Improvement of Cold Filter Plugging Point of Jatropha-Corn Biodiesel Blend Using Acrylic Copolymer

By

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CERTIFICATION OF APPROVAL

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May 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

HO MAY YUN

ABSTRACT

The aim of this study is to investigate the influence of fatty acid compositions in biodiesel on some parameters such as the oxidation stability, iodine value and cold flow properties. Edible oil is represented by refined corn oil and non-edible oil represented by jatropha curcas oil. In order to overcome the shortcomings of jatropha-corn biodiesel, acrylic copolymer is introduced as a Cold Flow Improvers (CFIs) additive to reduce the cold filter plugging point (CFPP). Crude jatropha oil was pre-treated to minimize the high free fatty acid content. The treated jatropha oil and refined corn oil were then transesterificated using sodium methoxide,CH_3ONa as catalyst at standard reaction conditions (reaction time, 1.5 h; weight of catalyst 1 wt.% of initial oil weight; molar ratio methano:oil/ 6:1; reaction temperature, 64°C) to produce jatropha methyl ester (JME) and corn methyl ester (CME) respectively. The biodiesel is then blended at different mass ratios. Each jatropha-corn biodiesel blend parameters such oxidation stability, iodine value, density, calorific value, fatty acid content and cold flow properties are investigated. The biodiesel was tested accordingly to the standard UNE-EN 14214 for quality assurance. Results show that ratio blend CME:JME (20:80) gives 6.42 hours of oxidation stability and -2°C for CFPP which complies with the EN 14214 standards. Acrylic copolymer as CFI is then added to the same blend ratio to reduce the CFPP. CFI successfully reduced the CFPP from -2°C to -6°C which gives better cold flow properties to the corn-jatropha biodiesel blend.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The world's total energy supply comes mainly from petroleum, coal and natural gas. Prediction of worldwide petroleum reserves is ambiguous but the general prediction of maximum production in or before the period 2010-2020 will be decline to the 1960 level by the year 2050. Consequently, the world can no longer afford to rely merely on fossil oil and the best way is to maintain energy reliability is through diversity in sources of energy (Bart, Palmeri, & Cavallaro, 2010). Recently in Malaysia, the Renewable Energy (RE) act is established to meet the 40% carbon emission intensity reduction target by 2020 (Invest Malaysia). Many countries such as Europe have raised their share of renewable energy to 6-10%, expected to increase to 20% by the year 2020(Ibrahim, 2012). Biodiesel can be one of the alternative fuels to the current market concentration of oil supply and potentially improves the environmental aspect (Wetzstein & Wetzstein, 2011).

There are several types of biodiesel. The first type of biodiesel is derived from vegetable oil mainly from food crops. Biodiesel can also be made from animal fat can be raw, processed or used. The second type is liquid fuels which can be derived from biomass such as ethanol. At present, large-scale biodiesel production relies on plantation crops as feedstock due to the existing needs of food supply in agricultural industry.

Nevertheless, there are debates over the increase of food prices alongside with the increase of global biofuel production. Studies suggested that biofuel production does have a modest 3% to 30% of contribution to the growth in the commodity food prices perceived in 2007/2008 (Mueller, Anderson, & Wallington, 2011). The increase of food prices continues to affect the poorer countries, therefore, the competition of edible crops for biofuel production and food supply is not ideal (Gui, Lee, & Bhatia, 2008). One of the ways to overcome the food prices crisis is to use non-edible oils for biodiesel production instead (Sims, Mabee, Saddler, & Taylor, 2010).

1.2 PROBLEM STATEMENT

One of the main setbacks related with the use of biodiesel at cold climates are operability problems in diesel engines when high amount of saturated fatty acid methyl ester components clogged fuel lines and filters when solidified(Boshui, Yuqiu, Jianhua, Jiu, & Jiang, 2010). Most non-edible oils contained more saturated fatty acid in the range of C_{16}-C_{18}. Meanwhile, edible oils that contained more unsaturated fatty acids are prone to oxidation but have good low temperatures properties (Das, Bora, Pradhan, Naik, & Naik, 2009).

Over the last few years, several ways has been studied to resolve the low-temperature problems of biodiesel. These include the blending of biodiesel with conventional diesel fuels, winterization, adding additives and blending with branched-chain esters. Of all methods, chemical additives was seems to be convenient and economical, and thereby the most attractive (Boshui et al., 2010). The aim of this work deals with the correlation of fatty acid methyl ester composition with important parameters; such as the oxidation stability, CFPP and iodine value (IV) of the biodiesel. As an effort to promote the usage of non-edible oil as feedstock in biodiesel production, an investigation of the blending of methyl ester from non-edible oils and methyl ester from edible oil is done. In this study, edible oil represented by refined corn oil and non-edible oil represented by jatropha curcas oil. In order to overcome the shortcomings of jatropha-corn biodiesel, acrylic copolymer is introduced as CFI to further reduce the CFPP.

1.3 OBJECTIVE

The main objectives of this research project are as the following;

1. To produce methyl ester from jatropha curcas L. oil and refined corn oil
2. To blend jatropha curcas L. methyl ester and refined corn oil methyl ester; and obtain the best blend that achieved oxidation stability of 6 hours and parameters such as iodine value and cold flow properties that complies with EN14214 standards.
3. To observe and investigate the effectiveness of commercial CFI in enhancing the cold flow properties of jatropha-corn methyl ester

1.4 SCOPE OF STUDY

In this project, the study aspects are the cold flow properties, oxidation stability and iodine value of the biodiesel blend. The scope of study includes three main parts. The first one is the production of corn methyl ester (CME) and jatropha curcas L. methyl ester (JME) followed by the blending of both biodiesel as the following mass ratios :

i. CME:JME (0:100)
ii. CME:JME (20:80)
iii. CME:JME (40:60)
iv. CME:JME (60:40)
v. CME:JME (80:20)
vi. CME:JME (100:0)

The second part is the study of relation between fatty acid methyl ester compositions of each blend with oxidation stability, iodine value and CFPP. The third part is the investigation of CFPP before and after the addition of acrylic copolymer at several concentrations; 0.0mass%, 0.5mass% and 1.0mass%.

CHAPTER 2

LITERATURE REVIEW

Vegetable oil comprises of 98% triglycerides and a small amount of monoglycerides and diglycerides(Ayhan, 2009). Triglycerides have one glycerol with three fatty acids. Direct usage of triglycerides in diesel engine is discouraged due to its long molecule chains and highly viscous characteristic (Çaynak, Gürü, Biçer, Keskin, & İçingür, 2009). Efforts have been given in finding ways to reduce the viscosity of vegetable oils. Methods that were discovered to reduce the viscosity are: dilution (blending) with hydrocarbons, microemulsification, pyrolysis or thermal cracking, catalytic cracking and transesterification(Schwab, Bagby, & Freedman, 1987).

Transesterification is the most conventional method where reaction between triglyceride and alcohol with the presence of catalyst gives biodiesel or fatty acid alkyl ester (FAME) and gylcerols. Biodiesels are suitable to replace diesel fuel without any modification of engines hardware. One study on the life cycle assessment (LCA) shows biodiesel is more environmentally friendly than the diesel based on the global warming and renewable energy aspect scores of biodiesel and diesel production (Jinglan).

Comparatively to the making of diesel fuel, diesel fuel is processed from fossil fuel through fractional distillation. Extracted crude oil contained different hydrocarbon compounds that are separated through difference in boiling point. Diesel is separated from the crude oil when the distillation chamber reaches 200°C to 350°C in temperature (Leffler, 2008). Biodiesel on the other hand, is biodegradable and have environmental benefits as it rarely contain sulfur(Balat & Balat, 2008).

2.1 CORN ZEA MAYS OIL

Corn oil was ever considered as a biodiesel fuel in 1952. However, due to its relatively expensive and high values as edible oil, biodiesel made from corn oil is not economically feasible. Corn is the third most vital grain in the world after wheat and rice. It is the most extensively used cooking oil in the US as a fast food frying oil. Corn oil's benefits include its very low level of linolenic acid, high level of unsaponifable and stability during frying. It also has a mild nutty flavor, contain high amount of unsaturated fatty acids and low content of saturated fatty acids (Bart et al., 2010).

2.2 JATROPHA CURCAS L. OIL

There is a growing in jatropha curcas L. as a biodiesel to help alleviate the energy crisis, reduce the countries dependence on foreign imports and generates income in rural areas of developing countries. The estimates of the oil content in seeds range from 35-40% and in the kernels 55-60%. Many developing countries cannot afford to use edible oils as an energy source because they are already in short supply. Thus, non-edible oils from under researched plants such as Jatropha, Pongamia, Neem, Kusum and Pilu are being advocated (Wright & Evans, 2008). Of the above Jatropha is considered the most potential source as non-edible biodiesel producing plant because it can be grown on almost any soil type. Jatropha curcas. L oil contain high free fatty acid (FFA) content and requires acid-catalyzed esterification.

2.3 TRANSESTERIFICATION

Transesterification (alcoholysis) is an equilibrium reaction and occurs essentially by mixing the reactants (Schwab et al., 1987). Transesterification occur when triglyceride (vegetable oil) reacts with an alcohol (methanol) in the presence of a strong acid or base catalyst (Figure 2.1)(Ma & Hanna, 1999).

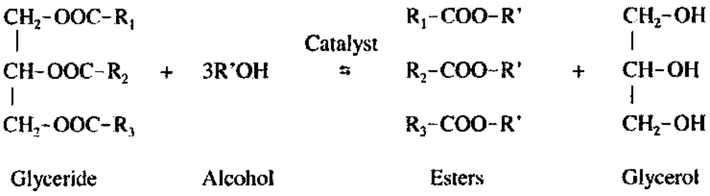

Figure 2.1 : Transestrification process (Ma & Hanna, 1999).

In biodiesel production, the choice of acid and alkali catalyst can varied depending on the free fatty acid (FFA) content in the raw vegetable oil. During the reaction, FFA may react with alkali catalyst to form soap and water which deters the ester formation (Ayhan, 2009). Therefore, alkali catalyst reaction should not exceed the recommended limit of acidity value (2mg KOH/g oil) and FFA (1%) to avoid deactivation of catalyst, formation of soaps and emulsion. This decreases the final yield of ester and consumes alkali. High FFA needs two-step transesterification process, acid transesterification followed by alkali-transesterification to get high biodiesel yield (Keskin, Gürü, & Altıparmak, 2008; Patil & Deng, 2009). Methanol is preferable as the solvent comparatively to ethanol because of it is a polar short chain alcohol that is low in cost. Alkali catalyst, potassium methoxide effects complete transesterification more quickly than sodium methoxide, CH_3ONa at equivalent molar concentration with the same triglyceride samples. Due to the danger possess in metallic potassium handling, sodium methoxide, CH_3ONa is preferable (Ayhan, 2009).

2.4 IODINE VALUE (IV)

Iodine value is used for the determination of the quality of diesel fuel derived from vegetable oil. Denote as grams of I_2 absorbed/100g sample under standard conditions, the iodine value is a degree of the unsaturation of oils and fats and their fatty acid derivatives, which can be determined in many different methods. There are many methods used to determine iodine value. One of the methods used is the American Oil Chemist' Society (AOCS) method Cd 1d-92 (Balat & Balat, 2008). The test begins with 0.1gm of tested oil taken in to 250ml of glass stopper iodine flask. The oil is dissolve in 20ml of carbon tetrachloride and 25ml of Wij's solution. The contents of the flask are shaken well and are placed in the dark for half an hour. At the end of this time 20 ml of 15% potassium iodide solution is added followed by the addition of 100ml of distilled water. The contents are then titrated against 0.1N sodium thiosulfate, $Na_2S_2O_3.5H_2O$ using starch as indicator until the yellow iodide color disappeared. The solution is again titrated until the disappearance of color. Same procedure was done for blank solution. Iodine value was then calculated by the following formula.

$$IV = \frac{(Blank\ titration - Sample\ titration) \times Normality\ of\ Na_2S_2O_3.5H_2O\ \times Equivalent\ weight\ of\ iodine}{Sample\ weight\ (gram)}$$

Where,

Normality of sodium thiosulfate, $Na_2S_2O_3.5H_2O = 0.1$

Equivalent weight of iodine = 127

According to EN-14214 for determination of the iodine number the mass percentage of the fatty acid methyl esters is multiplied by an assigned weighting factor. In this project, the EN-14214 method is used. Table 2.1 shows the weighting factors for each fatty acid composition.

Table 2.1: Weighting Factors for Common Fatty Acids to Determine Iodine Value (EN 14214:2003)

Methyl Ester	**Formula**	**Factor**
Saturated fatty acids	C n:0	0
Palmitoleic	C16:1	0.950
Oleic	C18:1	0.860
Linoleic	C18:2	1.732
Linolenic	C18:3	2.616
Gadoleic	C20:1	0.785
Erucic	C22:1	0.723

2.5 OXIDATION STABILITY

The oxidation stability of biodiesel differs extensively on the source of oil where the biodiesel is derived, processing conditions, contaminants particularly trace metals, water, radicals and peroxides and storage stability can be influence by humidity, sunlight, microorganisms, temperature, oxygen and presence of organic occurring stabilizers (Bart et al., 2010). Oxidation can form volatile small-chain fatty acids, which can lead to corrosion in the engine. Meanwhile, polymers can formed, which agglomerates as "gums" which may cause deposition of residue in the engine. Oxidation involves both storage and thermal stability. The oxidation stability is determined via the Rancimat method. This test is based on the period of time where methyl ester aged under constant air flow. When there is an increase of conductivity of deionized water contained in the reservoir, it retains the volatile acid liberated during the oxidation of fatty material. More volatile acids dissociates when methyl ester deteriorates rapidly. According to European Committee for Standardization, an oxidation curve is obtained when the conductivity is recorded continuously and this is known as the IP or oil stability index. The European standard EN14112 establishes that the oxidative stability of biodiesel should be determined at 110°C and required a minimum value of 6 hours for the induction period (Dantas et al., 2011).

2.6 COLD FLOW PROPERTIES

In the previous study on optimization of biodiesel from edible and non-edible vegetable oil, the jatropha and corn methyl ester show similar fuel properties to conventional diesel compare to canola and karanja methyl ester(Patil & Deng, 2009). One of the disadvantages of biodiesel is poor temperature operability, along with inferior oxidative and storage stability, lower volumetric energy content, and higher nitrogen oxides exhaust emissions(Joshi, 2011). Biodiesel with high unsaturated ester content show better cold flow properties but have lower oxidation stability(Patil & Deng, 2009;Garcia-Perez, Adams, Goodrum, Das, & Geller, 2010). Saturated fatty acid in the range of C_{16}-C_{18} has high oxidation stability while unsaturated fatty acids, such as oleic and linolenic, are prone to oxidation(Das et al., 2009).The biodiesel that has higher level of saturated methyl ester has higher cetane number however it is susceptible to the free-radical attack(Knothe, Krahl, & Van Gerpen, 2005).

Biodiesel with poor cold flow properties tend to cause formation of micro solid wax crystal nuclei at low temperatures. As temperature decrease further, these crystal starts to grow visibly and known as the cloud point (CP). At temperature below CP, larger crystals fuse together to form large agglomerates that tend to cut off flow through fuel pipes and filters causing start-up difficulties (Knothe et al., 2005). The temperature at which fuel crystals have agglomerated in sufficient amounts to cause a test filter to plug is the CFPP. Pour point is the temperature at which the fuel contains so many agglomerated crystals it is essentially a gel and will no longer flow. The definition of CP, PP and CFPP is as the following and illustrated in Figure 2.2;

i. **Cloud Point:** The temperature at which the first appearance of small solid crystals visibly when observed as the fuel is cooled (D 2500).

ii. **CFPP:** The lowest temperature at which 20ml of sample safely passed through the filter (wire mesh filter screen) under vacuum within 60 sec (EN 116) (Fernández, Ramos, Pérez, & Rodríguez, 2010).

iii. **Pour Point:** The temperature at which the fuel is fully agglomerated, become gel-like and will no longer flow when pour (D 97).

Numerous researches on the improvement of cold flow properties in biodiesel were carried out. Biodiesel mixed with regular petroleum diesel at various ratio reduced CP and CFPP (Kleinová, Paligová, Vrbová, Mikulec, & Cvengroš, 2007 ; Knothe et al., 2005). Winterization technique such as crystallization filteration with methanol is used to improve the cold flow properties of peanut biodiesel(Pérez, Casas, Fernández, Ramos, & Rodríguez, 2010). By adding CFIs as fuel additives into soybean diesel, olefin-ester copolymers (OECP) were found to reduce PP and CFPP(Boshui et al., 2010).

There are also a study on Differential Scanning Calorimetry(DSC) mixing bio-oil and biodiesel shows improvement on oxidation stability. Bio-oil contain hindered phenols and nano-particles of oligometric that modify crystal behavior by inhibiting wax crystals from growing and subsequently improving the cold flow of soybean diesel (Garcia-Perez et al., 2010).Metallic-based additive; magnesium, nickel and manganese is added into biodiesel and resulted in decrease of viscosity, flash point and pour point effectively as well as greenhouse gases emission reduction(Gürü, Koca, Can, Çınar, & Şahin, 2010; Keskin, Gürü, & Altıparmak, 2007; Çaynak et al., 2009). A study on ethyl levulinate, an inexpensive bio-based additive appears to be an acceptable CFI for biodiesel with high saturated fatty acid content such as cottonseed methyl ester(Joshi, Moser, Toler, Smith, & Walker, 2011).

Evidently, extensive work has been done on the flow properties of biodiesel production; however less significant work has been done concerning the improvement of cold flow of blended methyl ester from different sources of oil. One of the study on the blend of jatropha and palm methyl ester had achieved improvement in oxidation stability, and resulted in reasonable cold flow properties that are suitable for tropical climate but not for production of winter grades diesel fuels (Sarin, Sharma, Sinharay, & Malhotra, 2007).

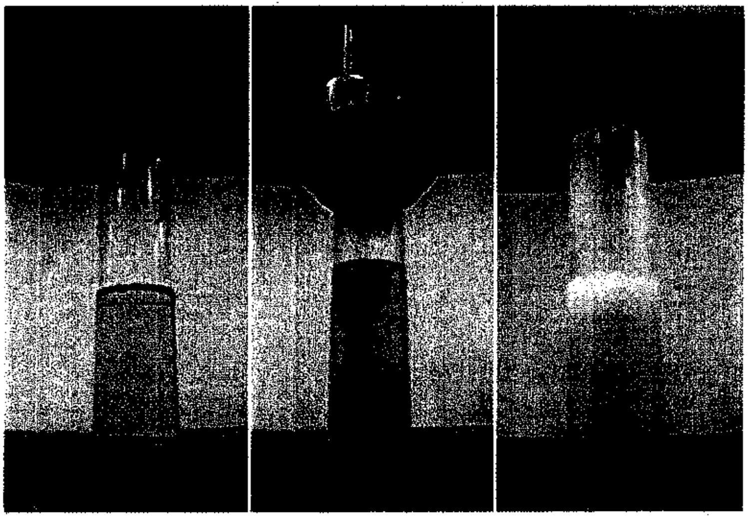

Figure 2.2 : Almost clear appearance of biodiesel after cloud point test (left), Cloudy appearance of biodiesel after CFPP test (middle), Fully crystallized after pour point test (right)

2.6.1 Cold Flow Improver (CFI)

One research reported the evaluation on the effectiveness of CFI in different blended biodiesel (Echim, Maes, & Greyt, 2012). High saturated methyl esters, such as tallow, palm, chicken and jatropha methyl ester were blended with high level of unsaturated methyl ester such as soybean and rapeseed biodiesel samples followed by the usage of CFI. However, there were no blend on jatropha methyl ester and corn methyl ester was made. CFPP of the biodiesel blends were improved when CFI were added (Echim et al., 2012). Hence, the aim of this study is to investigate the potential of acrylic copolymer as CFI to further improve the cold flow properties of jatropha-corn methyl ester blend. Another advantage is to allow biodiesel works in winter conditions and to reduce the dependency and usage of edible-oil.

CFI behave by hindering crystal growth, but do not prevent crystal initiation. They have little effect on the temperature at which crystals that has already form. To be more precise, CFI co-crystallize on the edges of the growing crystal plates when crystals form, thereby inhibiting the continued agglomeration of the plate(Bart et al., 2010). The CFI results in smaller size of crystals (d = 10μm-

100μm) enabling it to pass through filters without clogging (Knothe et al., 2005). The impact on cold flow properties is that, while CP is little affected, considerable improvements in CFPP and PP can obtained.

CFI are usually Pour Point Depressant (PPD) having low molecular weight copolymers in similar structure and melting point to the n-alkane paraffin molecules, allowing them to co-crystallize after nucleation has been initiated (Knothe et al., 2005). Types of copolymer includes polymethacrylates, polyalkylmethacrylates, copolymer of vinyl acetate-maleate esters and many more (Knothe et al., 2005). Polymethacrylates are the most widely used pour point depressants. R in the ester has a major effect on the product, and is usually represented by a normal paraffinic chain of at least 12 carbon atoms that ensure solubility is shown in Figure 2.3. Typically it has a molecular weight of 7000-10000 number in average. Commercial materials normally contain mixed alkyl chains which can be branched.

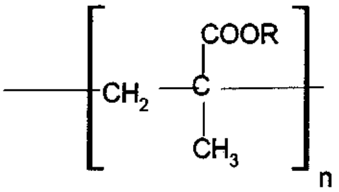

Figure 2.3 : A polymethacrylate molecule

CHAPTER 3

METHODOLOGY

3.1 MATERIALS

Crude jatropha oil was procured from Eco Energy Solution Pty. Ltd. Refined corn oil was Mazola/Sweet Yet Development Sdn. Bhd obtained from a local store. Anhydrous methanol (99.8%), Sulphuric Acid reagent (95-98%) and Sodium Methoxide, CH_3ONa (25% in methanol solution) were obtained from Sigma-Alrich. Chemicals procured from Merck via Avantis Laboratories Sdn. Bhd. were Toluene, Isopropanol and Anhydrous Sodium Sulfate. Potassium Hydroxide and Phenolphthalein were obtained from R&M Chemicals and Fisher Scientific respectively. All the chemicals used were analytical reagent grade. Tables 3.1-3-4 shows the materials required for each analytical methods.

Table 2.1 : Materials required for Acidity Check

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

Table 3.2: Materials and required for Pre-esterificaton reaction

Aspect	Item	Brand/Procured from
Oil	Refined Corn Oil	Mazola/Sweet Yet Development Sdn. Bhd.
	Jatropha Curcas L. Oil	Eco Energy Solution Pty. Ltd.
Alcohol	Methanol	Sigma-Alrich 34940
Acid	Sulphuric Acid	Sigma-Alrich ACS Reagant 95.0% - 98.0%
Drying Agent	Anhydrous Sodium Sulfate	Merck/Avantis Laboratories Sdn. Bhd.

Table 3.3: Materials required for Transesterification reaction

Aspect	Item	Brand/Procured from
Oil	Refined Corn Oil	Mazola/Sweet Yet Development Sdn. Bhd.
	Jatropha Curcas L. Oil	Eco Energy Solution Pty. Ltd.
Alcohol	Methanol	Sigma-Alrich 34940
Catalyst	Sodium Methoxide (25% solution in methanol)	Sigma-Alrich /Avantis Laboratories Sdn. Bhd.
Drying Agent	Anhydrous Sodium Sulfate	Merck/Avantis Laboratories Sdn. Bhd.

Table 3.4: Materials required for addition of cold flow improver

Aspect	**Item**	**Brand/Procured from**
Oil	Refined Corn Oil	Mazola/Sweet Yet Development Sdn. Bhd.
	Jatropha Curcas L. Oil	Eco Energy Solution Pty. Ltd.
Additive	Acrylic Copolymer	Viscoplex10-330/Platinum Energy Sdn. Bhd

3.2 EQUIPMENT

Esterification of crude jatropha oil and transesterification of jatropha oil and refined corn oil were carried out in a 250ml three-necked round bottom flask place in a water bath. The reactor was equipped with a reflux condenser, to avoid the evaporation of methanol; magnetic stirrer for rigorous stirring; and a heating plate for a constant heat supply (Figure 3.1).

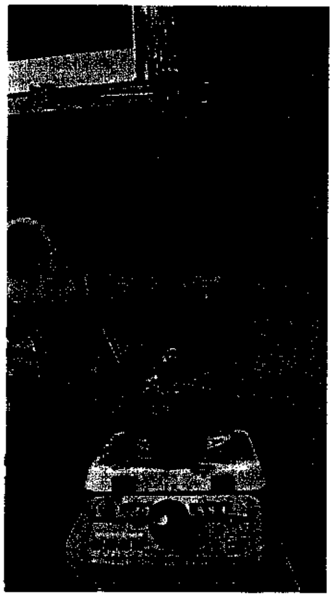

Figure 3.1 : Pre-esterification and Transesterification Experimental Setup

3.3 EXPERIMENTAL PROCEDURE

3.3.1 Pre-Esterification

Acid-catalyst pretreatment was carried out since the initial acid value of crude jatropha oil was 23.41% or 47 mg KOH/g oil. Refined corn oil yield an acidic value of 0.79% which is lower than 1%, thus, pre-esterification for refined corn oil is not required. 250g of Crude Jatropha Curcas L. Oil was taken in a three-necked round bottomed flask where 88 g of methanol was taken in a 200 ml measuring cylinder. 2.5g (1.0 wt%) of sulfuric acid (H_2SO_4) was measured and poured drop wise into a measuring cylinder containing the methanol. Oil was warmed by placing the round-bottomed flask in the water bath maintained at 64°C. Methanol and sulfuric acid were added into the oil for vigorous mixing by means of a mechanical stirrer fixed in the flask. The required temperature (64°C) was maintained throughout the stirring and after 4 hours, the mixture was left overnight. 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. Treated jatropha oil is washed with de-ionized water to further remove impurities. The residual methanol and water were separated from the oil by rotary evaporation under vacuum at 70°C for 30minutes. Finally, treated jatropha oil is swirled with anhydrous $NaSO_4$ to remove traces of moisture and then separated from the anhydrous via gravitational filtration. Acidity value test is repeated to ensure reduction of acidic value to less than 1 mg KOH/g oil.

3.3.2 Transesterification

200g of refined corn oil was taken in a three-necked round bottomed flask. 46.88 g of methanol was taken in a 200 ml beaker. 2 g of sodium methoxide, CH_3ONa was taken in a measuring cylinder. The oil was warmed by placing the round-bottomed flask in the water bath maintained at 64°C to avoid the evaporation of methanol. Sodium methoxide, CH_3ONa and methanol solution was added into the oil for vigorous mixing by means of a mechanical stirrer fixed in the flask. The required temperature (64°C) was maintained throughout the stirring and after 90 minutes. Mixture is then poured into a separating funnel and leaves it overnight. The 2 layer mixture of refined Corn biodiesel (CME) and the bottom layer (glycerol) is separated. CME is washed with de-ionized water carefully to further remove impurities (e.g catalyst, glycerol). The residual methanol and water were separated from biodiesel by rotary evaporation under vacuum at 70°C for 30minutes. Finally, biodiesel is swirled with anhydrous sodium sulfate, $NaSO_4$ to remove moisture. Mixture of CME and anhydrous $NaSO_4$ is then separated by gravitational filtration to pure, crystal clear biodiesel. Similar steps were repeated for treated jatropha oil to form jatropha biodiesel.

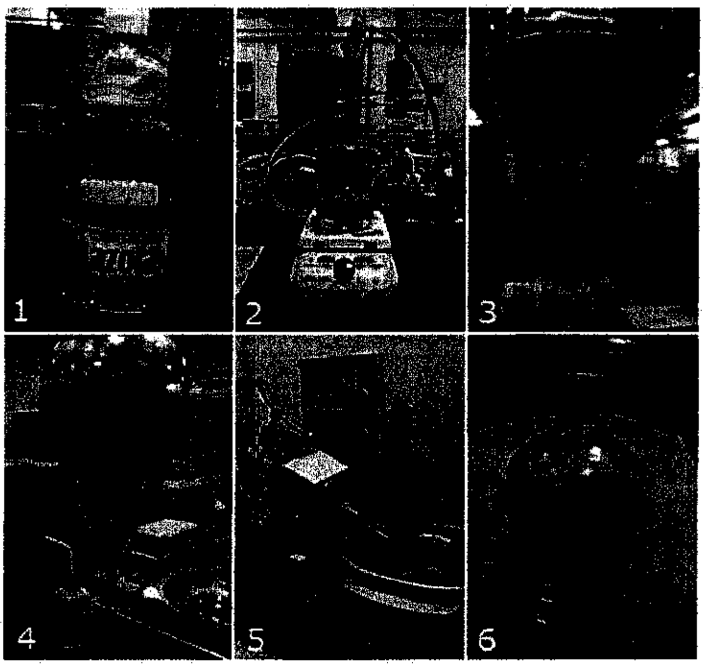

Figure 3.2: Transesterification process (1) Refined Corn Oil (2) Transesterification (3) Separation of biodiesel and glycerol (4) Washing with deionized water (5) Rotary Evaporator (6) Biodiesel as product

3.4 ANALYTICAL METHODS

3.4.1 Acid Value

Acid values (AV) of vegetable oil were determined according to American Oil Chemists' Society (AOCS) Method Cd 3d-63. Before proceeding with transesterification, the oil sample needs to be tested for acidity value. When an acid value of 2.0mg KOH/g oil or less was achieved, the oil can be used in alkali catalyzed transesterification reaction. When neat biodiesel is produced, acidity value is again tested to obtain EN14104 requirement of 0.5mg KOH/g oil and below.

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

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

$$\text{Acid Value} = \frac{[(\mathrm{A} - \mathrm{B}) \times \mathrm{N} \times 56.11]}{\mathrm{W}}$$

Where:

A = Volume of titrant used for sample
B = Volume of titrant used for blank
N =0.02
W =2

3.4.2 Fatty Acid Composition

The fatty acid composition at different blend ratios are analyzed by gas chromatography on a 7890A GC system from Agilent Technologies, equipped with Triple Axis inert XL El/Cl MSD detector and Quadrupole mass analyzer. The scan rate is 125,000 amu/sec and the inlet has a direct insertion probe and pyrolizer.

3.4.3 Density

Density meter Anton Paar DMA 4500M is used to measure the density of the neat biodiesel. The conversion factor for the correction of density, determined by EN ISO 3675 over a range of temperatures from 20°C to 60°C to density at 15°C is calculated by the formula :

$$\rho_{(15)} = \rho_{(T)} + 0.723\,(T - 15)$$

3.4.4 Oxidation Stability

The induction period (IP) of each biodiesel blend ratios was quantified using the Metrohm 873 Rancimat instrument with the method EN14112 for the neat biodiesel and its blends. In this method, 3g of sample were heated at 110°C under constant air flow (10 L/h).

3.4.5 Cold Flow Properties

CP and PP of each neat biodiesel was measured using ISL CPP 5Gs using D2500 and D97 method respectively. An automatic tester ISL FPP 5Gs was used to quantify the CFPP of neat biodiesel and each biodiesel blend ratios. Each test required a 45ml of biodiesel sample.

CHAPTER 4

RESULT AND DISCUSSION

4.1 CALCULATIONS FOR BIODIESEL PREPARATION

4.1.1 Pre-esterification of Crude Jatropha Oil

The calculations of the amount of methanol, and the amount of catalyst used for pre-esterification of crude jatropha oil to produce treated jatropha oil are shown. The methanol:oil ratio used is 10:1. Catalyst used is sulfuric acid (H_2S0_4) at 1wt% of total oil used.

Mass of crude jatropha oil = 250g

Molecular weight of jatropha oil = 910.23g/mol

Moles of jatropha oil $= \frac{\text{Mass of jatropha oil}}{\text{Molecular Weight of jatropha oil}}$

$= \frac{250g}{910.23g/mol}$

$= 0.275mol$

Mass of methanol =
Ratio of methanol: oil x Moles of jatropha oil x Molecular weight of methanol

$$= \frac{10}{1} \text{ x } (0.275) \text{x } 32.04 = 88g$$

Mass of H_2S0_4 = 1wt% x Mass of jatropha oil

$= \frac{1}{100} \text{ x } 250g$

$= 2.5g$

4.1.2 Transesterification of Treated Jatropha Oil/Refined Corn Oil

The calculations of the amount of methanol and the amount of catalyst used for transesterification of corn oil to produce corn methyl ester are shown. The methanol:oil ratio of 6:1 is used with alkalized catalyst sodium methoxide,CH_3OMe at 1wt% of total oil used. Same calculations were repeated for treated jatropha oil to produce jatropha methyl ester.

Mass of corn oil = 200g

Molecular weight of corn oil = 820.13g/mol

$$\text{Moles of corn oil} = \frac{\text{Mass of corn oil}}{\text{Molecular Weight of corn oil}}$$

$$= \frac{200g}{820.13g/mol}$$

$$= \mathbf{0.244}\ \boldsymbol{mol}$$

Mass of methanol =
Ratio of methanol: oil x Moles of corn oil x Molecular weight of methanol

$$= \frac{6}{1} \text{ x } (0.244) \text{x } 32.04 = \mathbf{45.37g}$$

Mass of CH_3OMe = 1wt% x Mass of corn oil

$$= \frac{1}{100} \text{ x } 200\text{g}$$

$$= \mathbf{2.00}\boldsymbol{g}$$

4.2 CHARACTERIZATION OF BIODIESEL SAMPLES

4.2.1 Titration for Acidity Value

To avoid the formation of soap and loss of ester during alkaline catalyst transesterification, acidity value titration was carried to identify the acidity value. It is found that pre-esterification reaction is needed to be carried for crude jatropha oil since an initial acidity value of 46.81 mg KOH/g oil or 23.41% FFA was obtained. The acidity value greatly reduced to 1.40 mg KOH/g oil after the pretreatment with sulfuric acid catalyst.

On the other hand, corn oil advanced to the transesterification reaction to form CME since the acidity value scored 1.57 mg KOH/g oil or 0.79% FFA. It did not exceed the maximum allowable specification at 2.0mgKOH/g oil or 1% FFA.

The acidity value of the neat biodiesel was examined again after transesterification reaction. CME and JME met the EN14104 requirement. Table 4.1 shows the summarized results of the acidity value test.

Table 4.1 : Acidity Value Test

Acidity Value Test	**Test Method**	**Limits**	**Average Acid Value (mg KOH/g oil)**	
			JME	**CME**
Initial Crude/Refined Oil	-	-	46.81	1.57
After Pre-esterification (Oil)	-	2.0 max	1.40	1.57
After Transesterification	EN14104	0.5 max	0.12	0.11

4.2.2 General Quality Parameters

Standards are vital for commercialization and market of biodiesel. The European norm EN14214 sets specifications and test methods for biodiesel (FAME) to be used as automotive fuel for diesel engines. The European standard tends to be stricter than the American ASTM D6751 standard, displaying more stringent limits. Table 4.2 shows some of the general properties of the biodiesel to ensure a good quality assurance of biodiesel.

Table 4.2 : General quality parameters of biodiesel

Properties	**Test Method**	**Limits**	**Methyl ester**	
			JME	**CME**
Ester Content (%)	EN 14103	96.5 min	95.7	95.9
Cloud Point (°C)	D 2500	-	4	0.1
Pour Point(°C)	D 97	-	3	0
CFPP(°C)	EN 116	+5 to -20	-1.2	-4
Density (kg/m3) at 15°C	EN ISO 3675	860 to 900	882.46	885.70
Acidity Value (mg KOH/g oil)	EN14104	0.5 max	0.12	0.11
Calorific Value (MJ/kg)	ASTM D240	-	39.75	39.82

4.2.3 Fatty Acid Compositions

Gas chromatography is used to analyze the fatty acid compositions of JME and CME; also the fatty acid composition of each blend ratios. Table 4.3 shows the common chemical structures of common fatty acids used to identify each component obtained from the GC results. Table 4.4 is a comparison table where the fatty acid components of this work are compared to available journal sources.

Table 4.3 : Chemical structures of common fatty acids(Barnwal & Sharma, 2005)

Fatty Acid	**Formulas**	**Methyl Ester Terms**
Myristic	C14:0	Methyl tetradecanoic acid
Palmitic	C16:0	Hexadecanoic acid
Palmitoleic	C16:1	9-Hexadecenoic acid
Margeric	C17:0	Heptadecanoic acid
Stearic	C18:0	Octadecanoic acid
Oleic	C18:1	9-Octadecenoic acid
Linoleic	C18:2	9,12-Octadecadienoic acid
Linolenic	C18:3	9,12,15-octadecatrienoic acid
Arachidic	C20:0	Eicosanoic acid
Gadoleic	C20:1	9-eicosenoic acid
Behenic	C22:0	Docosanoic acid
Lignoceric	C24:0	Tetracosanoic acid

Table 4.4 : Neat jatropha methyl ester and neat corn methyl ester major fatty acid component

Fatty Acid (%)	**Formula**	**JME**		**CME**	
		This work	**Source***	**This work**	**Source***
Palmitic	C16:0	22.45	16.02	22.11	11.54
Stearic	C18:0	10.00	10.21	4.09	2.02
Oleic	C18:1	8.04	38.54	8.14	28.32
Linoleic	C18:2	52.90	33.08	59.06	55.78
Others	Cn	6.61	2.15	6.60	2.32

Source*: (Wright & Evans, 2008), (Chiou, 2008)

Table 4.5 shows the fatty acid compositions of the neat biodiesel and biodiesel blends at Corn methyl ester (CME) :Jatropha methyl ester (JME) mass ratio of ;

i. CME:JME (0:100)
ii. CME:JME (20:80)
iii. CME:JME (40:60)
iv. CME:JME (60:40)
v. CME:JME (80:20)
vi. CME:JME (100:0)

Saturated fatty acid is methyl ester with no double bond. Unsaturated fatty acid is methyl ester with one double bond or more. Observation from Table 4.5, neat JME contained more saturated fat than neat CME. Vice-versa, CME contained more unsaturated fat than the neat JME. The percentage of saturation lessens as CME mass ratio increased in each blending. In the meantime, the total amount of monosaturated fat remained the same with little almost no increment or decrement in the total percentage while, the percentage of polysaturated fat escalated as the amount CME blend ratio increased.

Table 4.5 : Fatty acid compositions of Jatropha methyl ester(JME) and Corn methyl ester(CME) with its respective blend ratios

Fatty Acid (%)	**Formula**	**CME :JME (0:100)**	**20:80**	**40:60**	**60:40**	**80:20**	**CME :JME (100:0)**
Myristic	C14:0	0.28	0.22	0.22	0.21	0.23	0.17
Palmitic	C16:0	22.45	22.08	22.24	22.32	22.70	22.11
Palmitoleic	C16:1	3.27	2.84	2.31	1.82	1.42	1.14
Margeric	C17:0	-	0.39	0.52	0.47	0.45	0.34
Stearic	C18:0	10.00	9.19	7.94	6.77	5.42	4.09
Oleic	C18:1	8.04	7.63	6.73	7.53	7.49	8.14
Linoleic	C18:2	52.90	54.18	55.91	57.18	58.04	59.06
Linolenic	C18:3	0.23	0.50	0.20	0.20	0.70	0.24
Arachidic	C20:0	1.12	1.22	1.46	1.62	1.92	1.95
Gadoleic	C20:1	0.50	0.76	1.01	1.28	1.64	1.86
Behenic	C22:0	1.22	0.59	1.03	0.59	-	0.49
Lignoceric	C24:0	-	0.40	0.44	-	-	0.41
Saturated (Cn:0)		**35.06**	**34.09**	**33.85**	**31.99**	**30.71**	**29.57**
Monounsaturated (Cn:1)		**11.81**	**11.23**	**10.05**	**10.63**	**10.56**	**11.13**
Polyunsaturated (Cn:2,3)		**53.13**	**54.68**	**56.11**	**57.38**	**58.73**	**59.30**
Total		100.00	100.00	100.00	100.00	100.00	100.00

4.3 IODINE VALUE

The iodine value is quantified using the EN-14214 calculation method for determination of the iodine value adapted for biodiesel from the AOCS Recommended practice Cd1c-85. This method uses the mass percentage of the fatty acid methyl esters and multiplied it by an assigned weighting factor (Table 4.6). One example calculation is shown as the following.

Iodine value calculation (EN14214,2003) for CME:JME(100:0),

$$\boldsymbol{Iodine\ value\ (IV)} = mass\ \%\ fatty\ acid\ \times weighting\ factor$$

$$= (0.950 \times 1.139\%) + (0.86 \times 8.139\%) + (1.732 \times 59.055\%) + (2.616 \times 0.241\%) + (0.785 \times 1.856\%)$$

$$= \mathbf{112.45}$$

Table 4.6 : Weighting Factors for Common Fatty Acids to Determine Iodine Value (EN 14214:2003)

Methyl Ester	Formula	Factor
Saturated fatty acids	C n:0	0
Palmitoleic	C16:1	0.950
Oleic	C18:1	0.860
Linoleic	C18:2	1.732
Linolenic	C18:3	2.616
Gadoleic	C20:1	0.785
Erucic	C22:1	0.723

Expressed in gram I_2/100gram sample, Table 4.7 shows the correlation between the iodine value and the degree of unsaturation reported in one decimal place. CME:JME is represented by shortform C:J. Table 4.8 shows the comparison of the iodine value of this work with existing journal source.

Table 4.7: Fatty acid composition in total of saturated, monounsaturated and polyunsaturated with iodine value

Fatty Acid (%)	C:J (0:100)	20:80	40:60	60:40	80:20	C:J(100:0)
Saturated (Cn:0)	35.06	34.09	33.85	31.99	30.71	29.57
Monounsaturated (Cn:1)	11.81	11.23	10.05	10.63	10.56	11.13
Polyunsaturated (Cn:2,3)	53.13	54.68	56.11	57.38	58.73	59.30
Iodine value (gI_2/100g)	**102.6**	**105.0**	**106.1**	**108.8**	**111.4**	**112.5**

Table 4.8 : Iodine value

Methyl ester	**Iodine value ($gI_2/100g$)**	
	This work	**Source***
JME	102.6	96 to 106
CME	112.5	101 to 119.41

Source*:(Wright & Evans, 2008),(Ramos, Fernández, Casas, Rodríguez, & Pérez, 2009)

Iodine value is limited to 120g I_2/100g in the European biodiesel standard EN14214. The limitation of unsaturated fatty acids prevents the formation of deposits when heating higher unsaturated fatty acids can result in polymerization of glycerides(Ramos et al., 2009). Both JME and CME have iodine value below 120 which are 102.6g I_2/100g and 112.5g I_2/100g respectively. Iodine value is a measure for degree of unsaturation in methyl ester. In the table, as more the unsaturation is present, the iodine value increased as well. The increment of polyunsaturated fatty acid contributes to the increment of iodine value in this study.

4.4 OXIDATION STABILITY

The European standard EN14112 establishes that the oxidative stability of biodiesel should be determined at 110°C by the Rancimat method, requiring a minimum value of 6 hours for the induction period. Figure 4.1 shown is Metrohm 873 Biodiesel Rancimat instrument used to determine the oxidation stability for neat biodiesel and biodiesel blends.

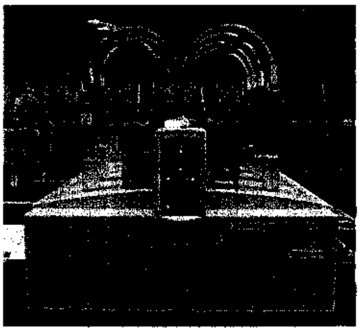

Figure 4.1 : Metrohm 873 Biodiesel Rancimat

The oxidation stability of biodiesel varies significantly depending on the source of oil/fat from which the biodiesl is derived, processing conditions, contaminants particularly trace metals, water, radicals and peroxides and storage stability can be influence by humidity, sunlight, microorganisms, temperature and oxygen(Bart et al., 2010). Figure 4.2 shows a graph of Induction Period (IP) against the biodiesel blends of jatropha mass fraction. Biodiesel blend at 0.6 and 0.8 of mass fraction jatropha indicates CME:JME (40:60) and CME:JME (20:80), respectively. Both blend ratios managed to achieve the minimum requirement at 6.18 hours and 6.42 hours respectively. The IP escalated as the degree of saturation increased with the higher amount of JME in the blends. Since the objective of the study is to maximize the usage of non-edible oil in biodiesel production, blend ratio at 0.8 mass fraction jatropha or CME:JME (20:80) is selected to be further improve for cold flow properties.

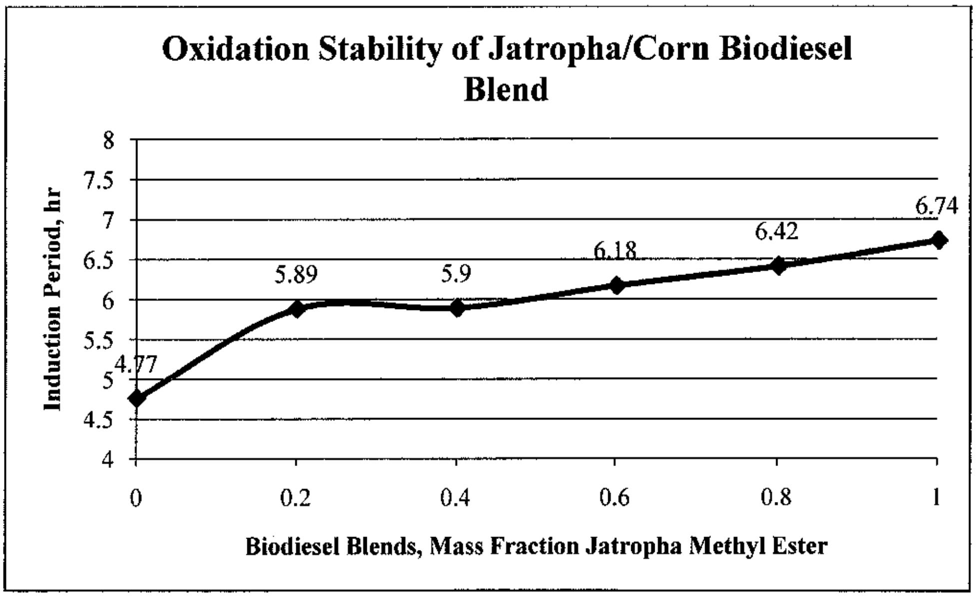

Figure 4.2: Oxidation Stability of Jatropha/Corn Biodiesel Blend

4.5 Cold Fiter Plugging Point

CFPP test calls for cooling a FAME sample at a specified rate and drawing it under vacuum through a wire mesh filter screen (Knothe et al., 2005). CFPP is then defined as the lowest temperature at which 20ml of sample safely passes through the filter within 60s (EN 116). An automatic tester ISL FPP 5Gs was used to carry out the determination of the CFPP at each biodiesel blend ratio and after the addition of CFI. Figure 4.3 shows the equipment used to test CFPP which is the automatic tester ISL FPP 5Gs.

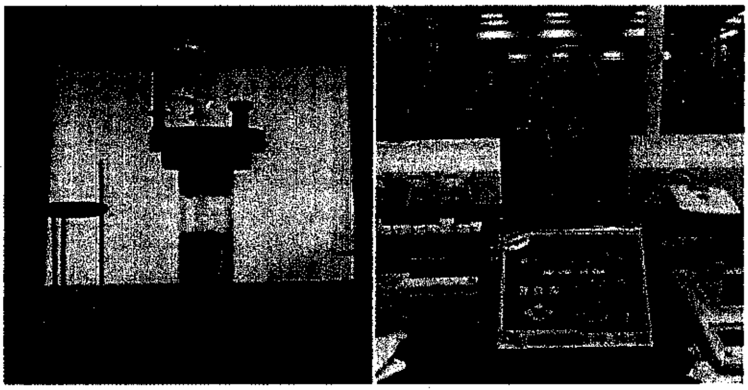

Figure 4.3 : Automatic tester ISL FPP 5Gs

4.5.1 Improvement of CFPP by blending of JME and CME

Figure 4.4 shows that pure CME has a CFPP value of -4°C which is lower than pure JME which has a value of -1.2°C. It can be seen that the edible oil has a better CFPP compared to the inedible JME. At the blend of 20:80 (CME:JME), it can be observed that the CFPP value lowers from -1.2°C to 2.0 °C. The trend continues as the mass fraction of CME increased, and the lowest temperature achieved is -3.7°C for the blend ratio at 80:20 (CME:JME). Methyl ester that has long chained saturated fatty acids like behenic (C20:0) and lignolenic(C24:0) acid tend to have the worse low-temperature properties. Low temperature properties depend mostly on the saturated fats while the effect of unsaturated ester is negligible.

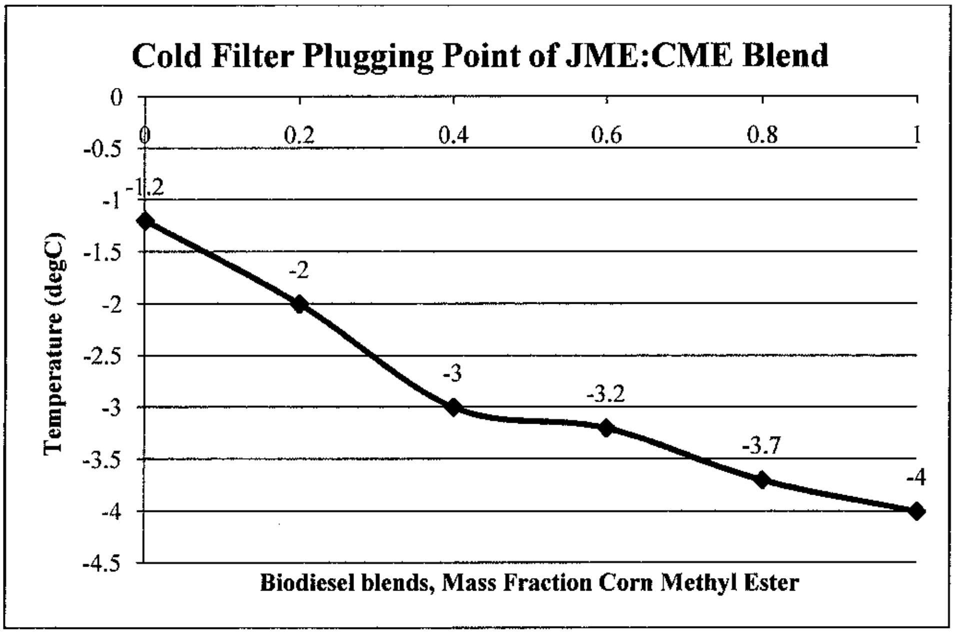

Figure 4.4: CFPP of JME:CME blend

Although blend ratio at 80:20 (CME:JME) has the lowest CFPP, the oxidation stability of this blend is 5.89 hours and it did not meet the oxidation stability requirement. Therefore, the blend 20:80 (CME:JME) with an oxidation stability of 6.42 hours and CFPP of -2°C is used for the investigation of CFI additive addition.

4.5.2 Performance of Acrylic Copolymer as Cold Flow Improver (CFI)

Figure 4.5 shows the effect of acrylic copolymer on the CFPP of the 20:80 (CME:JME) blend. Concentration of 0.0mass%, 0.5mass% and 1.0mass% of acrylic copolymer was added to the blend to observe the changes in temperature. The maximum allowable amount of additive used in the biodiesel is 1.0mass%.

The result of -3°C was obtained when 0.5mass% was added. When 1.0 mass% of additive was added, the temperature greatly reduced to -6°C. The function of the acryclic copolymer as additive is that it significantly reduces growth and agglomeration rates as temperature drops below cloud point. Acrylic copolymer behaves by hindering crystal growth, but do not prevent crystal initiation. They have little effect on the temperature at which crystals that has already form. To be more precise, the additive co-crystallize on the edges of the growing crystal plates when crystals form, thereby inhibiting the continued agglomeration of the plate(Bart et al., 2010).

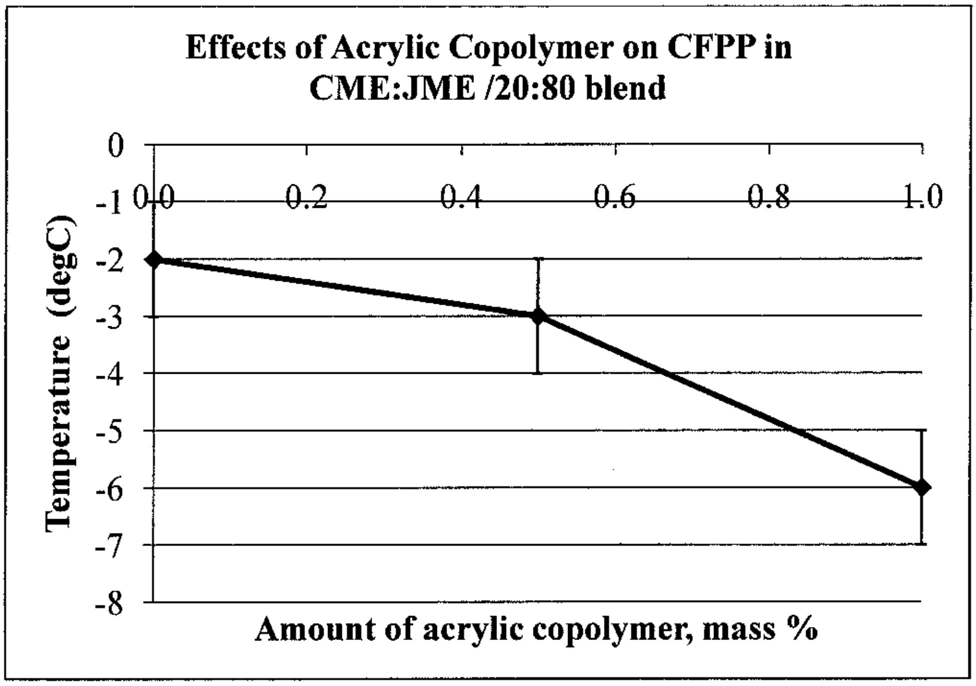

Figure 4.5: Effects of Acrylic Copolymer on CFPP in CME:JME/20:80 Blend

CHAPTER 5

RECOMMENDATION AND CONCLUSION

As an effort to promote the usage of non-edible oil as feedstock in biodiesel production, an investigation of the blending of methyl ester from non-edible oils and methyl ester from edible oil is done. The blend ratio of 20:80 (CME:JME) has achieved an oxidation stability of 6.42 hour with CFPP of -2°C.

Some critical parameters like oxidation stability, iodine value and CFPP were succesfully correlated with the methyl ester composition of each biodiesel, according to the parameter: degree of unsaturation.

In this study, in order to overcome the shortcomings of jatropha-corn biodiesel, acrylic copolymer is introduced as CFI additive to further reduce the CFPP. It is found out that the addition of CFI can enhance the cold flow properties of the biodiesel blend and in this case is the Jatropha-Corn biodiesel. The 20:80 (CME:JME) blend manage to achieve a reduction of CFPP from -2°C to -6°C after the addition 1.0 mass% of acrylic copolymer. Acrylic copolymer significantly helps to reduce growth and agglomeration rates as temperature drops below cloud point. Acrylic copolymer behaves by hindering crystal growth, co-crystallize on the edges of the growing crystal plates when crystals form, thereby inhibiting the continued agglomeration of the plate.

More parameters can be further tested to ensure the biodiesel has met the EN14214 standard; such as the cetane number, flash point, water and sediment content as these parameters are quite crucial in affecting the cold flow properties of biodiesel.

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APPENDIX

APPENDIX A

A1- GANTT CHART

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	■	■	■	■	■	■	■	Mid-Semester Break								
2	Submission of Progress Report									●							
3	Project Work Continues									■	■	■	■	■			
4	Pre-EDX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

APPENDIX B

B1) ACID VALUE

Crude Jatropha Curcas L. oil

Table B1: Acidity of Crude Jatropha Curcas L. oil

Trial	Condition	Volume of Titrant used (ml)	Acid Value FFA (%)	Average FFA(%)
1	Before titration (no sample added)	8.5	25.16	23.41
	After titration (no sample added)	9.1		
	After titration (2g of sample added)	32		
2	Before titration (no sample added)	10.5	21.65	
	After titration (no sample added)	10.8		
	After titration (2g of sample added)	30.3		

Treated Jatropha Curcas L. Oil

Table B2: Acidity for Treated Jatropha Oil

Trial	Condition	Volume of Titrant used (ml)	Acid Value FFA (%)	Average FFA(%)
1	Before titration (no sample added)	3.5	0.6600	0.69772
	After titration (no sample added)	4.1		
	After titration (2g of sample added)	7.1		
2	Before titration (no sample added)	12.6	0.72943	
	After titration (no sample added)	12.9		
	After titration (2g of sample added)	15.8		

Refined Corn Oil

Table B3: Acidity of Refined Corn Oil

Trial	Condition	Volume of Titrant used (ml)	Acid Value FFA (%)	Average FFA(%)
1	Before titration (no sample added)	7.7	0.89776	0.78554
	After titration (no sample added)	8.1		
	After titration (2g of sample added)	8.8		
2	Before titration (no sample added)	11	0.67332	
	After titration (no sample added)	14		
	After titration (2g of sample added)	19.2		

B2) TEMPERATURE PROFILES FOR NEAT BIODIESEL

Cloud Point

Table B4: Cloud Point Runs

Cloud Point	Experimental	
	JME	CME
Run 1	3.9	0.1
Run 2	4	0.1
Run 3	4	0.2
Average	4	0.1

Pour Point

Table B5 : Pour Point Runs

Pour Point	Experimental	
	JME	CME
Run 1	3	0
Run 2	3	0
Run 3	3	0
Average	3	0

Cold FilterPlugging Point

Table B6 : Cold Filter Plugging Point Runs

CFPP	Experimental	
	JME	CME
Run 1	-1.2	-4.1
Run 2	-1.1	-4.0
Run 3	-1.2	-4.0
Average	-1.2	-4

B3) OXIDATION STABILITY

Oxidation stability data (Conductivity,µS/cm vs Induction Period,hour)

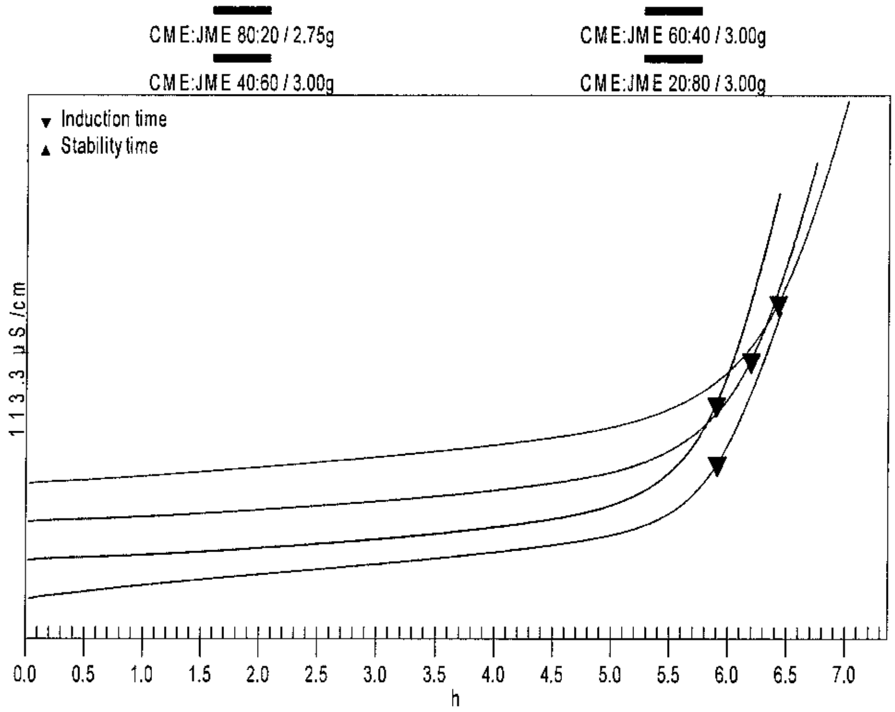

Figure B1: Comparison of the Induction Period of the Blends

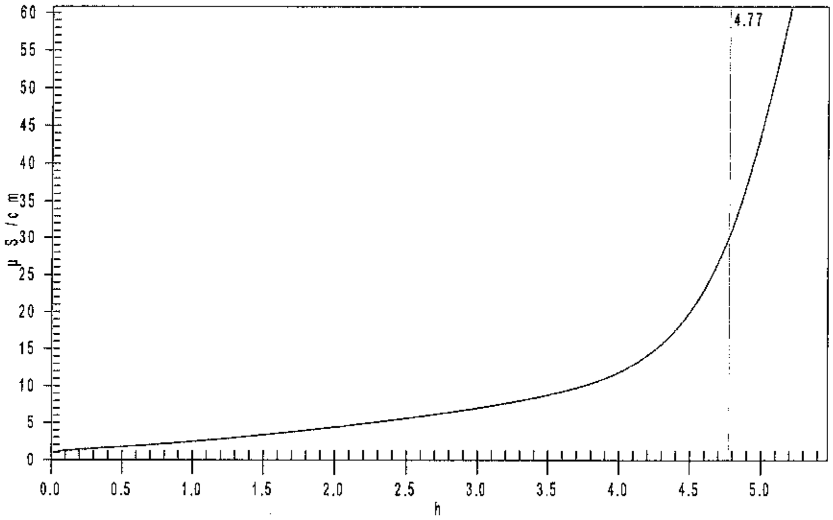

Figure B2: Induction Period at CME:JME (100:0)

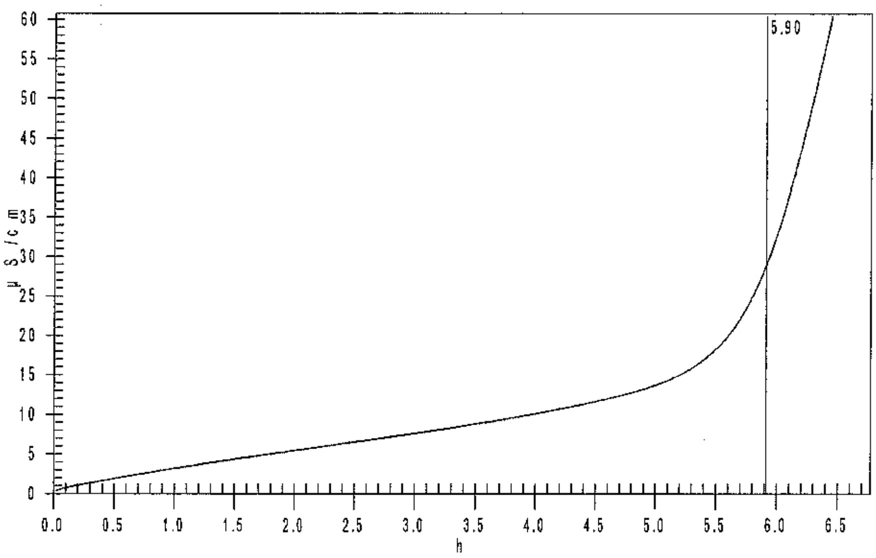

Figure B3: Induction Period at CME:JME (80:20)

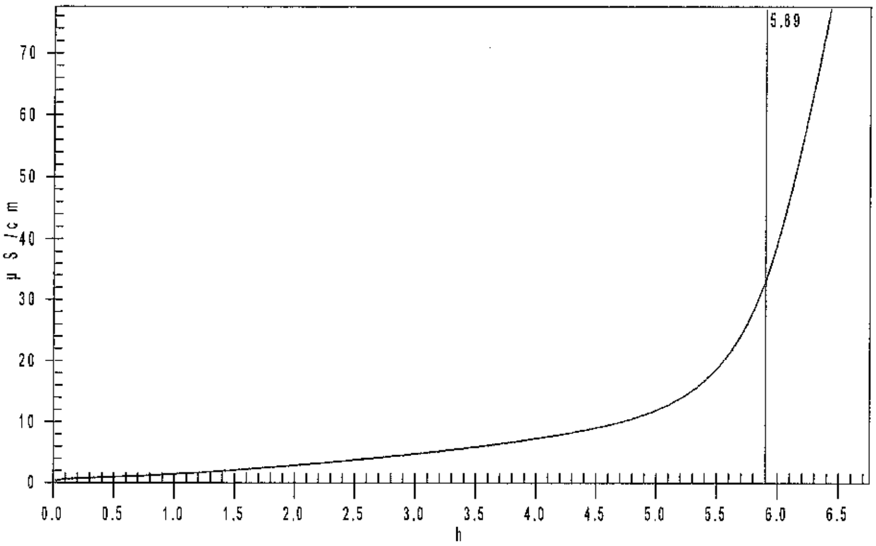

Figure B4: Induction Period at CME:JME (60:40)

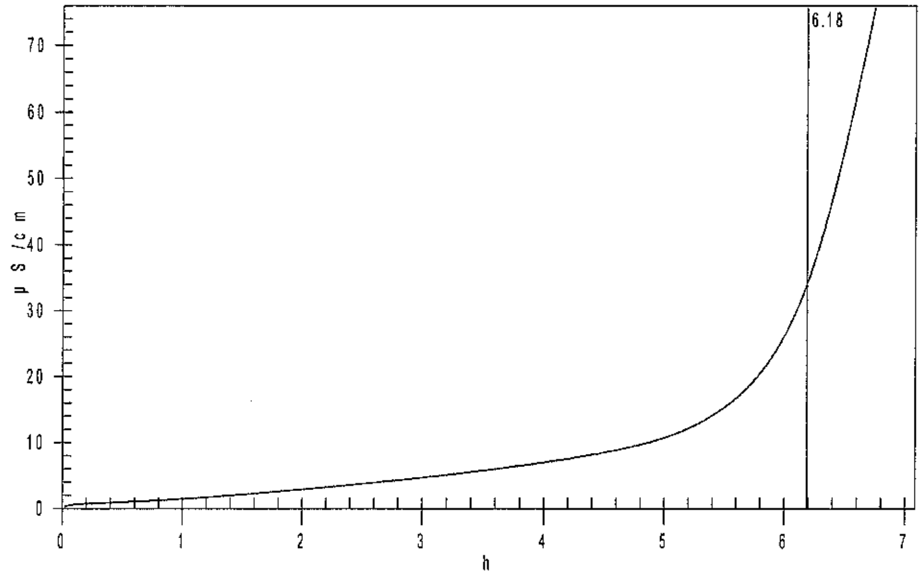

Figure B5: Induction Period at CME:JME (40:60)

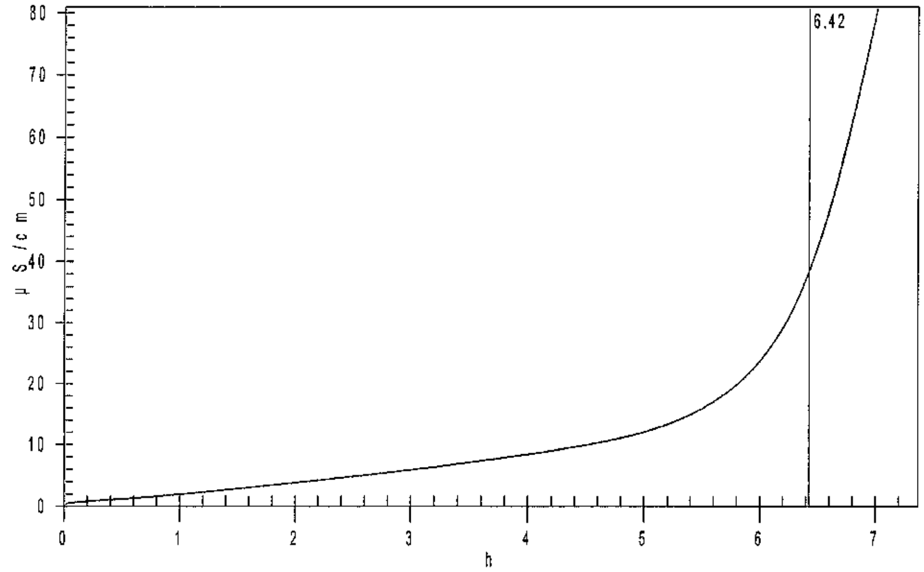

Figure B6: Induction Period at CME:JME (20:80)

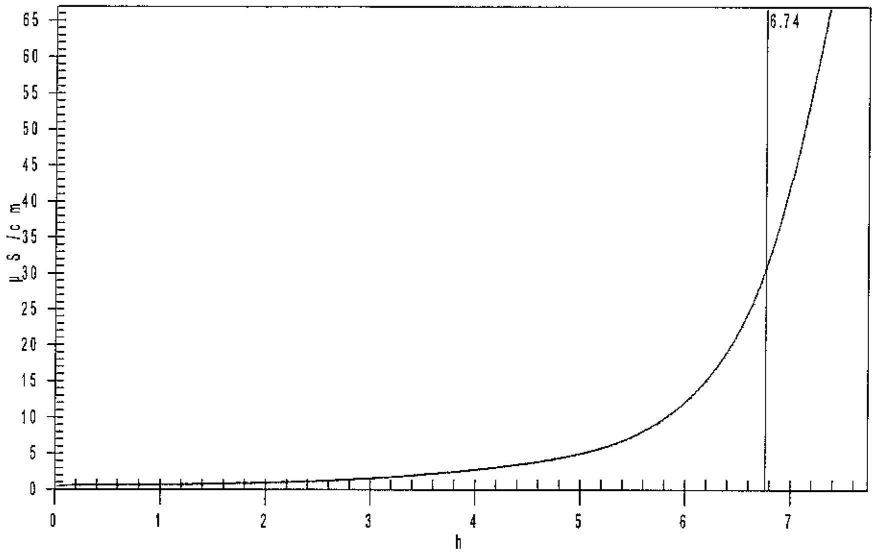

Figure B7: Induction Period at CME:JME (0:100)