CHAPTER 1
INTRODUCTION

1.1 BACKGROUND OF STUDY

Biodiesel is a mixture of alkyl esters, produced from an elementary organic chemical reaction between a triglyceride and a specific short-chain alcohol mainly methanol or ethanol. Biodiesel has been introduced as an alternative fuel of wide acceptance because of its higher cetane number and lubricity and its lower environmental impact as compared to diesel petroleum fuels. [7] The reaction catalyst and alcohol together with triglyceride feedstock are chosen so as to optimize both the combustion characteristics of the resulting biodiesel product and the percent yield of the transesterification reaction. The product of this reaction is a two-phase liquid in which the top layer is biodiesel (product) while the bottom phase is glycerol (byproduct). Being that the rate of this reaction is controlled by equilibrium conditions (reversible reaction), a molar excess of alcohol is used to shift the equilibrium to produce high conversions of the triglyceride. Co-solvent is used to increase the rate of reaction by making the oil soluble in methanol, thus increasing the contact of the reactants. The co-solvent that is generally used in this reaction is n-hexane or isopropyl alcohol. [2] The triglyceride is converted stepwise to a diglyceride, a monoglyceride and finally, to glycerol by removal of a carbonyl group in each step as shown in figure 2. For each of the step different activation energy is required in order for the reaction to occur. [11]

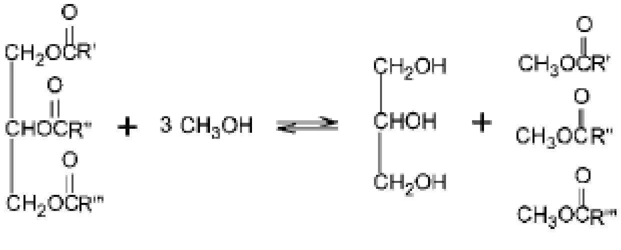


Figure 1: The general reaction for the transesterification of a triglyceride with an alcohol to form alkyl esters (biodiesel) and glycerol. ‘R’s represent hydrocarbon chains of various lengths. [10]

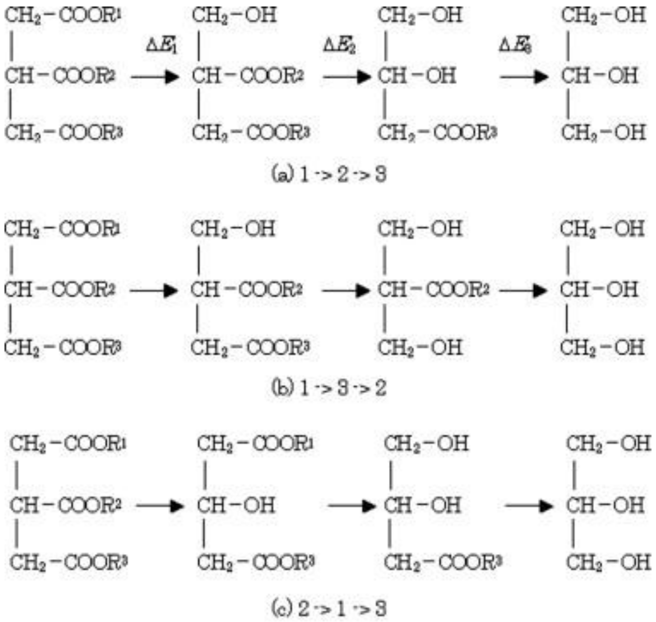


Figure 2: Three different pathways of transesterification. The meaning of the numbers 1, 2, and 3 is the position of the carboxyl group, either in the center (2) or on the outside (1 and 3). [11]

The acid-catalyzed process often uses sulfuric acid and hydrochloric acid as catalysts; however, the reaction time is very long (48-96 h), even at reflux of methanol, and a high molar ratio of methanol to oil is needed (30-150:1, by mole). Potassium hydroxide, sodium hydroxide, and their carbonates, as well as potassium and sodium alkoxides, such as $NaOCH_3$, are usually used as base catalysts for this reaction. As the catalytic activity of a base is higher than that of an acid, and acid catalysts are more corrosive, the base-catalyzed process is preferred to the acid-catalyzed one, and is thus most often used commercially. However, removal of the base after reaction is a major problem since aqueous quenching results in the formation of stable emulsions and saponification and requires large amount of wastewater to separate methyl ester and clean the catalyst [7], [10], [18] Therefore, conventional homogeneous catalysts are replaced by environmentally friendly heterogeneous catalysts, mainly due to environmental constraints and simplification of the existing processes. [1]

There are many resources which are being used as feedstock especially edible oil for producing this alternative fuel at industrial scale. Examples are palm oil, sunflower, soybean and rapeseed. [14-16]. However the use of the edible feedstocks in producing biodiesel will increase its price since it needs to compete with cooking oil. As a result, the cost of biodiesel production increases. Therefore non-edible oil such as Jatropha curcas is applied as a feedstock to produce biodiesel. [17]

For this project, the author will use Mg-Al hydrotalcites in the form of solids (heterogeneous catalyst). They are weak basic catalysts that have some acidic properties so that it is expected to be used directly to transesterify high free fatty acid content oils (jatropha oil). This is because if we use the homogeneous base catalyst directly towards the reaction, then there will be formation of soap which disturbs the process. The hydrotalcite $Mg_6Al_2(OH)_{16}CO_3.4H2O$ has attracted much attention during the development of new environmental friendly catalysts. Their chemical composition can be represented by the general formula $[M^{2+}_{(1-x)}M^{3+}_{x} (OH)_2]^{x+}(A_{x/n})^{n-}.yH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations respectively, A^{n-} is an n-valent anion, and x usually has a value between 0.25 and 0.33. [1]. The structure of hydrotalcites is based upon layered double hydroxides with brucite like ($Mg(OH)_2$) hydroxide layers containing octahedrally coordinated M^{2+} and M^{3+} cations. A^{n-} is the counter anion which resides in the interlayer space to balance the residual positive charge of the hydroxide layers which results from isomorphous substitution of M^{2+} by M^{3+}. [18] Synthetic hydrotalcite-like compounds have found a variety of uses in heterogeneous catalysis, polymer processing, and pharmacy. They are also known as good adsorbents and anion exchangers. [10]. Figure 3 shows the structure of hydrotalcite catalyst that has a brucite like layers and interlayer anions. [18]

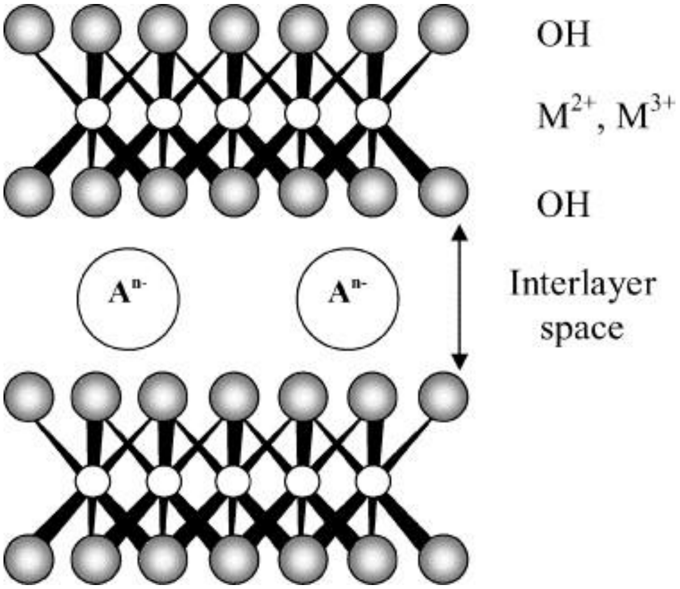


Figure 3: Hydrotalcite structure showing the brucite like layers and interlayer anions. [18]

1.2 PROBLEM STATEMENT

For more than two centuries, the world's energy supply has relied heavily on non-renewable crude oil derived (fossil) liquid fuels. Out of which 90% is estimated as to be consumed for energy generation and transportation. It is also known that emissions from the combustion of these fuels such as CO_2, CO, NO_X and sulfur containing residues are the principal causes of global warming. On the other hand, known crude oil reserves could be depleted in less than 50 years at the present rate of consumption. Thus, increased environmental concerns, tougher clean air act standards necessitates the search for a viable alternative fuels, which are environment friendly. [7] The current manufacturing processes, however, have several disadvantages: shifting the equilibrium to fatty esters by using an excess of alcohol that must be separated, making use of homogeneous catalysts that require neutralization (causing salt waste streams), expensive separation of products from the reaction mixture, and high costs due to relatively complex processes involving one to two reactors and several separation units. Moreover the high cost of biodiesel is due to the feedstock that uses edible oil such as soybean oil shown in figure 4. Therefore such oil needs to be substituted with other non-edible oil such as Jatropha oil which can lower the feedstock cost. [16]

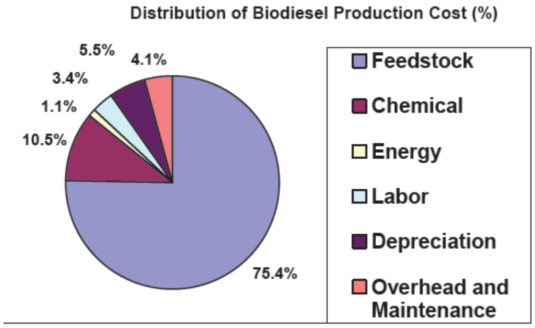


Figure 4: Pie chart showing distribution of biodiesel production cost for soybean oil. [16]

1.3 OBJECTIVE AND SCOPE OF STUDY

The main objectives of this research are:

- To produce biodiesel from jatropha oil which is a nonedible oil
- To develop hydrotalcite-derived mixed oxide catalyst which is a multifunctional catalyst that possesses both basic and acidic properties for transesterification process to avoid saponification process and to ease the separation by using this solid catalyst
- To investigate the activity of hydrotalcite derived Mg-Al oxide catalyst in light of the following parameters:
    1.) The alcohol to oil ratio (feed ratio)
    2.) Catalyst loading (catalyst to oil ratio)
    3.) Time of the reaction

The scope of study is to produce biodiesel by transesterification of jatropha oil which is a promising alternative fuel to diesel because of limited fossil fuel resources and environmental concerns. For this project the author need to use heterogeneous catalysts (solid catalyst) because they simplify the technological process of separation of the post-reaction mixture. The catalyst that is used which is to increase the rate of reaction of production of methyl esters or ethyl esters from jatropha oil is Mg-Al hydrotalcites.

1.4 RELEVANCY OF PROJECT AND FEASIBILITY OF PROJECT

The cost of the project is expensive because jatropha oil is very hard to get especially in Malaysia and the heater with magnetic stirrer cost around RM 2000, thus the author used the other alternative which is to extract the oil from the seeds. The hydrotalcite catalyst of Mg-Al needs to be prepared by the author himself. The preparation of hydrotalcite catalyst requires a lot of time since the catalyst need to be dried in owen and calcined at the furnace overnight. The catalyst need to be tested using XRD. The tedious work here is that the author must extract the oil from jatropha seed. The time required to get the amount of oil needed for transesterification is about one month. If the author used liquid catalyst such as sodium hydroxide, then the separation becomes harder since all the three components (alchohol, biodiesel and catalyst) will be on the top layer.

CHAPTER 2

LITERATURE REVIEW

Jatropha seeds and green leaves are poisonous, because it works as a barrier to animals from grazing the crops. Jatropha plant is now being increasingly used in reforestation programs in tropical countries because it thrives in poor-quality soil. Within the biodiesel industry, the Jatropha Curcas tree is one of few feedstock crops that can be used on non-food land. Thus growing Jatropha plant does not displace the food crops. [4]

The concept of using vegetable oils as fuel is not new since 1890 when Rudolph Diesel invented diesel engine. The diesel engine works on four strokes of piston inside the cylinder and this engine is called four-stroke engine. The fuel is injected from the nozzles and it is burnt due to compression of air inside the cylinder which is called Compression Ignition (CI) engine. Although the engine invented by him is being run widely on petroleum diesel throughout the world, Rudolph Diesel had envisioned in the days of engine discovery itself that his engine could be powered by the vegetable oil and used in remote areas of the world, where petroleum fuel is not available. Moreover this invention will benefit the farmers since his engine uses vegetable oils. Now, the modern biodiesel is made from renewable sources like vegetable oil and animal fats which make the dreams of Rudolph Diesel came true. [5]

The actual biodiesel industry was established in the late 1980s in Europe but the earliest research on biodiesel was carried out in 1930s in Belgium. In the early 1970s during the world oil crisis, a lot of interest was shown but due to the high viscosity of the vegetable oils, the diesel engines during that time could not operate. In the year 1937, a belgian scientist suggested the most effective method to reduce the viscosity of biodiesel fuel is by transesterification. In this method vegetable oil is converted into fatty acid alkyl esters and used as a biodiesel which can be used easily in the petroleum diesel engines. The concern for environment due to pollution in the early 1980s caused by petroleum diesel brought back the focus on vegetable oils. The market of vegetable oils started developing never to look back again. [5]

The British businessman Richard Branson's Virgin Voyager train, number 220007 *Thames Voyager*, billed as the world's first "biodiesel train" was converted to run on 80% petrodiesel and only 20% biodiesel, and it is claimed it will save 14% on direct emissions. On 15 September 2007, The Royal Train completed its first ever journey run on 100% biodiesel fuel supplied by Green Fuels Ltd. The Royal Train has operated successfully on B100 (100% biodiesel) since then. Similarly, a state-owned short-line railroad in Eastern Washington ran a test of a 25% biodiesel / 75% petrodiesel blend during the summer of 2008, purchasing fuel from a biodiesel producer seated along the railroad tracks. The train will be powered by biodiesel made in part from canola grown in agricultural regions. Also in 2007 Disneyland began running the park trains on B98 biodiesel blends (98% biodiesel). The program blipped in 2008 due to storage issues, but in January 2009 it was announced that they are now running all the trains on biodiesel manufactured locally from used cooking oils from the park. [5]

Vegetable oils have the potential to substitute a portion of the petroleum distillates in the near future since right now their price are higher compare to the petroleum fuels. However with the recent increases in petroleum prices and also in some country the tax for normal diesel is more expensive than biodiesel, there is renewed interest in using this vegetable oil in diesel engines. Biodiesel is a renewable source compare to petroleum oil which one day will disappear from this world and it also reduces the emission of CO_2 (lead to less global warming). Biodiesel also provides new markets for agricultural products and stimulate rural development because it is generated from crops; it holds enormous potential for farmers. [6]

Biodiesel is a liquid which varies in color (between golden and dark brown) depending on the reactants (alcohol and the vegetable oil). Biodiesel has a higher octane number compare to petroleum fuel (the higher the octane number the faster the ignition time). It is immiscible with water and has a high boiling point and low vapor pressure. The flash point of biodiesel (>130 °C) is significantly higher than that of petroleum diesel (64 °C) or gasoline (−45 °C). Higher flash point makes it safer to handle, use and store. Biodiesel has a density of ~ 0.88 g/cm^3, less than that of water. Biodiesel has virtually no sulfur content, and it is often used as an additive to Ultra-Low Sulfur Diesel (ULSD) fuel.

[10]. Combustion of biodiesel does not significantly contribute to the net atmospheric carbon level because of its closed carbon cycle. This reduction of green house gas emission due to biodiesel is in line with Kyoto Protocol. [8]

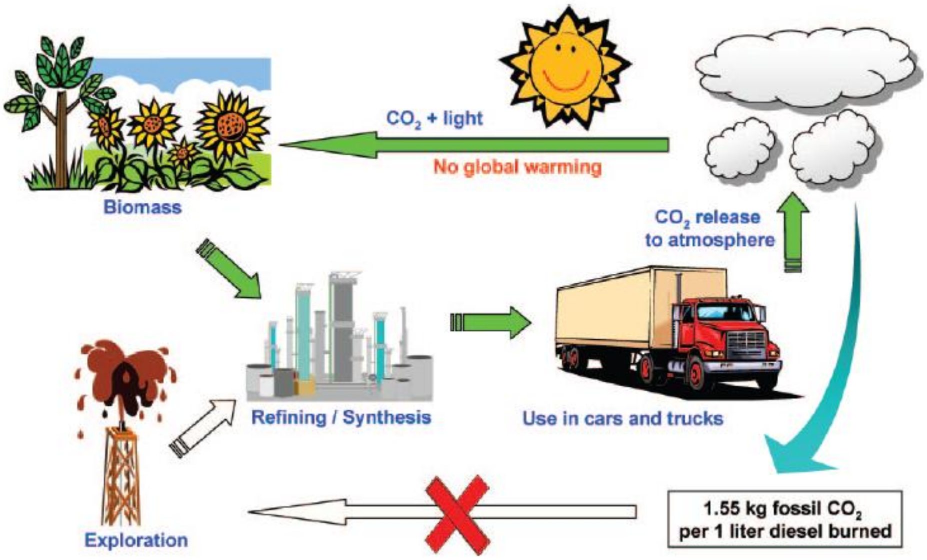


Figure 5: Life cycle of diesel versus biodiesel as an environmentally friendly fuel. The CO_2 cycle is closed for biodiesel but not for diesel. [8]

The general process of producing biodiesel is alcoholysis of triglyceride of oil known as transesterification. There are several effects on biodiesel production that were investigated which are molar ratio of alcohol to oil, reaction temperature, concentration of catalyst, reaction time and hydrotalcite catalyst loading. The following result is taken from several literatures to compare the results that have been obtained by other researchers.

2.1 EFFECT OF MOLAR RATIO OF ALCOHOL TO OIL

The transesterification process consists of a sequence of 3 consecutive reversible reactions in which the triglyceride is successively changed into diglyceride, monoglyceride, and finally into glycerin and three fatty acid methyl esters. The molar ratio of methanol to oil is an important factor that affects the conversion of methyl esters. Stoichiometrically, 3 moles of methanol are required for each mole of triglyceride because there are three reactions involves (triglyceride transformed into diglyceride and monoglyceride) but in practice a higher molar ratio is employed in order to drive the reaction towards completion because the it is an reversible reaction and so equilibrium limited. [11]

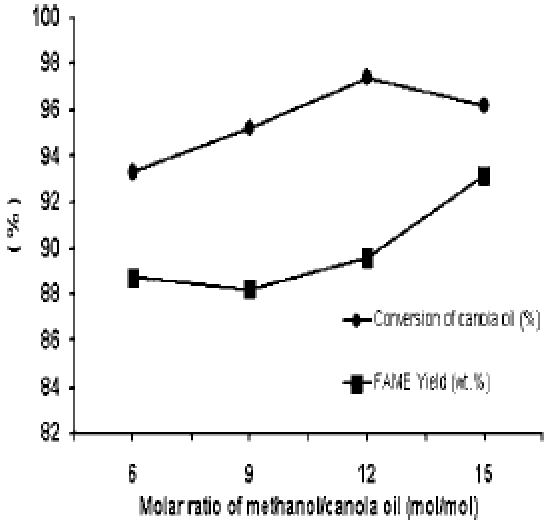


Figure 6: Conversion of canola oil and FAME yield as a function of the methanol/canola oil molar ratio using KOH/MgO as catalyst [7]

The dependence of conversions of canola oil and yield of esters on the methanol/canola oil molar ratio was studied at four different ratios higher than the stoichiometric ratio in the presence of 10 wt % KOH/MgO catalyst. As shown in figure 6, the highest FAME (fatty acid methyl ester) yield was obtained in the reaction carried out at a 15:1 methanol/canola oil molar ratio at 60 ^{o}C with the reaction time of 9 hours and the highest conversion of canola oil was obtained in the reaction carried out at a 12:1 methanol/canola oil molar ratio at the same temperature. It was reported that excess methanol can promote the transesterification reaction forward and also extract products, such as glycerin and methyl esters, from the system to renew the surface of the catalyst. To remove excess methanol usage because of environmental and economical reasons, the minimum possible amount of the methanol/oil ratio (6:1) was used to obtain higher FAME yields close to the ones obtained at a 15:1 alcohol/oil ratio. This is because the higher the amount of alcohol used, the more alcohol will be wasted. [7]

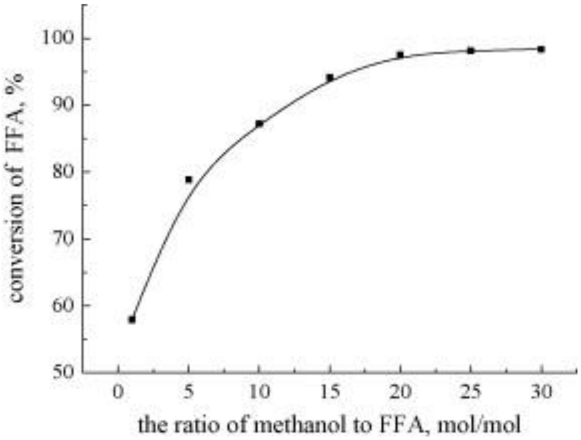


Figure 7: Effect of the ratio of methanol to FFA of jatropha oil on conversion at 90 °C for 3 h with 4 wt% of SO_4^{2-}/TiO_2 solid acid catalyst in oil [12]

As we can see from figure 7 as the ratio of methanol to jatropha oil increases, the conversion also increases. The maximum conversion is reached at a ratio of 20:1 of methanol to jatropha oil. The reason is that when there is more methanol in the reaction, the equilibrium will push towards producing more biodiesel (methyl ester). [11]

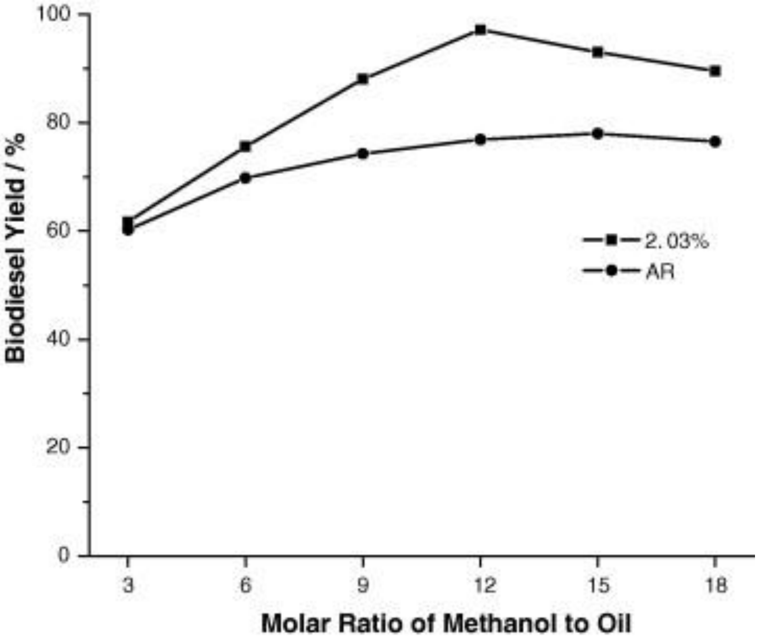


Figure 8: Effect of molar ratio of methanol to oil on biodiesel yield. CaO/oil mass ratio: 8%; reaction temperature: 65 °C; reaction time: 1.5 h; water content: 2.03%. [12]

The biodiesel yield could be improved by introducing excess amounts of methanol to shift the equilibrium to the right-hand side. The experimental results, illustrated in Figure 8, indicate the molar ratio of methanol to oil has a significant impact on the biodiesel yield. The biodiesel yields grew as the molar ratio increased, and the yield was 75% at a 12:1 molar ratio of methanol to oil when analytical reagent methanol was used. In comparison, the biodiesel yield increased from 61% to 97% when the molar ratio was increased from 3:1 to 12:1 at 2.03% water content in methanol. However, the yields were slightly reduced when the ratio of methanol to oil was higher than 12:1, and the biodiesel yield was only 90% at 18:1. The reason is that the catalyst content decreased with increase of methanol content. Therefore, the optimum molar ratio of methanol to oil was 12:1. [12]

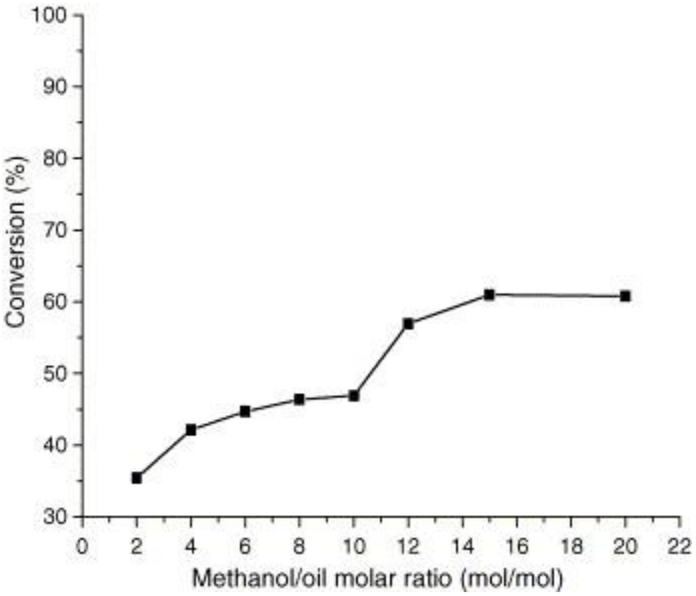


Figure 9: Influence of methanol/soybean oil molar ratio on the conversion. Reaction conditions: hydrotalcite Mg-Al catalyst amount 6.3%, reaction time 7 h and methanol reflux temperature. [19]

Stoichiometrically, the methanolysis of soybean oil requires three moles of methanol for each mole of oil. However, in practice, the methanol/oil molar ratio should be higher than that of stoichiometric ratio in order to drive the reaction towards completion and produce more methyl esters as product. It is observed that lower molar ratio required longer reaction period. Figure 9 reflects the effect of methanol/oil molar ratio on the conversion. As shown in this figure, by increasing the methanol amount, the conversion was increased considerably. The conversion reached the maximum value when the methanol/oil molar ratio was very close to 15:1. Beyond the molar ratio of 15:1, the excessively added methanol had no significant effect on the conversion. Therefore, we could conclude that to elevate the conversion an excess methanol feed was effective to a certain extent. [19]

2.2 EFFECT OF TEMPERATURE

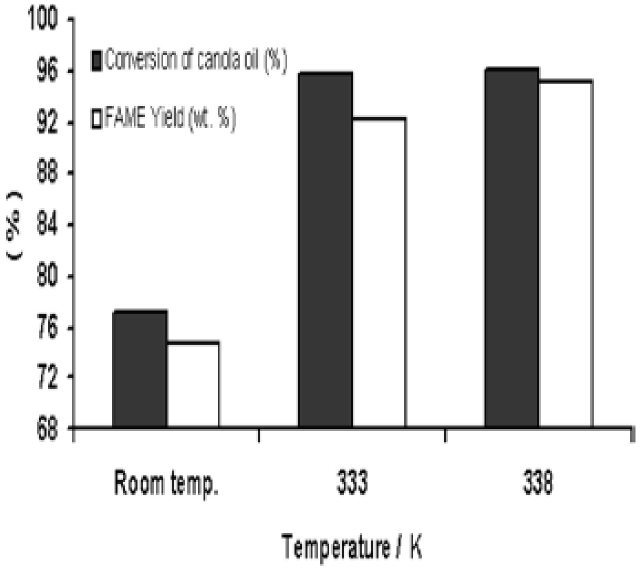


Figure 10: Conversion of canola oil and FAME yield as a function of the reaction temperature. Reaction conditions: methanol/oil molar ratio, 6:1; catalyst amount, 3 wt % of total amount; reaction time, 9 h. [7]

The reaction temperature can influence the reaction rate and the biodiesel yield because the intrinsic rate constants are strong functions of temperature. Commonly, the methanolysis is conducted close to the boiling point of methanol at atmospheric pressure. The effects of the reaction temperature on the conversions of canola oil and yields of esters were investigated at three different reaction temperatures, such as room temperature, boiling point temperature of methanol (65 °C, and 60°C (slightly less than boiling temperature). The catalyst used in this experiment was 20 wt % KOH/MgO. The results are shown in Figure 10. The conversion of canola oil and FAME yield increased with the rise of the reaction temperature from room temperature to the boiling point (338 K) of methanol. The conversion of canola oil and FAME yield at 338 K was obtained as 96.18 and 95.05%, respectively. [7]

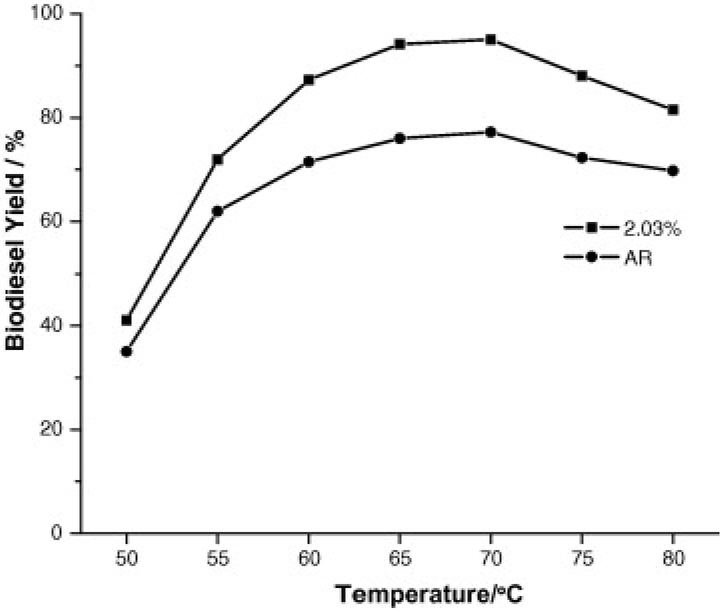


Figure 11: Effect of reaction temperature on biodiesel yield. CaO/oil mass ratio: 2%; methanol/oil molar ratio: 6:1; water content: 2.03%. [12]

In the presence of heterogeneous catalysts, the reaction mixture constitutes a three-phase system, oil–methanol-catalyst, in which the reaction would be slowed down because of the diffusion resistance between different phases. However, the reaction rate can be accelerated at higher reaction temperatures. As shown in Figure 11, the reaction rate was slow at low temperatures, but the biodiesel yield first increased and then decreased with the increase of the reaction temperature. Generally, a more rapid reaction rate could be obtained at high temperatures, but at high temperatures, methanol was vaporized and formed a large number of bubbles, which inhibited the reaction on the three-phase interface. Therefore, the optimum reaction temperature was 65 °C. [12]

2.3 EFFECT OF HYDROTALCITE MG-AL CATALYST LOADINGS, CATALYST AMOUNT AND THE CALCINED TEMPERATURE ON CONVERSION

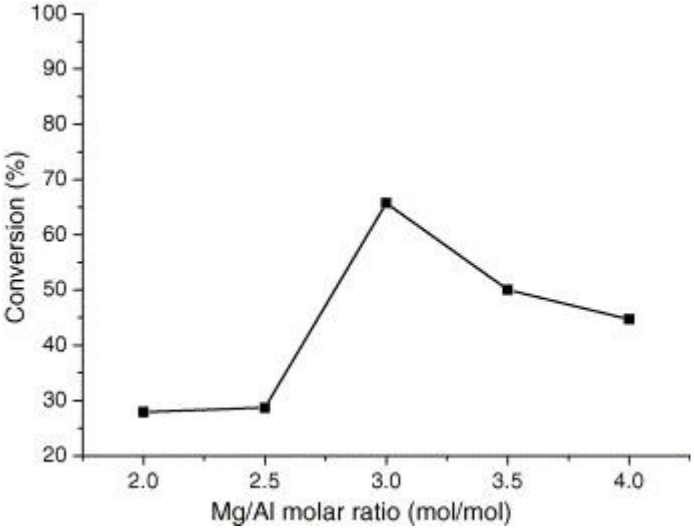


Figure12: Influence of Mg/Al molar ratio of calcined hydrotalcites on the conversion of soybean oil. Reaction conditions: methanol/oil molar ratio 15:1, catalyst amount 7.5%, reaction time 9 h and methanol reflux temperature. [19]

In order to determine the influence of the Mg/Al molar ratio of calcined hydrotalcites on their catalytic activity, hydrotalcites with different Mg/Al molar ratios were prepared and used to catalyze the methanolysis reaction after being calcined at 773 K for 8 h. The experimental results are illustrated in Figure 12, which indicates that the catalytic activity was improved with the increase in Mg content when the Mg/Al molar ratio was below 3.0, but when the Mg/Al molar ratio was above 3.0, the catalytic activity dropped. Clearly, such a tendency could be correlated well to that for the variation of the catalyst basicity with various Mg/Al ratios. As expected, a catalyst with a 3:1 molar ratio of Mg to Al, which had the highest basicity as mentioned above, showed the highest activity. [19]

It is known that all the Al^{3+} cations occupy the octahedral sites in hydrotalcites before calcination and the structure rearranges at high temperature, i.e. Al^{3+} cations transfer from octahedral to tetrahedral sites, substituting Mg^{2+} cations isomorphously in the mixed oxides. The positive charge generated by this isomorphous substitution could be compensated by the formation of two types of defects: cationic vacancies and/or inclusion of intersticial oxygens in the structure. The amount of tetrahedral aluminium decrease with increasing the Mg/Al ratio in the hydrotalcite calcined at high temperature, and at least a part of the tetrahedral aluminium is located at tetrahedral positions in MgO lattice. [19]

This structure could give rise to the formation of clusters of Mg–Al inverse spinel type. The Al^{3+} located at the tetrahedral or octahedral sites produces the defect of Mg^{2+} or Al^{3+} in the framework in order to compensate the positive charge generated. The O^{2-} ions adjacent to the Mg^{2+} or Al^{3+} defects become coordinatively unsaturated and could provide strong basic sites. On the other hand, Since Al is more electronegative than Mg, an increase in Al should increase the average electronegativity of the catalyst, and thus, a decrease in the average electronic density of the unsaturated framework oxygens could be expected, with the corresponding effect on their basicity and catalytic activity. As a result, the basicity and catalytic activity increased with elevating of Mg/Al molar ratio. However, when the Mg/Al molar ratio exceeds 3.0, the catalytic activity decreases. It may be due to the formation of new weaker basic sites and thus decrease of strong basic site amount. [19]

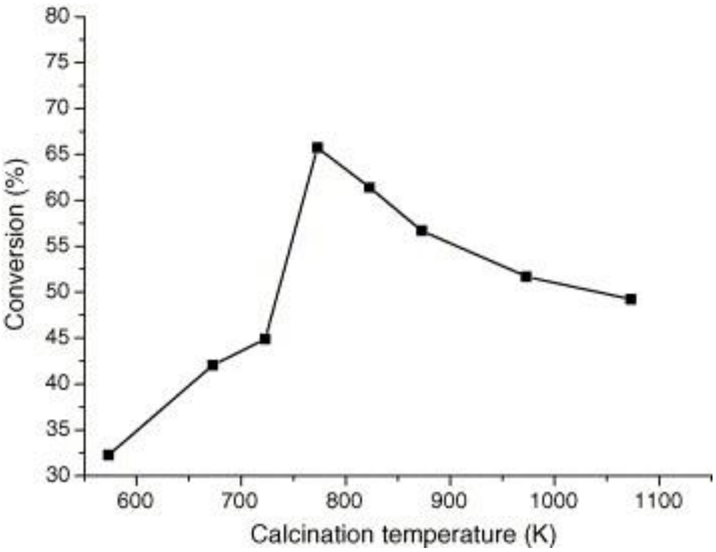


Figure 13: Influence of calcination temperature of catalyst on the conversion soybean oil. Reaction conditions: methanol/oil molar ratio 15:1, catalyst amount 7.5%, reaction time 9 h and methanol reflux temperature. [19]

The influence of calcination temperature on the catalyst activity is displayed in Figure 13. From the results obtained, it is shown that calcination temperature affected significantly the catalytic activity. With the rise of calcination temperature from 573 to 773 K, the conversion of soybean oil increased gradually and came up to the maxima of 66% when the calcination temperature was 773 K, which could be correlated well with the increase of the catalyst basicity with the increase of calcination temperature between 573 and 773 K. However, when the calcination temperature was higher than 773 K, resulting in lower basicity and corresponding to the formation of the spinel phase, the conversion dropped considerably. When being calcined at 773 K, the catalyst exhibited the highest basicity and, for this reasons the highest activity in the process of soybean oil methanolysis, giving a maximum conversion of 66%. Under this temperature, Al^{3+} substitutes isomorphously Mg^{2+} at the highest level, and Mg^{2+} coordinates with O^{2-} as most as possible. However, the basicity of coordination of Mg^{2+} with O^{2-} is higher than that of Al^{3+} with O^{2-}. Consequently, it has the most active centres and highest catalytic activity when 3.0 Mg/Al calcined at 773 K. [19]

But when the hydrotalcite is calcined above 773 K, the bulk $MgAl_2O_4$ spinel phase is formed, and due to this, the catalytic activity decrease. Such effect of calcination temperature on the catalytic activity has already been reported in the literature for the aldol condensation reaction. [19]

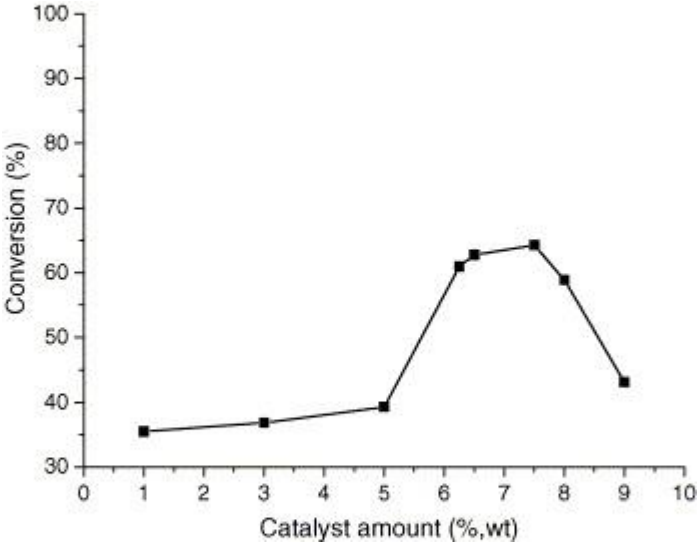


Figure 14: Influence of catalyst amount on the conversion. Reaction conditions: methanol/oil molar ratio 15:1, reaction time 7 h and methanol reflux temperature. [19]

The effect of the catalyst amount was investigated. The catalyst amount is varied in the range of 1.0–9.0wt%. These percentages are weight fractions of the oil supplied for this reaction. The reaction profiles of Figure 14 indicate that the conversion of soybean oil was increased first with the increase of catalyst amount from 1.0 to 7.5%. However, with further increase in the catalyst amount the conversion was decreased, which was possibly due to the rise of mixing problem of reactants, products and solid catalyst. At 7.5% catalyst amount, high conversion of up to 66% was obtained. [19]

2.4 EFFECT OF TIME

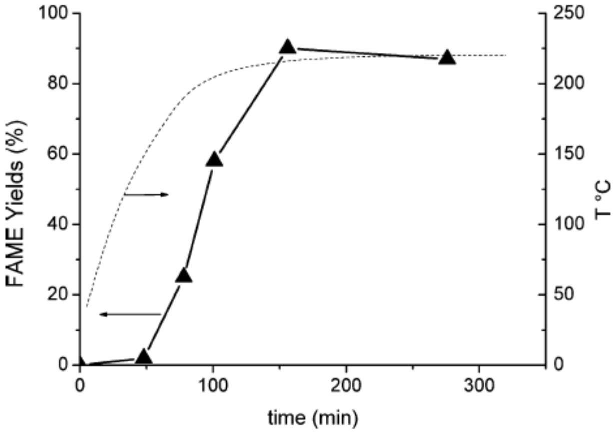


Figure 15: Run performed in autoclave on neutral soybean oil by using TiO2/SiO2 (TS) catalyst. [13]

From Figure 15, we can see that as time increases the yield increases until 90% at the time of 150 minutes or two hours and half. The yield decreases because as time goes by; the transesterification process consists of a sequence of three consecutive and reversible reactions transforming the triglyceride into a diglyceride, following a monoglyceride, and finally a glycerin, where FAME is produced from each step. These results indicate that monoglycerides are poorly stable intermediates under these reaction conditions and, once formed, are not easily converted to glycerol and methyl ester. Moreover the reaction is reversible and the product that is formed can turn back into reactant. [13]

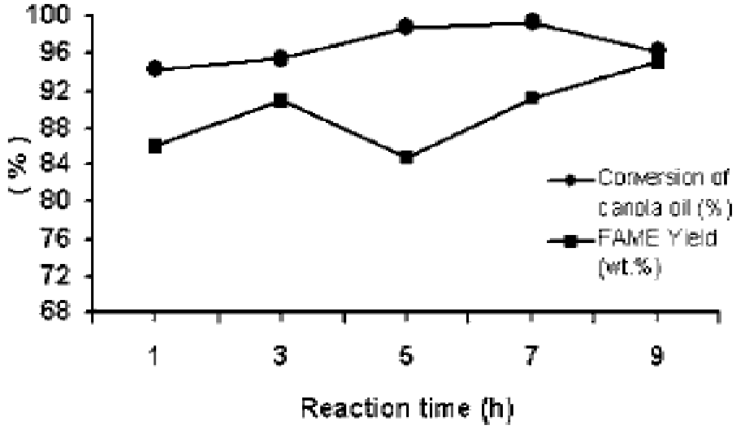


Figure 16: Conversion of canola oil and FAME yield as a function of the reaction time. Reaction conditions: methanol/oil molar ratio, 6:1; catalyst amount, 3 wt %; temperature, 65 °C on KOH/MgO catalyst

The dependence of conversions of canola oil and yields of esters on the reaction time was studied in the presence of 20 wt % KOH/MgO catalyst at reflux of methanol as shown in Figure 16. The reaction time was varied in the range of a 1-9 h period, including five different reaction times performed at different batches. Figure 16 reflects the effect of the reaction time on the conversion and FAME yield. As shown in this figure, conversion increased in the reaction time range between 1 and 7 h. However, an increasing reaction time to 9 h caused a slight decrease in conversion due to the same condition which is poor conversion produced by monoglyceride and reversible reaction. Although the FAME yield decreased in the reaction time range between 3 and 5 h, after 5 h of reaction time, the FAME yield of reaction was increased. The highest conversion of canola oil of 99.36% was obtained after 7 h of reaction time, and the highest FAME yield of 95.05% was obtained after 9 h of reaction time. [7]

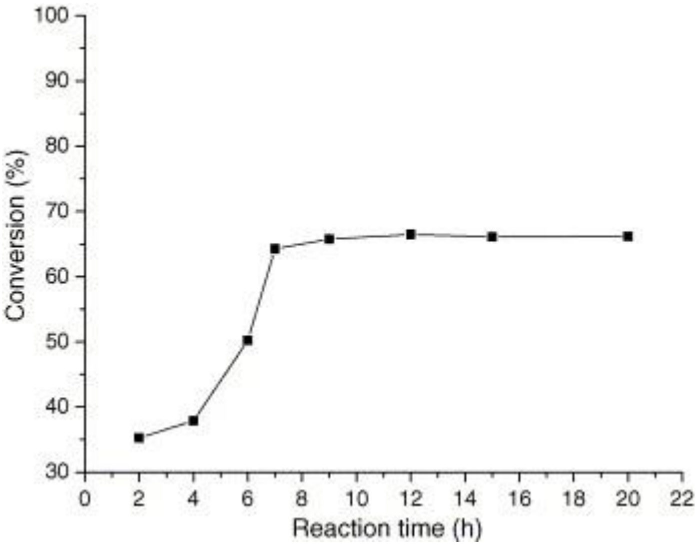


Figure 17: Influence of reaction time on the conversion. Reaction conditions: methanol/oil molar ratio 15:1, catalyst amount 7.5% and methanol reflux temperature. [19]

Commonly, the methanolysis is conducted close to the boiling point of methanol at atmospheric pressure. In Figure 17, the conversion versus reaction time is presented. It can be seen that the conversion increased steadily with reaction time and then reached a plateau value representative of a nearly equilibrium conversion. A nearly maximum conversion of 65% is obtained after 9 h reaction time. [19]

2.5 PRODUCT ANALYSIS USING THIN LAYER CHROMATOGRAPHY (TLC)

After sampling, the reaction mixture was stopped acidifying the mixture with sulfuric acid (1.0 mol/L) to neutralize the remaining catalyst. TLC is used to check the conversion of vegetable oil into biodiesel. TLC was chosen as a rapid analytical method and it gives quite accurate indication of oil and biodiesel content in the mixture. Silica-gel TLC plates (20 × 20 cm) were used and several samples were analyzed in each plate. Silica-gel TLC plates were obtained from Sigma-Aldrich. A mixture of hexane, ethyl ether and acetic acid (80:20:2 v/v/v) was used as mobile phase. [22]

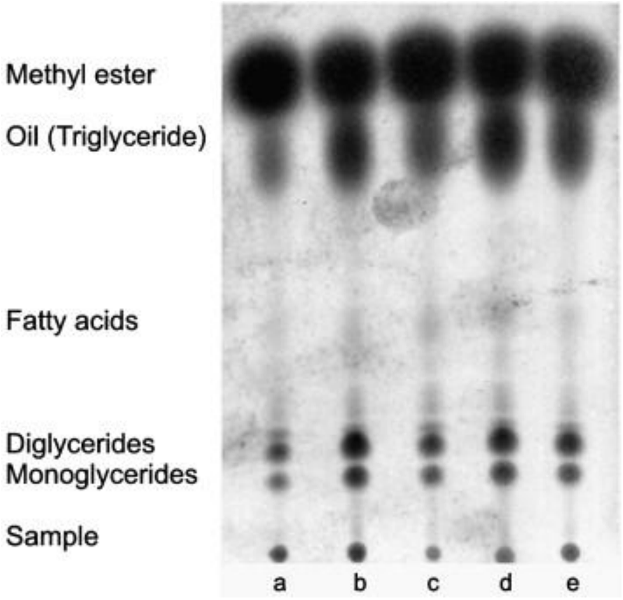


Figure 18: TLC plate indicating the positions of methyl esters, triglycerides, fatty acids, diglycerides, monoglycerides and sample. [22]

Figure 18 presents results for one silica-gel plate showing the positions of methyl esters, triglycerides, diglycerides, monoglycerides and fatty acids. The spots show that, for high biodiesel yields, the biodiesel spots are larger and darker, while the spots of oil are smaller and lighter indicating lower concentration of oil the sample. The samples presented low concentration of free fatty acids (FFA) as indicated by the very light spots in the FFA position. [22]

CHAPTER 3

METHODOLOGY

3.1 RESEARCH METHODOLOGY

In order to obtain the methodology for this experiment, the author needs to find several article related to transesterification of vegetable oils into biodiesel. For this project there will be four parts which the first method is preparation of catalyst, the second is extracting the oil from jatropha seeds, the third is the transesterification of jatropha oil and finally the separation process of the products and reactant. For the first one, the catalyst which is Mg-Al hydrotalcite will be coprecipitate by using Na_2CO_3. After the coprecipitation process has done, the catalyst is derived to make hydrotalcite-derived Mg-Al mixed oxide by using calcination process in the furnace at 500^oC. The catalyst is then tested using XRD. The next step is to extract the oil from the jatropha seed. When the catalyst and the oil are prepared, the author can proceed to the next step which is the transesterification of jatropha oil. Next, since there are two products of the reaction which are glycerin and ethyl ester (biodiesel), separation need to be done using hexane. Finally, the compatibility of the biodiesel produced will be tested using Thin Layer Chromatography.

3.2 TOOLS AND EQUIPMENT

The chemicals required are Aluminium Nitrate Nonahydrate, Magnesium Nitrate Hexahydrate, Sodium Carbonate, Ethanol, Hexane, Diethyl Ether, Acetic Acid and Jatropha seed. The equipment used to prepare the catalyst and biodiesel are 1-necked and 3-necked round bottomed flask with reflux condenser, heater with magnetic stirrer, heating mantle, soxhlet extracter, thermometer, silica plate, iodine chamber, TLC chamber, sample bottles and stopwatch. [6]

3.3 EXPERIMENTAL PROCEDURE

3.3.1 Preparation of Catalyst (hydrotalcite-derived Mg-Al mixed oxide-2.5)

1.) 31.5g of magnesium nitrate hexahydrate and 18.5g of aluminium nitrate nonahydate are dissolved in 250 ml distilled water to make solution A.

2.) 10% excess of theoretical requirement of Na_2CO_3, which is 31.42g $Na_2CO_3.10H_2O$ is dissolved in 250ml of distilled water to make solution B.

3.) The solution A and solution B from the respective burets are put drop by drop into the beaker. The precipitation solution is maintained at 50^{o}C with continuous stirring. The pH is maintained at about 9.

4.) After the precipitation, the slurry is stirred for 2 hours under nitrogen at room temperature, then filtered and dried overnight in an oven at 100^{o}C.

5.) Hydrotalcite-derived Mg-Al mixed oxide is prepared by calcining the Mg-Al NO_3-HT at 500 ^{o}C overnight.

6.) The dry precipitate is analyzed by X-Ray Diffraction (XRD) method. [6]

Figure 19: Titration of magnesium and aluminium nitrate to sodium carbonate

3.3.2 Extraction of Jatropha seed to Jatropha oil

1.) Husks from the seeds are removed to get the inner white seeds as shown in Figure 20:

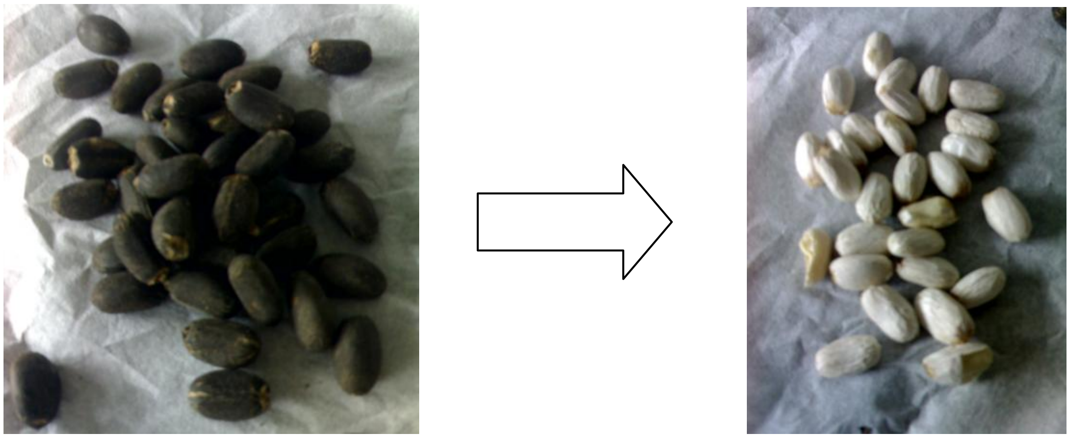


Figure 20: Removal of husks to get the white seeds

2.) The seeds are grinded to have a large contact area when extracting as shown in Figure 21.

Figure 21: Grinded seeds

3.) The seeds are then dried in the oven overnight.

3.) 20g of grinded seeds are positioned inside the thimble. The thimble is then placed inside the soxhlet extractor.

4.) 140 ml of hexane is prepared in the 1-necked flask.

5.) The hexane is heat up with heating mantle at it’s boiling point for six hours.

6.) The oil that is extracted need to be separated with hexane using rotary evaporator. The set up of extraction is shown in Figure 22.

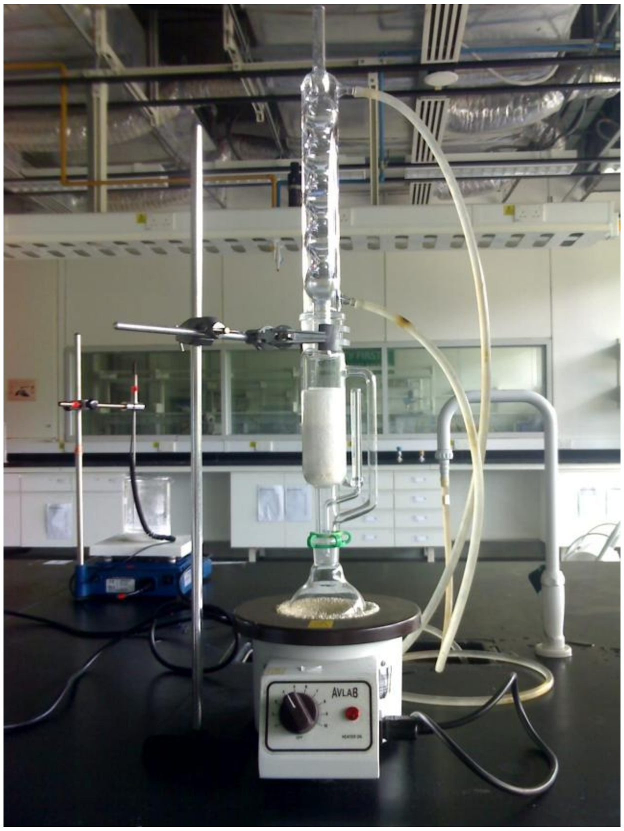


Figure 22: Soxhlet extraction set up

3.3.3 Transesterification of jatropha oil

1.) The transesterification reactions are performed in a 250ml, 3-necked round bottomed flask equipped with a reflux condenser and a hot plate stirrer with a temperature sensor as shown in Figure 23.

2.) Initially, the 3-neck flask is filled with 15g of jatropha oil and heated to the desired reaction temperature 70 ^{o}C.

3.) Ethanol of different ratio and different catalyst loading for 2.5 ratio of hydrotalcite derived Mg-Al mixed oxide catalyst are then added to the jatropha oil and stirring is begun. Time is taken when the catalyst is added in the reaction. Finally for varying the ratio of alcohol to oil needed is 6:1, 12:1 and 18:1. The concentration of the catalyst that is used is 2.0 wt%, 4.0 wt% and 6.0 wt%. The varying time is from 1 hour to 4 hours.

4.) Samples of approximately 1-2ml of the reaction mixture are pipetted out at 1, 2, 3 and 4 hours respectively. [6]

5.) The sample that is taken out need to be first added with 1ml of water to stop the reaction. Then, around 2ml of hexane is added to separate the glycerol from biodiesel.

6.) All the samples are labeled to be tested later.

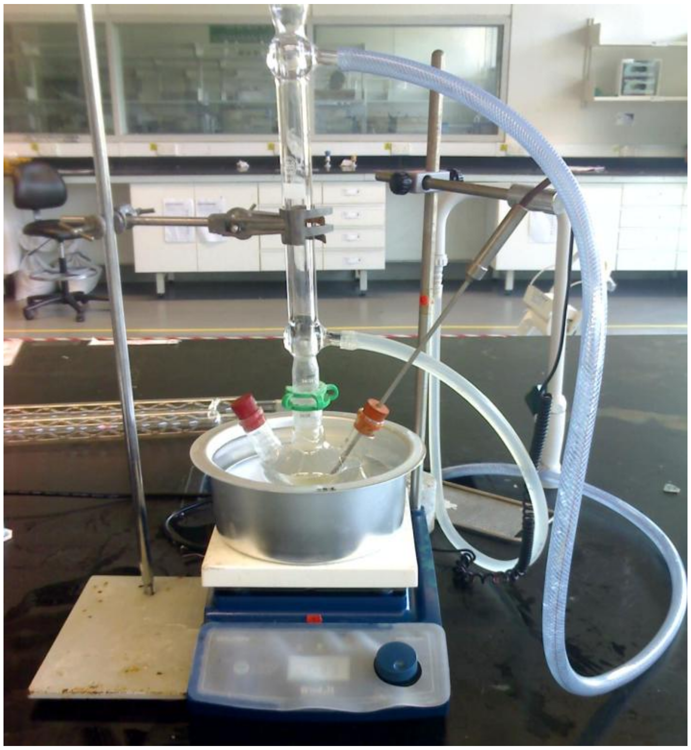


Figure 23: Experimental set up for transesterification of jatropha oil using three neck flask, condenser and a thermometer.

3.3.4 Analysis of Products.

3.3.4.1 TLC (Thin Layer Chromatography) analysis

1.) A solution containing 80% hexane, 20% diethyl ether and 1% acetic acid is prepared in the TLC chamber.

2.) A silica plate is cut into pieces of 10cm in length and 2cm in width. In between the length, both ends are drawn with a 1.5cm of line to separate the middle part as the part for analysis.

3.) A drop of the sample is tipped into the silica plate using capillary pipett at the 1.5cm line of the bottom end.

4.) Then, the silica plate is placed in the TLC chamber until the solvent reaches the top end.

5.) The silica plate is taken out and placed in the iodine chamber overnight for the spots to appear.

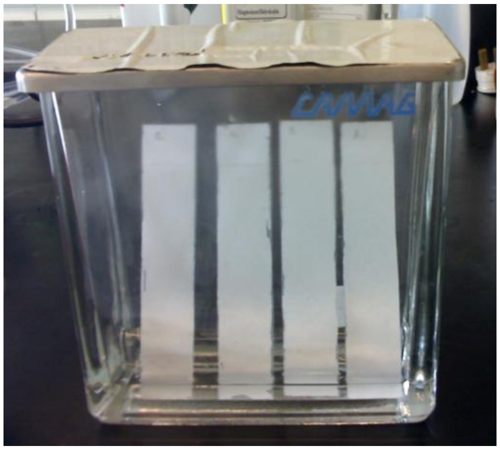


Figure 24: Analysis of sample in silica plate inside TLC chamber

Figure 25: Iodine chamber

3.3.4.2 Calculation for the area of the brown spots on the silica plate after TLC (Image-J software)

1.) When Image-J software is opened, go to the top menu and the oval type is selected.

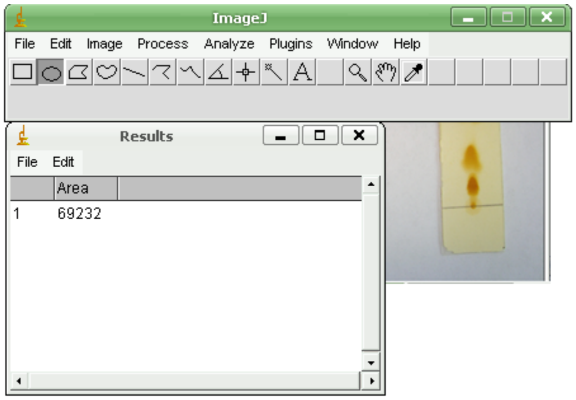
2.) Then, the area of the brown spots for triglyceride for the plate A3 is chosen as shown in Figure 26.

3072x2304 pixels; RGB; 27MB

Oval selections

Figure 26: Selecting the area of the triglyceride

3.) After that, the analyze command is clicked and the command measure will appear. Then click it to get the value for the area of triglyceride which is 69232 as shown in Figure 27.

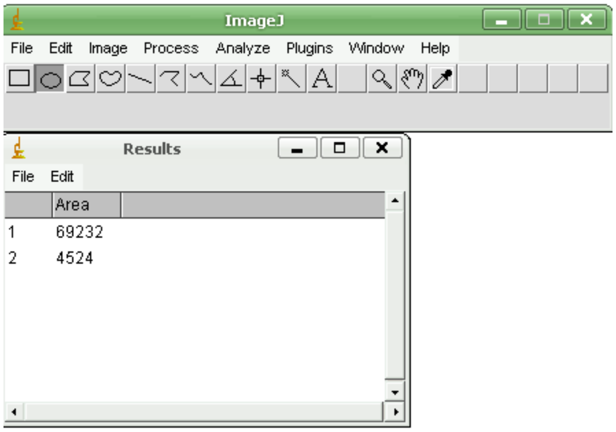


	Area
1	69232

Figure 27: The value of the triglyceride area

4.) Perform the same thing for diglyceride and monoglyceride to see the area of the components as shown in Figure 28 which is 4524.

5.) After all the area on the silica spots has been calculated; the composition of monoglyceride and diglyceride is found by dividing the area of monoglyceride and diglyceride to the total area.



	Area
1	69232
2	4524

Figure 28: The value of the triglyceride area is 68232 while diglyceride with monoglyceride is 4524

6.) From the composition, the data can be analyzed to see the conversion of triglyceride to diglyceride and monoglyceride.

CHAPTER 4

RESEARCH, OBSERVATIONS, RESULTS AND DISCUSSIONS

4.1 RESULTS AND DISCUSSION ON HYDROTALCITE DERIVED MG-AL OXIDE

As the author has mentioned in the methodology part, there are four steps involved. The first step is to prepare the hydrotalcite derived Mg-Al oxide catalyst. The steps were shown in methodology chapter. First, the author prepared the hydrotalcite catalyst without calcining it and tests it with XRD. Then the author calcined and test it again with XRD to see the difference before and after calcining. The hydrotalcite is shown below:

Figure 29: Hydrotalcite derived Mg-Al oxide catalyst

The ratio used is 2.5 Mg-Al since from the literature the basicity is the highest at a ratio of 2.5-3.0 Mg-Al ratio. The higher the basicity the better the transesterification reaction so that it can generate higher conversion and yield of biodiesel. To test whether the catalyst produced is correct; the author used XRD analysis to see the peaks and the wavelength of the graph. Figure 30 and 31 show the analyses of XRD before calcined and after calcined in the furnace.

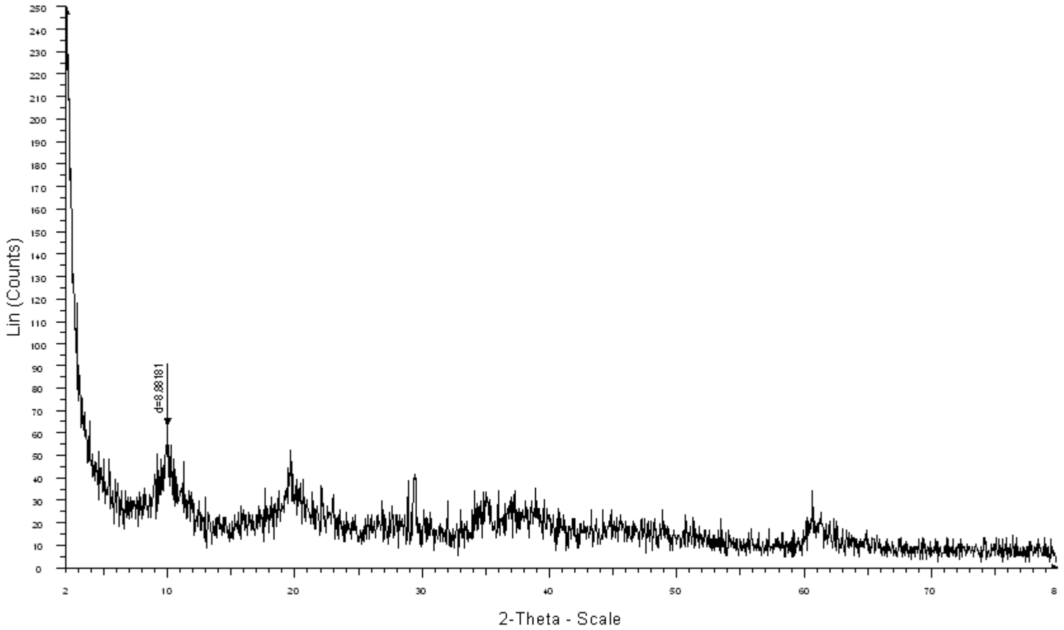


Figure 30: The hydrotalcite Mg-Al catalyst before calcining

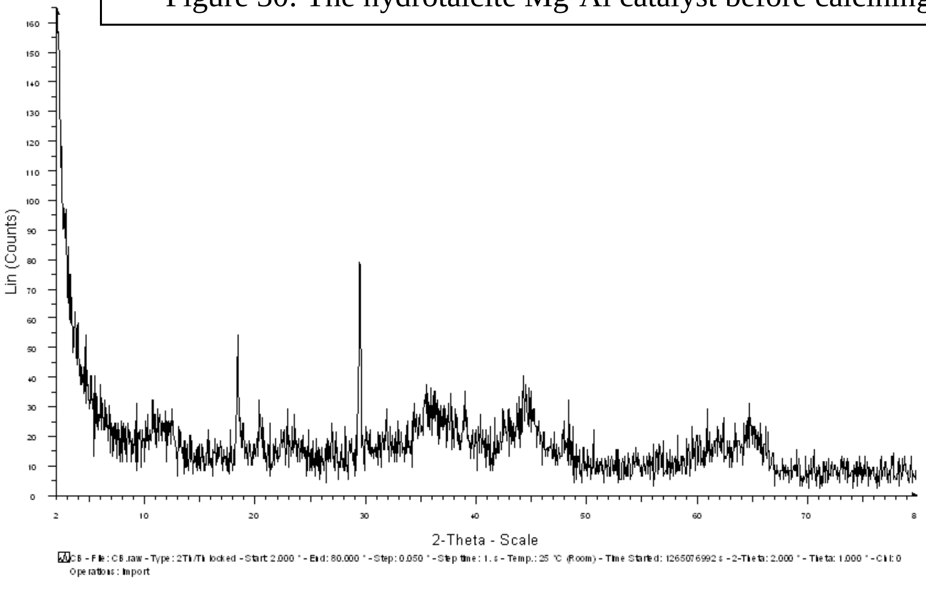


Figure 31: The hydrotalcite Mg-Al catalyst after calcining

Four peaks are observed in Figure 31 which is at the angle (2θ) of 11.5°, 18°, 23°, 29° and 36°. The standard spacing, d of Mg-Al hydrotalcite is 7.68cm and 3.88cm. From the equation wavelength, $\lambda = 2d \sin \theta$ where d is spacing and θ is angle, the angles, θ are around 6° and 11.5° when the wavelength is 1.54cm. Therefore the standard angles, 2θ of

Mg-Al hydrotalcite are around 11.5° and 23°. The value of first and second peak is almost the same as the standard angles for Mg-Al hydrotalcite. Although the first and second peak are corresponding to Mg-Al hydrotalcite structure, the peaks can not be seen clearly. It is because the obtained precipitate is not well-crystalline and causes the peaks to be broad. Therefore, the crystal size is small. [6] The other peaks corresponding to the magnesium-hydroxide-nitric-carbonate compounds. The aluminium compound are usually amorphous, and do not show peaks.

4.2 RESULTS AND DISCUSSIONS ON PREPARATION OF JATROPHA OIL

For the second step which is the extraction of seeds to get the oil, the author has tried two methods. The first one is using soxhlet extractor. The set up is shown in Figure 22 in the methodology part. The yield that the author got from the extraction is about 47% which the author calculated from 9.48g of oil from 20g of seeds. The oil that the author extracted can’t be used because for different extraction experiments, different oil will be produced shown in Figure 32 and affect the result of transesterification to produce biodiesel later. Thus the author need to first extract the oil with hexane together without doing the evaporation (removal of hexane) and mix all of the extract product together to get the same type of oil which is shown in Figure 33. About three times extraction need to be done to get around 20g of oil to prepare a sample of biodiesel. Therefore approximately 24 times of extraction required. The duration of the one extraction is around six hours. Therefore it is a tedious work to do.

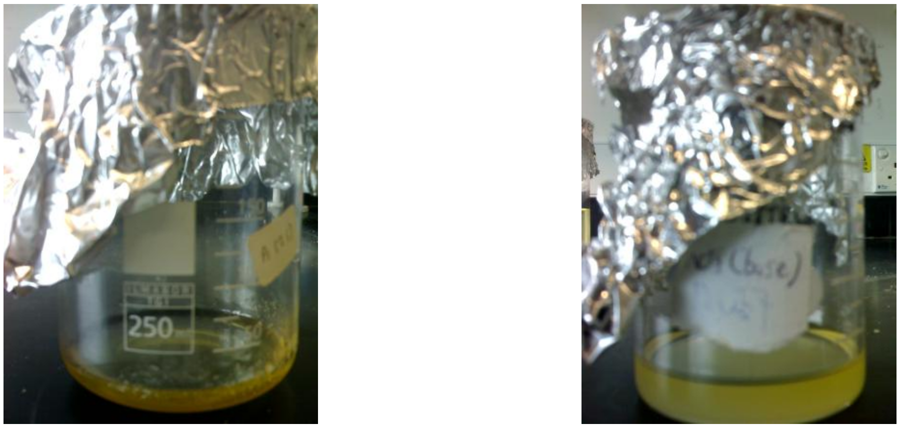


Figure 32: Different colour and viscosity of oil can be seen from both extractions

Figure 33: Pictures of mixture between hexane and jatropha oil

The other method is using ultrasonic wave to extract the oil. This method is still under study and is not showing a positive sign since the author tried twice but there is no outcome and no oil produced. The set up of ultrasonic wave is shown in Figure 34:

Figure 34: Ultrasonic bath to extract oil

The mixture of the oil and ethanol is tested using TLC to see the amount of free fatty acid in the oil. The picture is shown in Figure 35.

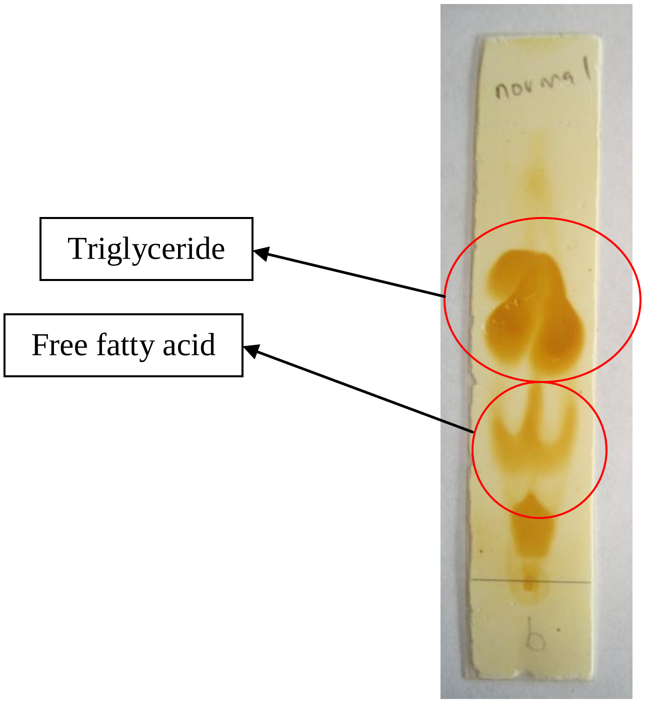


Figure 35: Mixture of oil and ethanol only without addition of catalyst

As we can see from the silica plate, the amount of free fatty acid is high around 30% from the overall mixture of triglyceride and free fatty acid of the oil. This indicates that if the author used straight liquid alkaline catalyst like sodium hydroxide, there is a chance where formation of soap will occur.

4.3 RESULTS AND DISCUSSIONS ON TRANSESTERIFICATION PROCESS

For the transesterification process all the parameters are choosen base on previous research and with the help of postgraduate student, Mr. Muhamad Surya Abadi Ginting. The sample taken out from the reaction is separated using hexane. The top part of the sample is the mixture between the unconverted jatropha oil and biodiesel which will be analyzed using TLC and the bottom part of the hexane is the glycerol. The lowest phase is the mixture of alcohol and water.

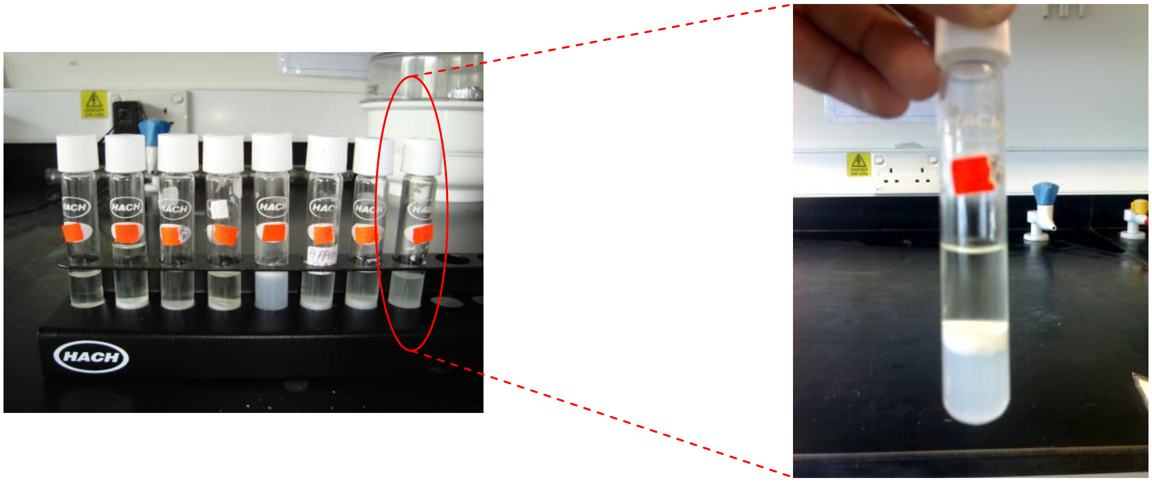


Figure 36: The different phase from the sample taken for transesterification process

Table 1: The labels in TLC analysis using silica plate

Parameters	Catalyst 2wt%	Catalyst 4wt%	Catalyst 6wt%
6:1 alcohol to oil ratio	Experiment 1	-	-
12:1 alcohol to oil ratio	Experiment 2	-	-
18:1 alcohol to oil ratio	Experiment 3	Experiment 4	Experiment 5
Extended for 9 hours (12:1)	Experiment 6	-	-

The alphabet for A represent 1 hour, B represent 2 hours, C represent 3 hours and finally D represent 4 hours of reaction. All the reaction is conducted at 70^{0}C.

4.3.1 Effect of time

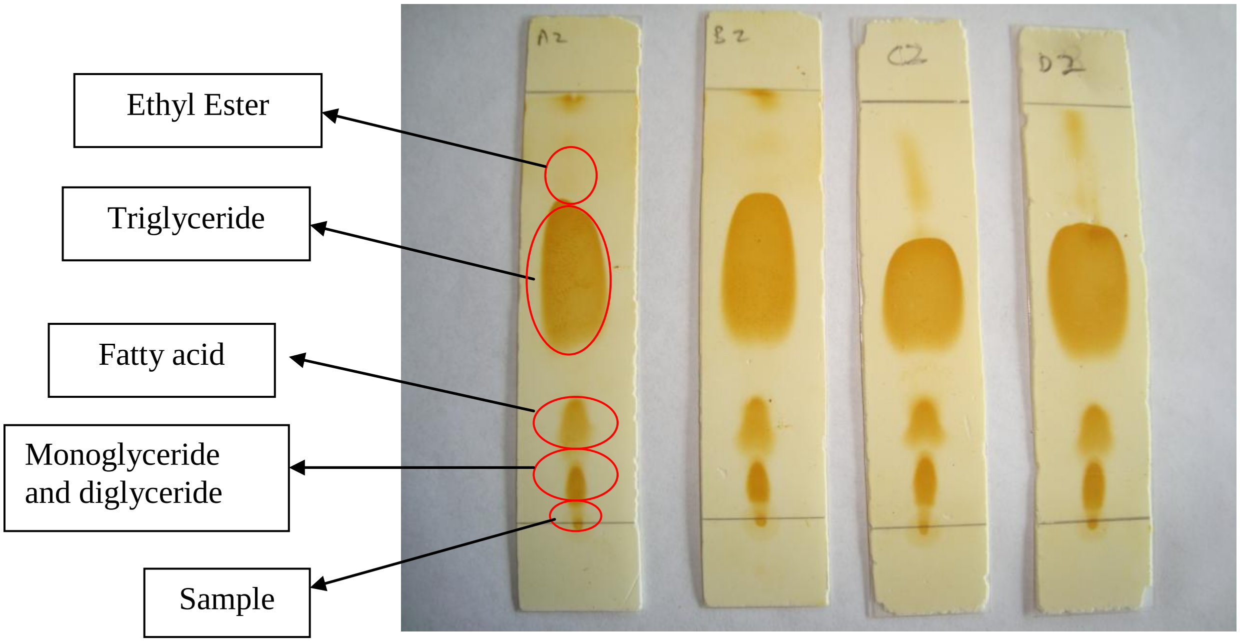


Figure 37: Effect of changing the time from A2 (1 hour), B2 (2 hours), C2 (3 hours) and D2 (4 hours). All the reactions are conducted at the same catalyst amount 2wt%, T=70^{0}C and 12:1 molar ratio of alcohol to oil. **(Experiment 2)**

Table 2: Image-J result for **experiment 2**

	Triglyceride	Diglyceride+monoglyceride	Ethyl ester	total	%tri	%di & mono
A2	109856	9284	0	119140	92.20749	7.79251301
B2	127734	10960	0	138694	92.09771	7.902288491
C2	104224	12636	0	116860	89.18706	10.81293856
D2	117394	15236	0	132630	88.5124	11.48759707

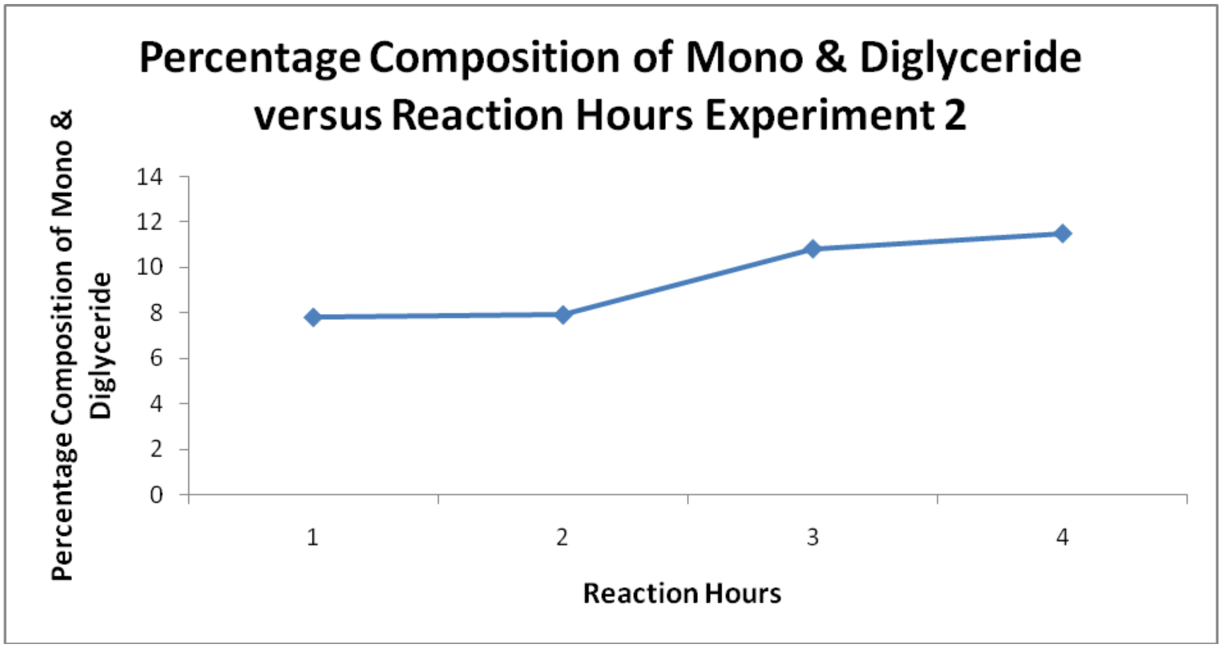


Figure 38: Graph Percentage Composition of Mono & Diglyceride versus Reaction Hours for **experiment 2**

As we can see from the result in Figure 37 no biodiesel is produced for four hours of reaction. However, the monoglyceride and diglyceride spots become larger. The darkness seems to be the same throughout the time. Darkness represents the concentration of the oil and biodiesel. Biodiesel has the darkest colour which differentiates it from other components. [22] Therefore this indicates that the concentration of the oil stays the same throughout the time. The longer the reaction time, triglyceride will change to diglyceride and monoglyceride as seen in Figure 2 because more reaction will happen as time goes by. This means that there is a reaction between the jatropha oil and ethanol with the presence of the catalyst. To see the amount of the diglyceride and monoglyceride, the area of the brown spots on the plate is measure using Image-J software. From Table 2 and Figure 38, the composition of diglyceride and monoglyceride increase from 7.79% to 11.49% from the first hour to the fourth hour. As the time increases, more reaction will happen.

To further investigate the problem, the author tried the reaction for six to nine hours of reaction. The result is shown in Figure 39.

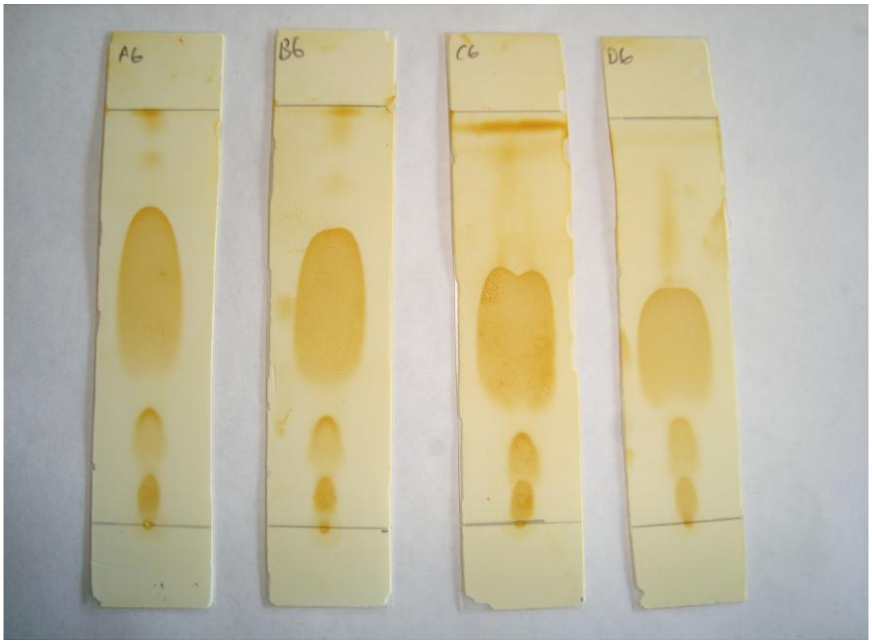


Figure 39: Effect of changing the time from A6 (6 hours), B6 (7 hours), C6 (8 hours) and D6 (9 hours). All the reactions are conducted at the same catalyst amount 2wt%, $T=70^0$C and 12:1 molar ratio of alcohol to oil. **(Experiment 6)**

Table 3: Image-J result for **experiment 6**

	Triglyceride	Diglyceride+monoglyceride	Ethyl ester	total	%tri	%di& mono
A6	110324	7792	0	118116	93.4031	6.596904738
B6	111152	9172	0	120324	92.37725	7.622751903
C6	116756	11624	0	128380	90.94563	9.05436984
D6	86564	10068	0	96632	89.58109	10.41890885

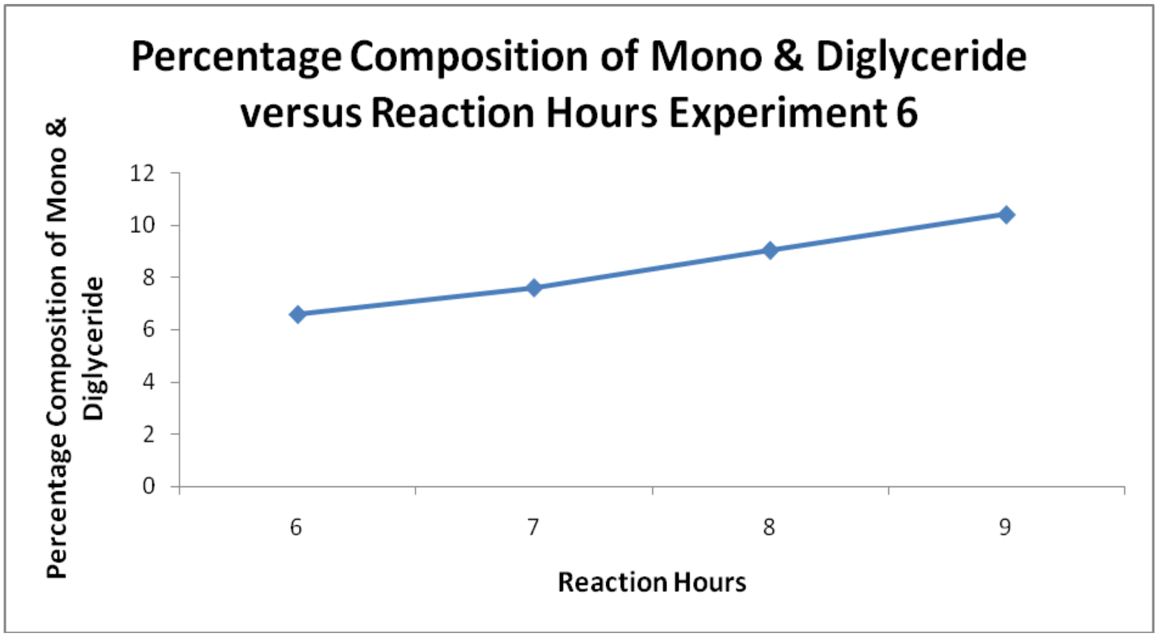


Figure 40: Graph Percentage Composition of Mono & Diglyceride versus Reaction Hours for **experiment 6**

The reason for the author to increase the time is to see whether nine hours for the reaction is enough to form biodiesel. We can see from Figure 39 the same effect as from previous result which showed the spot of mixture between monoglyceride and diglyceride increases from A6 for reaction of six hours to D6 for reaction of nine hours. This is because as time goes by more and more triglyceride will be converted to diglyceride and monoglyceride but the no biodiesel is produced. Therefore the problem here is not due to the time since the time for reaction is nine hours and from the literature, biodiesel is produced already in the second hour of reaction and the maximum conversion of biodiesel is at the seventh hour. [19] The spot area is analyzed again using Image-J software. From Table 3 and Figure 40, when the time increases from six hours to nine hours, the composition of diglyceride and monoglyceride increase from 6.6% to 10.42%.

4.3.2 Effect of alcohol to oil ratio

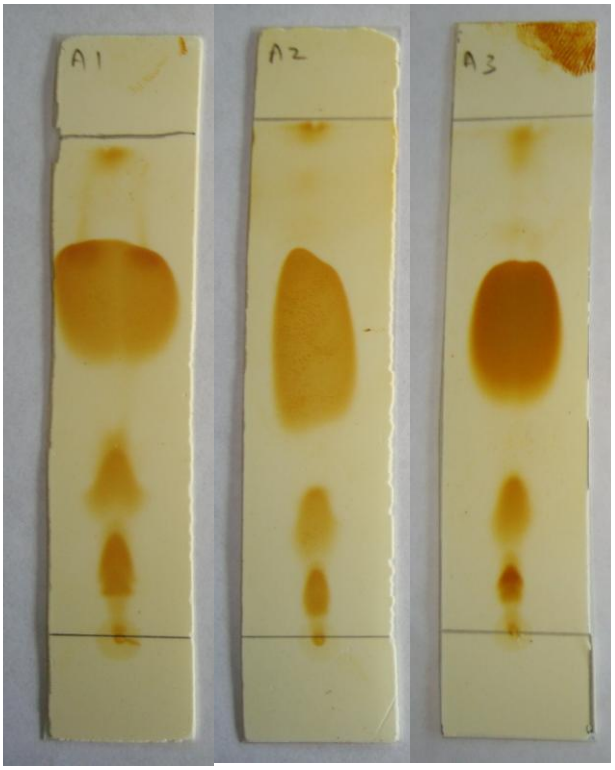


Figure 41: Effect of changing alcohol to oil ratio from A1 (6:1), A2 (12:1), A3 (18:1). All the reaction is conducted at the same catalyst amount 2wt%, T=70^{0}C and 1 hour of reaction.

Table 4: Image-J result for **different alcohol ratio analysis (A1=6:1, A2=12:1 and A3= 18:1)**

	Triglyceride	Diglyceride+monoglyceride	Ethyl ester	total	%tri	%di& mono
A1	111300	15100	0	126400	88.0538	11.94620253
A2	109856	9284	0	119140	92.20749	7.79251301
A3	65108	5432	0	70540	92.2994	7.700595407

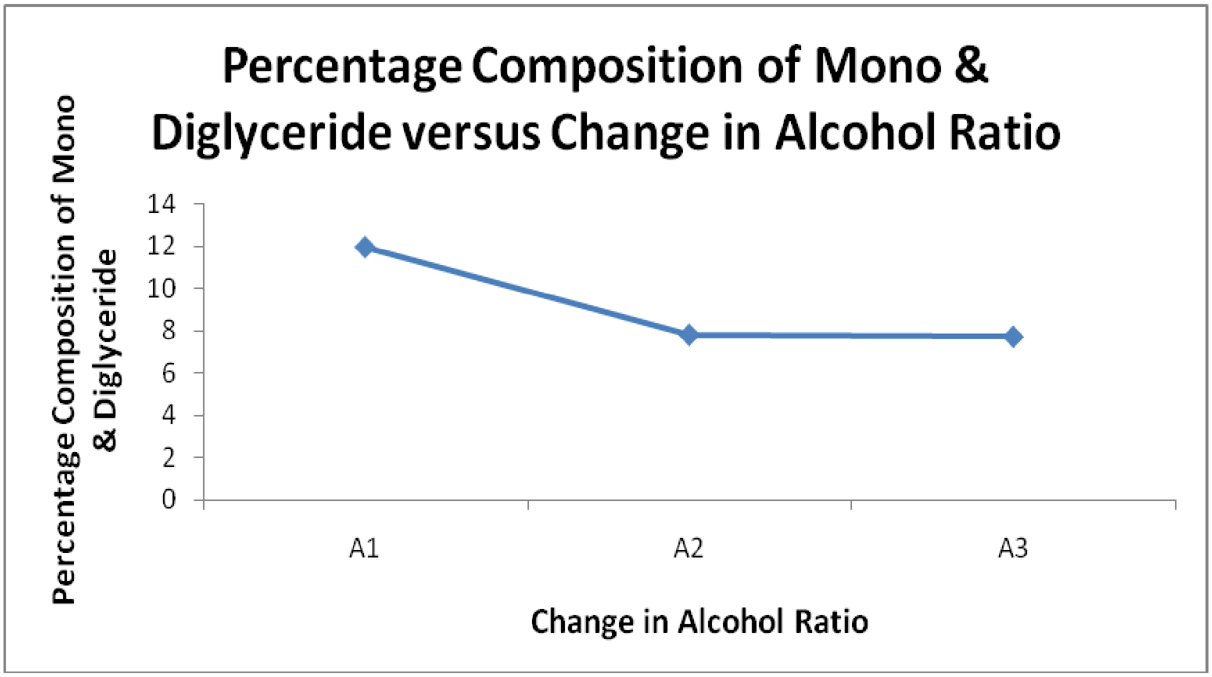


Figure 42: Graph Percentage Composition of Mono & Diglyceride versus Change in Alcohol Ratio

Wenlei Xie, Hong Peng and Ligong Chen et al showed that when alcohol to oil ratio increases, the amount of biodiesel produced increases. The oil used there is soybean oil and the author here used the jatropha oil. [19] Jatropha oil has a higher viscosity compare to the soybean oil. Therefore the author found out that that when the alcohol to oil ratio increases from 6:1 ratio to 18:1 ratio for 1 hour reaction with 2wt% of catalyst, the amount decreases from 11.95% to 7.7% is due to diffusion limitation between ethanol, solid catalyst and the oil where the three of them can not mix together. Therefore a co-solvent need to be used to make the oil dissolves in the ethanol to become a single phase and thus only two phases exist in the reaction which is the mixture of ethanol, co-solvent and oil with the solid catalyst. The other method is to use low viscosity oil rather than jatropha oil.

4.3.3 Effect of catalyst loading

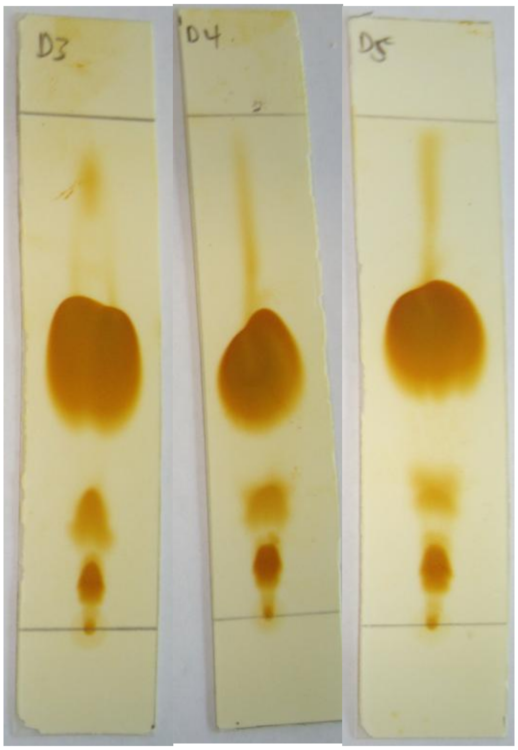


Figure 43: Effect of changing catalyst loading from D3 (2wt%), D4 (4wt%), D5 (6wt%). All the reaction is conducted at the same alcohol ratio of 18:1 and 4 hours of reaction.

Table 5: Image-J result for **different wt% of catalyst (D3=2wt%, D4=4wt% and D5= 6wt%)**

	Triglyceride	Diglyceride+monoglyceride	Ethyl ester	total	%tri	%di& mono
D3	62864	7476	0	70340	89.37162	10.62837646
D4	72984	8809	0	81793	89.23013	10.76987028
D5	79636	9772	0	89408	89.07033	10.92967072

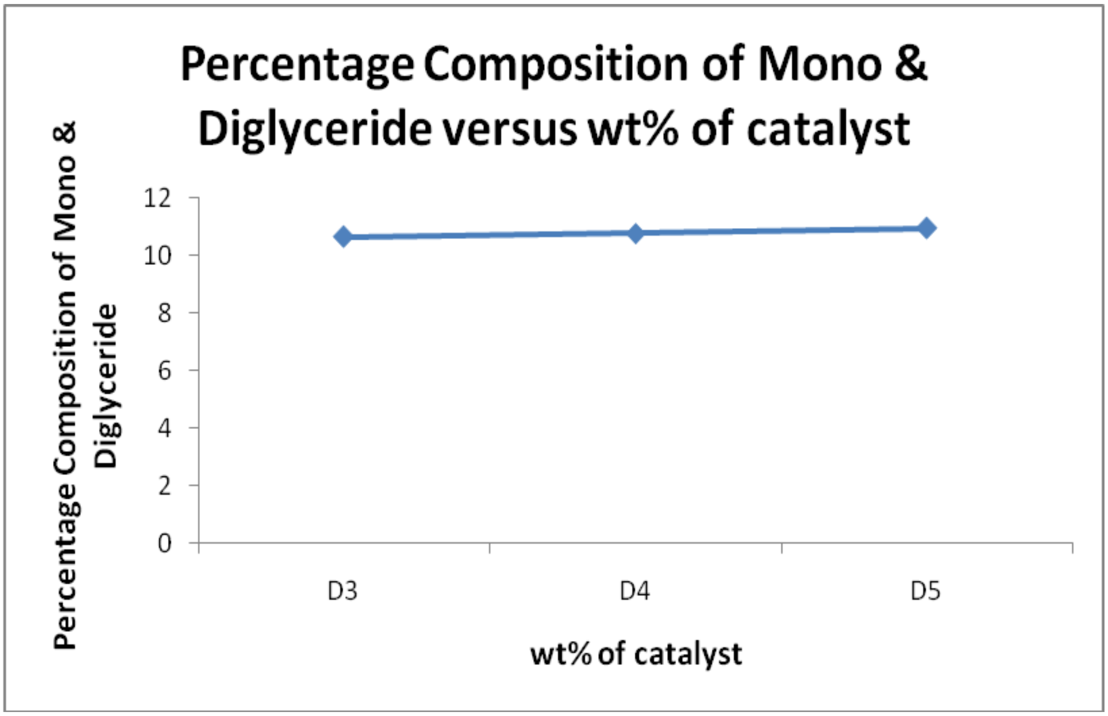


Figure 44: Graph Percentage Composition of Mono & Diglyceride versus Change in wt% of catalyst

The effect of catalyst from the Figure 43 can be seen that as the author increases the amount of catalyst from 2wt% to 6wt%, there is not much significant difference in the amount of monoglyceride and diglyceride. The only change can be seen is only in the free fatty acid amount. From here, the author can conclude that the nonreactive catalyst is the main problem that causes no production of biodiesel.

The factor that made the catalyst not active is because:

(a) The acidity-basicity tuning of the catalyst which means that the tuning of molar ratio between Mg to Al. The author use 2.5 Mg/Al.

(b) The calcination time for the catalyst. The author uses only 3 hours of calcination time.

(c) The calcination temperature of the catalyst. The author uses 500^{o}C to calcined the catalyst.

(d) The diffusion limitation of the heterogeneous catalyst. The reactants need to enter the pore of the catalyst, react and then diffuse out to get the product. It is not the case for homogeneous catalyst which is miscible in alcohol.

The Image-J analysis from Table 5 and Figure 44 proof that the catalyst is not reactive because the increase in 2wt% to 6wt% of catalyst increase the composition of monoglyceride and diglyceride by 0.3% only (from 10.63 to 10.93).

Table 6: The effect of parameters to the amount or concentration of the mixture between monoglyceride and diglyceride

Operating Parameters	Increase/Decrease	Amount or concentration of the mixture of Monoglyceride and Diglyceride
Molar ratio of ethanol to oil	⇧	⇩
Catalyst concentration	⇧	No effect because the catalyst is not reactive
Reaction time	⇧	⇧

Table 6 shows the summary of the results founded by the author which shows that the increase in molar ratio of ethanol to oil decreases the amount of monoglyceride and diglyceride. The increase in catalyst concentration does not affect the amount of the mixture of diglyceride and monoglyceride. Finally, as the time increases, the amount of monoglyceride and diglyceride increase.

CHAPTER 5

RECOMMENDATIONS

1.) The catalyst first need to be tested with soybean oil to see whether it works or not. Then it can be tested on the jatropha oil. This is to set the benchmark for research purposes.

2.) FESEM or SEM can be used to see the structure of the catalyst and pores size. Moreover for further research purposes BET can be used to check the surface area of the catalyst.

3.) Jatropha oil needs to be bought rather than extracted to get enough and consistent quality oil for transesterification reaction and to reduce the work load for extracting the oil from the seed. This is because the author focused is on testing the activity of the catalyst rather than the usage of the jatropha oil.

4.) Acidity and basicity tuning need to be done between the molar ratios of Mg to Al of the catalyst or by substituting with high basicity metal oxide or by increasing the catalyst loading to increase the activity of the catalyst. (The highest molar ratio is 3.0)

5.) Instead of using TLC which depends on manual preparation of standard solvent, GC (Gas Chromatography) can be use to get an accurate result. GC standard graph need to be installed in the computer by the technician and the technician incharge must know how to operate them.

6.) Increase the amount (mass) of the reactants so that when sample is taken for example 1ml for certain time will not affect the mass ratio of reactants in the reactor (3-necked flask).

7.) Methanol can be used instead of using ethanol because of its low cost and its physical and chemical advantages which is polar and shortest chain of alcohol.

8.) The reaction can also be done in the room condition temperature to see if temperature is the factor.

9.) Different type of oil can also be used due to the high viscosity and free fatty acid content of jatropha oil.

CHAPTER 6

CONCLUSION

The first objective based on this report which is to prepare the hydrotalcite derived Mg-Al oxide catalyst is done. The result shows that the peak from XRD analysis for the catalyst is 11.5°, 18°, 23°, 29° and 36°. These peaks coincide with the peak shown from the previous thesis done by Rita Chan Sok Nga. Therefore the author has achieved the first objective.

The second objective is to investigate the activity of catalyst, which the author has found that the catalyst is not reactive. As discussed in recommendations, this is due to three main factors which is first the basicity of catalyst (molar ratio between Mg-Al). Next is the calcination time and temperature of the catalyst and finally the diffusion limitation of the heterogeneous catalyst.

The final objective for this project is to study the parameters that affect transesterification process such as molar ratio of alcohol to oil, concentration of catalyst and the time. The author found that there were no production of biodiesel due to unreactive catalyst but the observation here is that when the author increased the time, the amount of monoglyceride and diglyceride increases while vice versa for the molar ratio of alcohol to oil. However, there is only a minor effect when changing the loading of catalyst.

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APPENDICES

APPENDIX A: CALCULATIONS

Molar ratio of ethanol to oil

$$(\frac{gram}{MW})_{\text{alcohol}} \text{ x } (\frac{MW}{gram})_{\text{oil}} = 6$$

$$(\frac{0.789g(v)}{46.09g/mol})_{\text{alcohol}} \text{ x } (\frac{919.443g/mol}{20g})_{\text{oil}} = 6$$

$V_{ethanol}$ = 7.621 ml by using 20g of jatropha oil

Concentration of catalyst that need to be used (wt%)

1.0 wt% of hydrotalcite Mg-Al means $(\frac{1.0}{100})$ x 20g = 0.2g of catalyst

Catalyst loading which will be used

A = $Mg(NO_3)_2.6H_2O$, Ma =284 g/gmole

B = $Al(NO_3)_3.9H_2O$, Mb = 417 g/gmole

C = $Na_2(CO_3)10H_2O$, Mc=286 g/gmole

Equations that are used

(i) $2[Mg(NO_3)_2.6H_2O] + Na_2(CO_3)10H_2O \rightarrow Mg_2(OH_2)_2.CO_3 + 2NaNO_3 + H_2O$

(ii) $Al(NO_3)_3.9H_2O + Na_2(CO_3)10H_2O \rightarrow Al(OH)CO_3 + 2NaNO_3 + H_2O$

The amount of $Mg(NO_3)_2.6H_2O$ & $Al(NO_3)_3.9H_2O$ needed

(a) Molar ratio of 1.5

$m_A + m_B = 50g$

$$(\frac{\text{Mole of A}}{\text{Mole of B}}) = 1.5 = (\frac{mA/MA}{mB/MB}) = (\frac{mA/284g/mo\ l}{mB/417g/mo\ l})$$

$m_A = 1.0216\ m_B$

$m_A + m_B = 50g$

$1.0216\ m_B + m_B = 50g$

m_B = **24.733g** while m_A = **25.267g**

(b) Molar ratio of 2.5

$m_A + m_B = 50g$

$$\left(\frac{\text{Mole of A}}{\text{Mole of B}}\right) = 2.5 = \left(\frac{mA/MA}{mB/MB}\right) = \left(\frac{mA/284g/mo\ l}{mB/417g/mo\ l}\right)$$

$m_A = 1.7026\ m_B$

$m_A + m_B = 50g$

$1.7026\ m_B + m_B = 50g$

m_B = **18.5g** while m_A = **31.5g**

To get the amount of Na2CO3.10H2O needed: Based on equation (i) and (ii):

(a) Mg:Na = 2:1

$$\left(\frac{NA}{NC}\right) = 2$$

$$\left(\frac{mA/MA}{mC1/MC}\right) = 2$$

$$\left(\frac{mA/284g/mo\ l}{mB/286g/mo\ l}\right) = 2$$

$m_A = 1.986\ m_{C1}$

$m_{C1} = 0.504\ m_A$

(b) Al:Na = 1:1

$$\left(\frac{NB}{NC}\right) = 1$$

$$\left(\frac{mB/MB}{mC2/MC}\right) = 2$$

$$\left(\frac{mB/417g/mo\ l}{mC2/286g/m\ ol}\right) = 1$$

$m_{C2} = 0.686\ m_B$

$m_C = m_{C1} + m_{C2}$

$= 0.504\ m_A + 0.686\ m_B$

Molar ratio 1.5 → $M_C = 0.504\ (25.267\text{g}) + 0.686\ (24.733\text{g})$

$= 29.70$ g

By using excess amount of 10% = (1.1) (29.70g)

= **32.67g**

Molar ratio 2.5 → $M_C = 0.504\ (31.5\text{g}) + 0.686\ (18.5\text{g})$

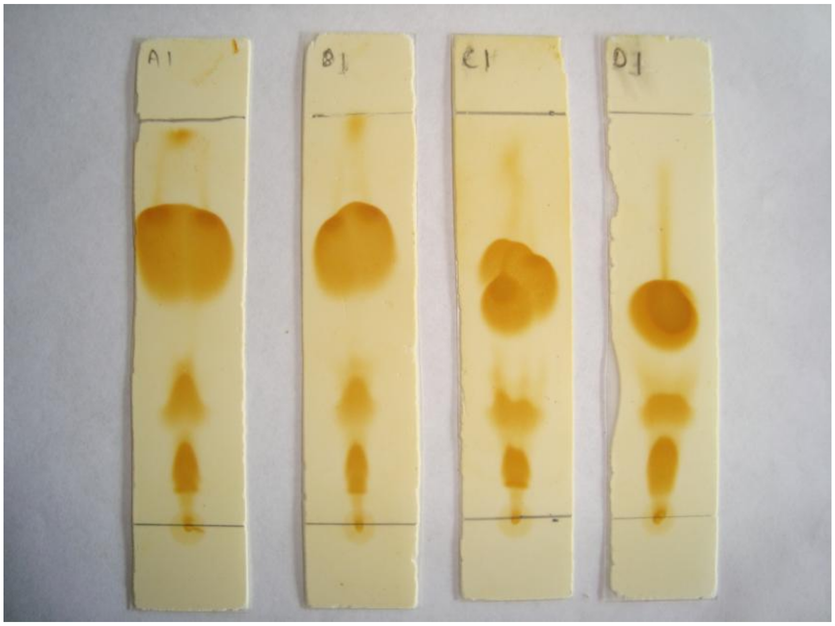
$= 28.567$ g

By using excess amount of 10% = (1.1) (28.567g)

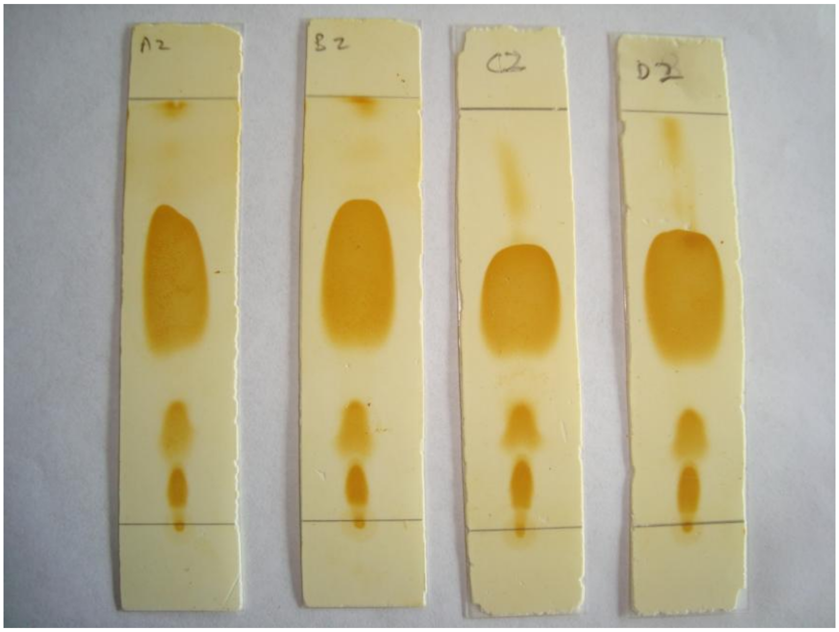
= **31.4237g**

APPENDIX B: TLC ANALYSIS

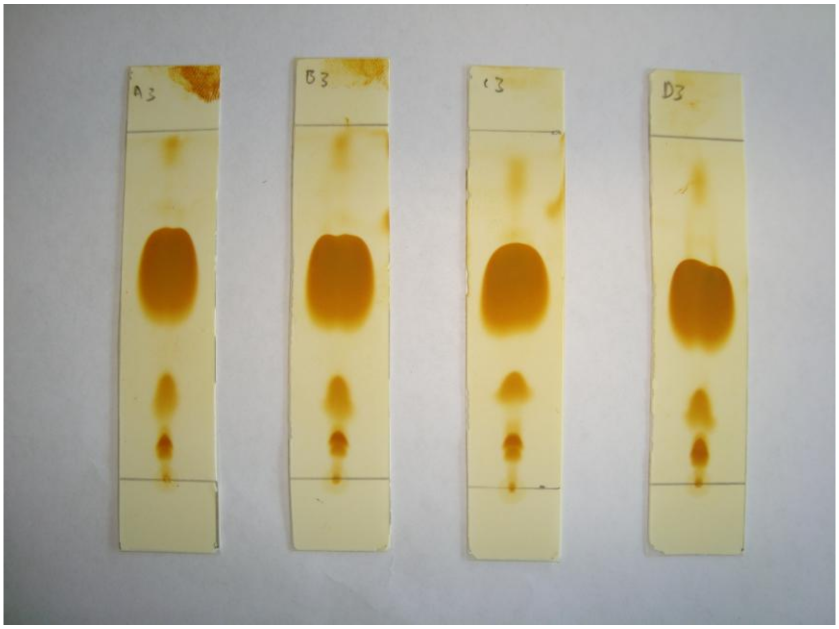
Experiment 1: 6:1 molar ratio of alcohol to oil, 2 wt% catalyst, T=70^{o}C and reaction time 4 hours



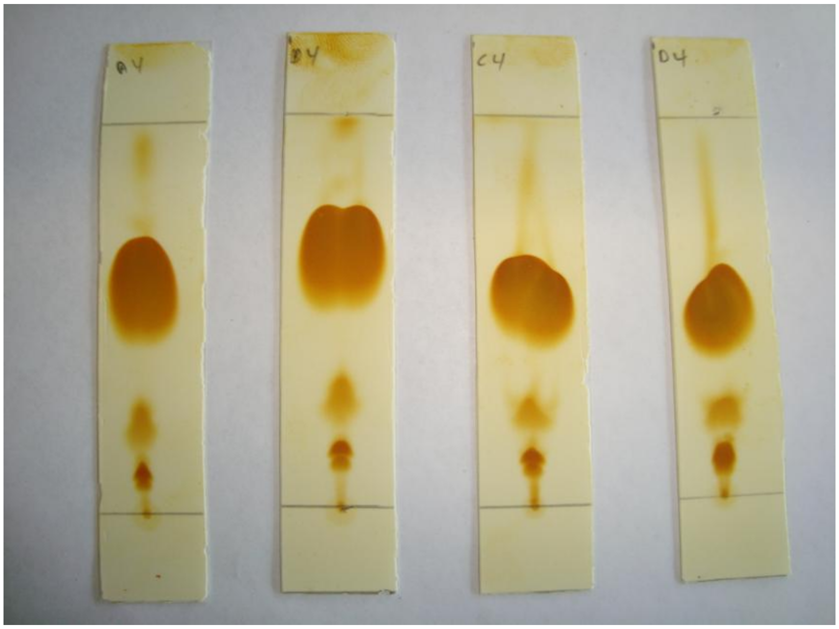
Experiment 2: 12:1 molar ratio of alcohol to oil, 2 wt% catalyst, T=70^{o}C and reaction time 4 hours



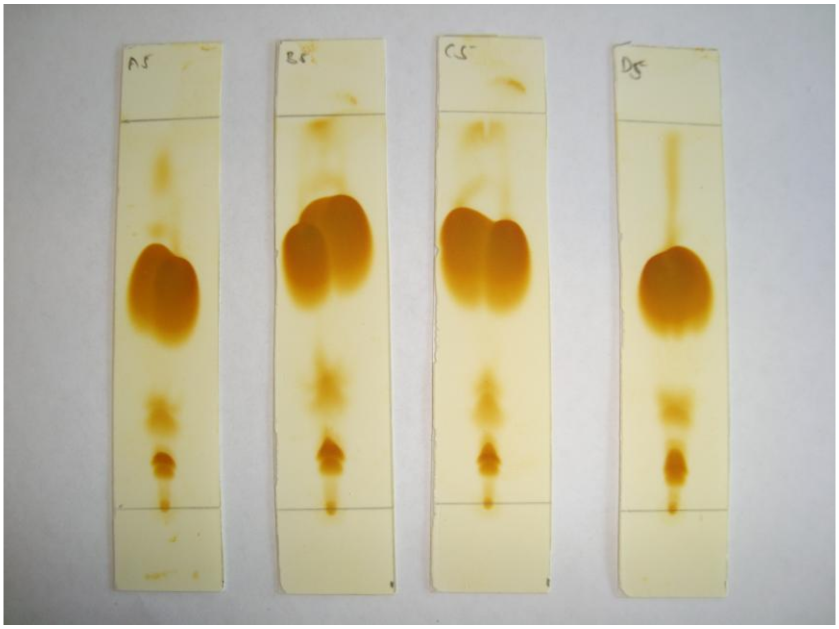
Experiment 3: 18:1 molar ratio of alcohol to oil, 2 wt% catalyst, $T=70^{o}C$ and reaction time 4 hours



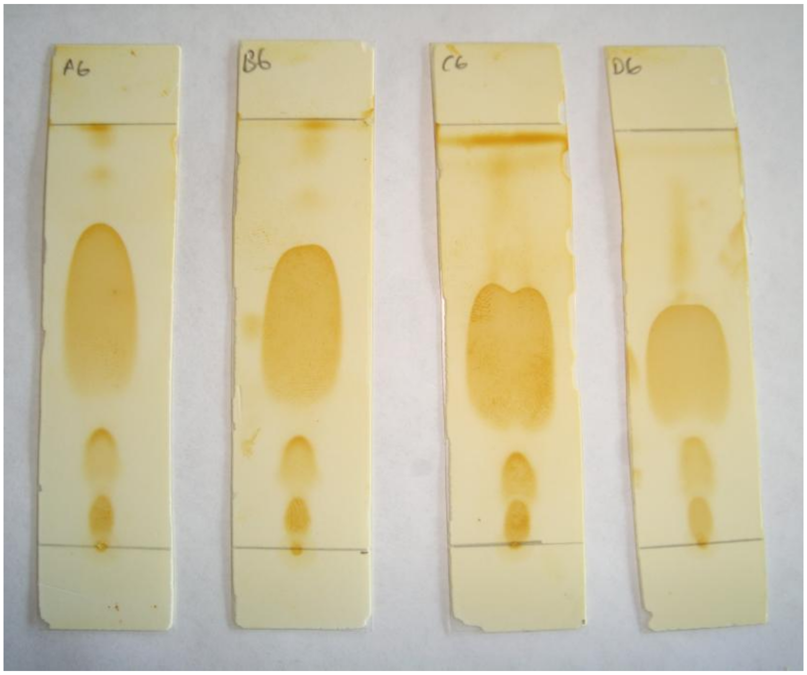
Experiment 4: 18:1 molar ratio of alcohol to oil, 4 wt% catalyst, $T=70^{o}C$ and reaction time 4 hours



Experiment 5: 18:1 molar ratio of alcohol to oil, 6 wt% catalyst, $T=70^{o}C$ and reaction time 4 hours



Experiment 6: 12:1 molar ratio of alcohol to oil, 2 wt% catalyst, $T=70^{o}C$ and reaction time 9 hours



APPENDICES

Detail/Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Briefing and update on student progress	🟦									🟪				
Project work commences		🟦	🟦	🟦						🟪				
Submission of progress Report 1					●					🟪				
Project work commences				🟦	🟦	🟦	🟦	🟦	🟦	🟦				
Submission of progress Report 2 (Draft of final report)										🟪	●			
Poster exhibition/ preedx										🟪	●			
EDX										🟪		●		

Submission of Final Report (CD softcopy & softbound)										▨				●
Final Oral Presentation										▨				31 May to 11 June
Submission of Final report hardbound										▨				18-Jun