

CHAPTER 1

INTRODUCTON

1.1 BACKGROUND OF STUDY

Currently, the energy re quirement of the world are mainly met through fossil fuels, such as gasoline, petroleum-based diesel, and natural gas. Such fossil-derived resources are scarce toward fulfilling the future energy demands and meeting the challenges of rapid human population growth and technological developments. The anticipated decreasing supply of fossil fuels coupled with environmental safety concerns has provoked the efforts to encourage the use of bio-based fuels as renewable energy source. Several types of biofuels, such as vegetable oil/animal fat (raw, processed or used), methyl esters from oil/fat, and ethanol or liquid fuels from biomass have been searched as a replacement for gasoline and petroleum diesel. ^[1]

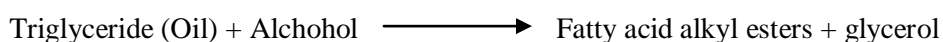
Biodiesel has a significant amount of low emissions compared to petroleum-based diesel when it is burned, whether used in its pure form or blended with petroleum diesel. It does not increase the level of carbon dioxide, CO₂ in the atmosphere which in turn reduces the green house effect. ^[2,3] It should be added that biodiesel is better than diesel fuels in terms of sulfur content, flash point, aromatic content and biodegradability. ^[4]

Currently, a heavy focus is on biodiesels made from crops such as corn, sugar cane, soybeans, sunflower and palm, for use as renewable energy sources. More than 95% of the world biodiesel is produced from edible oils which are easily available on large-scale from the agricultural industry ^[5]. Though it may seem beneficial to use renewable plant material for biodiesel, the use of crop residues and other biomass raises many concerns about vital environmental impact including food shortages ^[6]. It has to be added that the great concern about this issue is that continuous large-scale production of biodiesel from edible oils sparks the food versus fuel dispute. There are concerns that biodiesel feedstock may compete with food supply in the long term ^[7].

The rapidly growing world population and rising consumption of biodiesel are increasing the demand for both food and biodiesels. This extends to both food and fuel shortages. Extensive use of edible oils may cause other significant problems such as starvation in developing countries. With nearly 60% of humans in the world now currently malnourished, the need for grains and other basic food crops continues to be critical ^[8, 9].

One of the alternatives to edible oil for biodiesel production is non-edible oils. Non-edible plant oils have been found to be hopeful crude oils because of their significance in developing countries due to the high demand for edible oil as food, and their high expense to be used as fuel at present times.

The production of biodiesel comprises the conversion of vegetable oils/animal fats using alcohol and a catalyst to produce fatty acid alkyl esters and crude glycerol through a process called transesterification. Transesterification is an equilibrium reaction and occurs essentially by mixing the reactants. In this process, triglyceride reacts with an alcohol (methanol) in the presence of a strong acid or base (base in our case). ^[10]



The base-catalyzed transesterification is much faster and less corrosive than the acid-catalyzed reaction ^[11, 12]. Thus alkali hydroxides are the most commonly used catalysts. However, if the oil has a high free fatty acid (FFA) content, excess of alkali causes loss of the free fatty acids as their insoluble soaps. This decreases the final yield of ester and consumes alkali. As an alternative, in these cases, one can conduct an acid-catalyzed reaction that requires higher reaction temperatures (100°C) and longer reaction times than the former ^[12, 13].

It is to be noted that the reactants (oil and ethanol) and the products (fatty acid ethyl ester and glycerol) are partially mutual soluble in the reaction process. The transesterification reaction

takes place in the ethanol phase. So, the reaction rate greatly depends on the solubility of oil in ethanol. On the other hand, the formation of glycerol and FAEE may change the distribution of reaction components in different phases. The final products also exist in two separate phases, thus glycerol can be separated from FAEE by settling. The solubility of glycerol in the product FAME directly influences the following purification of biodiesel. Unreacted ethanol distributes in both FAEE and glycerol phases. The inter-solubility is also essential data for ethanol recovery [14].

1.2` PROBLEM STATEMENT

Our main objective through this project is to reduce the dependency on edible oil and increase the usage of inedible oil in the production of biodiesels. The type of inedible oil chosen is Treated *Jatropha Curcas* L. Oil (JCO) which can grow in arid, semiarid and wasteland. Apart from that, it requires little water and fertilizer. It must be added that JCO has a good oxidation stability (OS) which is above the EN-14112 specification (> 6h). However, JCO has a bad cloud point (CP) and pour point (PP).

The type of edible oil that we have chosen is refined corn oil (RCO). RCO does not have a good OS (~3.13h only. Refer Page 28). However, RCO has a very good CP and PP [10]. Hence, *Jatropha Curcas* biodiesel (JCBD) is going to be blended with refined corn oil biodiesel (RCBD) and the effect on the OS, PP and CP is going to be observed.

1.3 OBJECTIVES

The objectives of this project are as follow:

- i) To produce biodiesel from Refined Corn Oil (RCO) and Treated Jatropha Curcas L. Oil (JCO)
- ii) To blend Refined Corn Oil Biodiesel (RCBD) and Treated Jatropha Curcas L. Oil biodiesel (JCBD) in varied compositions
- iii) To obtain the trend in the oxidation stability (OS), pour point (PP) and cloud point (CP) of all these varied compositions

1.4 SCOPE OF STUDY

The scope in this research covers two main major areas. The first one is the production of biodiesel from Refined Corn Oil (RCO) and Treated Jatropha Curcas L. Oil (JCO). The second one is the determination of the oxidation stability (OS), pour point (PP) and cloud point (CP) for the blend with various compositions. RCBD and JCBD were blended in volume percent:

100:0 (JCBD),

80:20 (JCBD-1),

60:40 (JCBD-2),

40:60 (JCBD-3),

20:80 (JCBD-4)

0:100 (RCBD).

CHAPTER 2

LITERATURE REVIEW

2.1 JATROPHA CURCAS L. OIL (JCO)

Jatropha Curcas is a nut belonging to the Euphorbiaceae family. It is cultivated in central and South America, South East Asia, India and Africa.⁸ In Malaysia, wild Jatropha Curcas tree is also known as Jarak Pagar particularly in Peninsular Malaysia area. J. curcas tree which can easily be propagated by cutting is widely planted as a hedge to protect the field's erosion, as it is not browsed by cattle. J. curcas can grow well under such adverse climatic because of its low moisture demands, fertility requirements and tolerance to high temperatures.^[15]

Table 1: Fatty Acids Composition of Malaysian Jatropha Curcas Oil

Type of Fatty Acid	Percentage (%)
Palmitic	13.89 +/- 0.06
Palmitoleic	0.61 +/- 0.33
Stearic	7.16 +/- 0.36
Oleic	46.40 +/- 0.19
Linoleic	31.96 +/- 0.20
Saturated Fatty Acid	21.05
Unsaturated Fatty Acid	78.95

* Source: Salimon, J., & Abdullah, R. (2008). Physicochemical Properties

Based on the above table, in general, Jatropha Curcas L. Oil contained more unsaturated fatty acid compared to saturated fatty acid. This made the oil suitable for biodiesel production. However, it needs to be added that the chemical compositions of the oil vary according to the climate and locality^[15].

2.2 CORN OIL

Zea mays L. or known as corn is a cereal crop, a member of the grass family. Corn is grown around the world and is one of the globe's most widely used food staples; corn varieties are directly used for food and animal feed or processed to make food and feed ingredients (such as high fructose corn syrup, corn starch and lysine) or industrial products such as ethanol and polylactic acid (PLA). The two primary methods of processing corn are referred to as "dry" and "wet" milling ^[16].

Corn oil, which is extracted from corn germ, has been used as bottled oil for consumer use, followed by margarine and industrial snack-frying operations. By removing free fatty acids and phospholipids from crude corn oil, the oil refining process gives corn oil one of the qualities consumers value most: its excellent frying quality and resistance to smoking or discoloration. It also has a pleasant taste, resists developing off-flavors ^[17].

Table 2: Fatty Acids Composition of Corn Oil

Type of Fatty Acid	Percentage (%)
Palmitic	12.0
Stearic	2.4
Linolenic	1.0
Oleic	27.3
Linoleic	55.8
Other/ Unknown	1.5

* Source: Ang, Catharina Y. W., KeShun Liu, and Yao-Wen Huang, eds. (1999). *Asian Foods*

2.3 TRANSESTERIFICATION

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis ^[16].

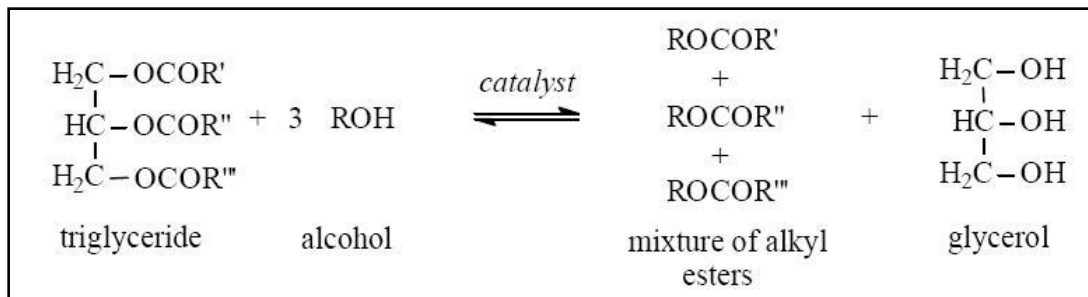


Figure 1: General Equation of Transesterification

Transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of a catalyst (typically a strong acid or base) accelerates considerably the adjustment of the equilibrium^[17].

2.3.1 Transesterification of Vegetable Oil

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol^[11,13]. The overall process is a sequence of three consecutive and reversible reactions, in which di- and monoglycerides are formed as intermediates^[5]. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol.

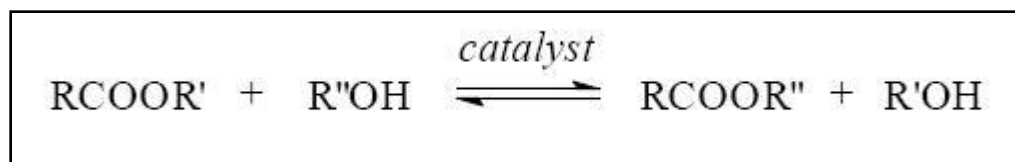


Figure 2: Transesterification of Vegetable Oil

However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed. Figure 2 above illustrates the transesterification of vegetable oils^[17].

2.3.2 Base-Catalyzed Process

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed process^[12,13]. Due to this reason, together with the fact that the alkaline catalysts are less corrosive than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides^[12,13,18] and hydroxides^[19-23].

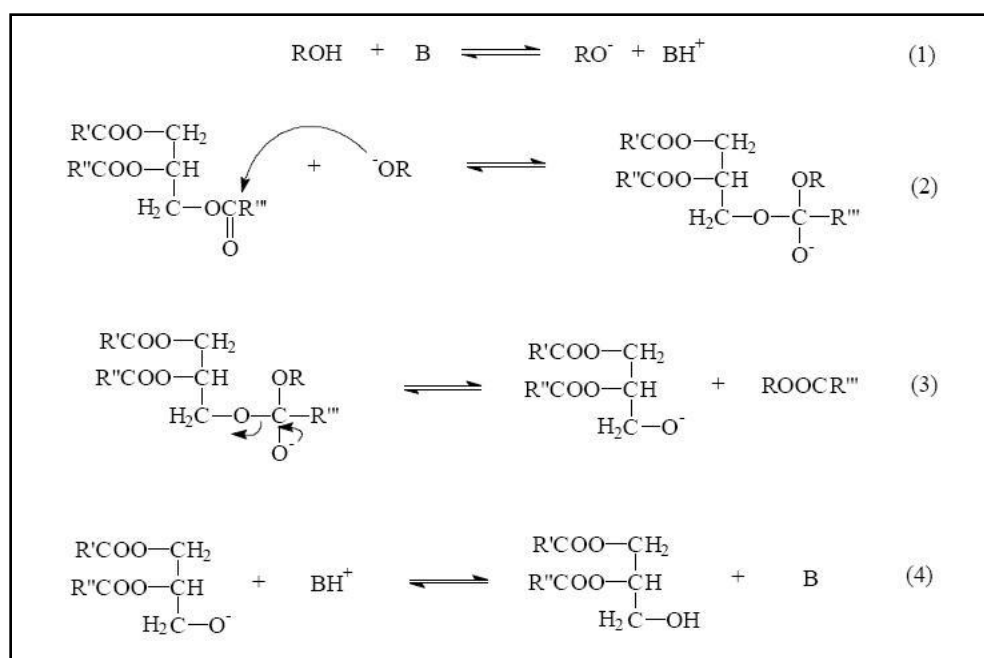


Figure 3: Mechanism of the base-catalyzed transesterification of vegetable oils

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Figure 3. The first step (Eq. 1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2)^[24,25], from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol^[17].

2.4 OXIDATION STABILITY

Numerous factors affect the oxidative stability of biodiesel during its commercialization. As the parent vegetable oil, biodiesel is susceptible to the oxidation of its unsaturated fatty acid esters [26, 27]. Ultraviolet irradiation, metal contamination enzymes, heating, humidity and pigments can change and further deteriorate biodiesel's performance [28, 29].

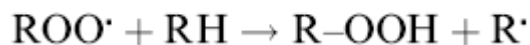
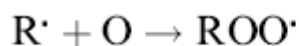
The quality of biodiesel is designated by several standards like EN-14214 and ASTM D-6751 and the oxidation stability (OS) is among the monitored parameters as EN-14214 calls for determining OS at 110°C with a minimum induction period (IP) of 6 hours by the Rancimat method [30, 31]. Both oxygen content and exposition time play an important role in the formation of undesired compounds, which can corrode the engines or clog the filters and injection systems of the engines [32]. Thus oxidative stability has to be considered as an essential characteristic in the control of the biodiesel properties [33, 34, 35].

Oxidation process is reported in literature and relative rates of oxidation are 1 for oleates, 41 for linoleates and 98 for linolenates [36, 37]. The positions allylic to the double bonds are the areas prone to be having oxidation chain reaction. Therefore, fatty acids with methylene-interrupted double bonds, for example, linoleic acid are more susceptible to oxidation because they contain methylene group that are allylic to two double bonds. Fatty acids with two such methylene groups, for example linolenic acid are even more prone of getting oxidized [38, 39, 37].

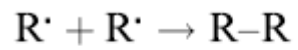
Oxidation stability begins with an initial chain reaction [40].



Followed by a propagating reaction that involves unstable peroxides and hydroperoxides [40]



Followed by the termination reactions resulting in aldehydes, alcohols and carbonic acids ^[40]



Due to these reasons, biodiesel is relatively unstable when kept apart from the mentioned above problems, it can also cause injector coking and corrosion of metal parts. This is why OS is such a vital criterion for biodiesel ^[41].

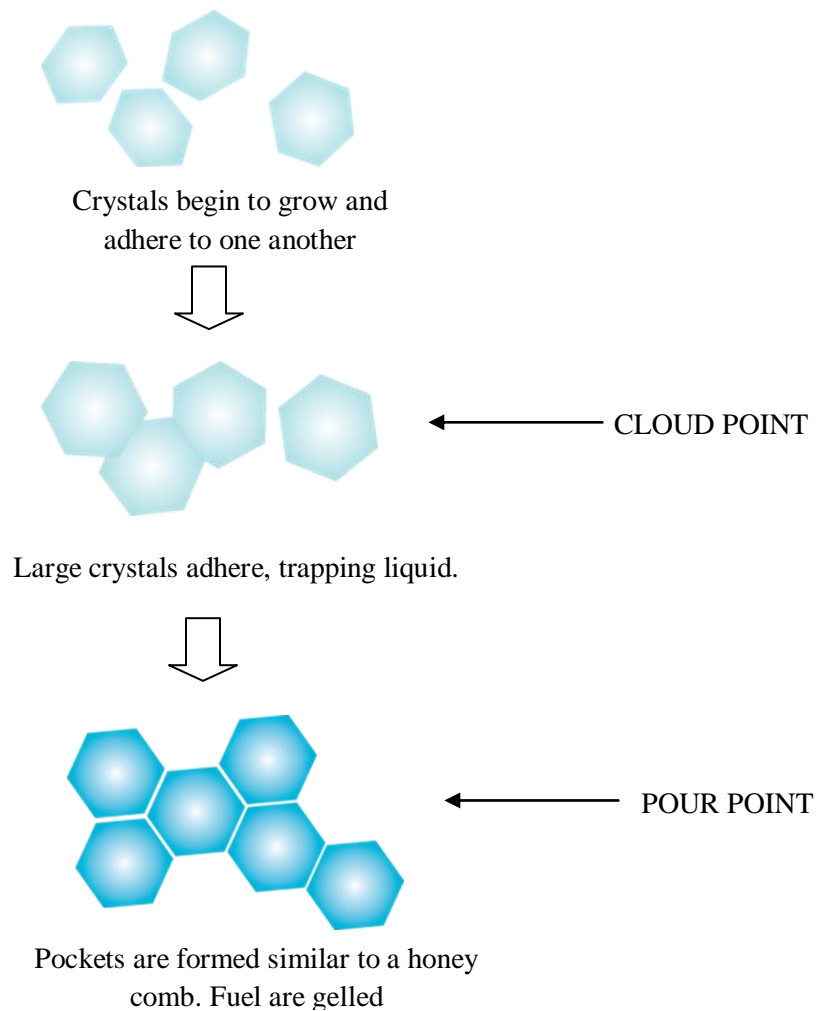
2.5 CLOUD POINT AND POUR POINT

2.5.1 Cloud Point

The cloud point is the temperature at which a cloud of wax first appears in a fuel sample that is cooled under conditions described by ASTM D2500. The cloud point is determined by visually inspecting for a haze in the normally clear fuel ^[42].

2.5.2 Pour Point

The pour point is the lowest temperature at which movement of the biodiesel sample can be determined when the sample container is tilted. The sample must be cooled following the procedure described in ASTM D97 ^[42].



CHAPTER 3

METHODOLOGY

3.1 MATERIALS AND EQUIPMENT

Table 3: Materials required for Acidity Check

Aspect	Name	Brand/Procured from
Solvent	2-Propanol	Merck/Avantis Laboratories Sdn. Bhd
	Toluene	Merck/Avantis Laboratories Sdn. Bhd
Titrant	Potassium Hydroxide	R&M Chemicals
Indicator	Phenolphthalein (General Purpose Grade)	Fisher Scientific

Table 4: Materials and required for Pre-esterification reaction

Aspect	Name	Brand/Procured from
Oil	Refined Corn Oil	Mazola/Sweet Yet Development Sdn. Bhd.
	Jatropha Curcas L. Oil	BERNAS
Alcohol	Methanol	Sigma-Alrich 34940
Acid	Sulphuric Acid	Sigma-Alrich ACS Reagent 95.0% - 98.0%
Drying Agent	Anhydrous Sodium Sulfate	Merck/Avantis Laboratories Sdn. Bhd.

Table 5: Materials required for Transesterification reaction

Aspect	Name	Brand/Procured from
Oil	Refined Corn Oil	Mazola/Sweet Yet Development Sdn. Bhd.
	Jatropha Curcas L. Oil	BERNAS
Alcohol	Methanol	Sigma-Alrich 34940
Catalyst	Sodium Methoxide (30% solution in methanol)	Merck/Avantis Laboratories Sdn. Bhd.
Drying Agent	Anhydrous Sodium Sulfate	Merck/Avantis Laboratories Sdn. Bhd.

Equipments and tools

1. 3-necked round bottomed flask
2. Thermometer
3. Separating funnel
4. Reflux condenser
5. Hot plate with magnetic stirrer
6. Burette

3.2 RESEARCH METHODOLOGY

3.2.1 MATERIAL PROCUREMENT

Materials needed for the transesterification process (e.g. RCO, JCO, methanol, sodium methoxide, anhydrous Na₂SO₄) and titration analysis (e.g. toluene, phenolphthalein and 2-propanol) have been listed and procured from suppliers. (Refer table 3, 4 and 5)

3.2.2 ACIDITY TEST

Before proceeding with transesterification, the oil sample needs to be tested for acidity value. An adaptation of the American Oil Chemists' Society (AOCS) Method Cd 3d-63 was used. Steps are as elaborated below:

Titrant	:	KOH (85% Assay); 0.66g/500mL Isopropanol
Solvent	:	Isopropanol : Toluene; (1:1)
Indicator	:	Phenolphthalein; 1.0g/100mL Isopropanol

1. Fill burette with KOH titrant
2. Aliquot 25mL solvent into beaker with magnetic stirrer and add 0.4 mL indicator
3. Note volume on burette
4. Add titrant drop-wise while stirring until faint pink color remains
5. Note volume on burette and record volume KOH used (B)
6. Add 2g (W) of oil sample and mix until fully dissolved
7. Add titrant drop-wise until faint pink color remains
8. Note volume on burette and note volume KOH used (A).
9. Acid Value is tabulated using the below equation:

$$\frac{[(A - B) \times N \times 56.11]}{W}$$

Where:

A – Volume of titrant used for sample

B – Volume of titrant used for blank

N – 0.02

W – 2

3.2.3 PRE-ESTERIFICATION EXPERIMENTAL PROCEDURE

Since the acidity test on *Jatropha Curcas* L. Oil (JCO) yielded an acidic value (> 3%), pre-esterification procedure was conducted to reduce the acidity value.

1. 250g of Crude *Jatropha Curcas* L. Oil was taken in a three-necked round bottomed flask.
2. 80 g of methanol was taken in a 200 ml measuring cylinder.
3. 0.4 ml (0.5 vol%) of sulfuric acid (H_2SO_4) was measured and poured into a measuring cylinder.
4. Oil was warmed by placing the round-bottomed flask in the water bath maintained at $65^\circ C$.
5. Methanol and sulfuric acid were added into the oil for vigorous mixing by means of a mechanical stirrer fixed in the flask.
6. The required temperature ($65^\circ C$) was maintained throughout the stirring and after 4 hours, the mixture was left overnight.
7. The 2 layer mixture of treated *Jatropha* Oil and residue are then poured into a separating funnel and the bottom layer (treated *Jatropha* Oil) is separated and stored.
8. Treated *Jatropha* Oil is washed with de-ionized until the washed de-ionized water's pH is around 7 (neutral) to further remove impurities (e.g excess ethanol and sulfuric acid).
9. Treated *Jatropha* Oil is mixed with anhydrous $NaSO_4$ to remove the water in it.
10. Mixture of treated *Jatropha* Oil and anhydrous $NaSO_4$ is poured into a separating funnel and pure, crystal clear Treated *Jatropha* Oil is obtained.
11. The pure Treated *Jatropha* Oil is then checked its acidity using the Acidity Test method shown in section 3.2.2.

3.2.4 TRANSESTERIFICATION EXPERIMENTAL PROCEDURE

3.2.4.1`Production of Refined Corn Oil Biodiesel (RCBD) using Methanol

1. 100g of Refined Corn Oil (RCO) was taken in a three-necked round bottomed flask.
2. 23.44 g of methanol was taken in a 200 ml beaker.
3. 1 g of sodium methoxide was taken in a measuring cylinder.
4. RCO was warmed by placing the round-bottomed flask in the water bath maintained at 65°C.
5. Sodium methoxide and methanol solution was added into the oil for vigorous mixing by means of a mechanical stirrer fixed in the flask.
6. The required temperature (65°C) was maintained throughout the stirring and after 90 minutes, the mixture was left overnight.
7. The 2 layer mixture of RCBD and glycerol are then poured into a separating funnel and the bottom layer (glycerol) is separated.
8. RCBD is washed with de-ionized water to further remove impurities (e.g catalyst, glycerol).
9. RCBD is mixed with anhydrous sodium sulfate, NaSO₄ to remove the water in it.
10. Mixture of RCBD and anhydrous NaSO₄ is poured into a separating funnel and pure, crystal clear biodiesel is obtained.

3.2.4.2`Production of Jatropha Curcas Oil Biodiesel (JCBD) using Methanol

1. 100g of Treated Jatropha Curcas Oil (JCO) was taken in a three-necked round bottomed flask.
2. 23.50 g of methanol was taken in a 200 ml beaker.
3. 1 g of sodium methoxide was taken in a measuring cylinder.
4. JCO was warmed by placing the round-bottomed flask in the water bath maintained at 65°C.
5. Sodium methoxide and methanol solution was added into the oil for vigorous mixing by means of a mechanical stirrer fixed in the flask.
6. The required temperature (65°C) was maintained throughout the stirring and after 90 minutes, the mixture was left overnight.
7. The 2 layer mixture of JCBD and glycerol are then poured into a separating funnel and the bottom layer (glycerol) is separated.
8. JCBD is washed with de-ionized water to further remove impurities (e.g catalyst, glycerol).
9. JCBD is mixed with anhydrous sodium sulfate, NaSO_4 to remove the water in it.
10. Mixture of JCBD and anhydrous NaSO_4 is poured into a separating funnel and pure, crystal clear biodiesel is obtained.

3.2.5 OXIDATION STABILITY EXPERIMENT USING METROHM 873 RANCIMAT

1. Appropriate method is selected from the method list under the method column on selected block (Block A or Block B or both).
2. The heat button is pressed from the software to heat the selected block.
3. 3.0g of biodiesel sample are weighed accurately into the reaction vessel.
4. The reaction vessel is fitted with the air inlet tube, sealing ring, and the connection nipple accordingly.
5. 50ml of distilled water is measured into the measuring vessel by using a measuring cylinder.
6. The measuring cylinder is closed with the cover (which comes with the conductivity electrode).
7. Once the required temperature is reached (appearance of a green light is sighted), the reaction vessel was placed into the opening provided in 873 Rancimat.
8. The white tubing that attached to the collecting tube is connected to the connection piece on the measuring vessel cover.
9. The START button is pressed on the selected channel of the selected Block from the software to start the measurement of the sample.
10. Steps 4 to 9 are repeated for other samples.

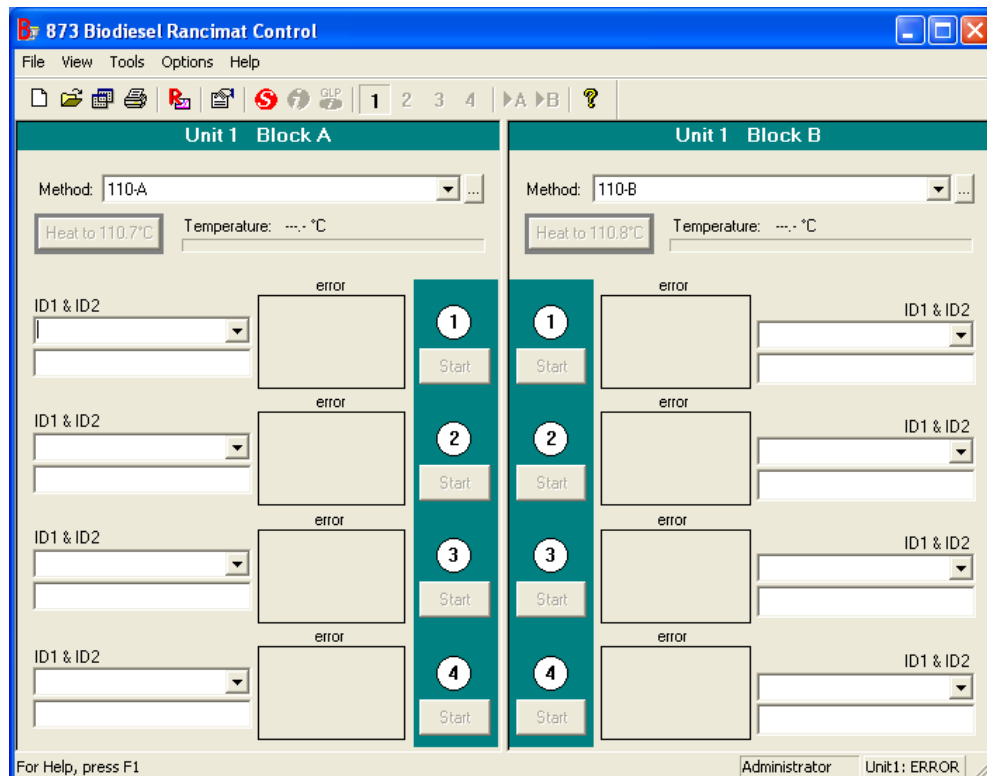


Figure 4: Graphical User Interface (GUI) for the 873 Rancimat

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. ACIDITY TEST

Acid Value is tabulated using the below equation:

$$\frac{[(A - B) \times N \times 56.11]}{W}$$

Where:

A – Volume of titrant used for sample

B – Volume of titrant used for blank

N – 0.02

W – 2

4.1.1 Refined Corn Oil

From Table 10 (Refer Appendix A.1), it can be concluded that the acidity of refined corn oil which is 0.78554% is way below the pre-requisite (3%). Thus, no pre-treatment is required for this oil.

4.1.2 Crude *Jatropha Curcas L.* Oil

From Table 11 (Refer Appendix A.2), it can be concluded that the acidity of refined corn oil which is 28.3905% is way above the pre-requisite (3%). Thus, pre-treatment is required for this oil.

4.1.3 Treated *Jatropha Curcas L.* Oil

From Table 12 (Refer Appendix A.3), it can be concluded that the acidity of treated *Jatropha* oil which is 0.2244% is way below the pre-requisite (3%). Thus, no further pre-treatment is required for this oil.

4.2 MOISTURE CONTENT

The moisture content of RCBD and JCBD were estimated following ASTM D95 using Mettler Toledo DL 39 (Karl Fischer Coulometer). The results are as follow:

Table 6: Moisture content of RCBD and JCBD

Sample	Moisture Content (ppm)
Refined Corn Oil Biodiesel (RCBD)	189.16
Treated Jatropha Biodiesel (JCBD)	148.11

The ASTM D95 method limits the moisture content to be less than 500ppm in order to make the biodiesel to qualify as a good sample. Low moisture content is an important aspect for a biodiesel because it will affect the cloud point and pour point of the sample. In this case, the moisture content of both RCBD and JCBD is well below the moisture content limit which makes it applicable for other usages.



Figure 5: Mettler Toledo DL 39 (Karl Fischer Coulometer)

4.3 FREE FATTY ACID PROFILE

The biodiesel samples (RCBD and JCBD) were analyzed by gas chromatography in order to assess the conversion of the triglycerides into their methyl esters. RCBD and JCBD fatty acid profile was determined by using 7890A gas chromatograph (Agilent Technology Inc., USA), equipped with a BP-X5 (SGE) capillary column (30 m x 0.25 mm x 0.25 mm) and a flame ionization detector.

The column temperature program: initial temperature 100°C, kept 3 min, and then to 200°C/min up to 170°C, kept 10 min, followed up to 260°C. Helium was used as the carrier gas. The injector temperature was programmed at 280°C. Approximately 0.1 mL of the sample was diluted in 1 mL of solvent (hexane) and a sample volume of 0.1 µL was injected onto the column. The retention time was used in the identification of the peaks by comparing them with authentic standards analyzed under the same conditions. Table 10 and 11 presents these results, as well as theoretical biodiesel compositions, based on the fatty acid compositions of corn oil and *Jatropha Curcas* L. Oil available in the literature respectively ^[43, 44].

Table 7: Free Fatty Acid Composition of RCBD

Fatty Acid	This work/wt%	[43]/wt%
Palmitic	0.39	11.8
Stearic	9.09	2.0
Oleic	44.45	24.8
Linoleic	46.07	61.3
Saturated Fatty Acid	9.48	13.8
Unsaturated Fatty Acid	90.52	86.1

Table 8: Free Fatty Acid Composition of JCBD

Fatty Acid	This work/wt%	[44]/wt%
Palmitic	16.45	19.50
Stearic	9.98	6.80
Oleic	37.67	41.30
Linoleic	35.90	31.40
Saturated Fatty Acid	26.43	26.30
Unsaturated Fatty Acid	73.57	72.70

Based on the comparison done in the table above, it can be said that the free fatty acid (FFA) contents of the RCBD and JCBD produced somehow coincides with the data in the journal. The results, as expected by the RCBD composition, indicated the abundance of linoleic acid (46.07 wt. %). The second richest ester in RCBD is oleic acid, with 44.45wt. %.

Where as, from table 11, JCBD composition indicates higher amount of palmitic acid (16.44 wt. %) and stearic acid (9.98 wt. %) as compared to RCBD. This shows that the amount of unsaturated fatty acid in RCBD is way higher (90.52 wt. %) compared to JCBD (73.57 wt. %). This will be an important aspect as these facts can be used in predicting the oxidation stability (OS) of the biodiesels.

Below are the gas chromatography (GC) results generated for both RCBD and JCBD:

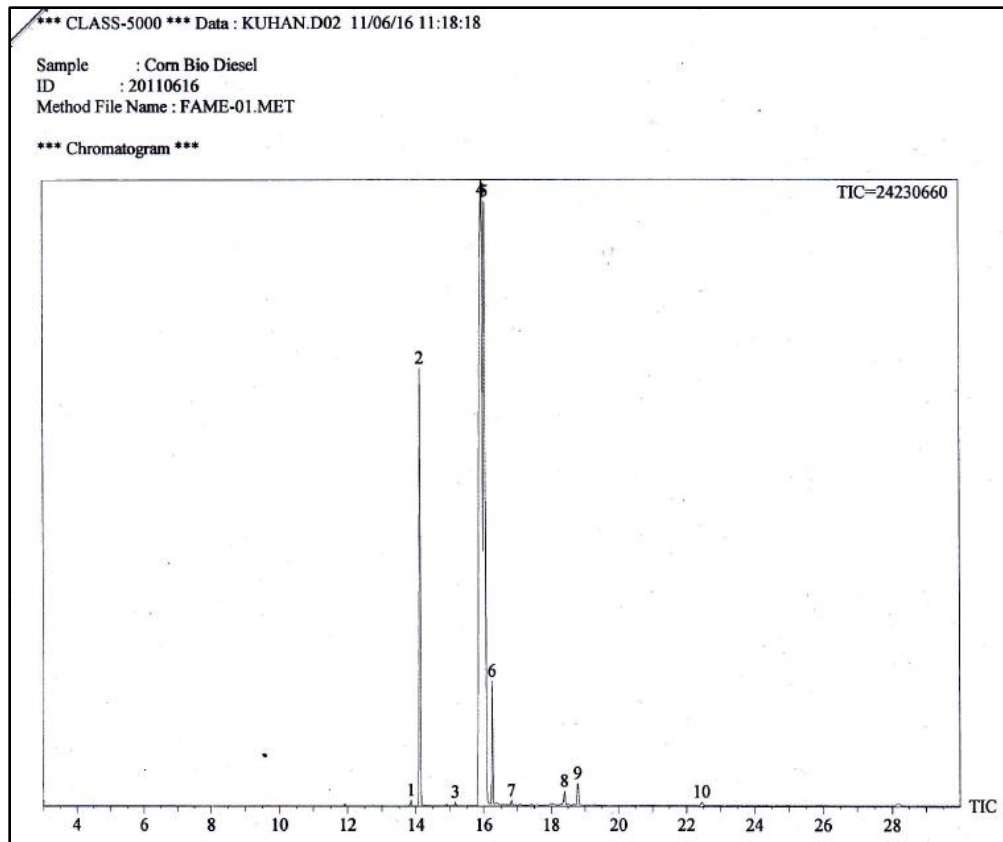


Figure 6: RCBD Free Fatty Acid Content

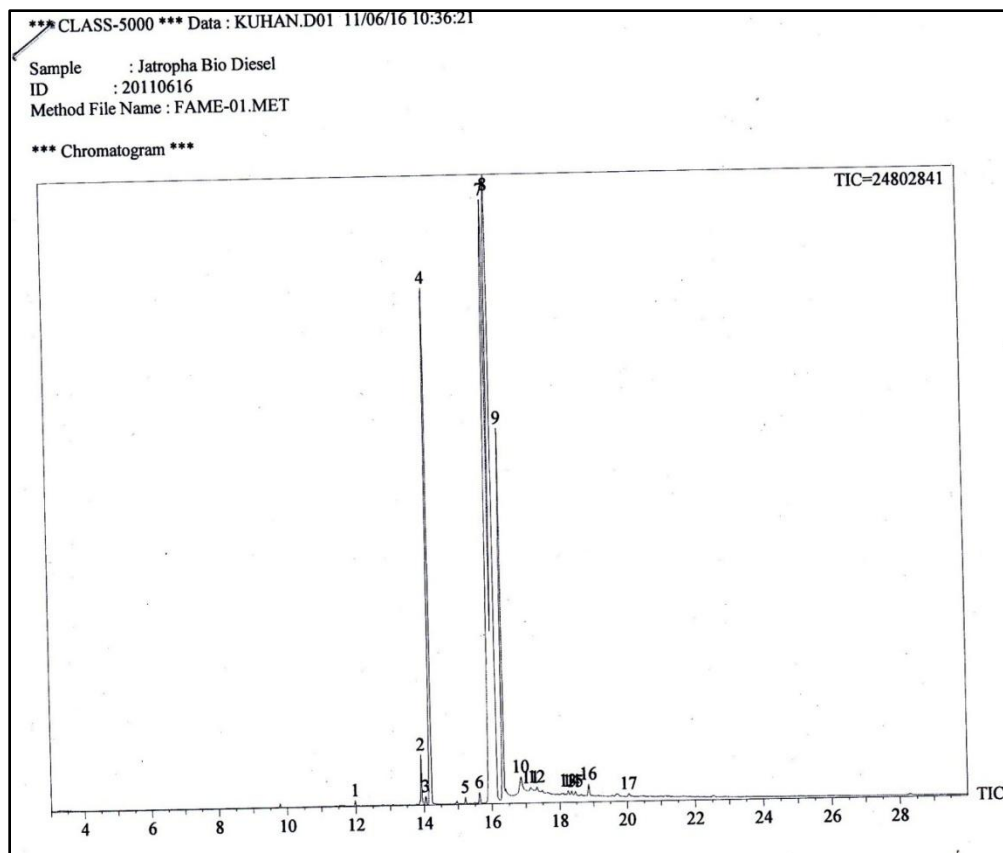


Figure 7: JCBD Free Fatty Acid Content

4.4 OXIDATION STABILITY (OS)

Rancimat equipment model 873 (Metrohm) was used to study the oxidation stability (OS) of biodiesel, according to EN-14112 specifications ^[41]. The Rancimat method is also called the automated swift test or accelerated oxidation test and is in general use today ^[45, 46, 47, 48]. In the Rancimat method, the oxidation is induced by passing a stream of air at the rate of 10L/h through a 3g biodiesel sample, kept at constant temperature 110°C. The vapors released during the oxidation process, together with the air, are passed into the measuring vessel containing 50mL of deionized water which has electrodes to measure conductivity ^[41].

Since the electrode is connected to a measuring device, the end of IP when the conductivity begins to increase rapidly is indicated. It should be added that this acceleration is caused by volatile carboxylic acids which are disassociated due to the oxidation process. An oxidation curve is obtained when the conductivity is recorded continuously and this is known as the IP or oil stability index ^[41].

RCBD and JCBD were blended in volume percent 100:0 (JCBD), 80:20 (JCBD-1), 60:40 (JCBD-2), 40:60 (JCBD-3), 20:80 (JCBD-4) and 0:100 (RCBD). Below are the result generated from the Rancimat equipment model 873 (Metrohm) for all the compositions.

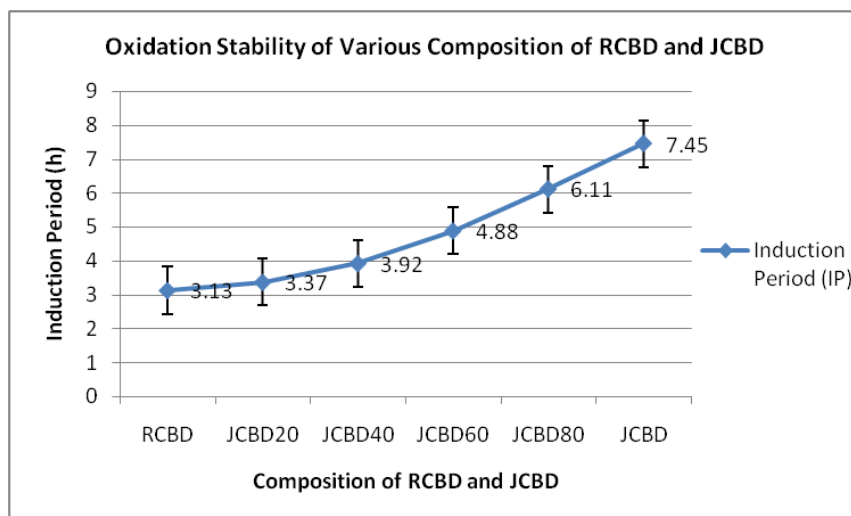


Figure 8: Oxidation stability of JCBD blended with RCBD

Figure 8 shows that the low oxidation stability (OS) of RCBD increases after blending the JCBD having a high OS. The graph above also shows that with a minimum dosing of 20 vol% of RCBD is all that is needed to make sure the induction period (IP) of the blend is still above 6 hours as required by EN-14112 specifications for biodiesel OS. In this case, the induction period for JCBD-1 is 6.11 hours.

4.4 CLOUD POINT (CP) & POUR POINT (PP)

Both RCBD and JCBD were assessed of their cloud point and pour point since these were the major criteria for determining low temperature properties of fuels, and were measured as per ASTM D97 and D2500 test methods respectively. This test method covers and is intended for use on any fuel products. Pour points are expressed in integers that are positive or negative multiplies of 3°C. Below is the equipment used in determining the cloud point and pour point of both RCBD and JCBD.

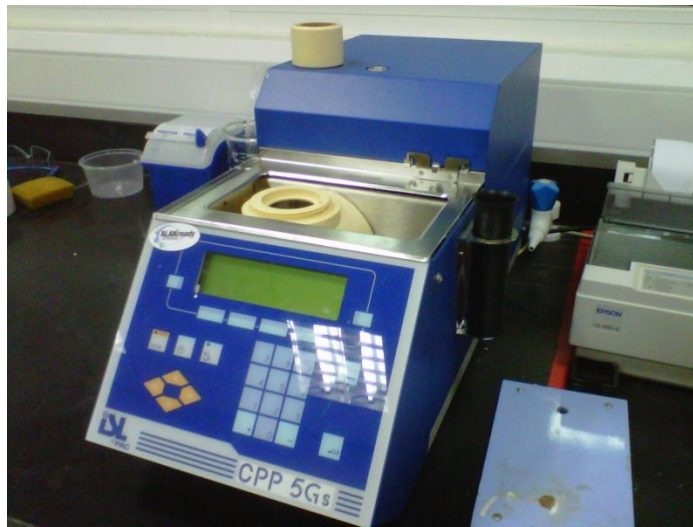


Figure 9: Cloud Point and Pour Point Analyzer, CPP 5Gs

Table 12 presents these results, as well as theoretical biodiesel compositions, based on the cloud point and pour point of corn oil and Jatropha Curcas L. Oil.

Table 9: Cloud Point and Pour Point of RCBD and JCBD

Biodiesel Sample	Cloud Point (°C)	Pour Point (°C)
JCBD	3.4	3.0
JCBD-1	2.1	3.0
JCBD-2	1.7	0.0
JCBD-3	-1.0	0.0
JCBD-4	-2.3	-3.0
RCBD	-3.1	-3.0

The trend in the changes in the cloud point and the pour point can further be viewed clearly from the graph below.

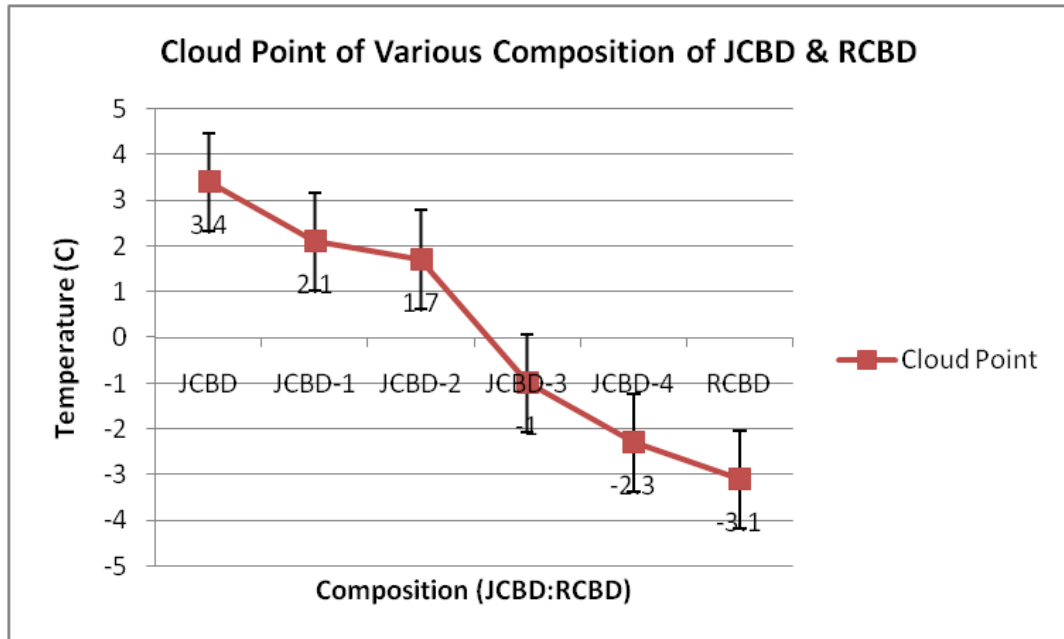


Figure 10: Cloud point of various compositions of JCBD and RCBD

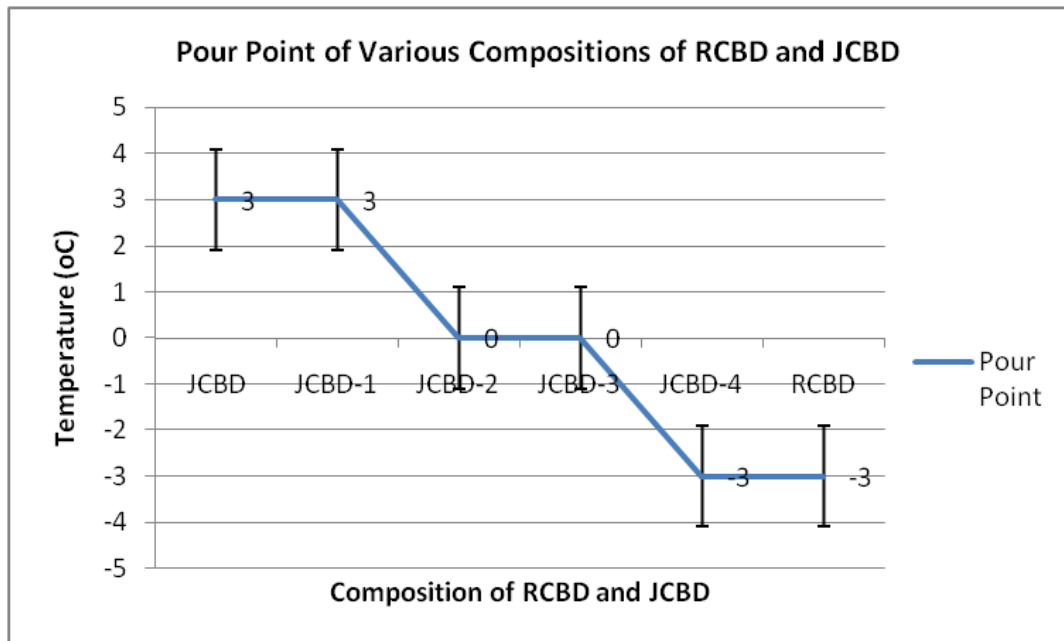


Figure 11: Pour point of various compositions of JCBD and RCBD

From Table 9, Figure 10 and Figure 11, it can be seen that the edible oil biodiesel, RCBD has a better cloud point and pour point compared to the inedible oil biodiesel, JCBD. The cloud point and pour point of RCBD is -3.1°C and -3.0°C respectively.

When RCBD is blended to JCBD starting with 20 vol. %, it can be observed that the cloud point of JCBD lowers from 3.4°C to 2.1°C . When 40 vol. % of RCBD is blended with 60 vol. % of JCBD, the cloud point is further lowered to 1.7°C . Next, when 60 vol. % of RCBD is blended with 40 vol. % of JCBD, the cloud point lowers to -1.0°C and when 80 vol. % of RCBD is blended with 20 vol. % of JCBD; the cloud point is further lowered to -2.3°C .

The same trend can be noticed in the pour point as well. When RCBD is blended to JCBD starting with 20 vol. %, it can be observed that the pour point of JCBD remains at 3.0°C . When 40 vol. % of RCBD is blended with 60 vol. % of JCBD, the cloud point is further lowered to 0.0°C . Next, when 60 vol. % of RCBD is blended with 40 vol. % of JCBD, the pour point remains at 0.0°C and when 80 vol. % of RCBD is blended with 20 vol. % of JCBD; the pour point is further lowered to -3.0°C .

The dominant factor influencing the cloud point and pour point of biodiesel is the number of double bonds in the alkyl chain of the fatty methyl ester. To develop a predictive model for predicting the cloud point of biodiesel, a thermodynamic study was performed ^[49]. It was concluded that cloud point of the biodiesel could be predicted solely depending on the amount of saturated fatty acids. It is said that the biodiesels with higher amount of saturated fatty acids will have a higher cloud point.

This can be proven with RCBD and JCBD itself. JCBD has a higher amount of saturated fatty acid (26.43 wt. %) compared to RCBD (9.48 wt. %) and prediction can be made that the cloud point of JCBD is going to be higher than RCBD and the result from the Cloud Point and Pour Point Analyzer, CPP 5Gs indicated the same thing.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

In this work, it is very evident that we are trying to reduce the dependence with edible oils and find ways to increase the usage of inedible oils to produce good biodiesels [21]. Non-edible plant oils have been found to have a bright future for the production of biodiesel. In this case we have chosen to blend *Jatropha Curcas L.* Oil biodiesel (JCBD) with refined corn oil biodiesel (RCBD) [22].

Although corn oil is a very good source of edible oil in producing biodiesel, there have been issues regarding the usage of edible oil in the provision of food worldwide. JCO appears to have several advantages as a renewable diesel feedstock. Mainly, it is both inedible, can be grown on marginal lands and most importantly, it will not compete with food crops [46].

One of the most important aspects for biodiesel is oxidation stability and it is imperative that it meets storage requirements and also EN-14112 specifications. RCBD has poor oxidation stability, around 3.13 hours, whereas, JCBD has a good oxidation stability, amounting to 7.45 hours. This is well above the 6 hours OS as required by EN-14112 specifications.

Hence, when JCBD is blended with RCBD with various compositions (JCBD-1, JCBD-2, JCBD-3 and JCBD-4), it is clearly shown that by just adding 20% of RCBD into JCBD, it is able to maintain the 6 hours OS requirement. Thus, this reduces the usage of edible oil and makes non-edible oil much more stable to be used. Therefore, this adheres to the motive of our project.

The next characteristic that was examined was the cloud point (CP) and the pour point (PP) of RCBD and JCBD. The cloud point and pour point of RCBD is proven to be better than JCBD hence blending was done in the same compositions like the oxidation stability. It was evident

that the cloud point and pour point decreased as higher amount of RCBD was blended with JCBD. Thus this meets the next project objective.

Although the cloud point and pour point of JCBD is still not that good after blended with small amount of RCBD (20 vol. % and 40 vol. %), it is to be noted that pour point depressants (PPD) can be used to further decrease the cloud and pour point. The blending further decreases the amount and cost of depressants used.

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APPENDICES

APPENDIX A

A.1 Refined Corn Oil

Table 10: Acidity of Refined Corn Oil

Trial	Condition	Volume of Titrant used (ml)	Acid Value (%)	Average (%)
1	Before titration (no sample added)	4	0.89776	0.78554
	After titration (no sample added)	7.2		
	After titration (2g of sample added)	12		
2	Before titration (no sample added)	12	0.67332	
	After titration (no sample added)	15		
	After titration (2g of sample added)	19.2		

A.2 Crude Jatropha Curcas L. Oil

Table 11: Acidity for Crude Jatropha Oil

Trial	Condition	Volume of Titrant used (ml)	Acid Value (%)	Average (%)
1	Before titration (no sample added)	14	27.38	28.3905
	After titration (no sample added)	14.4		
	After titration (2g of sample added)	63.6		
2	Before titration (no sample added)	15.7	29.401	
	After titration (no sample added)	16.2		
	After titration (2g of sample added)	69.1		

A.3 Treated *Jatropha Curcas* L. Oil

Table 12: Acidity for Treated *Jatropha* Oil

Trial	Condition	Volume of Titrant used (ml)	Acid Value (%)	Average (%)
1	Before titration (no sample added)	0	0.2244	0.2244
	After titration (no sample added)	0.5		
	After titration (2g of sample added)	1.4		
2	Before titration (no sample added)	2.9	0.2244	
	After titration (no sample added)	3.4		
	After titration (2g of sample added)	4.3		

APPENDIX B

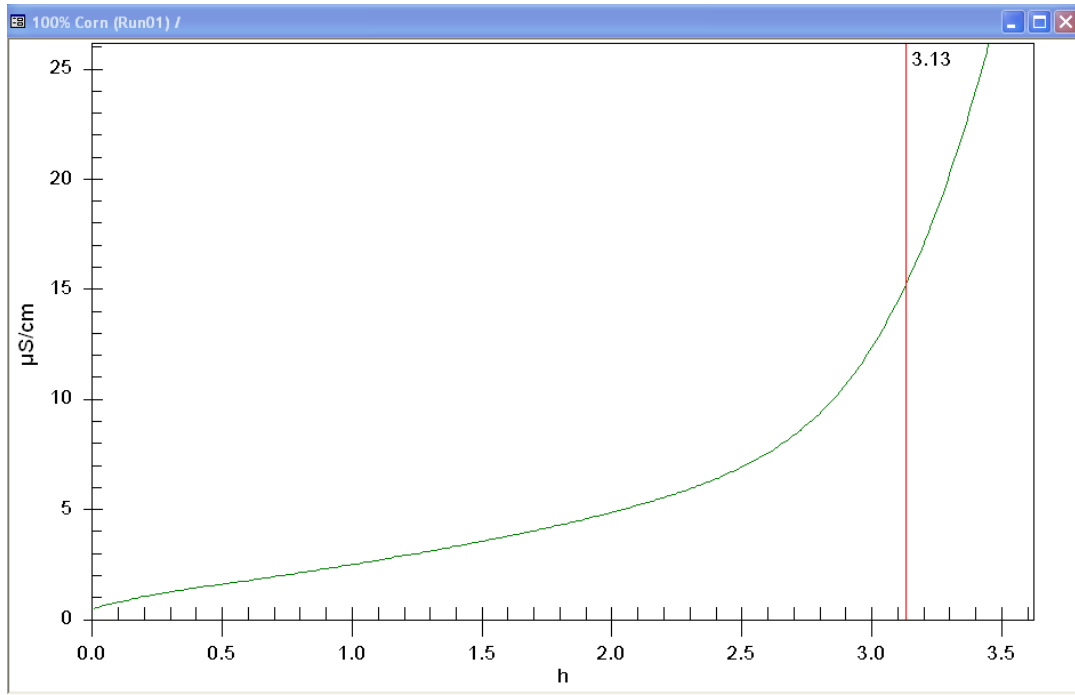


Figure 12: Oxidation stability for RCBD

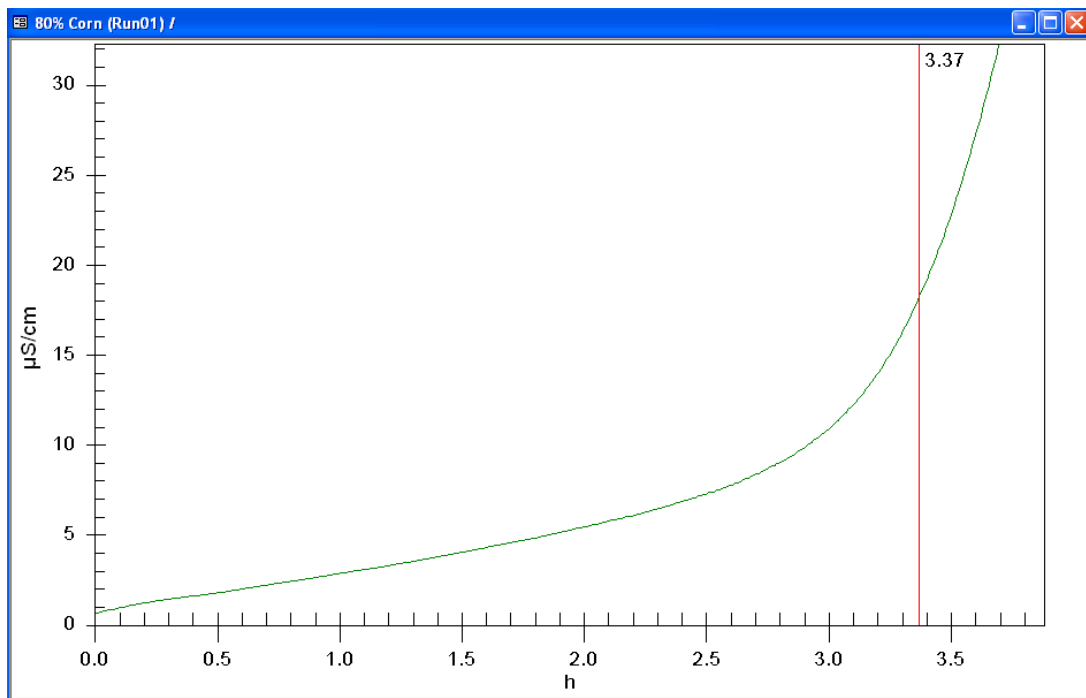


Figure 13: Oxidation stability for JBCD-4

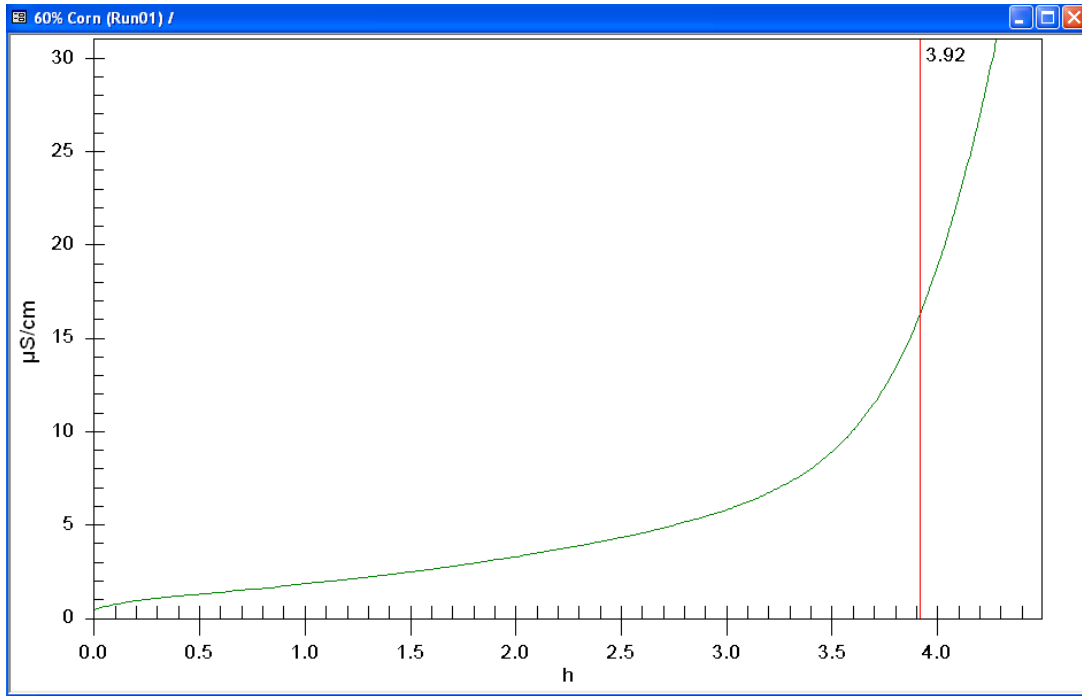


Figure 14: Oxidation stability for JCBD-3

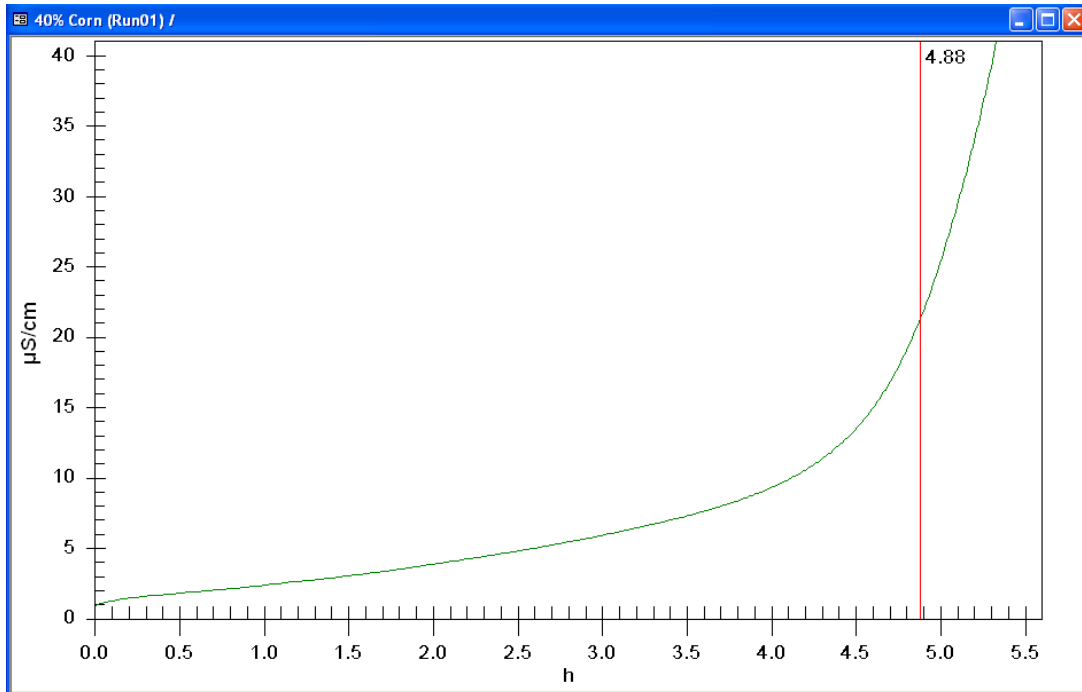


Figure 15: Oxidation stability for JCBD-2

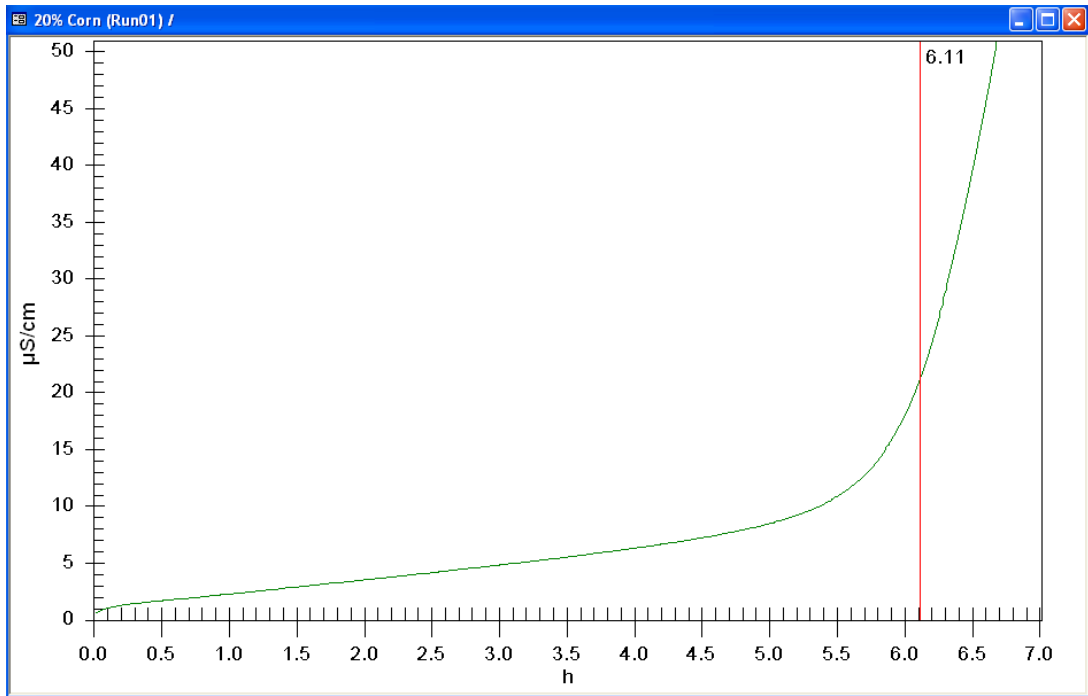


Figure 16: Oxidation stability for JCBD-1

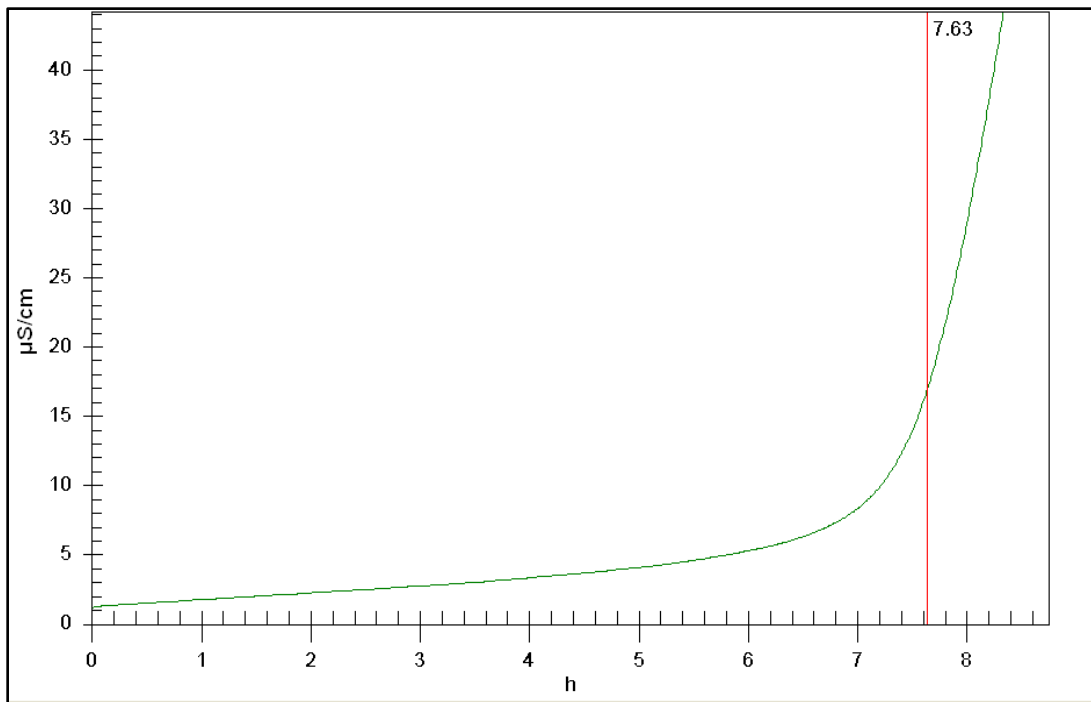


Figure 17: Oxidation stability for JCBD