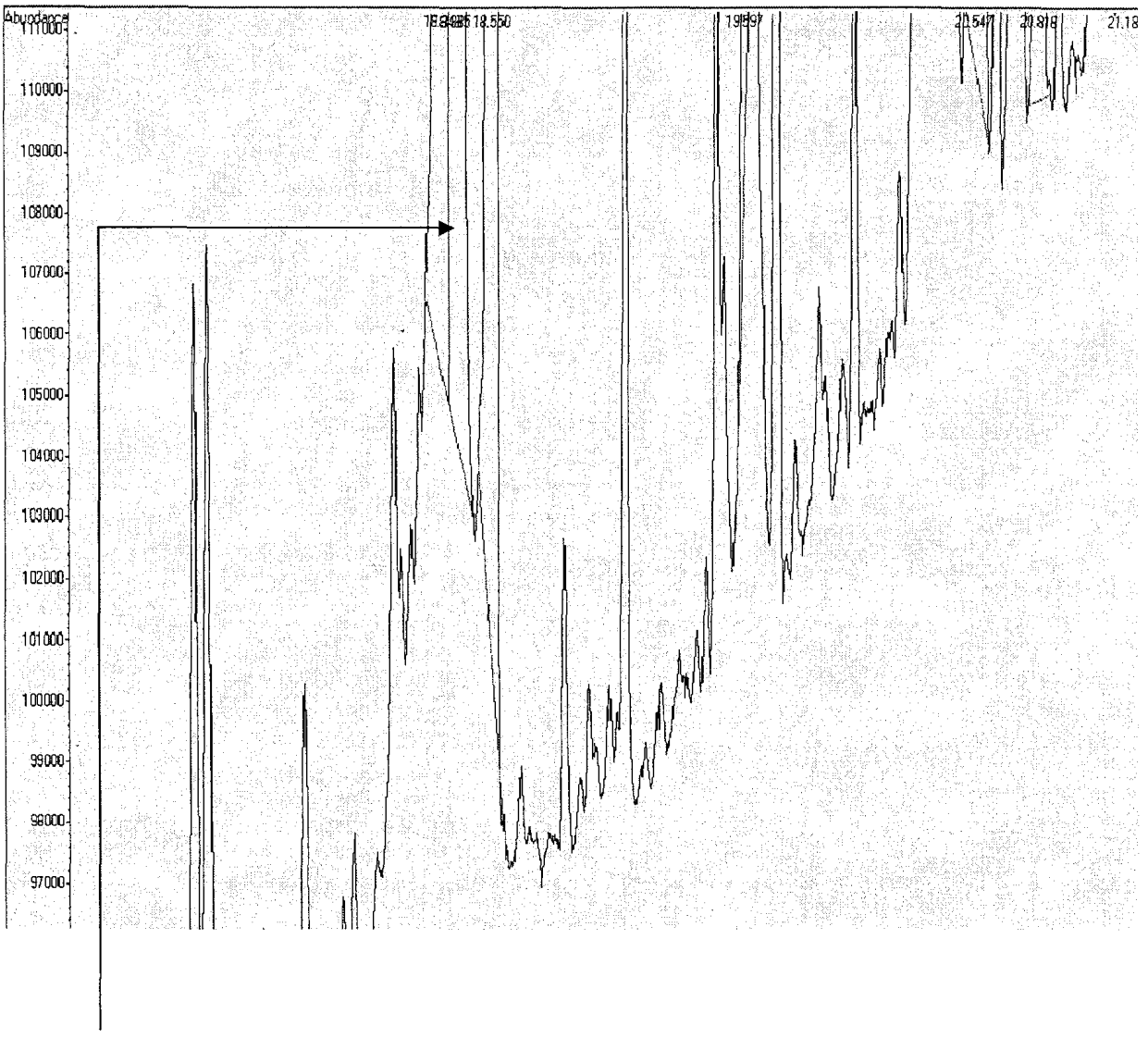


Fig B.9 Spectra of raw oil

B.10

Table B.10.1 Composition of the oil feedstock residue after reaction samples were taken for the reactor

[PBM Apex]

Time=	Tue Sep 16 02:35:04 2008			
Header=	PK	RT	Area Pct	Library/ID
1=	1	4.4431	0.3232	Cyclopentanone, 2-(1-methylpropyl)-
2=	2	6.9109	7.9677	Tetracosane
3=	3	6.9737	5.6109	Tetracosane
4=	4	7.2665	7.3515	Heneicosane
5=	5	7.4129	12.143	Nonacosane
6=	6	8.4168	1.8251	Trimethylsilyl ether of glycerol
7=	7	16.8241	12.7438	Hexadecanoic acid, trimethylsilyl ester
8=	8	18.4554	41.3133	Oleic acid, trimethylsilyl ester
9=	9	18.6227	7.3012	Octadecanoic acid, trimethylsilyl ester
10=	10	20.6514	0.4394	1-Octadecanamine, N-methyl-
11=	11	20.9232	0.5966	Benzaldehyde, 2-nitro-, diaminomethylidenhydrazone
12=	12	25.0433	2.3843	dl-Alanyl-l-phenylalanine

B. 11

Table B.11.1 Percent mole conversion obtained in run 9 from samples prepared using 20 mL wash water (Table 4.13)

Run No.	Replicate No.	Mole conversion%	Average % mole conversion of the raw oil	Error% at 95% confidence level
9	1	98.328	98.356	0.166
	2	98.308		
	3	98.432		

Table B.11.2 Significance test between run 6 & run 9 using 20 mL wash water

	Washed sample using 20 mL wash water
t value obtained (t_{stat})	2.931
Critical value of t(t_{crit})	2.776
Difference significant	**Yes**

B.12

Table B.12.1 Overall material loss: (reactor content)

Parameter Combination	Run no.	Material loss wt%	Average material loss wt%	Error%
D	1	0.323	0.293	0.065
	2	0.28		
	3	0.276		