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Declaration

I hereby declare that the work presented in this thesis has been carried out independently and according to the rules and regulations for getting Master's degree in Environmental Technology at the University of Stavanger, Norway.

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I would like to express my sincere gratitude and thanks to my thesis supervisor Prof. Kåre Bredeli Jørgensen for his guidance, suggestions and many good advices and his patience during the correction of the manuscript.

I would also like to express heartiest thanks to my family members in Pakistan for their patience, ever constant encouragement and love during my studies.

Abstract

This research work has dealt with kinetics of biodiesel production (Fatty Acid Methyl Ester "FAME") from triglyceride oils through transesterification. This project is divided into two parts: literature study and a small experimental testing of kinetics measurements.

A focus of the literature study has been on the kinetic models and experiments for transesterification. It briefly touches various biodiesel synthesis techniques that are of being researched. It also describes applications and problems that are associated with different types of transesterifications.

We found that lot of work has been done on optimizing the reaction conditions for biodiesel production. We need to do more research on biodiesel process optimization incorporating high free fatty acids.

In the experimental part is described the synthesis of Jatropha methyl ester from Jatropha oil, methanol and homogenous alkali catalyst as raw materials. Kinetic experiments were made and carried out in laboratory for small scale production of biodiesel. A simple and accurate NMR method was implemented to determine fatty acid methyl esters (FAMEs) in biodiesel product from Jatropha oil. The kinetic parameters based on NMR analysis gave activation energy that fits with the literature value. This method of FAME synthesis can be used and these results are reproducible.

Symbols and abbrevations

A	-	frequency factor for a reaction (in Arrhenius equation)
AV	-	Acid Value
ASTM	-	American Society for Testing and Materials
arom	-	aromatic
bf	-	biofuels
B100	-	pure biodiesel
BXX	-	Percentage of Biodiesel contained in the blend
CN	-	Cetane Number
CI	-	Compression Ignition
cSt	-	centistokes
DG	-	Diglyceride
ds	-	desulpherization
E	-	Alkyl esters
EPA	-	Environmental Protection Agency
EE	-	Ethyl Ester
EU	-	European Union
E_a ($E^{\pm}$)	-	Activation Energy
et al	-	et alia (and others)
$\mathcal{E} r^2$	-	sum of error squares
FAME	-	Fatty Acid Methyl Ester
FFA	-	Free Fatty Acid
GC	-	Gas chromatography
in situ	-	in place

JCO	-	Jatropha Curcas Oil
JME	-	Jatropha Methyl Ester
K	-	Kelvin
kj	-	kilo joule
Ln*k*	-	natural log of rate constant
min	-	minutes
MG	-	Monoglyceride
ME	-	Methyl Ester
MR	-	Molar Ratio
Max	-	maximum
n-PAH	-	Nitro polyaromatic hydrocarbons
NMR	-	Nuclear Magnetic Resonance
N/A	-	not available
N/S	-	not specified
ppm	-	parts per million
R	-	Universal molar gas constant (in Arrhenius equation)
RBD	-	Refined, bleached and dried
rxn	-	reaction
PAH	-	Polyaromatic hydrocarbons
TG	-	Triglyceride
TMS	-	Tetramethylsilane
temp	-	temperature
wt%	-	weight percentage

Contents

1 Introduction

1.1 Background

Energy consumption is rising everywhere in the world. At the same time, natural resources are decreasing and CO_2 emissions are becoming a real threat for the ecosystem equilibrium. Diminishing fossil fuel resources, coupled with the steady increase in energy consumption, has spurred research interest in alternative and renewable energy sources. In this context, the European Union is promoting the use of alternative renewable resources and a new directive has been implemented for the promotion of the use of biofuels or other renewable fuels for transport, by replacing diesel and petrol up to 2% by 2005 and 5.75% by 2010 [1]. This directive is a strategy to decrease Europe's dependence on energy imports, especially for the transport sector, based 95% on oil – 80% of which is imported. Energy consumption in this sector is expected to increase at a rate of 1.5% a year in developed countries and 3.6% in developing countries. This directive will contribute to meet the goals set out by the Kyoto Protocol, reducing the emissions of greenhouse gases. It also represents a sustainable solution to prevent the dramatic depletion of fossil resources.

Recently, developing countries such as India and China have experienced a significant increase in energy demand. Moreover, the persistent hike in global prices of crude oil is becoming the major issue in every country. This exacerbates the situation in the form of dwindling production rate, the instabilities in the petroleum production and the processing costs such as; desulphurization in order to meet stringent emission norms etc [2]. This, inevitably, reflects an adverse impact on the local economy of many countries, especially the oil importing countries, by posing a severe burden on their foreign exchange [3]. Therefore, the aforementioned obsessive issues were considered to be the important trigger for many initiatives, to search for the alternative source of energy, which can supplement or replace fossil fuels [4].

1.2 Biodiesel Definition

Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from renewable biolipids via transesterification process, which conform to ASTM D6751 specifications for use in diesel engines [5]. “Bio” represents the renewable and biological source in contrast to petroleum-based diesel fuel and “Diesel” refers to its use in diesel engines. Biodiesel refers to the pure fuel before blending with diesel fuel. Biodiesel blends are denoted as, "BXX" with "XX" representing the percentage of biodiesel contained in the blend (i.e. B20 is 20% biodiesel, 80% petroleum diesel, B100 is pure biodiesel) [6].

Biodiesel is the name of a clean burning alternative fuel, produced from domestic, renewable resources like vegetable oils, recycled cooking oils, or animal fats. Because plants produce oils from sunlight and air, and can do so year after year on cropland; these oils are renewable. Animal fats are produced when the animal consumes plant oils and other fats, and they too are renewable. Used cooking oils are mostly made from vegetable oils, but may also contain animal fats. Used cooking oils are both recycled and renewable. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression-ignition (CI-diesel) engines with little or no modifications. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics [7].

1.3 Biodiesel as a Fuel

Biodiesel is registered as a fuel and fuel additive with the Environmental Protection Agency (EPA) and meets clean diesel standards established by the California Air Resources Board (CARB). Neat (100 percent) biodiesel has been designated as an alternative fuel by the Department of Energy (DOE) and the U.S. Department of Transportation (DOT) [8].

In petrodiesel the energy content can vary upto 15% but in biodiesel it is much less variable. Pure biodiesel contains up to 10-12% oxygen by weight, while diesel contains almost 0% oxygen. The presence of oxygen allows more complete combustion, which

reduces hydrocarbons, carbon monoxide, and particulate matter emission. However, higher oxygen content increases nitrogen oxides emissions [9] .

The primary reason, why biodiesel is suitable as an alternative fuel for petrodiesel, lies in the cetane number (CN). The cetane number indicates the ignition quality of a diesel fuel. It measures a fuel's ignition delay, which is a period between the start of injection and start of combustion (ignition) of the fuel. Fuels with a higher cetane number have shorter ignition delays, providing more time for the fuel combustion process to be completed [10].

The term “cetane number” is derived from a straight chain alkane with 16 carbons ($C_{16}H_{34}$), hexadecane or cetane (figure 1.1) [11].

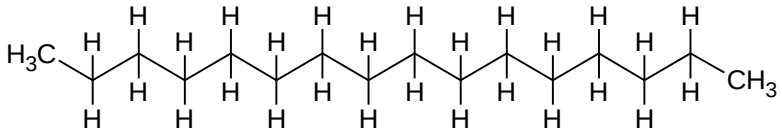


Figure 1.1: Hexadecane

This long unbranched hexadecane, is the high quality standard on the cetane scale and has been assigned as having a cetane number of 100. On the other hand, highly branched alkanes are low quality compounds on the cetane scale and have low cetane numbers. Biodiesel’s long chain fatty acids methyl esters; (figure 1.2) are similar to long chain alkanes with number of carbons ranging from 14 to 22. This makes biodiesel suitable for alternative diesel fuel [12].

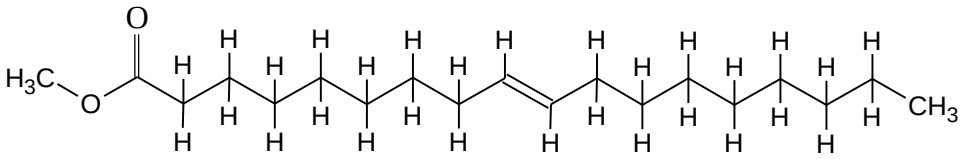


Figure 1.2: Fatty Acid Methyl Ester (FAME)

1.4 Sources of Biodiesel

Biodiesel is produced from any fat or oil; such as Jatropha oil through a refinery process called transesterification. Several hundred plants and animals produce fats and oils in sufficient quantities to warrant processing into edible oils; however, only a few sources are commercially significant. Table 1.1 summarizes the major sources in the world and the method of processing. The primary raw materials used in the production of biodiesel are vegetable oils, animal fats, and recycled greases. These materials contain triglycerides, free fatty acids, and other contaminants depending on the degree of pre-treatment they have received prior to delivery. Since biodiesel is a mono-alkyl fatty acid ester, the primary alcohol used to form the ester is the other major feedstock [13]. Fuel-grade biodiesel must be produced to strict industry specifications (ASTM D6751) in order to insure proper performance. A number of studies have shown that triglycerides (vegetable oils/animal fats) hold promise as alternative fuels for diesel engines. However, the high viscosity, low volatility and poor cold flow properties of triglycerides, which result in severe engine deposits, injector choking and piston ring sticking, have prevented triglycerides from being used directly in diesel engines [14]. Raw vegetable oil cannot meet biodiesel fuel specifications, it is not registered with the Environmental Protection Agency (EPA), and it is not a legal motor fuel [15]. Hence, Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the United States Clean Air Act Amendments of 1990 [16].

Table 1.1: Major edible fats and oils in the world and processing method [17].

Source	**Oil content (%)**	**Prevalent method of recovery**
Soybean	19	Direct solvent extraction
Corn (germ)	40	Solvent extraction
Jatropha curcas(Physic Nut)	27-40	Mechanical/solvent extraction
Canola	42	Prepress solvent extraction
Coconut (dried copra)	66	Hard pressing
Lard (edible tissue)	70-95	Wet or dry rendering
Palm	47	Hard pressing
Sunflower	40	Prepress solvent extraction
Peanut (shelled)	47	Hard pressing or prepress

1.5 Biodiesel Specifications

The American Society for Testing and Materials International (ASTM) specification for biodiesel (B100) is ASTM D6751-02. It is summarized in Table 1.2 and Appendix 10. Some of the test methods listed in it performs more than one role. These methods ensure that the fuel performs same as intended in CI engines and as tests to ensure that the manufacturer produced a high quality B100 [18]. Each of these properties and the test method used to measure it are briefly described below. Detail explanations about its property requirements and specific methods can be found in literature [13].

Table 1.2: Specifications for Biodiesel [13].

Property	**Units**	**ASTM D-6751**		**EN 14214**	
		Limits	Test methods	Limits	Test methods
Kinematic Viscosity (40 ^{0}C)	mm^2/s	1.9-6.0	D445	3.5-5.0	EN ISO 3104
Density (15 ^{0}C)	kg/m^3	N/S	N/S	860-900	EN ISO 3675
Ester content	mass %	N/S	N/S	96.5 min	EN 14103
Cetane number	-	47 min	D 613	51 min	EN ISO 5165
Flash point	^{0}C	130 min	D 93	120 min	ISO/CD 3679
Water content	volume %	0.050 max	D 2709	500 max	EN ISO 12937
Sulphated ash	mass %	0.020 max	D874	0.02 max	ISO 3987
Copper Corrosion	grade	No.3 max.	D130	No.1	EN ISO 2160
Acid number	mg KOH/g	0.80 max	D 664	0.5 max	EN 14104
Free glycerol	mass %	0.02 max	D 6584	0.02 max	EN 14105
Total glycerol	mass %	0.240 max	D 6584	0.25 max	EN 14105
Phosphorous content	mass %	0.001 max	D 4951	10 max	EN 14107
Iodine number	-	N/S	N/S	120 max	EN 14111
Oxidative stability (110 ^{0}C)	h	N/S	N/S	6 min	EN 14112
Monoglycerols	mass %	N/S	N/S	0.8 max	EN 14105
Diglycerols	mass %	N/S	N/S	0.2 max	EN 14105
Triglycerols	mass %	N/S	N/S	0.2 max	EN 14105
Methanol	mass %	N/S	N/S	0.2 max	EN 14110
High calorific value	MJ/kg	N/S	N/S	N/S	N/S
Low calorific value	MJ/kg	N/S	N/S	N/S	N/S
Oxygen Content	%	N/S	N/S	N/S	N/S

Flash point: it is defined as the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mmHg), at which application of an ignition source causes the vapors of a specimen to ignite under specified conditions of test. For biodiesel, this test is a measure of residual alcohol and determinant for flammability classification of materials.

Water and Sediment: It is a test that determines the volume of free water and sediment in middle distillate fuels having viscosities at 40 °C in the range 1.0 to 4.1 mm^2/s and densities in the range of 700 to 900 kg/m^3. This test is a measure of cleanliness of fuel. For biodiesel, this test is determinant of presence of free water droplets and sediment particles.

Kinematic Viscosity: It is defined as the resistance to flow of a fluid under gravity. It is a basic design specification for fuel injectors used in diesel engines. For biodiesel it is quick and easy method for estimating the degree of completion of batch reaction.

Sulfated Ash: It is the residue remaining after a fuel sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to a constant weight. This test monitors the mineral ash residual when fuel is burned. For biodiesel, this test is an important indicator of the quantity of residual metals in the fuel that came from the catalyst used in the esterification process.

Sulfur: This method covers the determination of total sulfur in liquid hydrocarbons, boiling in the range from approximately 25 to 400 °C, with viscosities between approximately 0.2 and 20 cSt (mm^2/s) at room temperature. Biodiesel feedstocks typically have very little sulfur, but this test is an indicator of contamination of protein material and/or carryover catalyst material or neutralization material from the production process.

Copper Strip Corrosion: The copper strip corrosion is used for detection of the corrosiveness to copper of fuels and solvents. This test monitors the presence of acids in the fuel. For B100, the most likely source of a test failure would be excessive free fatty acids, which are determined in accordance with an additional specification.

Cetane Number: The cetane number is a measure of the ignition performance of a diesel fuel obtained by comparing it to reference fuels in a standardized engine test. This test is a measure of how easily the fuel will ignite in the engine. For biodiesel, the cetane number is seldom an issue because all of the common fatty acid esters have cetane numbers near or above 47.

Cloud Point: The cloud point is the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled down under specific conditions. The cloud point is a critical factor in cold weather performance for all diesel fuels. For biodiesel, cloud point is typically higher than the cloud point of conventional diesel. It can then be modified in following ways to get the lower cloud point.

- The use of additives that retard the formation of solid crystals in the B100 by various mechanisms.
- The blending feedstock that is relatively high in saturated fatty acids with feedstock that have lower saturated fatty acid content.

Carbon Residue: In petroleum products, the part remaining after a sample has been subjected to thermal decomposition, is the carbon residue. The carbon residue is a measure of how much residual carbon remains after combustion. The test basically involves heating the fuel to a high temperature in the absence of oxygen. The most common cause of excess carbon residues in biodiesel is an excessive level of total glycerin.

Acid Number: The acid number is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specified end point. The acid number is a direct measure of free fatty acids in B100. The free fatty acids can lead to corrosion and may be a symptom of water in the fuel.

Free Glycerin: Free glycerol is the glycerol present as molecular glycerol in the fuel. It results from incomplete separation of the ester and glycerol products after the transesterification reaction. This can be a result of imperfect water washing or other approaches that do not effectively separate the glycerol from the biodiesel.

Total Glycerin: Total glycerol is the sum of free and bonded glycerol. Bonded glycerol "is the glycerol portion of the mono-, di-, and triglyceride molecules." High values of total glycerin are indicators of incomplete esterification reactions and predictors of excessive carbon deposits in the engine.

Phosphorous: This test covers the quantitative determination of barium, calcium, copper, magnesium, phosphorus, sulfur, and zinc in unused lubricating oils and additive packages. In the case of B100, phosphorus can come from incomplete refining of the phospholipids (or gums) from the vegetable oil and from bone and proteins encountered in the rendering process.

Vacuum Distillation end point: The vacuum distillation end point test covers the determination, at reduced pressures, of the range of boiling points for petroleum products that can be partially or completely vaporized at a maximum liquid temperature of 400 °C. Petroleum fractions have tens to hundreds of individual compounds mixed together. In B100 there are, at most, ten different esters present, and they can be identified using gas or liquid chromatography and NMR.

1.6 Environmental Impacts of Biodiesel

As an alternative fuel, biodiesel is becoming increasingly important due to diminishing petroleum reserves and adverse environmental consequences of exhaust gases from petroleum-fuelled engines [19]. In contrast to conventional petrodiesel, it is environmental friendly and creates substantial reduction in emission, hence, these properties make Biodiesel a good alternative fuel to petroleum-based diesel oil [20].

Biodiesel has many other environmental benefits, such as it is biodegradable, non-toxic, and has low emission profile (including potential carcinogens) [20, 21]. It can be used in today's vehicle fleets worldwide and may also offer a viable path to sustainable transportation fuel [22]. Moreover, it does not contribute to global warming due to its closed carbon cycle because the primary feedstock for biodiesel is a biologically-based material that can be grown season after season. And, since the carbon in the fuel was

originally removed from the air by plants, there is no net increase in carbon dioxide levels [23].

Biodiesel is safer fuel as it has high flash point temperature of 154 ^{o}C [24]. It is regarded as clean fuel since it does not contain carcinogenic substances and its sulphur content level is also lower than its content in petrodiesel [25].

It is well known that biodiesel is non-toxic, contains no aromatics and is less pollutant to both water and soil. It is the most suitable fuel in environmentally sensitive areas (national parks, lakes, rivers) or in confined areas where environmental conditions and worker protection must meet high standards (underground mines, quarries) [26]. Moreover, it contains about 10% built in oxygen, which helps it to burn fully and also expected to reduce exhaust emissions. Its higher cetane number (CN) improves the ignition quality even when blended with petroleum diesel [27].

Nevertheless, diesel engines emit particulate matter, nitrogen oxides, greenhouse gases, and air toxics [28]. Hence, the important property of Biodiesel is, then, its ability to reduce such pollutants as carbon monoxide, unburned hydrocarbons and particulate emission from engines [23]. Studies also showed significantly lower levels of emissions of specific toxic compounds for Biodiesel and Biodiesel blends, including aldehydes, polyaromatic hydrocarbons (PAH), and nitro-polyaromatic hydrocarbons (nPAH) [29].

2 Modern Processes of Biodiesel Production

2.1 The Basic Concept

Biodiesel is defined as the mono-alkyl esters of long chain fatty acids (derived from vegetable oils or animal fats). It is the product of the reaction of a straight chain alcohol, such as methanol or ethanol (in the presence of catalyst NaOH, KOH or CH_3ONa) with a fat or oil (triglycerides) to form the mixture of fatty esters of long chain fatty acids (Biodiesel) and glycerol (glycerin) [30, 31]. Biodiesel represents a suitable renewable substitute for petroleum based diesel and is accepted as an alternative diesel fuel in a steadily growing number of countries around the world. Fatty acid methyl esters or ethyl esters (FAME/EE), from vegetable oils, have shown promise as Biodiesel, as the result of improved viscosity, volatility and combustion behavior relative to raw triglycerides, while maintaining their cetane number (around 50) [32].

2.2 Technological Platforms

Vegetable oils are produced from numerous oil seed crops with varying fatty acid composition. While all vegetable oils have high-energy content, most require some processing to assure safe fuel use in internal combustion engines [26].

Various methods were used to produce fuels from vegetable oils or fats including; direct use of vegetable oils & fats and/or blending at different proportions with diesel, microemulsions with simple alcohols, thermal cracking (pyrolysis) to alkanes, alkenes, alkadienes etc., batch wise transesterification (alcoholysis) (figure 2.1) and the continuous base-catalyzed process (Appendix 1) [33, 34]. More literature related to advantages and disadvantages of different methods of biodiesel production can be studied in the review on biodiesel production [56].

The continuous base-catalyzed process is the most widely used biodiesel process in the European Union and US which is divided into three main sections, namely; crude oil

degumming and refining; transesterification reaction and ester washing; methanol recovery and glycerol refining. But, in the case of batch wise process, transesterification is most commonly used method [14, 35, 36]. Because of the simple process and glycerol obtained as byproduct, which has a commercial value, transesterification is preferred over others [37].

There are a number of approaches available for ensuring that the transesterification reaction occurs quickly enough to be practical [23]. The following groups classify these options:

- Homogenous/Heterogeneous base catalyst such as NaOH, KOH, NaOMe.
- Homogenous/Heterogeneous acid catalyst, using H_2SO_4, H_3PO_4, HCl, BF_3.
- Lipase Enzymes.
- Non-catalyst options such as supercritical processes, and co-solvent systems.

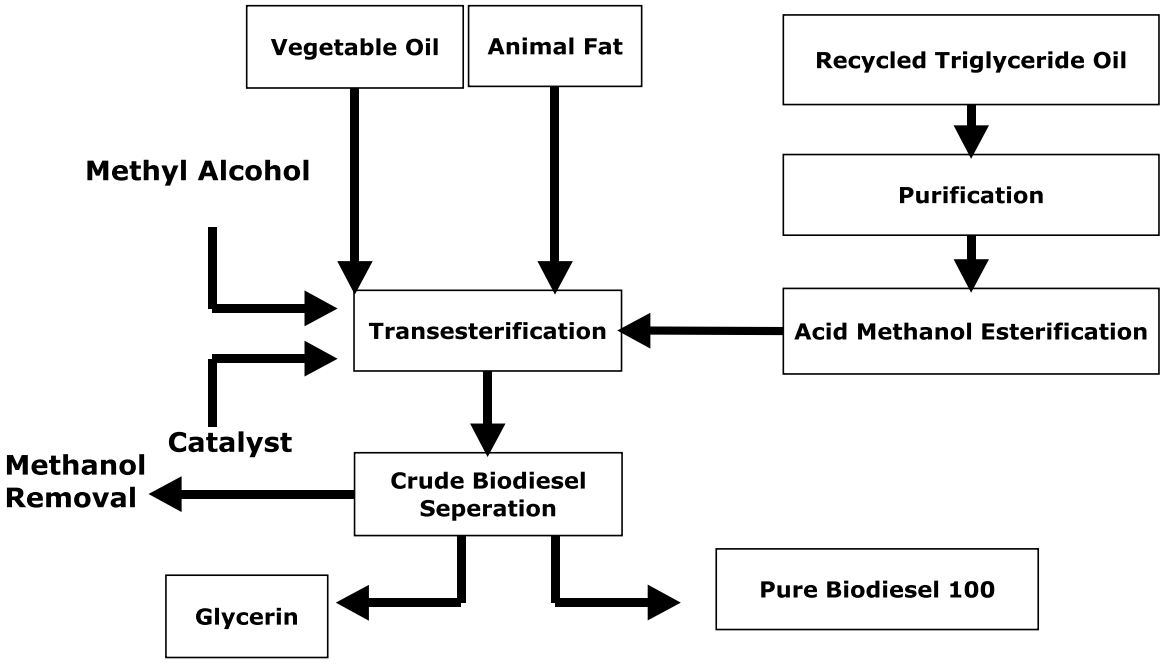


Figure 2.1: Biodiesel Production Process [33].

2.3 Alkali Catalyzed Reaction

Most of the biodiesel produced today is done with the alkali catalyzed reaction for several reasons:

- It is carried out at low temperature and pressure.
- It yields high conversion (98%) with minimal side reactions and reaction time.
- It is a direct conversion to biodiesel with no intermediate compounds.
- No exotic materials are needed [37].

The base-catalyzed process is relatively fast but is affected by water content and free fatty acids of oils or fats. Free fatty acids can react with base catalysts to form soaps and water. Soap not only lowers the yield of alkyl esters but also increases the difficulty in the separation of biodiesel and glycerol and also in the water washing because of the formation of emulsions [19].

2.3.1 Transesterification of Triglycerides

Transesterification is, in principle, the action of one alcohol displacing another from an ester, referred to as alcoholysis [38]. In the transesterification of different types of oils, triacylglycerol react with an alcohol, generally methanol or ethanol, to produce esters and glycerin [39]. The main factors affecting transesterification are the amounts of alcohol and catalysts; reaction temperature, pressure and time; the contents of free fatty acids and water in oils [40].

Transesterification is conducted to produce biodiesel with the objective to reduce the viscosity of the parent vegetable oil or animal fat, since it is an order of magnitude greater than that of the corresponding methyl esters (Biodiesel) [23, 41]. The kinematic viscosity of Jatropha oil significantly reduces after transesterification [42].

The overall transesterification process is a sequence of three equivalents, consecutive and reversible reactions, in which di- and monoglycerides are formed as intermediates

[43]. At each reaction step, one molecule of methyl or ethyl ester is produced for each molecule of methanol or ethanol consumed. The transesterification reaction is represented by the general equation shown in figure 2.2.

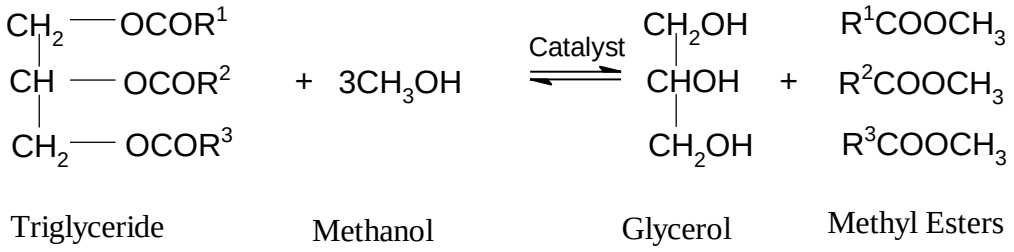


Figure 2.2: General equation for transesterification of triglycerides [43].

The reactions, as shown below, are reversible, and thus an excess of alcohol is usually used to force the equilibrium to the product side. The stoichiometry for the reaction is 3:1 alcohol to oil. However, in practice this is usually increased to 6:1 to raise the product yield [38]. The three stages of the transesterification reaction are indicated in figure 2.3.

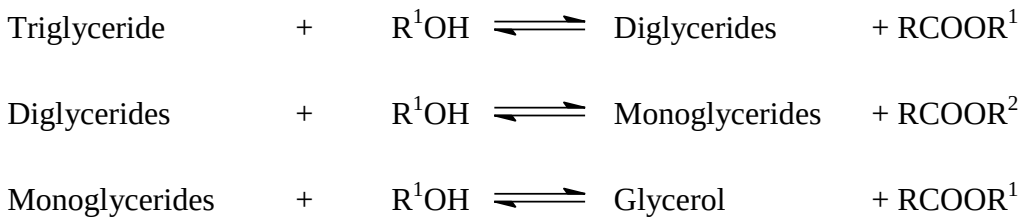


Figure 2.3: Stages of transesterification of triglycerides [43].

2.3.2 Catalyst Selection

The catalyst used has a determinant effect on the reaction, raising the rate notably. It is known that basic catalysts require short times (30 min) to complete the reaction even at room temperature, while acid catalysts, such as sulfuric acid, require higher temperatures (100 °C) and longer reaction times (3–4 h) [38]. The alkali catalysts are the most commonly used in the biodiesel industry, because the process proves faster and the reaction conditions are moderated. These catalysts include sodium hydroxide, potassium hydroxide and sodium methoxide. However, sodium methoxide is more

expensive than the hydroxides and also more difficult to manipulate since it is very hygroscopic. Potassium hydroxide has the advantage that it can be neutralised with phosphoric acid after the reaction, resulting in potassium phosphate, which may be used as fertilizer [44].

2.3.3 Ethanol / Methanol Selection

Ethanol is a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment. However, Methanol is considerably easier to recover and find than the ethanol. Ethanol forms an azeotrope with water so it is expensive to purify the ethanol during recovery. If the water is not removed it will interfere with the reactions. Methanol recycles easier because it does not form an azeotrope. These two factors are the reason that evens though methanol is more toxic, it is the preferred alcohol for producing biodiesel. Methanol has a flash point of 283 K, while the flash point of ethanol is 281 K, so both are considered highly flammable [45].

2.4 Acid Catalyzed Reaction

Acid catalyzed reactions are used to convert FFAs to esters, or soaps to esters as pre-treatment step for high FFA feedstock [46]. Although it requires a longer reaction time and a higher temperature than the alkali-catalyzed reaction, acid catalysis is more efficient when the amount of free fatty acids in the oil exceeds 1%. An economic analysis study has shown that the acid-catalyzed procedure, being a one-step process, is more economical than the alkali-catalyzed process, which requires an extra step to convert free fatty acids to methyl esters, thus avoiding soap formation [47].

Studies of the acid-catalyzed system have been very limited in number. No commercial biodiesel plants to date have been reported to use the acid-catalyzed process. Despite its relatively slow reaction rate, the acid catalyzed process offers benefits with respect to its independence from free fatty acid content and the consequent absence of a

pretreatment step. These advantages favor the use of the acid-catalyzed process when using waste cooking oil as the raw material [48].

2.5 Enzyme (Biocatalyst) Catalyzed Reaction

Enzymatic transesterification especially those using lipase has drawn researcher's attention in last ten years due to the downstream processing problem posed by chemical transesterification. Huge amount of wastewater generation and difficulty in glycerol recovery are among problems that eventually increase the overall biodiesel production cost and being not environmental benign [49].

In contrast, enzyme catalysis proceeds without the generation of by-products, easy recovery of product, mild reaction conditions, insensitive to high FFA oil and catalyst can be reuse. These advantages prove that enzyme catalyzed biodiesel production has high potential to be an eco-friendly process and a promising alternative to the chemical process. However, it still has its fair share of constraints especially when implemented in industrial scale such as high cost of enzyme, slow reaction rate and enzyme deactivation [49].

The advantages and disadvantages of different types of catalysts used in transesterification of triglyceride oils can be studied in more detail in review article [49].

2.6 Parallel Reactions affecting yield of Biodiesel from Triglyceride Oil

2.6.1 Hydrolysis

Triglyceride oils can be hydrolyzed to long chain fatty acids and glycerol by water and lipases [50]. The naturally occurring fatty acids are chiefly straight-chain compounds containing an even number of carbon atoms and conveniently divided into saturated and unsaturated chain acids [51]. Hydrolysis of triglyceride oils and fats is an endothermic reaction (Scheme 1) [52].

Triglyceride + Water ⇌ Diglycerides + Fatty acids

Diglycerides + Water ⇌ Monoglycerides + Fatty acids

Monoglycerides + Water ⇌ Glycerol + Fatty acids

Overall reaction:

Triglycerides + 3Water ⇌ Glycerol + 3Fatty acids

Scheme 1: Hydrolysis of Triglyceride oils [51].

The extent of hydrolysis increases with an increase in temperature. Additionally, the miscibility of water in lipid increases at high temperatures and pressures, thereby enhancing the rate of the hydrolysis reaction. At high temperatures, these triglycerides and the fatty acids derived from them undergo undesired thermal decomposition leading to deterioration in color or odor and to a reduced yield of fatty acids. Additional major drawbacks of the high temperature–pressure fat splitting process include:

- It is an energy intensive process.
- It uses considerable amount of superheated steam as a reagent.
- It requires the use of large reactors made of expensive corrosion-resistant material.
- The quality of the product is poor and necessitates additional process steps to purify the fatty acids and glycerol escalating the cost of the overall manufacturing process.

Enzymatic hydrolysis is a good alternative to overcome these disadvantages as the use of enzymes for the hydrolysis not only gives colorless pure products but also reduces the by-product formation, due to enzyme specificity [53]. Enzymatic hydrolysis is an advantageous approach because it can be performed at lower temperature to save energy, and it exhibits high selectivity, leading to products with high purity [54].

2.6.2 Saponification

The production of soap, sometimes called alkaline hydrolysis, converts tri-alkylglycerols to glycerol and form a mixture of salts of long chain carboxylic acids [55]. The saponification reaction of the catalyst (sodium hydroxide) and the FFA, forming soap and water is shown in figure 2.4.

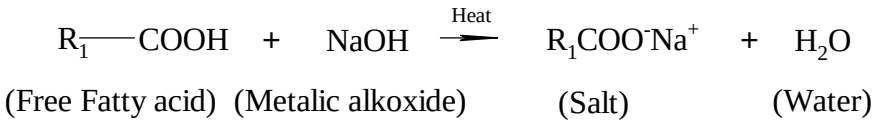


Figure 2.4: Saponification reaction [56].

This reaction is undesirable because the soap lowers the yield of the biodiesel and inhibits the separation of the esters from the glycerol. In addition, it binds with the catalyst meaning that more catalyst will be needed and hence the process will involve a higher cost [56].

The biodiesel industry has dealt with the problem of saponification by replacing the hydroxides traditionally used as catalysts (KOH and NaOH) with methoxides (mainly CH_3ONa). Although this proceeding does not completely prevent saponification, using a methoxide catalyst can significantly reduce its occurrence. Additionally, some studies affirm that, provided the vegetable oil is refined, the yield loss resulting from the formation of soaps is sufficiently small to be neglected [57]. Hence, inorder to prevent the biodiesel yield loss due to the saponification reaction, oil and alcohol must be dry and the oil should have a minimum amount of free fatty acids (less than 0.1 wt%) [58].

2.6.3 Esterification

The acid catalyzed esterification (a condensation reaction) occurs by the reaction of carboxylic acid (fatty acids) and alcohols in the presence of strong acids [59, 60]. The parameters which mostly influence the esterification reaction are catalyst amount, reaction temperature, reaction time and molar ratio of alcohol to oil. To enable

biodiesel production from acid raw materials in a more cost-effective way, the study of such reaction is necessary [61].

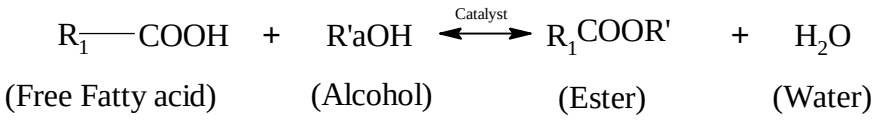


Figure 2.5: Esterification Reaction

This side reaction is of great importance due not only to the possible increase on the biodiesel production, but also because it will affect the properties of future biodiesel [62].

3 Kinetic Models

3.1 Introduction to Kinetic Models

Kinetic studies on the transesterification reaction of oils provide parameters for predicting the extent of reaction at any given time under particular reaction conditions. Kinetics usually includes the determination of reaction rate equation and rate constant as well as activation energy. Although the importance of biodiesel as an alternative fuel has grown during the past twenty years, the chemical kinetics of transesterification, the most common means of biodiesel production, remain controversial [63]. Most attempts in literature have been focused on finding the best fit of empirical data to simple models of reaction order [64]. However some of these results are contradictory. Numerous studies have been carried out on the kinetics for both acid and base catalyzed transesterification processes [65].

3.2 Freedman's Kinetic Model

The work on chemical kinetics specific to biodiesel production began with Freedman and colleagues in the early 1980s [66]. They reported the transesterification of soyabean and other oils with methanol and butanol to examine the effect of alcohol type, the reaction rate constants, catalyst type and concentration [65]. Their kinetic model was of limited use due to the consideration of only one overall reaction. In this case one molecule of triglyceride (TG) reacts with three molecules of alcohol (ROH) [67].

$$TG + 3ROH \rightleftharpoons G + 3E \qquad \text{Equation 3.1}$$

This reaction occurs as a sequence of three steps. The triglyceride (TG) decomposes to diglyceride (DG) and monoglyceride (MG) with the production of glycerol (G) and alkyl ester (E) [68]. This is represented as eq. 3.2.

$$TG + ROH \rightleftharpoons DG + E$$

$$DG + ROH \rightleftharpoons MG + E$$

MG + ROH ⇌ G + E Equation 3.2

Freedman's kinetic model appears to derive from the application of the law of mass action to the three steps of the reaction. The forward reactions are said to be second order, referring to the overall order of the proposed forward reaction step. When the molar ratio of alcohol to triglyceride is very high, the concentration of alcohol can be assumed constant. The rate of reaction then depends solely on the concentration of triglyceride, a condition which Freedman referred to as first order reaction. Finally, where the data does not fit the sequential model, Freedman proposed a "shunt reaction" in which three alcohols simultaneously attack the triglyceride [67]. The shunt reaction is said to be fourth order, presumably proportional to $[TG][ROH]^3$.

Freedman used butanol and methanol, with molar ratio of alcohol to oil of 30:1 and 6:1, at temperature ranging from 20 ^oC to 60 ^oC. He found reverse reactions appear to be second order, while forward reactions appear to be pseudo-first order or second order kinetics depending upon conditions used [66]. He also derived rate constants and activation energies (E_a) from the Arrhenius equation given by eq. 3.3

$$E = -RT \ln\left(\frac{k}{A}\right) \quad \text{Equation 3.3}$$

Where A is the frequency factor for reaction, R the universal molar gas constant, and T the temperature (K). Since the activation energy is dependent on temperature, and therefore the rate constants at any temperature can be computed using eq. 3.4.

$$\ln k = \ln A - \frac{E}{RT} \quad \text{Equation 3.4}$$

This is a linear equation and therefore a plot of Ln*k* vs 1/T should produce a straight line of slope $-\frac{E}{RT}$ [65].

In 1990, Mittelbach and Trathnigg of Karl Franzens [69] University Graz, Austria, studied the kinetics of alkaline catalyzed methanolysis of sunflower oil. They discussed

the parameters affecting the transesterification reaction. However, they did not propose any rate equations or derived any rate constants. Mittelbach found that the conversion of triglycerides did not follow second-order kinetics as indicated by Freedman. He was able to show that the first reaction step of methanol and triglyceride forming diglyceride is the rate limiting, whereas the other steps occur much faster [69]. He also found that the rate of reaction is temperature dependent but the percentage conversion is not a strong function of temperature, provided that the reaction proceeds for at least ten minutes [68, 70]. Figure 3.1 illustrates the effect of temperature on final yield. When experimenting with a small amount of vegetable oil, about ten minutes after the reaction, the temperature hardly affects the amount of methyl ester formed (under the same reaction conditions).

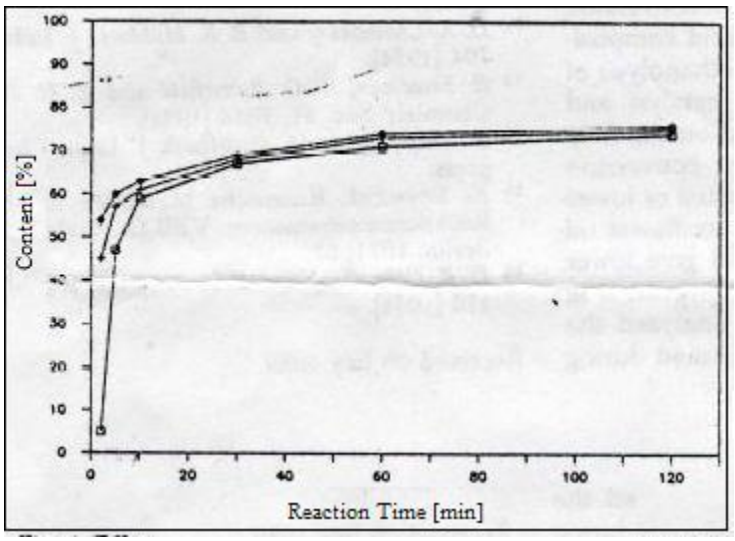


Figure 3.1: Effect of temperature on methanolysis for a molar ratio of methanol: sunflower oil = 3:1, 0.5% KOH, Temperature = 25 ^{o}C [70].

For the determination of the order of the reaction it has to be considered that the reaction mixture is non-homogenous throughout methanolysis. For the reaction studied by them, this non-homogenous phase distribution meant that significant conversion to methyl esters only set in after about two minutes, corresponding to the period of time necessary to bring about complete homogenization. Afterwards the reaction proceeds quit fast, following second order kinetics, until after about ten minutes methanolysis drastically slowed down [69].

In 1997, Noureddini and Zhu [71] of the University of Nebraska investigated the kinetics of the transesterification of soybean oil with methanol using NaOH as a catalyst. In their investigation, they borrowed Freedman's kinetic model [68]. They studied the effect of mixing intensity and temperature on the reaction rates for a 6:1 methanol to soybean oil molar ratio. A reaction mechanism was proposed, consisting of an initial mass transfer-controlled region followed by a second-order kinetically controlled region [71]. They took measurements at differing mixing intensities, as measured by the Reynolds number of the stirrer. In addition, they included temperature effects by computing Arrhenius parameters for both the standard Arrhenius equation, as well as a modified equation expressed as eq. 3.5.

$$k = A\, T^{n} \exp^{(-Ea/RT)} \qquad \text{Equation 3.5}$$

where n is an experimentally derived parameter. They concluded that the shunt reaction proposed by Freedman was negligible [68].

In 1998, Boocock and collegues [72] investigated the fast formation of high purity methyl esters from vegetable oils at University of Toronto. They conducted numerous experiments on coconut oil and soybean oil using tetrahydroforan as cosolvent. They found that the reaction slows down drastically over time. Their study suggests that the reaction rate drops off because of a fall in the catalyst concentration and polarity effect caused by mixing of methanol with the non-polar oil [72]. Figure 3.2 illustrates the kinetics of a typical methanolysis reaction. Further literature related to anomalies in Freedman's result can be read in Boocock et al [72].

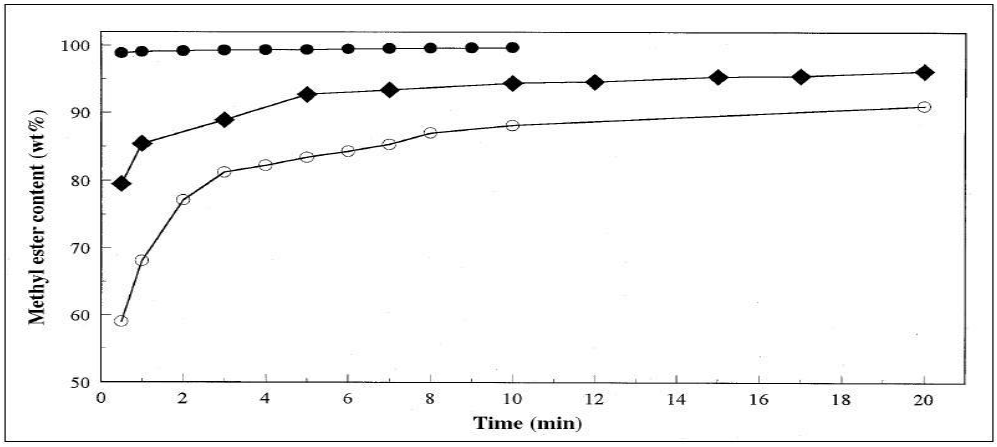


Figure 3.2: Schematic course of a methanolysis reaction. Reaction conditions; Methanol: Coconut and soybean oil = 6:1 (mol/mol) [72].

In 2000, Cheryan and Darnoko [69] studied the kinetics of Palm oil transesterification in a batch reactor at University of Illinois. They found that best kinetic model for their data appears to be pseudo second order model for the initial stages of the reaction, followed by first-order or zero-order kinetics. This phenomenon is explained by removal of glycerol from the reaction mixture, which also makes a significant amount of catalyst and methanol leave the reaction zone [69]. To test that hypothesis, a model was developed based on kinetics of triglyceride hydrolysis [73].

In 2002, Komers and his colleagues [74] at the University of Pardubice, Czech Republic, derived a kinetic model for all the consecutive competitive reactions that take place during transesterification. This kinetic model described the reaction of vegetable oil with methanol using potassium hydroxide as a catalyst. Presumed model of Komer for reaction of rapeseed oil include formation of methanol, methanolysis, and saponification [74]. Their kinetic model is the only attempt to formulate chemical kinetics reaction model of vegetable oil alcoholysis completely. The model assumed that the vegetable oil was purely triglyceride, FFAs concentration on the vegetable oil was negligible and the saponification of FFAs did not occur during alcoholysis [77]. This model supports Bikou research on negative effect of water on transesterification reaction progress [75].

In 2007, Franceschini and Macchietto [73, 76] studied Validation of a model for biodiesel production at Imperial College London. They used experimental design to elucidate the parameters of kinetic models for a biodiesel process. They indicated possible future developments for the optimal experiment design method in their exhaustive review. Modern model-based design of experiment techniques by Franceschini and Macchietto allow for the rapid development and assessment of dynamic models. It yields the most informative set of experimental data, in order to estimate precisely the parametric set of a given model.

3.3 Komers' Kinetic Model reviewed by Turner

A comprehensive investigation of the kinetics of alkali-catalyzed methanolysis of rapeseed oil was conducted by Komers et al. [72]. His model considers alcoholysis of triglyceride oil using potassium hydroxide as the catalyst. Review and reanalysis of Komers' kinetic model has been carried out by Turner by extending the kinetic model and involving the FFA saponification to the developed kinetic reaction model. However, Turner work focused only on theoretical aspects and examination of previous research and experimental data without implementing any real experiment to verify his developed kinetic reaction model [77]. In this research work, we described the reviewed proposed mechanisms for all competing reactions that take place during alcoholysis. Here, we change and simplify the Komer model for any alkyl alcohol, designated ROH, and any base catalyst.

The development of detailed kinetic models often requires simplifying assumptions. For theoretical processing of the mechanism assume that:

(1) Free Fatty acid concentration is negligible.
(2) Only two reactions from all theoretically possible are proceeding to form products: the alcoholysis of glycerides (TG, DG, and MG) and saponification of TG, DG, and MG or E (alkyl esters).
(3) All the isomers of TG, DG and MG and E react with the same rate and mechanism.
(4) Alcoholysis is catalyzed by OH^- or X^- (alkoxide) ions. Concentrations of OH^- and X^- ions are much smaller than those of TG and alkyl alcohol (ROH).

Based on proposed simplifications, following reactions presented in eq. 3.6, 3.7 and 3.8 are possible.

Formation of Alkoxide (RO^-):

$$ROH + OH^- \underset{k_{1r}}{\overset{k_1}{\rightleftharpoons}} X^- + H_2O \qquad (1) \quad \text{Equation 3.6}$$

Alcoholysis:

$$TG + X^- \underset{k_{2r}}{\overset{k_2}{\rightleftharpoons}} DG^- + E \qquad (2)$$

$$DG^- + ROH \underset{k_{3r}}{\overset{k_3}{\rightleftharpoons}} DG + X^- \qquad (3)$$

$$DG + X^- \underset{k_{4r}}{\overset{k_4}{\rightleftharpoons}} MG^- + E \qquad (4)$$

$$MG^- + ROH \underset{k_{5r}}{\overset{k_5}{\rightleftharpoons}} MG + X^- \qquad (5)$$

$$MG + X^- \underset{k_{6r}}{\overset{k_6}{\rightleftharpoons}} G^- + E \qquad (6)$$

$$G^- + ROH \underset{k_{7r}}{\overset{k_7}{\rightleftharpoons}} G + X^- \qquad (7)$$

Equation 3.7

Saponification:

$$E + OH^- \xrightarrow{k_8} ROH + A \qquad (8)$$

$$TG + OH^- \xrightarrow{k_9} DG + A \qquad (9)$$

$$DG + OH^- \xrightarrow{k_{10}} MG + A \qquad (10)$$

$$MG + OH^- \xrightarrow{k_{11}} G + A \qquad (11)$$

Equation 3.8

where A is the soap of the corresponding fatty acid chain [74].

However, this kinetic reaction model requires an additional reaction equation if it is used for studying the effect of FFA content. If participation of FFA in the kinetic reaction model has to be considered then saponification of FFA must be involved in the set of eq. 3.8. Thus, eq. 3.9 is additional saponification for the set of eq. 3.8.

$$FFA + OH^- \xrightarrow{k_{12}} A + H_2O \qquad \text{Equation 3.9}$$

The saponification of FFA is an adverse side reaction because it consumes catalyst to produce water and more soap. Therefore, as a result, the new system of kinetic reaction model that considers FFA saponification consist of 10 reaction components (TG, DG, MG, G, E, M, A, OH, FFA and water) [77].

From the above list of reactions, a system of differential equations is enumerated using appropriate rate laws, such as mass action kinetics. Rate laws use the product of a rate constant and concentrations of reactants to calculate reaction rates. Simplifying assumptions can be made to reduce the number of differential equations and their complexity. Two common approaches are steady state approximation and rate limiting step approximation. Rate-limiting step approximation is based on the assumption that the forward and reverse rates of the first step are much larger than the rate of second step. Steady state approximation consists of assumption that the rates of change of concentrations of all reactive intermediates are negligibly small. This is generally a good approximation if the concentrations of the intermediates are small since small variables have small time derivatives if they do not oscillate rapidly. The approach taken by Komers is steady state because this approximation often gives quite accurate results [78]. In other words, we presume that reaction (3), (5) and (7) in eq. 3.7 proceed faster than others (eq. 3.10), that is

$$k_2, k_{2r} << k_3, k_{3r}$$

$$k_4, k_{4r} << k_5, k_{5r}$$

$$k_6, k_{6r} << k_7, k_{7r}$$

$$k_3, k_{3r}, k_5, k_{5r}, k_7, k_{7r} > k_8, k_9, k_{10}, k_{11}, k_{12} \qquad \text{Equation 3.10}$$

On this basis the stationary state for following reaction components is valid. It therefore follows that

$$\frac{d[H_2O]}{dt} = \frac{d[X^-]}{dt} = \frac{d[DG^-]}{dt} = \frac{d[MG^-]}{dt} = \frac{d[G^-]}{dt} = 0$$

Komers normalized the corresponding species by initial concentrations of alcohols.

$TG = [TG] / a$	$DG = [DG] / a$	$MG = [MG] / a$
$G = [G] / a$	$A = [A] / a$	$OH = [OH^-] / a$
$H_2O = [H_2O] / a$	$ROH = [ROH] / b$	$X^- = [X^-]/b$
$b = [ROH]_0$	$E = [E] / a$	$a = [TG]_0$

Equation 3.11

The resulting system of rate equations for only 10 reaction components (TG, DG, MG, G, E, ROH, OH, A, FFA and H_2O) in the form of differential kinetic equations are

$$-\frac{dTG}{dt} = b \cdot OH \cdot (k'_2 \cdot TG \cdot ROH - k'_{2r} \cdot DG \cdot E) + a \cdot OH \cdot k_9 \cdot TG$$

$$-\frac{dDG}{dt} = b \cdot OH \cdot (-k'_2 \cdot TG \cdot ROH + k'_{2r} \cdot DG \cdot E + k'_4 \cdot DG \cdot ROH - k'_{4r} \cdot MG \cdot E) + a \cdot OH \cdot (-k_9 \cdot TG + k_{10} \cdot DG)$$

$$-\frac{dMG}{dt} = b \cdot OH \cdot (-k'_4 \cdot DG \cdot ROH + k'_{4r} \cdot MG \cdot E + k'_6 \cdot MG \cdot ROH - k'_{6r} \cdot G \cdot E) + a \cdot OH \cdot (-k_{10} \cdot DG + k_{11} \cdot MG)$$

$$-\frac{dG}{dt} = b \cdot OH \cdot (-k'_6 \cdot MG \cdot ROH - k'_{6r} \cdot G \cdot E) - a \cdot OH \cdot k_{11} \cdot MG$$

$$-\frac{dROH}{dt} = \frac{dE}{dt} = a \cdot OH \cdot (k'_2 \cdot TG \cdot ROH - k'_{2r} \cdot DG \cdot E + k'_4 \cdot DG \cdot ROH - k'_{4r} \cdot MG \cdot E + k'_6 \cdot MG \cdot ROH - k'_{6r} \cdot G \cdot E - k_8 \cdot E)$$

$$-\frac{dH_2O}{dt} = \frac{dFFA}{dt} = a \cdot k_{12} \cdot FFA \cdot OH$$

$$-\frac{dOH}{dt} = \frac{dA}{dt} = b \cdot OH \cdot k_8 \cdot E + a \cdot OH \cdot (k_9 \cdot TG + k_{10} \cdot DG + k_{11} \cdot MG)$$

Equation 3.12

In above equation (eq. 3.12), k_1 to k_{12} are reaction rate constants ($Lmol^{-1}s^{-}1$).

Reaction rate constants (eq. 3.14 and eq. 3.15) have following definition

$k'_2 = k_{2*} K_1/W$ $\quad k'_{2r} = k_{2r} * K_1/(K_{3*} W$

$k'_4 = k_4 * K_1/W$ $\quad k'_{4r} = k_{4r} * K_1/(K_5 * W)$

$k'_6 = k_6 * K_1/W$ $\quad k'_{6r} = k_{6r} * K_1/(K_7 * W)$ Equation 3.14

And

$K_1 = k_1/k_{1r} = [X^-][W] / [ROH][OH^-]$

$K_2 = k_2/k_{2r} = [DG^-][E] / [TG][RO^-]$

$K_3 = k_3/k_{3r} = [DG][X^-] / [DG^-][ROH]$

$K_4 = k_4/k_{4r} = [MG^-][E] / [DG][X^-]$

$K_5 = k_5/k_{5r} = [MG][X^-] / [MG^-][ROH]$

$K_6 = k_6/k_{6r} = [G^-][E] / [MG][X^-]$

$K_7 = k_7/k_{7r} = [G][X^-] / [G^-][ROH]$ Equation 3.15

The resulting system of rate equations in the form of balance equation (eq. 3.13) is then

$1 = TG + DG + MG + G$

$ROH + E = 1$

$p = OH + A$

$p = [OH^-]_0/ [TG]_0$

$n.E + 3.TG + 2.DG + MG + A = 3$

$n = [ROH]_0/ [TG]_0$ Equation 3.13

The initial relative concentrations of the reaction components are shown in eq. 3.16.

$[TG]_o = 1$

$[ROH]_o = 1$

$[OH]_o = p$

$[DG]_o = [MG]_o = [G]_o = [E]_o = [A]_o = 0$ Equation 3.16

Assuming that all reactions have reached equilibrium, the additional equilibrium equations (eq. 3.15) is

$K_2 = k_2/k_{2r} = [DG^-][E] / [TG][RO^-]$

$K_4 = k_4/k_{4r} = [MG^-][E] / [DG][X^-]$

$K_6 = k_6/k_{6r} = [G^-][E] / [MG][X^-]$ Equation 3.15

Combining products of pairs of original equilibrium constants, Komers defined new equilibrium constants (eq. 3.17).

$K'_2 = K_2.K_3 = [DG][E] / [TG][ROH] = k'_2/k'_{2r}$

$K'_4 = K_4.K_5 = [MG][E] / [DG][ROH] = k'_4/k'_{4r}$

$K'_6 = K_6K_7 = [G][E] / [MG][ROH] = k'_6/k'_{6r}$ Equation 3.17

It directly gives values for intermediates (eq. 3.18)

$DG = K'_2 * TG * (1-E)/E$

$MG = K'_4 * DG * (1-E)/E = K'_2 * K'_4 * TG * [(1-E)/E]^2$

$G = K'_6 * MG * (1-E)/E = K'_2 * K'_4. * K'_6. * TG * [(1-E)/E]^3$ Equation 3.18

The combination of eq. 3.13 and eq. 3.15 gives the relation TG vs. E in the form of

$$TG = \left[\frac{1}{1 + K'_2 [(1-E) / E] + K'_2K'_4 [(1-E) / E]^2 + K'_2K'_4 K'_6[1+ K'_6((1-E) / E)]^3} \right] \quad \text{Equation 3.19}$$

By substitution of eq. 3.19 and eq. 3.17 in to eq. 3.13, we get the desired result for initial molar ratio of alcohol to triglyceride.

$$n = \frac{1}{E} \left[P+3 - \frac{3 + 2K'_2 [(1-E) / E] + K'_2K'_4 [(1-E) / E]^2}{1 + K'_2 [(1-E) / E] + K'_2K'_4 [(1-E) / E]^2 + K'_2K'_4 K'_6[1+ K'_6((1-E) / E)]^3} \right] \quad \text{Equation 3.20}$$

Here P represents molar ratio of hydroxide to triglyceride.

By means of eq. 3.17 to 3.19, the values of n, TG, DG, MG and G can be theoretically calculated for every chosen alkyl ester. The corresponding value of alkyl alcohol can be obtained from eq. 3.13 as ROH = 1- E.

The work by Komers puts forward an analytical expression that can be used to predict the end concentrations of products. The described kinetic analysis showed us the antagonistic effect of a majority of the reaction conditions. For example, the increase of ROH concentration increases the total reaction rate i.e. the velocity of the consumption of TG, but more in behalf of the origin of soaps. The same can be discussed about the increase of the reaction temperature [74].

3.4 Yunus Kinetic study of Triglyceride Oils

In 2010, Yunus et al. from the University Putra Malysia [77], studied the alkaline-catalyzed transesterification for biodiesel production from the Jatropha curcas oil. This is the first investigation of its kind dealing with simplified kinetics of transesterification of Jatropha curcas-based triglycerides with an alcohol catalyzed by potassium hydroxide. Experiments were carried out at 6:1 molar ratio of methanol to oil and 1 wt% KOH concentration at various temperatures. A reaction kinetic model,

based on overall reaction (eq. 3.1), was proposed to fit the experimental data. Based on the kinetic model, the rate constant and the activation energy of the reaction were determined.

3.4.1 Determination of the Rate Constant

The rate constant of the reaction can be determined based on the increased amount of the product that occurs in some reaction time interval or alternatively based on the decreased amount of the limiting reactant, i.e. triglycerides. The determination of rate constant also depends on the order of the reaction. Using experimental data, the correct order would be determined by which function of rate equation best fit the linear requirement. Once the order of reaction is established, the rate constants are then estimated from the slope of the linear plot. Based on eq. 3.1, the rate of reaction at any time t is given by the following equation (eq. 3.21) [77].

$$\text{Rate} = \frac{-\,d\,[TG]}{dt} \qquad \text{(Equation 3.21)}$$

Where, TG and t denotes the triglyceride concentration and time. However, in this study, the transesterification of Jatropha based triglycerides with methanol in the presence of potassium hydroxide as catalyst occurred very rapidly. Therefore, the intermediate reactions were considered negligible. That phenomenon was evidenced from the GC chromatograms. In addition, the use of excess methanol minimized the rate of backward reaction [77].

The best kinetics model for this study appears to be a first order model for the initial stages of the transesterification as shown in figure 3.3. In order to test these experimental data, a model was developed based on the kinetics of triglycerides hydrolysis. As discussed before, the mathematical model for this reaction was defined by ignoring the intermediate reaction of monoglycerides, so the three steps can be simplified to be two steps. The first order rate is assumed as a function of the concentration of methyl ester. The rate constant of the reaction can be determined based on the decreased amount of one reactant in certain reaction time interval [77].

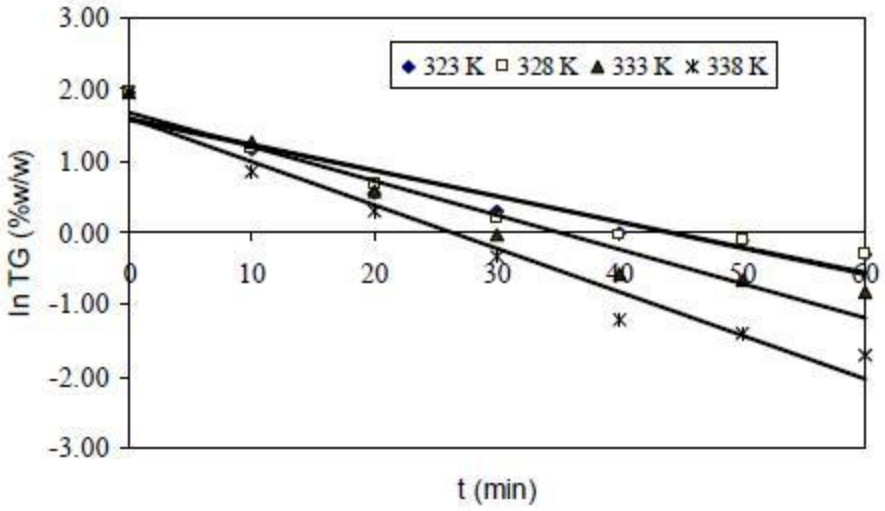


Figure 3.3: First order kinetics model for transesterification of Jatropha curcas-based triglycerides with methanol at various temperatures [77].

In this study, triglycerides are chosen as the decreased amount of one reactant. Therefore, the rate constant of the reaction can be given by eq. 3.22.

$$-\int_{TG\,0}^{TG} \frac{d(TG)}{TG} = k \int_0^t dt$$

$$k = \frac{1}{t} \ln \frac{d\,[TG\,0]}{[TG]}$$

Using logarithms base the 10:

$$k = \frac{2.303}{t} \log_{10} \frac{[TG\,0]}{[TG]} \qquad \text{Equation 3.22}$$

Where k is the overall rate constant for triglycerides, t is time of reaction and TG_0 is the initial triglycerides concentration. For the hydrolysis of triglycerides, a plot of reaction time (t) versus log (TG_0/TG) will be a straight line if the first order model (eq. 3.22) is valid. Figure 3.3 shows such plots at temperatures 323, 328, 333 and 338 K. The slope was 2.303/k with the units of $(min)^{-1}$. The values of k_{TG} and its corresponding correlation coefficient are shown in Table 3.1. In a similar study, Tapanes et al. [43] reported that the k values increases when the temperature is higher. However, if the

data is plotted in the second order model, the graph does not form a straight line. Therefore, the reaction does not match that for 2^{nd} order model. A similar calculation method is applied for determining the rate constant for diglycerides as tabulated in Table 3.2.

Table 3.1: Rate constant, K_{TG} for reaction between methanol and Jatropha curcas-based triglycerides [77].

Temperature (^{0}K)	**K_{TG} (1^{st} order)$(min)^{-1}$**	**R^2**
323	0.11	0.94
328	0.12	0.97
333	0.15	0.99
338	0.17	0.99

Table 3.2: Rate constant, K_{DG} for reaction between methanol and Jatropha curcas-based diglycerides [77].

Temperature (^{0}K)	**K_{TG} (1^{st} order)$(min)^{-1}$**	**R^2**
323	0.07	0.99
328	0.13	0.99
333	0.18	0.98
338	0.20	0.99

The rates of reaction are very sensitive to change in temperature. According to Noureddini and Zhu (1997) [71], reaction rates almost always increase with temperature for elementary irreversible reactions. Multiple and reversible reactions do occasionally exhibit an optimal temperature with respect to the yield of a desired product. Thus, indirectly, these findings show that their assumption of irreversible reaction is valid since the rate increases with temperatures (Table 3.1 and 3.2).

Rate constants for the first two reactions increase with temperature for the forward reactions. The kinetics study on rates of reaction for monoglycerides could not be performed because it occurs so fast that monoglycerides could not be detected on GC chromatogram.

3.4.2 Determination of Activation Energy $E^{\pm}$

It can be seen that the rate constant for any reaction depends on two factors: (a) the frequency of collisions between the reactant molecules, (b) the value of the activation energy. The dependency of rate constant, k on temperature follows the Arrhenius equation (eq. 3.23).

$$\log_{10}k = (-E^{\pm} / 2.303RT) + \log_{10}A \qquad \text{Equation 3.23}$$

Where T is expressed in K and R is the universal gas constant. The activation energy ($E^{\pm}$) was estimated from the slope of a plot of $\log_{10}$ k versus 1/T. In this term, k is equal to k_{TG} and k_{DG}. The frequency factor, A was determined from the y-intercept. The plot is shown in figure 3.4 for Jatropha methyl esters synthesis at 323 – 338 K. These data were used to determine the Arrhenius energy of activation. The activation energies for the transesterification reaction are comparable with other study as shown in Table 3.3.

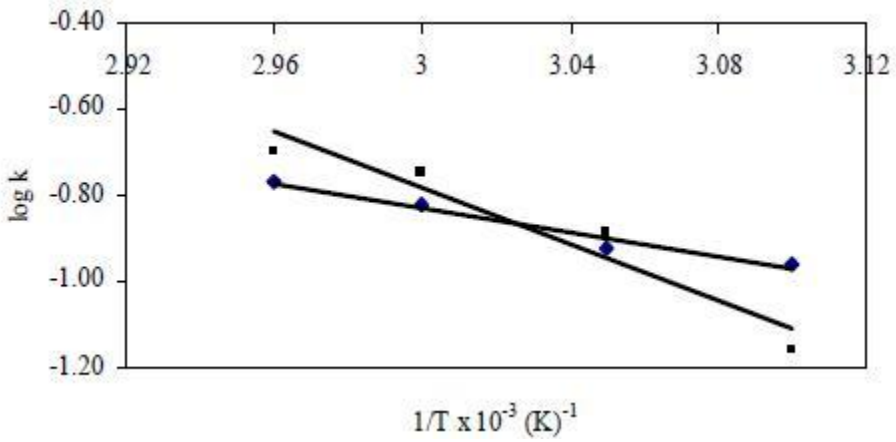


Figure 3.4: Arhenius plot showing the temperature dependency of reaction rate constants [77].

Activation energies which were determined for each step of the reaction mechanism, not considering the pre-step is common for all of the reactions. According to Tapanes et al. [77], the reaction scenario is described as follows. In the first step, the reaction passes through an initial complex and after a transition state with low activation energy forms the tetrahedral intermediate as the main product. In the next step, the tetrahedral intermediate dissociates via a second transition state with larger activation energy leads

to the methyl esters and the glycerol. This phenomenon was considered that the break of the tetrahedral intermediate to form the final product may play a key role in the base-catalyzed transesterification of triglycerides.

Table 3.3: Activation energy for transesterification of Jatropha curcas based triglycerides [77].

Reaction	$E^{\pm}$(kJmol^{-1})	$E^{\pm}$(kJmol^{-1})	R^2
TG ⟶ DG	27.38	17.53	0.97
DG ⟶ ME	46.72	42.84	0.93

Furthermore, Noureddini and Zhu, reported that normally, with multiple reactions, a high temperature favors the reaction of higher activation energy, and a low temperature favors the reaction of lower activation energy. In this study, the experimental data is comparable to other similar work. However, the transesterification of Jatropha curcas-based triglycerides in this study using potassium hydroxide as catalyst takes place at a much higher rate than the previous work caused by higher activation energy.

4 Kinetics of Triglyceride Oils

4.1 Introduction

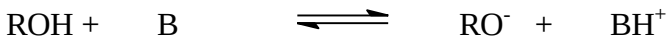
This chapter involves comparison and description of Homogenous Alkali and Acid catalyzed transesterification of triglyceride oils. It includes reaction mechanism and general catalyzed processes for both types of transesterification. Derivations for first and second order kinetics of Jatropha oil transesterification are also elaborated in this chapter. Kinetic models, reaction mechanisms and activation energies for transesterification of different triglyceride oils are presented in Appendix 9.

4.2 Homogenous Alkali Catalyzed Transesterification

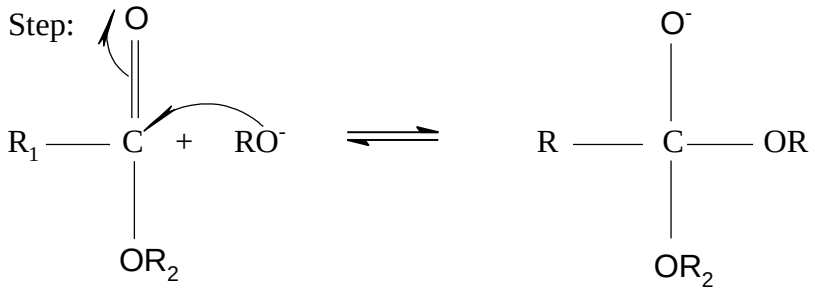
4.2.1 Reaction Mechanism

The reaction mechanism for alkali-catalyzed transesterification was formulated as three steps, as shown in figure 4.1 [79]. The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule, which results in the formation of a tetrahedral intermediate carrying a negative charge. The reaction of this intermediate with an alcohol produces the alkoxide ion in the second step. In the third step the rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride. After that, proton transfer to the diglyceride ion regenrates the catalytically active species (RO^-). This sequence is then repeated twice to yield first a monoglyceride intermediate and finally the glycerol product and biodiesel [35, 80].

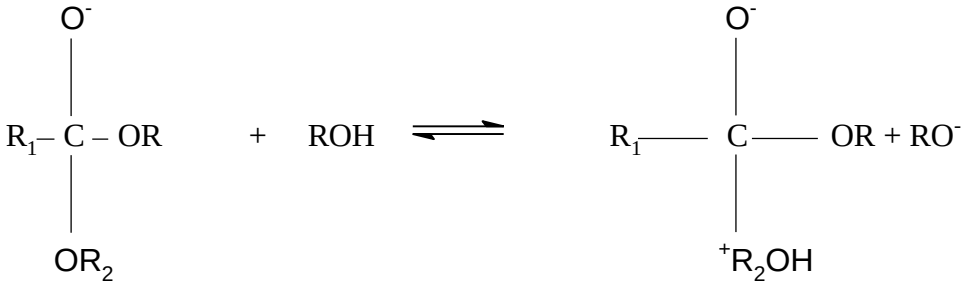
Pre-Step:



First Step:



Second Step:



Third Step:

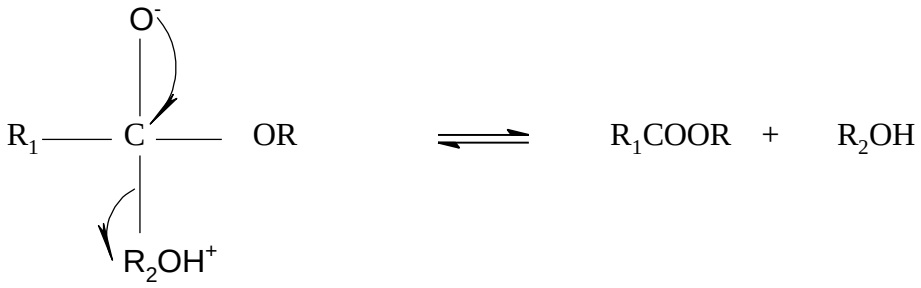


Figure 4.1: Homogeneous Alkali-catalyzed mechanism for the transesterification [81].

Where R_2 = CH_2(OCOR$_1$)–CH(OCOR$_1$)–CH_2(OCOR$_1$)

R_1 = Carbon Chain of fatty acid

R = Alkyl group of Alcohol

B = Base Catalyst

OR_2 = Leaving group

4.2.2 General Catalyzed Process

Currently, biodiesel is commonly produced using homogeneous base catalyst, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). These catalysts are commonly used in the industries due to several reasons:

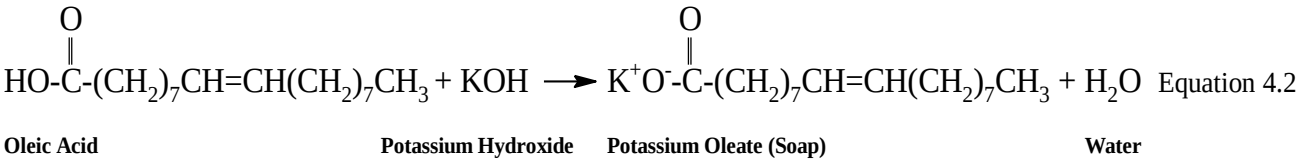
- Able to catalyze reaction at low reaction temperature and atmospheric pressure.
- High conversion can be achieved in a minimal time.
- Widely available and economical.

In fact, it was reported that the rate for base-catalyzed reaction would be 4000 times faster compared to acidic catalyst. However, the use of this catalyst is limited only for refined vegetable oil with less than 0.5 wt% FFA or acid value less than 1 mg KOH/g. Some researchers reported that base catalyst can tolerate higher content of FFA as shown in Table 4.1. Nevertheless, it is clear that the FFA content in oil feedstock should be as low as possible (ranging from less than 0.5 wt% to less than 2 wt%) for base catalyzed transesterification reaction [49].

Table 4.1: Level of FFA recommended for Homogeneous base catalyst transesterification [49].

Author/reference	**Recommended FFA (wt %)**
Ma and Hanna (1999)	< 1
Ramadhas et al. (2005)	≤ 2
Zhang et al. (2003)	< 0.5
Freedman et al. (1984)	< 1
Kumar Tiwari et al. (2007)	< 1
Sahoo et al. (2007)	≤ 2

FFA consists of long carbon chains that are disconnected from the glycerol backbone. They are sometimes called carboxylic acids. If an oil or fat containing high FFA such as oleic acid is used to produce biodiesel, the alkali catalyst will typically react with FFA to form soap; which is highly undesirable. Eq. 4.2 shows a typical reaction between FFA (oleic acid) and base catalyst (KOH). This reaction is highly undesirable because it will consume the catalyst and prevent it from the transesterification reaction. Furthermore, excessive soap in the products can drastically reduce the fatty acid methyl ester (FAME) yield and inhibit the subsequent purification process of biodiesel, including glycerol separation and water washing. Apart from that, high water content in waste cooking oil also affects the methyl ester yield. When water is present, particularly at high temperatures, it can hydrolyze triglycerides to diglycerides and form free fatty acid.



Equation 4.2

With the presence of base catalyst, the FFA will subsequently react to form soap as shown in eq. 4.2. Thus, when water is present in the reactant, it generally manifests itself through excessive soap production. Apart from that, the soaps of saturated fatty acids tend to solidify at ambient temperatures and thus a reaction mixture with excessive soap may gel-up and form a semi-solid mass which is very difficult to recover [49].

The basic process flow diagram of homogenous alkaline-catalyzed transesterification process is shown in figure 4.2 [82]. More detail about homogenous base catalyzed biodiesel processing can be studied in literature [80, 82].

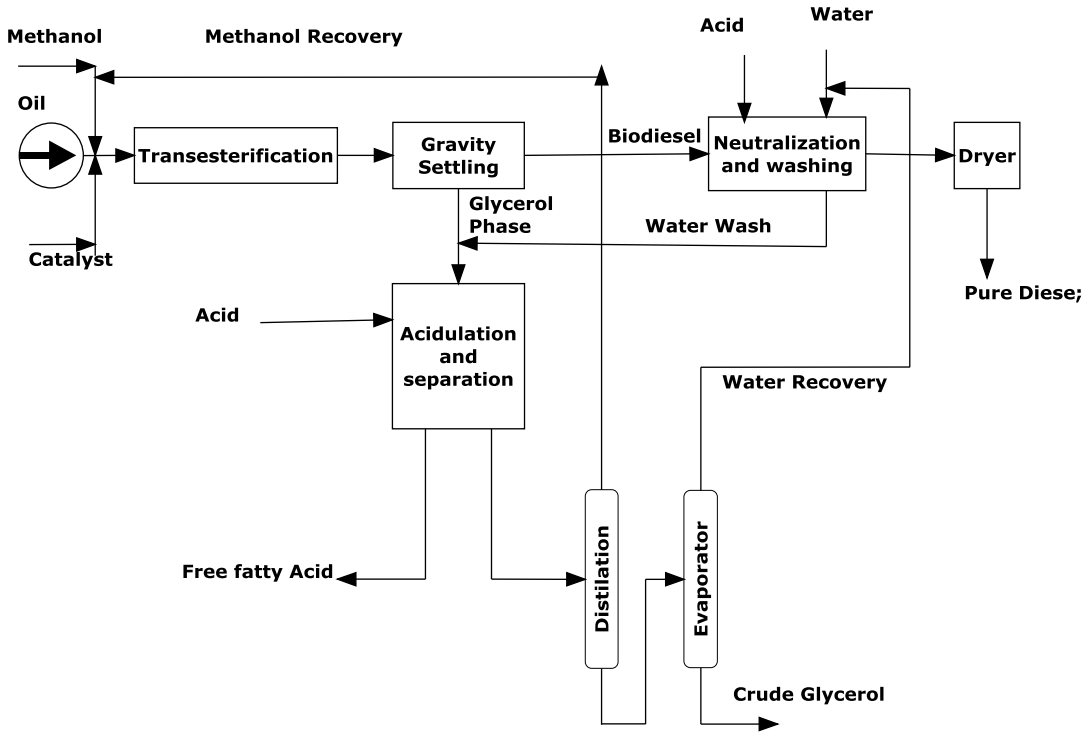


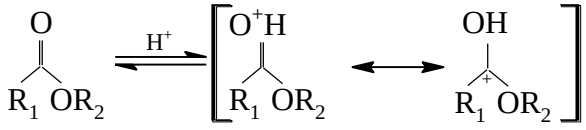
Figure 4.2: The process flow diagram of homogenous alkaline-catalyzed transesterification [82].

4.3 Homogenous Acid Catalyzed Transesterification

4.3.1 Reaction Mechanism

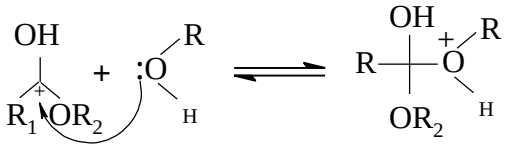
The mechanism of homogenous acid catalyzed transesterification of triglyceride oil (for a monoglyceride) is shown in figure 4.3. However, it can be extended to di- and triglycerides [81]. The sequence of steps can be summarized as follows: first, the TG carbonyl group is protonated by the acid catalyst.

a)



Second, the activated carbonyl group undergoes nucleophilic attack from an alcohol molecule, forming a tetrahedral intermediate.

b)



Third, solvent assisted proton migration gives rise to a good leaving group, promoting (fourth) the cleavage of hemiacetal species (tetrahedral intermediate) and yielding a protonated alkyl monoester and diglyceride molecule. Fifth, proton transfer regenerates the acid catalyst. This sequence is repeated twice to ultimately 3 alkyl monoesters and glycerol as products [80].

c)

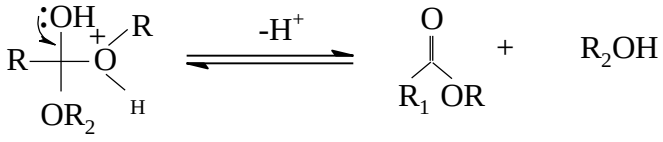


Figure 4.3 a,b,c: Homogeneous acid-catalyzed reaction mechanism for the transesterification of triglycerides.

From the figure 4.3c, it can be seen that the protonation of carbonyl group is the key step in the catalyst–reactant interaction. However, this initial chemical pathway has in turn increased the electrophilicity of the adjoining carbon atom, making it more susceptible to nucleophilic attack. In contrast, the base catalysis takes on a more direct route, at which alkoxide ion is created initially and directly acts as a strong nucleophile. As described earlier, figure 4.1 shows the mechanism of base-catalyzed reaction. This crucial different pathway (formation of electrophilic species by acid catalysis versus formation of stronger nucleophile by base catalysis) is ultimately responsible to the difference in catalytic activity in the transesterification reaction [49].

4.3.2 General Catalyzed Process

Since liquid base-catalyzed transesterification process poses a lot of problems especially for oil or fat with high FFAs concentration, liquid acid catalysts are proposed in order to overcome the limitations. To date, the most investigated catalysts for acid-catalyzed system are sulfuric acid (H_2SO_4) and hydrochloric acid (HCl). The

acid catalyzed process does not enjoy the same popularity in commercial application as its counterpart. However, Acid catalyzed transesterification holds an important advantage with respect to base-catalyzed process:

- Acid catalyst is insensitive to the presence of FFAs in the feedstock and
- Can catalyze esterification and transesterification simultaneously.

It was reported that acid catalysis is more efficient when the amount of FFA in the oil exceeds 1 wt%. In addition, economic analysis has proven that acid catalyzed procedure, being a one-step process, is more economical than the base-catalyzed process which requires an extra step to convert FFA to methyl esters. However, acid-catalyzed system is not a popular choice for commercial applications due to slower reaction rate, requirement of high reaction temperature, high molar ratio of alcohol to oil, separation of the catalyst, serious environmental and corrosion related problem [49].

It should be noted that increased water concentration affects transesterification more than it affects esterification. This is due to the presence of polar carboxylic functional groups in FFAs that allows FFAs to more easily interact with polar compunds, facilitating the alcolysis reaction [80].

Figure 4.4 show general block flow diagram for synthesis of biodiesel via acid catalyst. More detail about homogenous acid catalyzed biodiesel processing can be studied in literature [80, 83].

Literature related to Heterogenous acid catalyzed transesterification and heterogenous base catalyzed transesterification can be studied in review article [49].

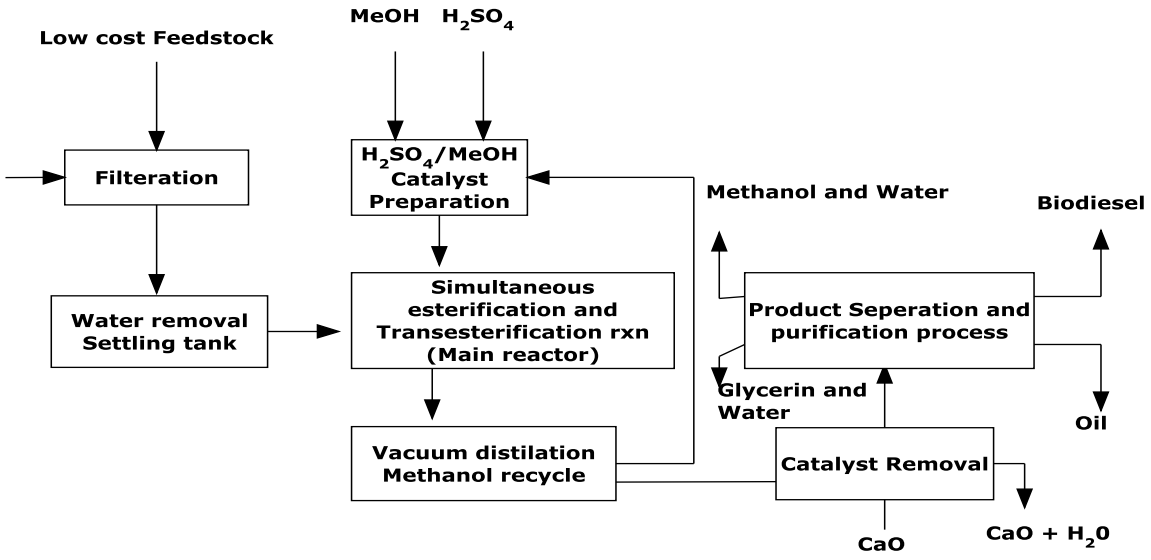


Figure 4.3: General block flow diagram for synthesis of biodiesel.

4.4 Derivation techniques for first and second order Kinetics of Jatropha Oil Transesterification

Transesterification of Jatropha oil with alcohol is multiple reactions consisting of a number of consecutive and reversible reactions as discussed in section 2.6.1 and section 3.2. Triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol as following equation (eq. 3.1 and eq. 3.2).

1) Triglyceride + Methanol $\rightleftharpoons$ Diglyceride + R_1-COO-CH_3
2) Diglyceride + Methanol $\rightleftharpoons$ Monoglyceride + R_2-COO-CH_3
3) Monoglyceride + Methanol $\rightleftharpoons$ Glycerol + R_3-COO-CH_3 Equation 3.1

Overall reaction

Triglyceride + 3 Methanol $\rightleftharpoons$ Glycerol + 3 FAME Equation 3.2

4.4.1 First order Homogenous differential equation

According to the above equation, whole transesterification results ultimately in the production of methyl ester and therefore, all the intermediate reaction products (e.g DG and MG) can be ignored and simple mathematical model expressing the whole

conversion as one step has been developed. The whole reaction is assumed to proceed as first order reaction, as a function of concentration of ME.

Rate Equation for methyl ester content:

Avrami equation also known as Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation is normally used to find out the rate equation. In this work, Avrami equation is used to find out rate equation for methyl ester content. From Avrami equation (eq. 4.1), we have

$$x_{(t)} = 1 - e^{-kt} \qquad \text{Equation 4.1}$$

Taking natural log of eq. 4.1 on both sides, we get eq. 4.2.

$$\text{Ln } x_{(t)} = \text{Ln}(1 - e^{-kt}) = \text{Ln } 1 - \text{Ln } e^{-kt} \qquad \text{Equation 4.2}$$

Taking derivative of eq. 4.2 with respect to time (t)

$$\frac{d}{dt} \text{Ln } x_{(t)} = \frac{d}{dt} [\text{ Ln } (1) - \text{Ln } e^{-kt}] \qquad \text{Equation 4.3}$$

$$\Rightarrow \quad \frac{1}{x} \frac{dx}{dt} = k \qquad \text{Equation 4.4}$$

$$\Rightarrow \quad \frac{dx}{dt} = kx \qquad \text{Equation 4.5}$$

Since we know that

$$\frac{dx}{dt} = \text{Rate} \qquad \text{Equation 4.6}$$

So we can replace x by methyl ester (ME) in eq. 4.6, thus eq. 4.5 becomes

$$\frac{d(ME)}{dt} = k\,(ME) \qquad \text{Equation 4.7}$$

$$\Rightarrow \quad \frac{d(ME)}{ME} = k\,dt \qquad \text{Equation 4.8}$$

Taking integration on both sides of eq. 4.8, we get

$$\int_{Me\,0}^{Met} \frac{d(ME)}{ME} = k \int_{Me\,0}^{Met} dt \qquad \text{Equation 4.9}$$

$$\Rightarrow \quad Ln\,(ME_t) - Ln\,(ME_0) = kt$$

$$\Rightarrow \quad k = \frac{Ln\,(ME_t) - Ln\,(ME_0)}{t} \qquad \text{Equation 4.10}$$

According to Avrami, eq. 4.10 should give us a straight line and data should fall on that line.

4.4.2 Second order Kinetics of Jatropha oil transesterification

According to the kinetic scheme in eq. 4.1 the second order kinetics obeys the following governing equations.

Case 1: With Shunt-reaction scheme

$$\frac{d[TG]}{dt} = -k_1[TG][MeOH] + k_2[DG][FAME] - k_7[TG][MeOH] + k_8[GL][FAME]^3$$

$$\frac{d[DG]}{dt} = -k_1[TG][MeOH] - k_2[DG][FAME] - k_3[DG][MeOH] + k_4[MG][FAME]$$

$$\frac{d[MG]}{dt} = k_3[DG][MeOH] - k_4[MG][FAME] - k_5[MG][MeOH] + k_6[GL][FAME]$$

$$\frac{d[GL]}{dt} = k_5[MG][MeOH] - k_6[GL][FAME] + k_7[TG][MeOH]^3 - k_8[GL][FAME]^3$$

$$\frac{d[FAME]}{dt} = k_1[TG][MeOH] - k_2[DG][FAME] + k_3[DG][MeOH] - k_4[MG][FAME] + k_5[MG][MeOH] - k_6[GL][FAME] + k_7[TG][MeOH]^3 - k_8[GL][FAME]^3$$

$$\frac{d[MeOH]}{dt} = -\frac{d[FAME]}{dt}$$

Case 2: Without Shunt-reaction scheme

For the case without shunt reaction scheme, k_7 and k_8 are set equal to zero. Since k_1 to k_8 are reaction rate constants (lit/mol.s), while [TG], [DG], [MG], [GL], [MeOH] and [FAME] are mole concentrations in a reaction mixture (mol/lit).

The differentiation of mole concentration with respect to time on left hand side of case1 equations are calculated by number of methods.

Some of the methods include

(1) Runge Kutta's method of fourth order.

(2) Three points numerical differential formulas. In this method, formulas can be used when the data points have a change in time increment.

4.5 Determination of Rate Constants

The coefficients of k_1 to k_6 (without shunt reaction) on the right side of above equations can be obtained from multiplication of experimental mole concentrations. Substitution of the differentiation of concentrations with respect to time and the coefficients of k_1 to k_6 into above equations for all measured data points and rearrangement of equations gave the system of linear equations of 6 unknowns in the following form.

$$\begin{vmatrix} a11 & a12 & a13 & a14 & a15 \\ a21 & a22 & a23 & a24 & a25 \\ a31 & a32 & a33 & a34 & a35 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ an1 & an2 & an3 & an4 & an5 \end{vmatrix} \begin{vmatrix} k1 \\ k2 \\ k3 \\ \vdots \\ kn \end{vmatrix} = \begin{vmatrix} b1 \\ b2 \\ b3 \\ \vdots \\ bn \end{vmatrix} \qquad \text{Equation 4.11}$$

Where n is equal to multiplication of number of subequations, with number of measured data points, a_{11} to a_{n5} and b_1 to b_n are the known constants obtained from experimental data.

The above system of linear equations (eq. 4.11) can be solved by various numerical techniques. However, least square regression is the best method that fits k_1 to k_6 into the experimental data. The ability of solver tool in Microsoft Excel 2007 program can be used to minimize a value of sum of error squares ($\mathcal{E}_r^2$) as shown in the following form.

$$\mathcal{E}_r^2 = \sum_{i=1}^{n} [bi - (ai1k1 + ai2k2 + ai3k3 + \cdots .. + ai6k6)]$$

To correspond with nature of reversible reactions, it is best to determine rate constants, based on constrains that k_1 to $k_6 \geq 0$.

Further literature, related to evaluation of second order kinetics mechanism and experimental results can be studied in article [84].

4.6 Determination of Rate equation for non-methyl ester content

Reaction rate equation for the reduction of triglyceride can be expressed as

$$\text{Rate} = \frac{-d\,[TG]}{dt} \qquad \text{Equation 4.12}$$

Where, [TG] refers to the content of triglyceride. Eq. 4.12 can be modified as

$$\text{Rate} = \frac{-d\,[nonME]}{dt} \qquad \text{Equation 4.13}$$

where, [nonME] refers to the content of the species excluding methyl esters and glycerol, i.e, the sum of the contents of TG, DG, MG, and FFA in the reaction mixture.

Then

$$[nonME] = 1 - [ME] \qquad \text{Equation 4.14}$$

The reaction is assumed to proceed in second order reaction as function of concentration of triglycerides and reaction temperature. As a result, the assumed reaction rate equation for transesterification reaction at temperature T can be represented as eq. 4.15:

$$\text{Rate} = \frac{-d\,[nonME]}{dt} \qquad \text{Equation 4.15}$$

By taking derivative of eq. 4.15, we get

$$\text{Rate} = k\,[nonME]^2 \qquad \text{Equation 4.16}$$

Substituting eq. 4.14 into eq. 4.16 and rearranging gives eq. 4.17.

$$\frac{d\,[ME]}{[1-[ME]]^2} = k\,dt \qquad \text{Equation 4.17}$$

Integrating of eq. 4.17 gives eq. 4.18.

$$\int_0^{Met} \frac{d(ME)}{(1-[ME]2)} = k\int_0^t dt \qquad \text{Equation 4.18}$$

$$\Rightarrow \quad 1 - \frac{1}{[1-[ME]_t]} = -kt$$

Where k = Pseudo rate constant

t = Reaction time

$[ME]_t$ = Methyl ester content at reaction time t and temperature T.

Plot of t vs $[1- 1/ (1 - [ME]_t)]$ should give us a straight line and data should fall on this line for assumed equation to be valid.

5 Kinetic studies of Jatropha Methyl Ester formation

5.1 Experimental procedure for determination of Kinetics of transesterification

Methyl esters were produced at room temperature and 40 °C by transesterification batch reactions of Jatropha oil. The batch reactions were performed with a stoichiometric molar ratio (6:1) of methanol/Jatropha oil. A 100 mL round-bottom flask was charged with 1.5 wt% KOH as catalyst and methanol (15 mL, 0.373 mol). With continuous stirring on a magnetic stir plate, the catalyst was completely dissolved in about 15 min. Once the catalyst was dissolved, Jatropha oil (60 mL, (54.80 g)) was added and the rate of stirring increased to approximate a homogeneous system. The batch reactions were performed in an oil bath (20 and 40 °C) to obtain the temperature dependent data for the reaction. The oil and alcohol/catalyst solutions were allowed to equilibrate at the desired temperature prior to mixing and initiation of the reaction.

Kinetic measurements were performed according to a procedure developed by Morgenstem et al [85]. Aliquots (1.0 mL) were removed from the batch reaction using an autopipet with disposable tips. The maximum rate of aliquot extraction was one sample every 30-60s using this method. The aliquots were immediately transferred into a test tube containing 12M HCL (2.5 µL, 0.030 mmol) and placed on ice to quench any further alcoholysis reaction in the test tube. Acetone (0.100 mL, 1.35 mmol) was added to each aliquot to serve as an internal standard for the ^{1}H-NMR analysis of concentrations present in each ten samples. For each sample, 0.100 mL acetone was mixed with 0.5 mL $CDCL_3$ and analyzed by ^{1}H-NMR.

5.2 Triglyceride Conversion and Identification of Peaks

The gross conversion of triglycerides in oil was assessed using the NMR-based method proposed by Gelbard et al [86]. The features of this method are described briefly in the following text, but more literature relevant to this method can be found in the article

[86]. NMR figure depicts A representative ^{1}H-NMR spectrum of the biodiesel sample as given in figure 5.1.

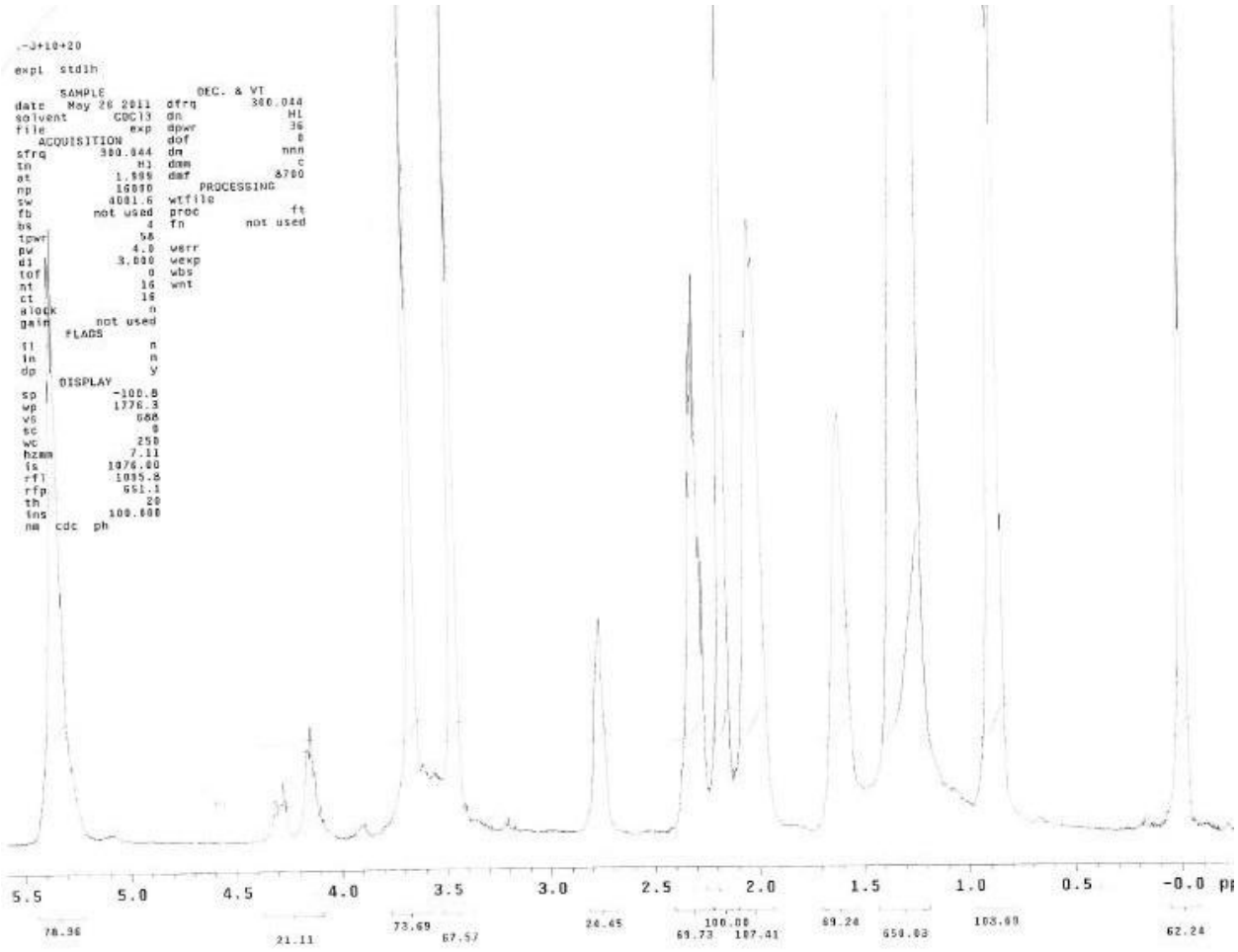


Figure 5.1: Fatty acid methyl ester from Jatropha Oil alcoholysis with methanol at 20^{o}C.

The molar ratio of methanol to oil was 6:1 for our experimental run in addition to base catalyst KOH. The signals at 4.1-4.3 ppm are caused by the protons attached to the glycerol moiety of mono-, di-, or triacylglycerols. The strong singlet at 3.6 ppm indicates methyl ester ($-CO_2CH_3$) formation. The signals at 2.3 ppm result from the protons on the CH_2 groups adjacent to the methyl or glycerol ester moieties ($-CH_2CO_2CH_3$ for methyl esters). Reference signal at 0 ppm represents $CDCl_3$ tetramethylsilane (TMS) and signal at 3.5 ppm in figure 5.1 is methanol. The ratio of

the integration value of the peak corresponding to the protons of the methylene group adjacent to the ester moiety in triglycerides to that of the protons in the alcohol moiety of the product methyl esters is used to monitor the gross yield of the transesterification reaction.

A simple equation that allows for the calculation of conversion in a transesterification from the NMR spectrum is given as follows:

$$C = 100\ (2A_{ME} / 3\ \alpha\text{-}CH_2) \qquad \text{Equation 5.1}$$

Where, C = Conversion of the triglycerides,

A_{ME} = Integration value of the protons of the methyl esters, and

$A_{\alpha\text{-}CH2}$ = Integration value of the methylene protons.

The factors 2 and 3, in eq. 5.1, are derived from the fact that the methylene carbon possesses two protons and the alcohol (methanol) carbon has three attached protons. This method, thus, enables the determination of the conversion in the transesterification reaction, without knowing the exact nature and amount of the reaction intermediates. The precision of the conversion calculated with this method, is determined by the accuracy of the integration of NMR signals [87].

For example, the percent conversion of triglyceride at 20 ^{o}C for Jatropha oil can be determined from eq. 5.1 and figure 5.1, in the following way.

In figure 5.1, Integration value of Jatropha methyl ester at 3.6 ppm is 73.69 (also mentioned in Table 5.2) and integration value of the methylene proton at 2.3 ppm is 69.73 (Table 5.2). Using the eq.5.1 to find out the percent conversion in transesterification reaction.

$$C = 100\ (2 \times 73.69 / 3 \times 69.73)$$

$$= 70\%$$

Thus at room temperature (20 ^{o}C), a low conversion of 70% was found with Jatropha curcas oil. Table 5.1 and 5.2 represents the integration values of Peaks that are measured for various samples at different temperatures. These integration values are not good enough. NMR-Spectrums, for starting material, intermediate and final product, are provided in Appendix 2 to 7.

Table 5.1: Integration values for NMR-Spectrum at 40^{o}C

S.Number	**Temprature 40^{o}C**		
	Methyl ester Signal	Methanol Signal	Methylene proton signal
1	9.32	143.69	58.07
2	55.94	101.67	62.35
3	38.28	85.58	53.25
4	49.31	101.14	60.89
5	52.01	116.23	45.48
6	38.87	62.15	39.08
7	130.33	91.03	123.18
8	57.3	75.11	22.52
9	47.64	26.46	18.63
10	40.02	39.34	10.29

Table 5.2: Integration values for NMR-Spectrum at 20^{o}C

S.Number	**Temprature 20^{o}C**		
	Methyl ester Signal	Methanol Signal	Methylene proton signal
1	1.6	60.07	71.37
2	3.42	106.74	99.87
3	8.52	95.19	74.63
4	8.18	101.43	85.85
5	36.21	74.9	56.85
6	18.39	64.58	37.32
7	30.65	98.03	60.55
8	57.04	77.61	79.95
9	112.61	84.78	68.45
10	73.69	67.57	69.73

5.3 Analysis of Jatropha Methyl Ester (JME)

Jatropha methyl ester was analyzed using NMR under two different temperatures. Results for these different transesterification conditions are shown in Appendix 2 to 7. The presence of triglyceride was found at shift value of 4.21 ppm as shown in appendix 2 and 5. A new peak was observed after expected reaction time, at shift value 3.67 ppm (Appendix 4), showing the presence of methyl ester formed during the reaction process. No traces of triglyceride group were observed in the final product of JME (Appendix 4). The glycerol product is not observed in the ^{1}H-NMR analysis because of insolubility in the system. This confirms the complete conversion of Jatropha oil into Jatropha methyl ester. Furthermore, Appendix 2 to 7 suggests fast formation of methyl ester product as compared to glyceride consumption. The major differences between the ^{1}H-NMR spectra of the starting Jatropha oil (Appendix 2) and the resulting fatty acid methyl ester (Appendix 5) are the disappearance of the glyceride protons at 4.21 ppm (4H) and the appearance of the methyl ester protons at 3.67 ppm (3H).

5.4 Calculations and Results

5.4.1 Calculations for Ester Concentration

The kinetics of the homogenous alkali-catalyzed transesterification reaction between methanol and Jatropha oil, in a 6:1 molar ratio was studied by ^{1}H-NMR at temperatures of 20 and 40^{o}C. Table 5.1 and Table 5.2 represent ester concentration for all samples at different temperatures with varying time period. Concentration of esters is calculated as an example for sample number 10 at 20 ^{o}C. Figure 5.1, Table 5.2 and the following data provides the basis for calculation of esters concentration example.

Volume of methanol	=	15 mL
Volume of Jatropha Oil	=	60 mL
Molar mass of methanol	=	32.04 g/mol
Density of methanol	=	0.791 g/mL

Based on above data, amount of methanol, total concentration of methanol is calculated in the following way.

$$\text{Amount of methanol} = \frac{\text{Volume of methanol} \times \text{Density of methanol}}{\text{Molar mass of methanol}}$$

$$= \frac{15 \text{ mL} \times 0.791 \text{ g/mL}}{32.04 \text{ g/mol}} = 0.3703 \text{ mol}$$

$$\text{Total concentration of methanol} = \frac{\text{Amount of methanol}}{\text{Volume of methanol} \times \text{Volume of Jatropha oil}}$$

$$= \frac{0.3703 \text{ mol} \times 1000 \text{ mL/mol}}{(15 \text{ mL} + 60 \text{ mL})} = 4.9376 \text{ M}$$

$$\text{Concentration of Ester} = \frac{\text{Methyl ester value} \times \text{Total concentration of methanol}}{\text{Methyl ester signal value} \times \text{Methanol signal value}}$$

$$= \frac{(73.69)}{(73.69 + 67.57)} \times 4.9376 \text{ M} = 2.58 \text{ M}$$

Thus the initial concentration of ester for sample number 10 at 20 ^{o}C is 2.58 M. Integration values for methyl ester and methanol are taken from Table 5.2 Calculations for ester concentration remain same for rest of sample, only the integration values for methyl ester and methanol varies with corresponding peaks respectively.

Table 5.1: Ester Concentration during kinetic runs from methanol peaks at 40^{o}C.

Sample Number	Time (Seconds)	Conc. of Esters (mol/lit)
1	30	0.30
2	60	1.75
3	90	1.53
4	120	1.62
5	180	1.53
6	240	1.90
7	330	2.91
8	420	2.14

9	540	3.17
10	720	2.49

Table 5.2: Ester Concentrations during kinetic runs from methanol peaks at 20^{o}C.

Sample Number	Time (Seconds)	Conc. of Ester(mol/lit)
1	30	0.13
2	60	0.15
3	90	0.41
4	120	0.37
5	180	1.61
6	300	1.09
7	420	1.18
8	540	2.09
9	720	2.82
10	900	2.58

5.4.2 Determination of Rate constants from Kinetic data

Methyl ester initial rates were calculated based on Table 5.1 and Table 5.2. Kinetic plots for the reaction at 40 ^{o}C and 20 ^{o}C are presented in figure 5.2 and figure 5.3.

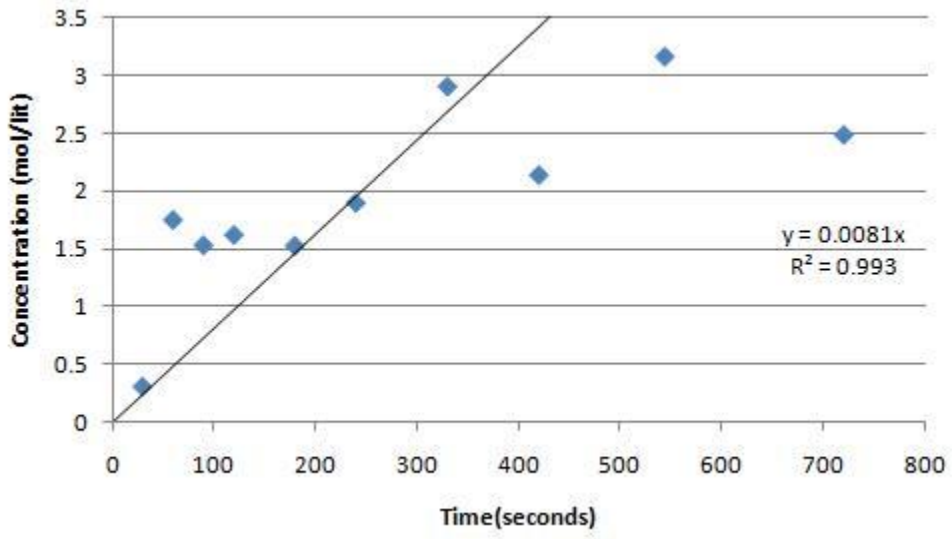


Figure 5.2: Kinetic plots of the KOH-catalyzed methanolysis of Jatropha Oil at 40^{o}C.

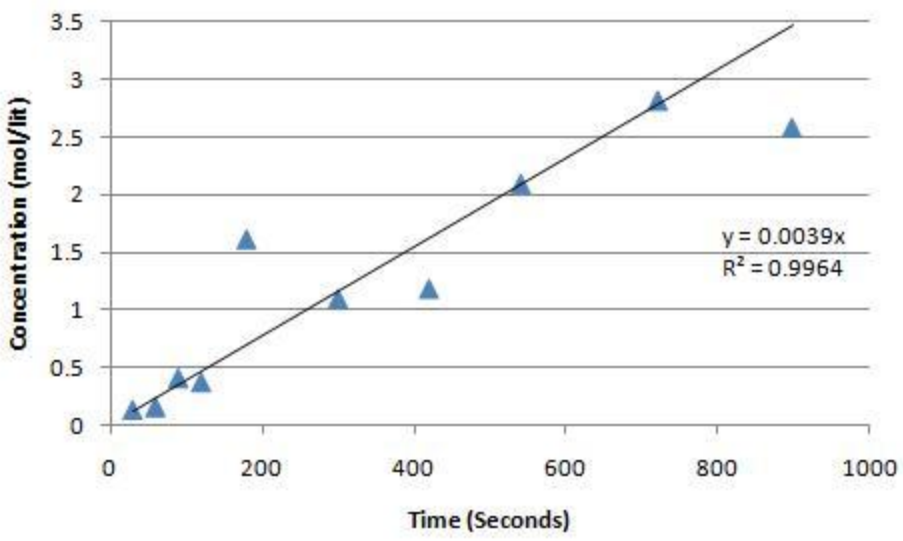


Figure 5.3: Kinetic plots of the KOH-catalyzed methanolysis of Jatropha Oil at 20^{o}C.

These plots show the development of rate of change of concentration with time t. The trend line shows the rate we want and we picked out only those signals that follow the linear region and regression among these. Those data points which are after the linear range are not used in calculations.

Analogous kinetic data using KOH as the catalyst provides the initial rates for methyl ester formation at several temperatures and are presented in Table 5.3 and 5.4. Table 5.3 represents our KOH values for initial rate of methyl ester and Table 5.4 represents article values [85] for methyl ester formation using NaOH as the catalyst.

Table 5.3: Methyl ester initial rate obtained by ^{1}H-NMR Analysis

Temprature (^{o}C)	**Methyl ester Initial rate (M/s)**
10*	2.7 x 10^{-3}
20	3.8 x 10^{-3}
40	6.1 x 10^{-3}

* Methyl ester initial rate for 10^{o}C in Table 5.3, was taken from literature [85].

Table 5.4: Temperature dependence of initial rates of methyl ester formation obtained by ^{1}H-NMR Analysis [85].

Temprature (^{o}C)	Methyl ester Initial rate (M/s)
10	6.4×10^{-3}
35	1.6×10^{-2}
45	2.3×10^{-2}

5.4.3 Determination of Activation Energy by Arrhenius Plot

Arrhenius plot is used to obtain the activation energy for the methanolysis of Jatropha oil using the KOH and NaOH catalyst. Figure 5.4 shows the Arrhenius plot, of the initial rates presented in Table 5.3 and Table 5.4.

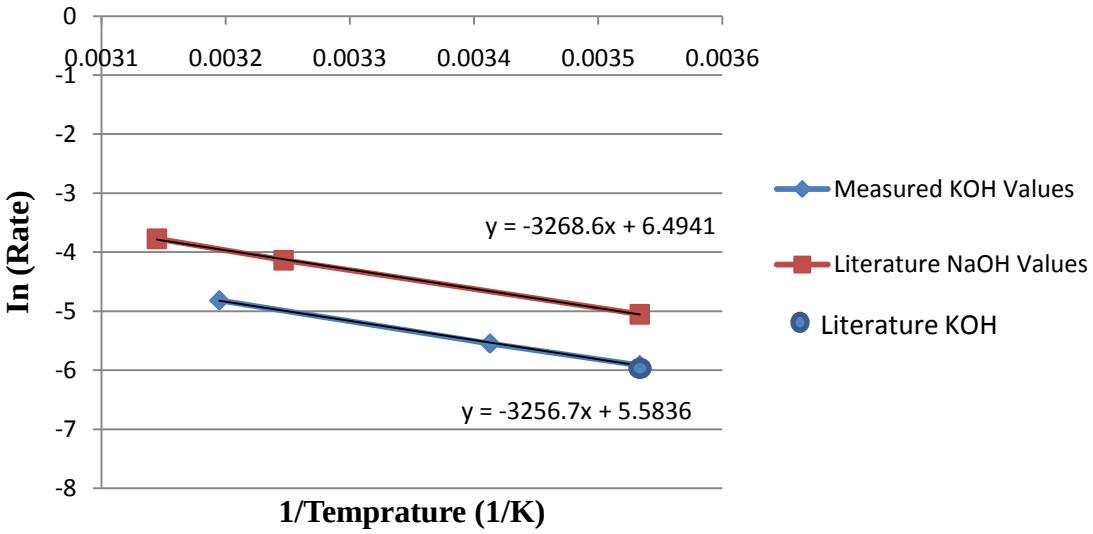


Figure 5.4: Arrhenius plot of data sets presented in Table 5.3 and Table 5.4.

This plot is based on both literature values and data set based on our experiments. The encircled data point is literature value for KOH taken from the article [85]. By plotting the article results and my results in the same plot, we get an excellent linear fit (R^2 = 0.99) for both plots.

An activation energy value of 27.2 kJ/mol was obtained from the slope of the plot according to the eq. 3.4 as shown below:

$$\text{Ln } k = -E_a/RT + C \qquad \text{Equation 3.4}$$

In this equation, R is the gas constant (8.31 $Jmol^{-1}K^{-1}$), T is the absolute temperature (in Kelvin), and C is a constant. In above equation, –Ea/RT represents slope.

$$\text{Slope} = \frac{-Ea}{RT} \qquad \text{Equation 5.2}$$

By simple plotation in Microsoft Excel, as shown in figure 5.4, values of slope and equation of slope can be calculated.

$$\text{Slope} = -3256.7x + 5.5836 \qquad \text{Equation 5.3}$$

$$\text{Slope} = -3256.74$$

Hence, Activation Energy (E_a) can be easily calculated from both eq. 5.2 and eq. 5.3.

$$Ea = 3256.74\ (8.314/100)$$

$$= 27.2\ \frac{kJ}{mol.K}$$

This value of activation energy, obtained using ^{1}H-NMR analysis, agree with the results reported by Yunus (section 3.4.2) and Morgenstern et al [85] using GC analysis of Jatropha oil transesterification reaction.

6 Conclusion

Literature Overview Conclusion:

This thesis summarized most important literature related to kinetic models, its development and the main ways it is done. Kinetic experiments were made according to literature procedure and its results fit with literature data. Future research directions for further study are indicated in recommendations.

Experimental Conclusion:

The Jatropha methyl ester production investigation via the kinetics study of transesterification of Jatropha based triglycerides, was successfully performed. Experiments were carried out at 6:1 molar ratio of methanol to JCO and 1.5 wt% KOH concentration at two different temperatures (20 ^{o}C and 40 ^{o}C). In this study, NMR-Spectroscopy provided an appropriate method for analyzing FAME in biodiesel product. The preparation methods for the samples have been established and analyses of triglyceride conversion yield of ester and kinetic plots have been demonstrated. Our results indicated that the homogenous alkaline catalyzed transesterification reaction took place relatively fast. The homogenous alkaline catalyzed reactions proved to be efficient and cheap, but the nature of the catalyst may limit any future use.

7 Recommendations

This thesis has extensively studied the literature related to kinetics of biodiesel production from triglyceride oils. Some issues still need to be addressed in the future as outlined below.

Published papers suggested that there are few studies reported on transesterification of triglyceride oils containing high free fatty acids. There is need to investigate an appropriate method for the transesterification of such triglyceride oils based on its properties. It can be done by properly analyzing the variables that affect the transesterification process and appropriate catalyst.

We performed experiments on Jatropha curcas oil containing high free fatty acid. Literature suggests that FFA content of triglyceride oils less than 1% is recommended for homogenous alkaline catalyst due to saponification possibility. Our parallel study in group showed that for Jatropha oil with 3% FFA content, the yield of ester formed was 83%. This yield was low because of significant amount of FFA that could not be transesterified by KOH catalyst completely into esters but to side product soap. The problem of FFA can be solved effectively by acid esterification and base transesterification process approach. Recently, researchers recommend this two stage process, an acid pretreatment process to convert FFA in Jatropha oil to esters, followed by alkali base-catalyzed transesterification process. Therefore, it is highly recommended for future experiments.

An efficient kinetic model could also be determined by technique of quantitatively measuring the content of the intermediates in ester product mixture. Some inconsistent results did not allow us to study properly the effect of various variables. Therefore, the experimental works on the kinetics study should be continued.

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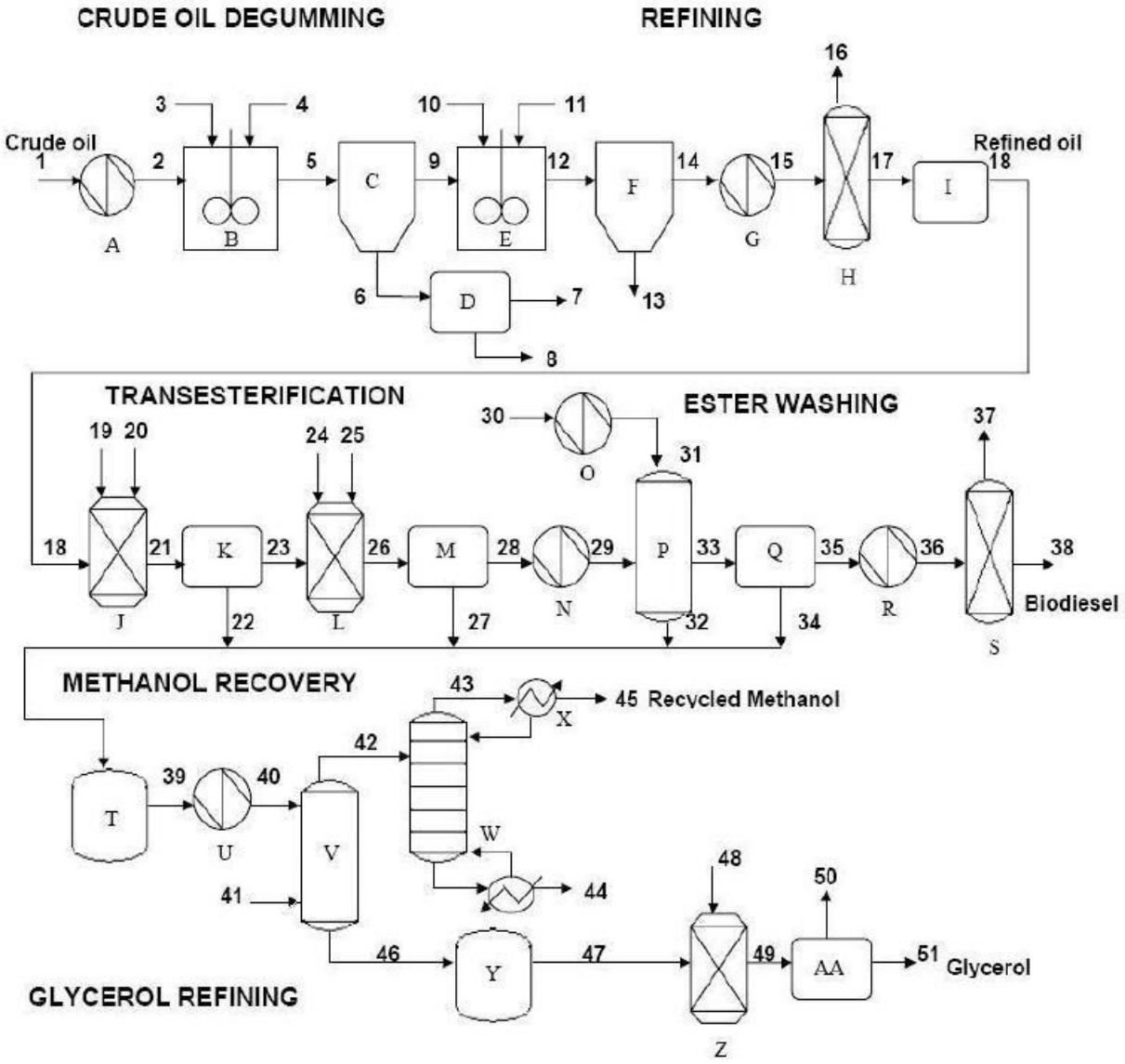
Appendices

Appendix 1

Continuous-based catalyzed biodiesel production process [34].

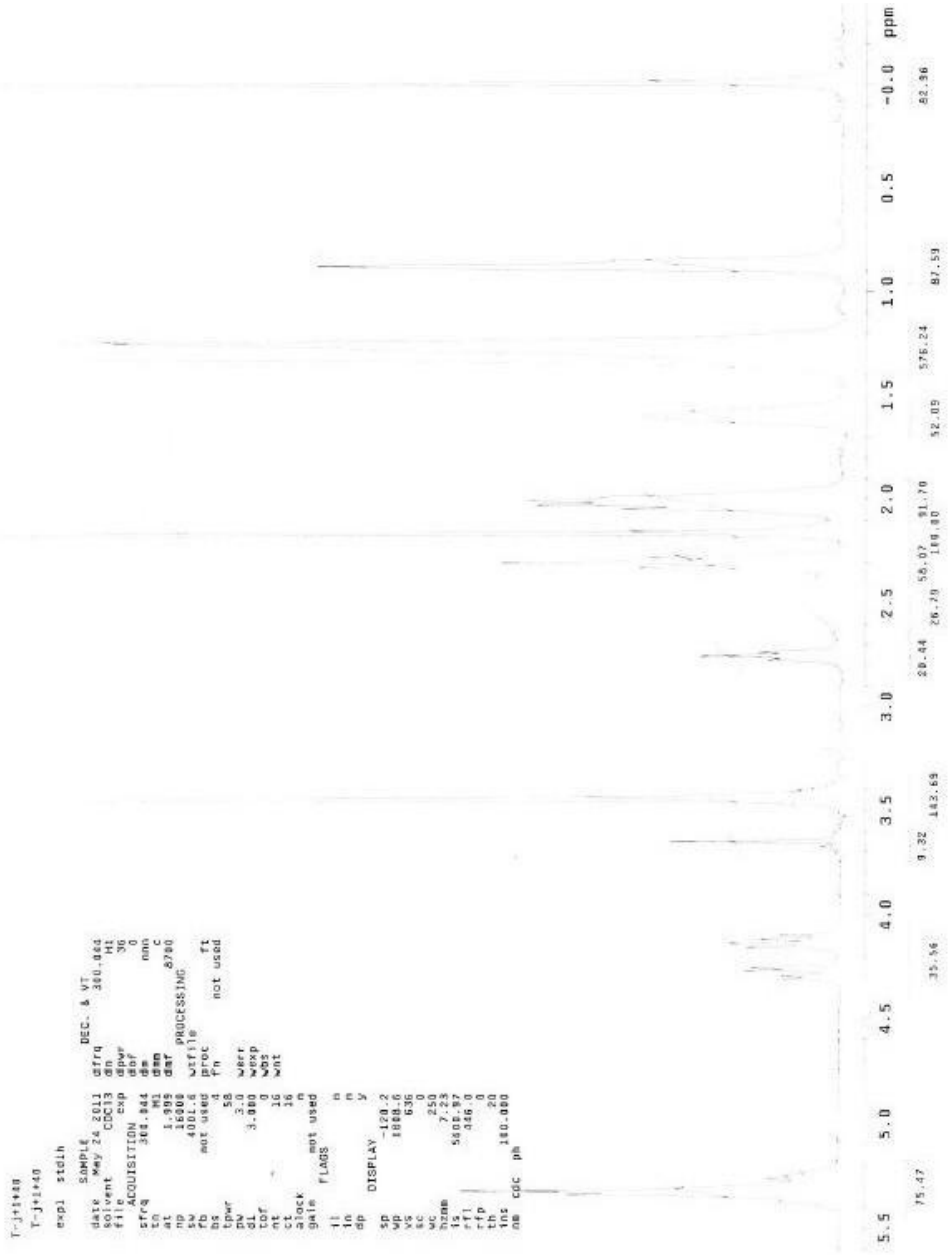


Continuous base-catalyzed biodiesel production process, used for model development. Equipment: (A) heater, (B) mixing tank, (C) centrifuge, (D) gums/water separator, (E) refining tank, (F) centrifuge, (G) heater, (H) vacuum oil dryer, (I) surge tank, (J) continuous stirred tank reactor (CSTR) 1, (K) decanter 1, (L) CSTR 2, (M) decanter 2, (N) heater, (O) heater, (P) wash columns, (Q) settler tank, (R) heater, (S) vacuum ester dryer, (T) collecting tank, (U) heater, (V) glycerol-alcohol stripper, (W) distillation column/reboiler, (X) reflux condenser, (Y) glycerol hold tank, (Z) acidulation reactor, and (AA) decanter. Streams: (1) crude oil, (2) heated crude oil, (3) phosphoric acid, (4) soft water, (5) mixing tank outstream, (6) gums-water mix, (7) gums, (8) water, (9) degummed oil, (10) NaOH solution, (11) wash water, (12) refining tank outstream, (13) soapstock, (14) centrifuge outstream, (15) heater outstream, (16) water vapor, (17) hot oil,

(18) refined oil, (19) sodium methoxide, (20) methanol, (21) CSTR 1 outstream, (22) glycerol phase, (23) ester phase, (24) sodium methoxide, (25) methanol, (26) CSTR 2 outstream, (27) glycerol phase, (28) ester phase, (29) heater outstream, (30) soft water, (31) heated wash water, (32) waste stream, (33) washed esters, (34) aqueous phase, (35) esters, (36) heated esters, (37) water vapor, (38) biodiesel, (39) glycerol/aqueous phase, (40) heater outstream, (41) super heated steam, (42) saturated methanol vapors and saturated steam, (43) methanol vapor, (44) distillation column bottoms, (45) recycled methanol, (46) hot glycerol solution, (47) glycerine, (48) HCl solution, (49) acidulation reactor outstream, (50) waste, and (51) product glycerol.

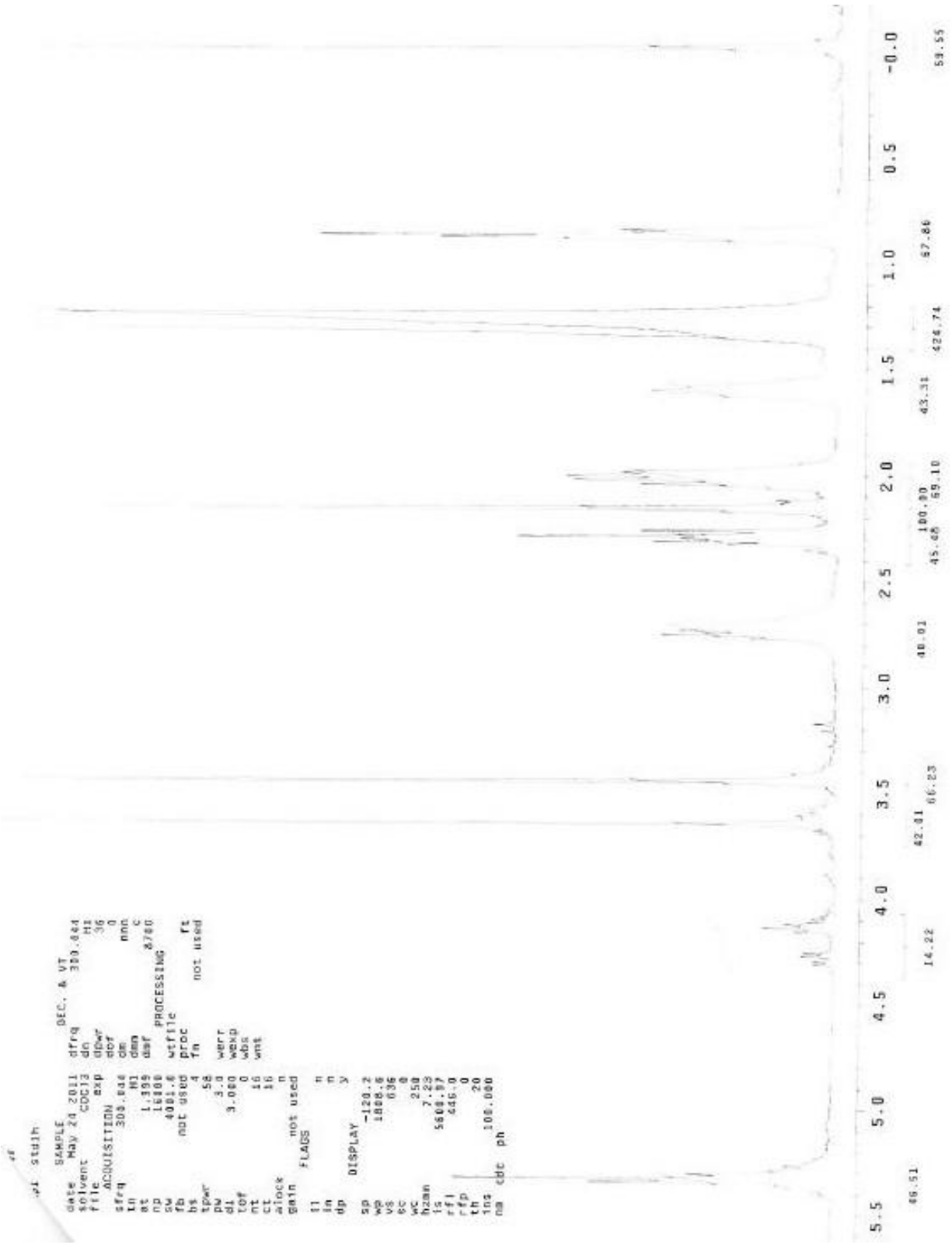
Appendix 2

NMR Spectra of FAME: starting material sample spectra at 40 ^{o}C.



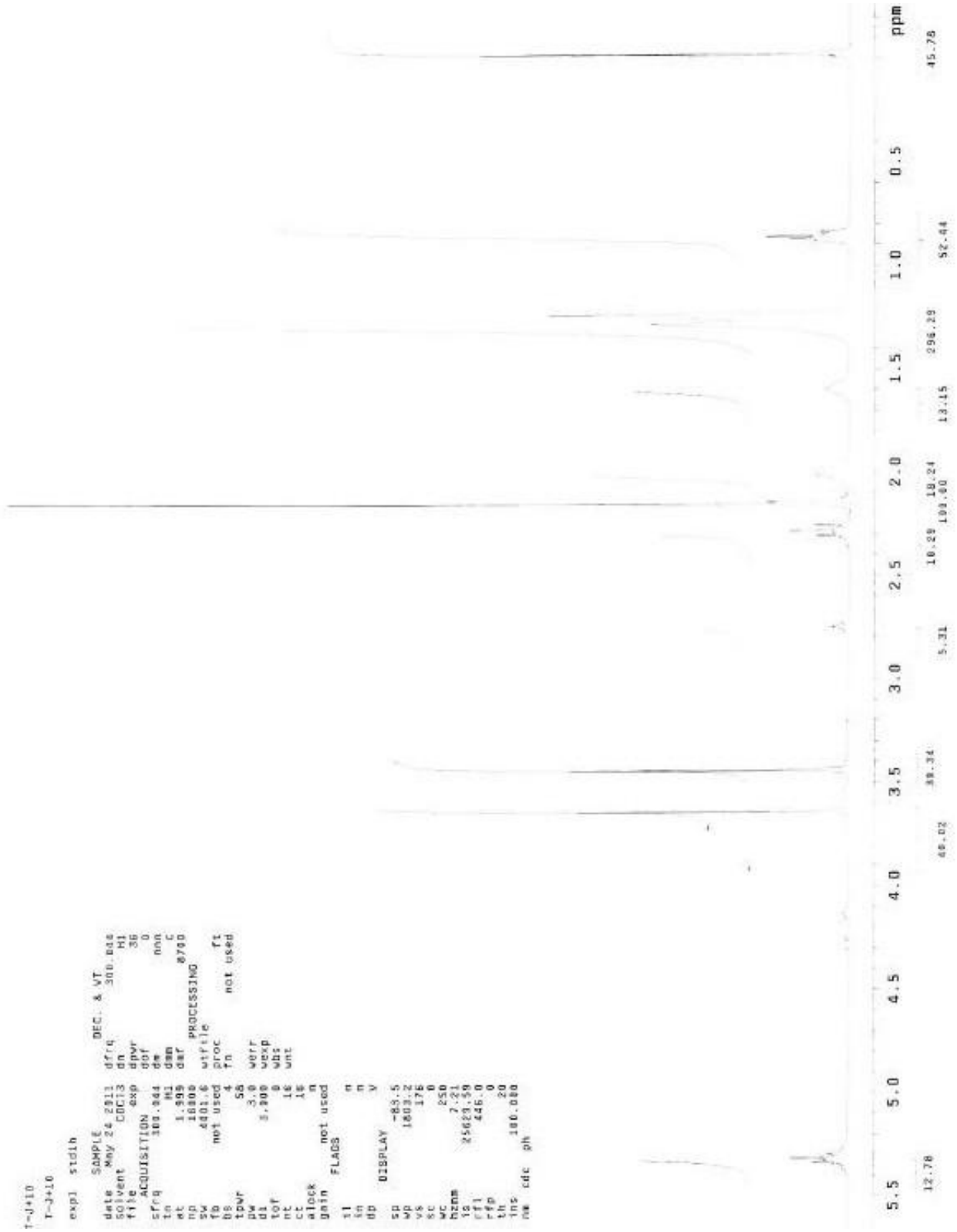
Appendix 3

NMR Spectra of FAME: intermediate sample spectra at 40 ^{o}C.



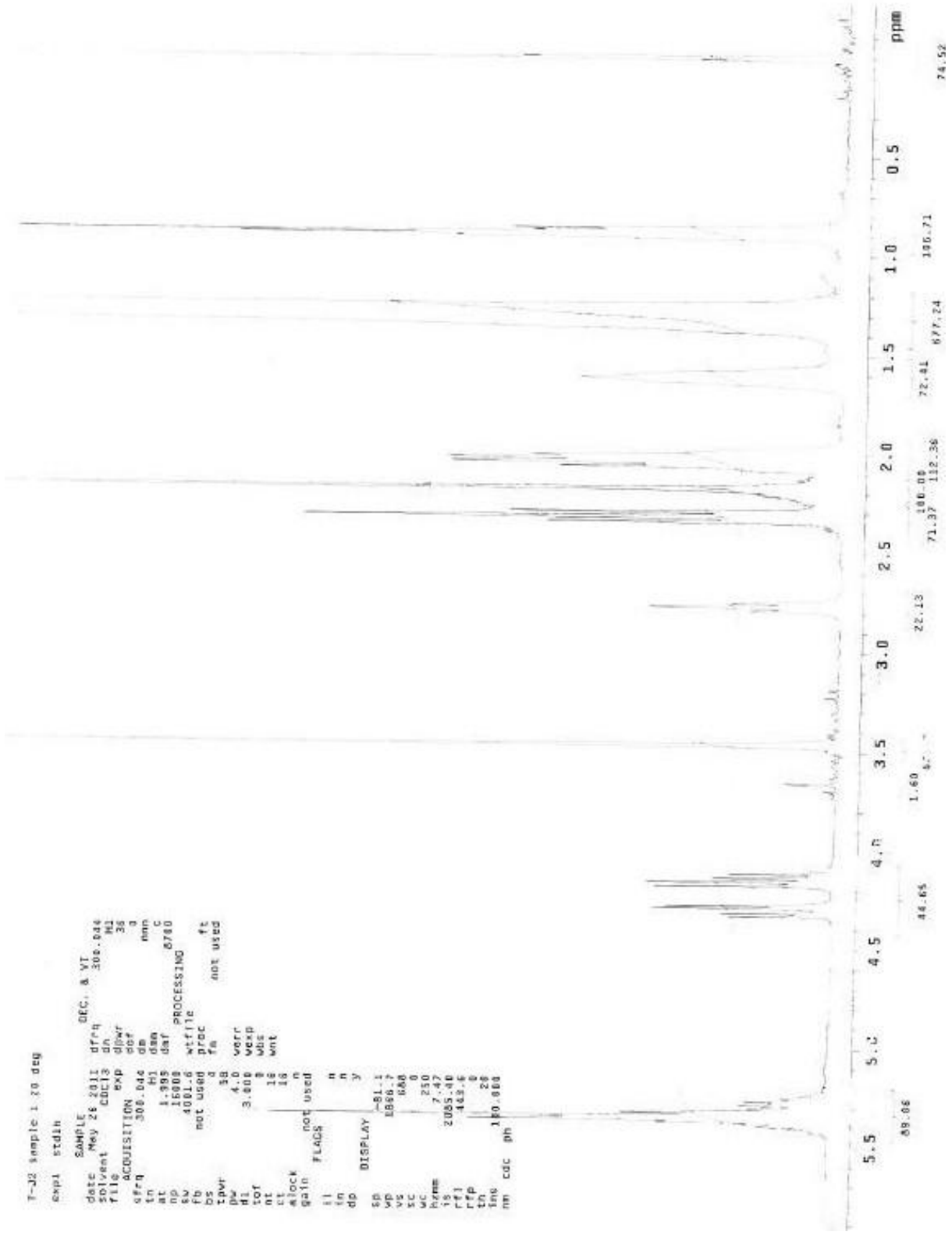
Appendix 4

NMR Spectra of FAME: final product sample spectra at 40 ^{o}C.



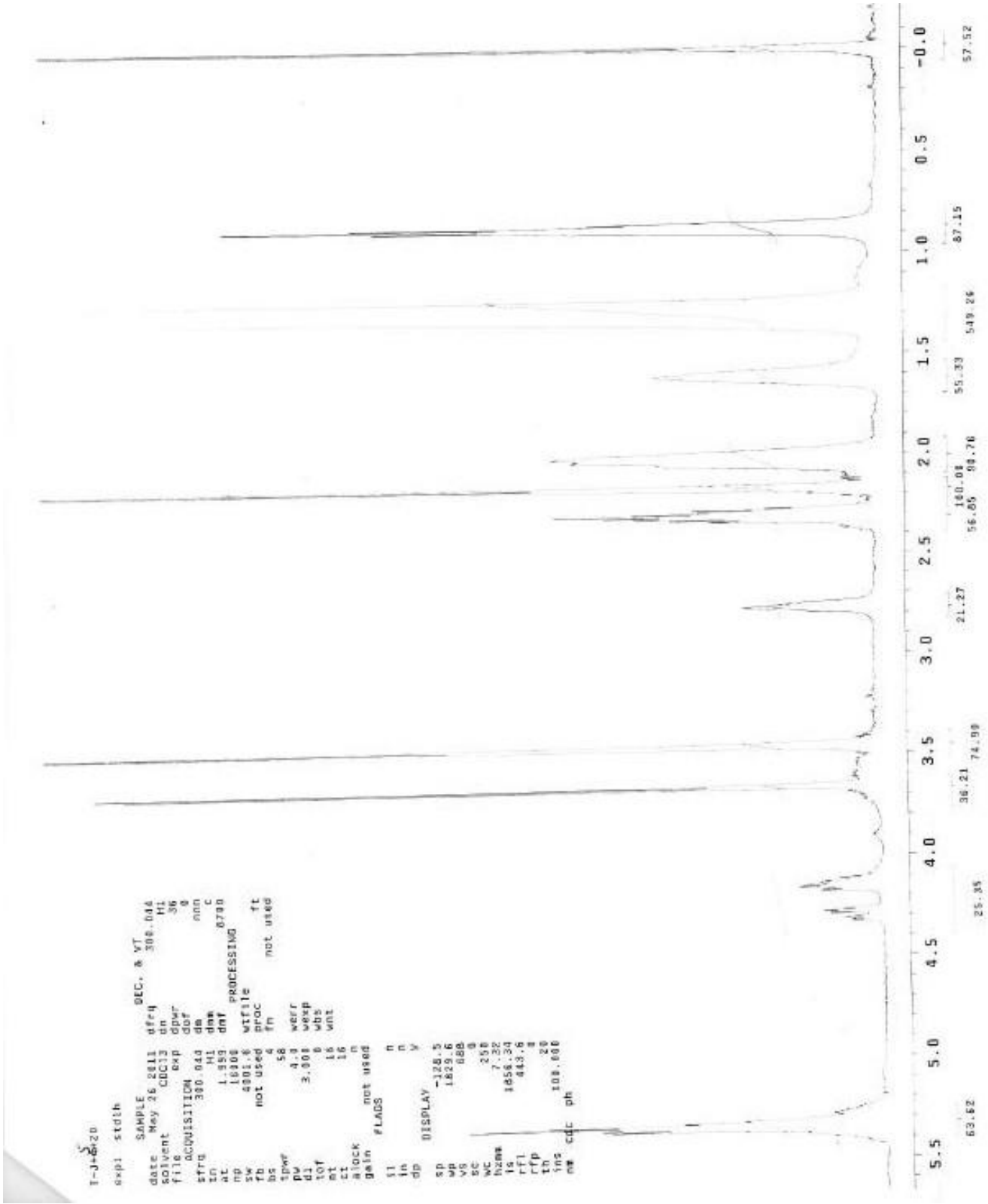
Appendix 5

NMR Spectra of FAME: starting material sample spectra at 20 ^{o}C.



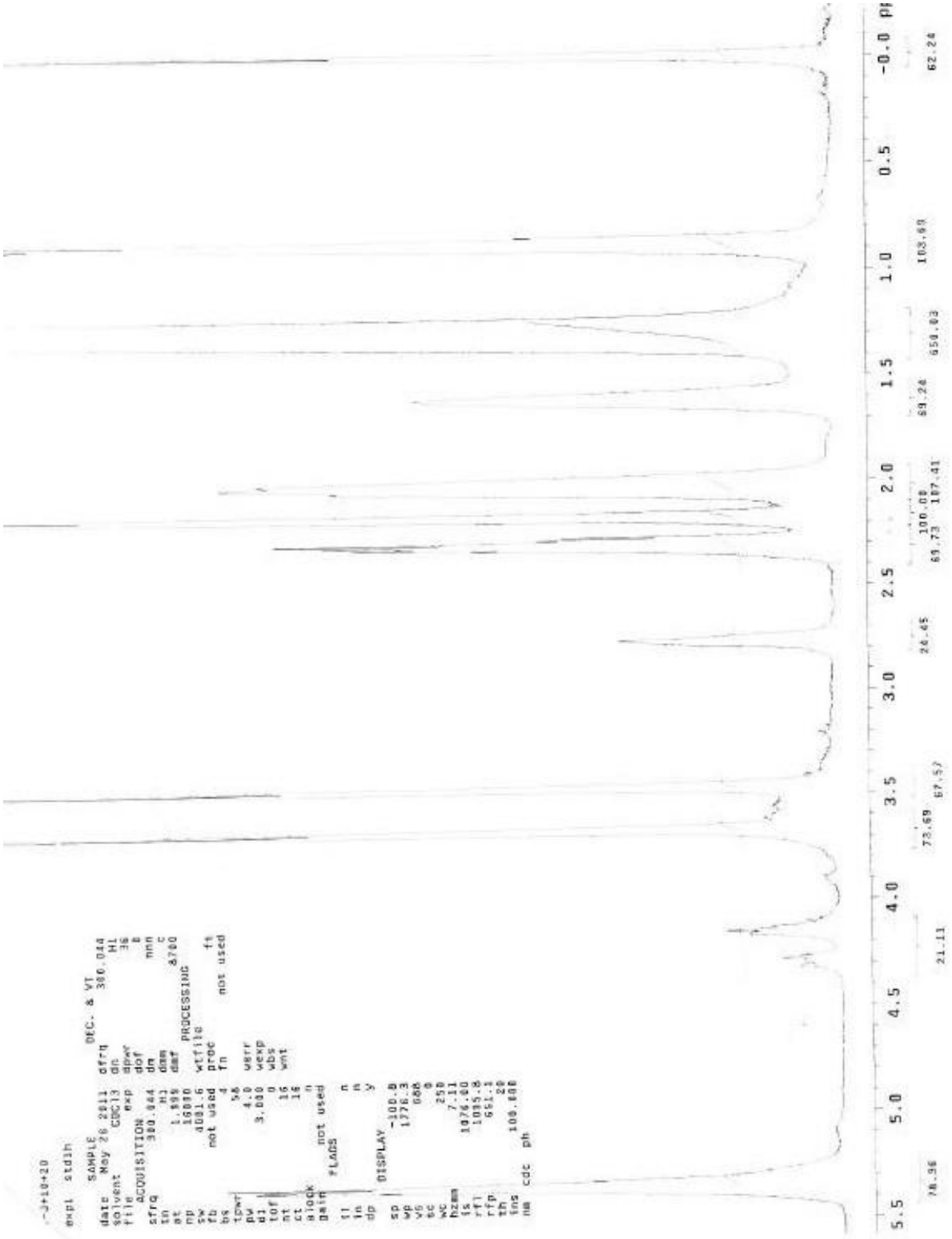
Appendix 6

NMR Spectra of FAME: intermediate sample spectra at 20 ^{o}C.



Appendix 7

NMR Spectra of FAME: final product sample spectra at 20 ^{o}C.



Appendix 8

A: An overview of Jatropha Methyl Ester production by various researchers using Homogenous Catalyst treatment. [43, 88-96]

No.	Alcohol	FFA in Oil	Ratio of Alcohol/Oil	Number of steps of Process*	Type of Catalyst	Catalyst Conc.
1.	Methanol	3.09%	20 wt%	Single step	NaOH	1 wt%
2.	Methanol Ethanol	N/A	9:1 mol	Single step	$NaOCH_3$	0.8 wt%
3.	Methanol	14.9%	70 wt%	Single step	NaOH	3.3 wt%
			1) 60 wt%	Double steps	1)H_2SO_4	1)1 wt%
			2) 24 wt%		2) NaOH	2)1.4wt%
4.	Methanol	14%	1) 0.28 v/v	Double steps	1) H_2SO_4	1)1.43% v/v
			2) 0.16 v/v		2) KOH	2)0.55% wt/v
5.	Ethanol	0.29 -- 1.27%	6.90 : 1.14 mol	Double steps	1) KOH	1) 1.5wt%
					2) H_2SO_4	2) 2 wt%
6.	Methanol	N/A	3:1 mol	N/A	NaOH/ KOH	1 wt%
7.	Methanol	44%	1) 0.20v/v	Double steps	1) H_2SO_4	1) 2 wt%
			2) 0.40v/v		2) KOH	2) 0.3 wt%
8.	Methanol	N/A	1) 0.20v/v	Double steps	1) HCl	1) 1 wt%
			2) 0.10v/v		2) NaOH	2) 0.5 wt%

*Single Step: Alkali-Transesterification; Double Steps: 1) Alkali-Transesterification 2) Acid Transesterification

B: An overview of Jatropha Methyl Ester production by various researchers using Homogenous Catalyst treatment. [43, 88-96]

No	Alcohol	Alcohol Vol. [mL]	Catalyst Weight [g]	Rxn temp. [^{o}C]	Time [min]	Stirring	Yield (%)	Ref.
1.	Methanol	299	9	60	90	Stirring	98	88, 89, 96
2.	Methanol	364	7.2	45^{o}C	30	300rpm	96	43, 89
	Ethanol	525			45			
3.	Methanol	796	29.7	65 ^{o}C	120	400rpm	55	90, 89
		955	1) 9 2) 12.6	50 ^{o}C	1) 60 2) 120		90	
4.	Methanol	955	1) 12.87 2) 5.3	60^{o}C	1) 88 2) 24	N/A	99	91, 89
5.	Ethanol	353	1) 13.5 2) 18	1) 75^{o}C 2) 80^{o}C	1) 90 2)360	Stirring	88	92, 89
6.	Methanol	N/A	N/A	N/A	120-240	Stirring	N/A	93, 89
7.	Methanol	N/A	N/A	60 ^{o}C	90	N/A	N/A	88,94, 89
8.	Methanol	N/A	N/A	60 ^{o}C	1) 42 2) 30	N/A	N/A	95, 89

Appendix 9

A: Kinetic models and activation energies for transesterification of vegetable oils. [97, 98, 99]

A: Kinetic models and activation energies for transesterification of vegetable oils. [97, 98, 99]

Oil Source	Alcohol	Catalyst/ quantity (% of oil)	MR	T (°C)	Reaction mechanism and kinetics model	Activation energy (kj/mol)
Palm	Methanol	KOH 1.0%	6:1	55-65	Three consecutive reversible reactions; second order.	26.8-61.5
		NaOH 0.2%			Three sequential reversible reactions and shunt (overall) reaction; second order	R_f=68.65 R_f= 56.93
Soybean	Butanol	NaOBu 0.5 and 1%	30:1	20-60	Three consecutive reversible reactions; pseudo-first order forward and second order reverse reactions.	46.9-72.0
		NaOBu 1.0%	6:1		Three consecutive reversible reactions; second order.	34.2-71.5
	Methanol	$NaOCH_3$ 0.5%	6:1	20-60	Combination of consecutive and shunt reactions; second and forth order for consecutive and shunt reactions, respectively.	56.8-83.8
		NaOH 0.2%	6:1	30-70	Three consecutive reversible reactions; second order.	21.7-83.1
Brassica	Methanol	KOH 0.5-1.5%	6:1	25-65	Three consecutive reversible reactions, second order.	12-104.8

Appendix 9

B: Kinetic models and activation energies for transesterification of vegetable oils. [97, 98, 99]

B: Kinetic models and activation energies for transesterification of vegetable oils. [97, 98, 99]

Oil Source	Alcohol	Catalyst/ quantity (% of oil)	MR	Temp. (^{0}C)	Reaction mechanism and kinetics model	Activation energy (kj/mol)
Sunflower	Methanol	KOH 0.5-1.5%	6:1	25-65	Three consecutive reversible reactions; second order.	6.0-41.6
		KOH 1.0%	6:1	10-30	Irreversible second order overall reaction in the middle period; the reversible second order overall reaction in the final period.	33.2-53.5
		CaO 1%, 2.5%, 5.0% and 10%		N/A	A mass controlled regime followed pseudo-first order by chemically controlled regime.	N/A
	Ethanol	NaOH 0.75%, 1% and 1.25%	6:1, 9:1, 12:1	25-75	Irreversible second order overall reaction in the initial period; the reversible second order overall reaction in the final period.	34-43.9
Rapeseed	Methanol	KOH 0.29-1.59%	1:1-6:1	22.7	Three consecutive reversible (methanolysis) plus saponification reactions; second order.	N/A
		Without catalyst	N/A	N/A	One overall reaction; first order	
RBD Palm	Methanol	Without catalyst	N/A	N/A	Three sequential reversible reactions.	

MR: Molar Ratio

RBD: Refined, bleached and dried

Appendix 10

Properties of Jatropha curcas oil methyl ester (biodiesel) compared to American and European standards. [56, 100, 101]

Properties of Jatopha curcas oil methyl ester (biodiesel) compared to American and European standards. [56, 100, 101]

Property	Units	Jatropha biodiesel	ASTM D-6751		EN 14214	
			Limits	Test methods	Limits	Test methods
Kinematic Viscosity (40 ^{0}C)	mm^2/s	4.4	1.9-6.0	D445	3.5-5.0	EN ISO 3104
Density (15 ^{0}C)	kg/m^3	884.2		Not Specified	860-900	EN ISO 3675
Ester content	mass %	98.9		Not Specified	96.5 min	EN 14103
Cetane number	-	58.5	47 min	D 613	51 min	EN ISO 5165
Flash point	^{0}C	172	130 min	D 93	120 min	ISO/CD 3679
Water content	volume %	590 mg/kg	0.050 max	D 2709	500 max	EN ISO 12937
Sulphated ash	mass %	0.01 max	0.020 max	D874	0.02 max	ISO 3987
Copper Corrosion	grade	1	No.3 max.	D130	No.1(3h at 50°C)	EN ISO 2160
Acid number	mg KOH/g	0.11	0.80 max	D 664	0.5 max	EN 14104
Free glycerol	mass %	0.02 max	0.02 max	D 6584	0.02 max	EN 14105
Total glycerol	mass %	0.03	0.240 max	D 6584	0.25 max	EN 14105
Phosphorous content	mass %	1 max	0.001 max	D 4951	10 max	EN 14107
Iodine number	-	93	N/S	N/S	120 max	EN 14111
Oxidative stability (110 ^{0}C)	h	6.7	N/S	N/S	6 min	EN 14112
Monoglycerols	mass %	0.01	N/S	N/S	0.8 max	EN 14105
Diglycerols	mass %	0.02	N/S	N/S	0.2 max	EN 14105
Triglycerols	mass %	0.02 min	N/S	N/S	0.2 max	EN 14105
Methanol	mass %	0.02 max	N/S	N/S	0.2 max	EN 14110
High calorific value	MJ/kg	41.3	N/S	N/S	N/S	N/S
Low calorific value	MJ/kg	38.9	N/S	N/S	N/S	N/S
Oxygen Content	%	11.2	N/S	N/S	N/S	N/S