

CERTIFICATION OF APPROVAL

Jatropha Biodiesel Blends: A Noble Solution for Global Fuel Crisis

by

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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.



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ABSTRACT

Biodiesel has been increasingly promoted as an alternative renewable fuel due to fossil fuel depletion and environmental degradation. In USA, Europe and Asia, biodiesel is derived from animal fats and vegetable oil to significantly reduce air pollution and dependence on fossil fuel, where resources are limited and localized to specific regions. Edible oil such as Soybean, sunflower and rapeseed are used as feedstock for the production of biodiesel in USA and Europe. Palm oil is used mainly in the Asia region. This calls for the exploration of non-edible seed oil as to reduce the dependency on edible oil as biodiesel raw materials, as an effective global solution without affecting the global food economy, depletion of food supply, feedstock cost and limited land availability for plantation of oil crop. In the present study, blends of Jatropha, Soybean and Palm biodiesel have been explored to determine a noble design with respect to optimum oxidation stability and low temperature properties (cloud point, pour point and cold filter plugging point). A two-step process consisting of pre-esterification and esterification were developed to produce biodiesel from crude *Jatropha curcas* L. and Soybean respectively. The process was carried out at optimized set of conditions: methanol/oil molar ratio (6:1), sodium methoxide catalyst concentration (1.00%), temperature (60°C) and mixing intensity (1200 rpm). The physicochemical properties showed that the methyl esters contained low moisture level (<500ppm) and acid value (<0.5 mg-KOH/ mg-oil) respectively. Characterization of the fatty acid methyl esters (FAMEs) was accomplished by gas-chromatography. The biodiesel produced were found to comply to the standards specifications of ASTM D 6751, EN 14214 and MS123:2008. The noble design of Jatropha and Soybean biodiesel blend has achieved better cold filter plugging point than PETRONAS B5 Dynamic Diesel. The noble design of Jatropha and Palm biodiesel blend is able to meet the industrial expectation of cold filter plugging point, delivering a natural additive effect on neat Palm biodiesel.

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Table of Contents

CERTIFICATION OF APPROVAL.....	ii
CERTIFICATION OF ORIGINALITY	iii
ABSTRACT.....	iv
ACKNOWLEDGEMENTS.....	v
1. CHAPTER 1: INTRODUCTION	1
1.1 Background	1
1.2 Problem Statement	2
1.3 Objectives and Scope of Study.....	2
1.3.1 Objectives	2
1.3.2 Scope of Study	3
2. CHAPTER 2: LITERATURE REVIEW AND/OR THEORY	5
2.1 Overview of Biodiesel.....	5
2.2 Advantages and Disadvantages of Biodiesel	5
2.3 Noble Design and Region of Interest	6
2.4 Soybean Oil	7
2.5 Jatropha Oil	7
2.6 Acidity and Free Fatty Acids	8
2.7 Low Temperature Properties.....	8
2.8 Oxidation Stability	11
2.9 Transesterification of Vegetable Oils.....	11
2.10 Experimental Strategies and Standard Specifications	12
3. CHAPTER 3: METHODOLOGY	13
3.1 Material and Apparatus	13
3.1.1 Material	13
3.1.2 Apparatus	14
3.2 Research Methodology.....	15
3.2.1 Material Procurement.....	15
3.2.2 Experimental Setup.....	15

3.2.3	Determination of Acid Value.....	16
3.3	Pre-treatment and Transesterification	16
3.3.1	Pre-esterification Procedure for Non-edible Oil	16
3.3.2	Transesterification Procedure for Edible and Non-edible Oils.....	17
3.3.3	Product Analysis	18
3.3.4	Product Characterization and Properties of Biodiesel	18
3.3.5	Blending of Biodiesel	21
4.	CHAPTER 4: RESULTS AND DISCUSSION.....	22
4.1	Calculations.....	22
4.1.1	Pre-treatment.....	22
4.1.2	Determination of Acid Value	22
4.1.3	Transesterification on Jatropha and Soybean Oil	23
4.2	Experimental Proceedings.....	24
4.2.1	Determination of Acid Value.....	24
4.2.2	Transesterification.....	24
4.3	Discussion	27
4.3.1	Oxidation Stability	31
4.3.2	Low Temperature Properties.....	35
5.	CONCLUSION AND RECOMMENDATION.....	39
6.	REFERENCES.	40
7.	APPENDIX I: GANTT CHART.....	44
8.	APPENDIX II: OXIDATION STABILITY.....	45
9.	APPENDIX III: GAS CHROMATOGRAPHY ANALYSIS.....	49

List of Tables

Table 1: Comparison between Acid-catalyzed and Alkali-catalyzed Process.....	12
Table 2: Expected Observation Before and After Titration for Acid Value Determination...	16
Table 3: Calculation of Iodine Value From Methyl Ester Composition.....	20
Table 4: Blending Proportions of Biodiesel.....	21
Table 5: Determination of Acid Value for Pre-treated Jatropha Oil.....	22
Table 6: Determination of Acid Value for Neat Biodiesel	23
Table 7: Observation Before and After Titration for Acid Value Determination.....	24
Table 8: Observation for Transesterification	24
Table 9: Fatty Acids Composition of Jatropha and Soybean Methyl Ester	27
Table 10: Fatty Acid Profile in Comparison with Previous Reports	29
Table 11: Physico-chemical Properties of Biodiesel	30

List of Figures

Figure 1: Structure of triglycerides and principle of the transesterification reaction (shown for methyl esters; R = (CH ₂) _x CH ₃ or unsaturated rests according to the fatty acids).....	12
Figure 2: Experimental Setup for Pre-esterification and Tranesterification	15
Figure 3: Oxidation Stability of Jatropha and Soybean Methyl Ester Blends	31
Figure 4: Relative Oxidation Stability at 6 hours	34
Figure 5: Low Temperature Properties for Jatropha and Soybean Methyl Ester Blends	35
Figure 6: Cold Filter Plugging Point of B5 Admixtures.....	36
Figure 7: Cold Filter Plugging Point of Jatropha and Palm Methyl Ester Blends.....	36

CHAPTER 1

INTRODUCTION

1.1 Background

Among the driving forces to promote biodiesel as an alternative renewable fuel are fossil fuel exhaustion and environmental dilapidation. Increasing environmental concerns, depleting petroleum reserves and agricultural economy foundation of our country have boosted the significance of biodiesel as an alternative fuel. In USA, Europe and Asia, biodiesel is derived from animal fats and vegetable oil to significantly reduce air pollution and dependence on fossil fuel, where resources are limited and localized to specific regions. Edible oil such as Soybean, sunflower and rapeseed are used as feedstock for the production of biodiesel in USA and Europe. Palm oil is used mainly in the Asia region. Neat biodiesel often has either the difficulties in terms of oxidation stability or low temperature operability. Biodiesel such as Soybean portrays excellent low temperature operability in which it does not clog the engine at moderate temperature climates during cold seasons. It is associated with their crystallization temperature due to high concentrations of high-melting point saturated long chain fatty acids [13]. However, Soybean biodiesel possesses low oxidation stability in which the biodiesel becomes rancid easily. Biodiesel such as Palm portrays excellent oxidation stability but bad in terms of low temperature operability. Palm biodiesel ceases to flow at a relatively higher temperature than Soybean.

This calls for the exploration of non-edible seed oil as to reduce the dependency on edible oil as biodiesel raw materials, as an effective global solution without affecting the global food economy, depletion of food supply, feedstock cost and limited land availability for plantation of oil crop [1]. In the present study, blends of Jatropha, Soybean and Palm biodiesel have been explored to determine a noble design with respect to optimum oxidation stability and low temperature properties (cloud point, pour point and cold filter plugging point).

1.2 Problem Statement

Large scale and continuous production of biodiesel from edible oil leads to depletion of food supply as biodiesel from edible oil is competing with food industry for plantation of oil crop in limited land availability. The issue of “Food versus Fuel” has been a resounding dilemma regarding the risk of diverting plantation of crops for biodiesel production.

The major economic factor to ponder for input cost of biodiesel production is the feedstock, which comprises about 80% of the total operating costs [2]. As edible oil in the energy markets competes with food markets for scarce land, an effect of higher food/fuel price is resulted.

1.3 Objectives and Scope of Study

1.3.1 Objectives

The objectives which the author intends to achieve are:

- To produce biodiesel from Soybean (edible oil) and *Jatropha curcas* (non-edible oil)
- To identify a noble design for edible and non-edible oil blend with respect to oxidation stability and low temperature properties
- To reduce dependency on edible oil for biodiesel production

All analytical tests and methods are conforming to ASTM (American Society for Testing and Materials) 6751, EN (European Normalization) 14214 and MS (Malaysian Standard for Diesel Fuel) 123:2008

1.3.2 Scope of Study

The following are the scopes of study:

- Determination of acid value of crude Jatropha and refined Soybean oil
- Acid pre-treatment (Pre-transesterification) of non-edible oil (Jatropha) at optimized conditions
- Transesterification of non-edible and edible oil at optimized conditions
- Characterization of neat biodiesel by means of gas-chromatography (GC-MS)
- Product analysis involving Density (at 15°C), Calorific Value, Flash Point, Water Content, Iodine Value, Sulfur Content, Oxidation Stability (at 110°C), Acid Value, Linolenic Acid Methyl Ester, Polyunsaturated Methyl Ester and Cold Filter Plugging Point. Product analysis ensures the compliance to the standards specifications.
- Product analysis of Low Temperature Properties (Cloud Point, Pour Point and Cold Filter Plugging Point) and Oxidation Stability (at 110°C) for neat biodiesel and biodiesel blends
- Blending of non-edible and edible oil to produce noble design
- Blending of noble design, neat biodiesel and fossil fuel (PETRONAS Dynamic Diesel) and analysis of Cold Filter Plugging Point
- Comparative study of Cold Filter Plugging Point of the blended noble design with fossil fuel and commercial PETRONAS B5 Dynamic Diesel

The strategy to achieve the objectives was to blend Jatropha methyl ester with Soybean methyl ester and Palm methyl ester. Jatropha and Soybean methyl esters were blended at volume fraction of JOME:SOME (20:80), JOME:SOME (40:60), JOME:SOME (60:40) and JOME:SOME (80:20). For the latter, oxidation stability and low temperature properties were investigated and compared for analysis. Jatropha and Palm methyl esters were blended at volume fraction of JOME:POME (5:95), JOME:SOME (10:90), JOME:SOME (20:80), JOME:SOME (40:60) and JOME: POME (60:40). For the latter, cold filter plugging point was the attribute under investigation to meet the industrial expectation of cold filter plugging point of 11°C.

Noble design of JOME:SOME was blended with PETRONAS Dynamic Diesel at 5% volume fraction and comparison was made with commercial PETRONAS B5 Dynamic Diesel, B5 JOME (5% Jatropha methyl ester, 95% PETRONAS Dynamic Diesel), B5 SOME (5% Soybean methyl ester, 95% PETRONAS Dynamic Diesel) and B5 POME (5% Palm methyl ester, 95% PETRONAS Dynamic Diesel) in terms of cold filter plugging point.

CHAPTER 2

LITERATURE REVIEW AND/OR THEORY

2.1 Overview of Biodiesel

Developing alternative fuels has become a necessity due to the fast depletion of fossil fuel for the coming years. The indiscriminate extraction and extreme consumption of fossil fuels have been reducing the petroleum reserves significantly. Many studies have been devoted in the last years to renewable energy and sustainable development but the economic viability due to low market prices of biodiesel and increasing prices of the starting oils for fuel has been questioned. Many researches have been conducted to optimize biodiesel production which includes design of active heterogeneous catalyst, use of supercritical fluid and search for new feedstock that does not compete with food market [32].

Increasing environmental concerns, depleting petroleum reserves and agricultural economy foundation of our country have boosted the significance of biodiesel as an alternative fuel. In USA, Europe and Asia, biodiesel is derived from animal fats and vegetable oil to significantly reduce air pollution and dependence on fossil fuel, where resources are limited and localized to specific regions [22]. Edible oil such as Soybean, sunflower and rapeseed are used as feedstock for the production of biodiesel in USA and Europe. Palm oil is used mainly in the Asia region.

2.2 Advantages and Disadvantages of Biodiesel

Biodiesel portrays several advantages and disadvantages compared to fossil fuel. The main disadvantages would be its lower oxidation stability and inferior storage, higher crystallization temperatures [32], poor temperature operability, high feedstock cost and lower heating value [22]. The advantages of the biodiesel over fossil fuel are improved lubricity; a more complete combustion and less emission of harmful particles and pollutants [5].

Biodiesel comprises of mono-alkyl esters of long-chain fatty acids derived from animal fats or vegetable oils. It now serves as a renewable and alternative fuel [26]. Biodiesel and its blend with fossil fuel can be introduced into diesel engines without any significant modification to the engine [18]. More importance is given to the alternative feedstock due to sustainability problems associated with food/feed and land/fuel discussions. Furthermore, the competition between food and fuel from edible oil feedstock results in high price of the traditional feedstock [8]. Among alternative feedstock are animal fats, tallow, waste greases, used cooking oils [35], vegetable oil refining wastes such as acid oils and deodorizer distillates [9], micro algal oils and non-edible oils. This calls for the exploration of non-edible seed oil as to reduce the dependency on edible oil as biodiesel raw materials, as an effective global solution without affecting the global food economy, depletion of food supply, feedstock cost and limited land availability for plantation of oil crop [1]. Conversely, the significant economic factor to ponder for input costs of biodiesel production is the feedstock that comprises up to 80% of the total operating cost [2]. Current price of crude Palm oil is around USD 936 per metric tonne [29] and current price of Soybean oil is around USD 1135 per metric tonne [27]. Alternative feedstock of Jatropha oil costs only around USD 400 per metric tonne [28].

2.3 Noble Design and Region of Interest

A noble design of edible and non-edible biodiesel blend was produced to provide a low-cost feedstock and at the same time, reduce the dependency on edible oil in biodiesel production. That would significantly prevent the negative effects on the global food economy. To achieve that, blending of edible and non-edible biodiesel is performed to create a noble design for the global fuel crisis. Low temperature properties (cloud point, pour point and cold filter plugging point) and oxidation stability have been set as the top priority ahead of other properties with Soybean and Palm as edible oil and Jatropha as the non-edible oil.

Blend of *Jatropha* and Soybean is aimed primarily to cater for the USA and European region and blend of *Jatropha* and Palm is aimed to cater for the Asian market with respect to low temperature properties and oxidation stability. Biodiesel and its blends were tested to comply with ASTM (American Society for Testing and Materials) 6751, EN (European Normalization) 14214 and MS (Malaysian Standard for Diesel Fuel) 123:2008.

2.4 Soybean Oil

Soybeans flower produce 60-80 pods, each holding three pea sized beans. In processing, Soybeans are cleaned, cracked, de-hulled and rolled into flakes. This breaks the oil cells for efficient extraction to separate the oil and meat component. After producing the Soybean oil, the remaining flakes can then be processed into many types of edible soy protein products, or used to make Soybean meal [24].

2.5 *Jatropha* Oil

On the other hand, *Jatropha Curcas* can grow in arid, semiarid and wasteland. It requires little water and fertilizer, can survive on infertile soils and is not browsed by cattle. It is also pest-resistant and has a high-seed yield that continues to be produced for 30-40 years. Oil content in the *Jatropha* seeds is around 30-40% [23]. Each fruit contains 2-3 oblong black seeds which can produce oil. *Jatropha* seeds are obtained, where the ripe seeds are collected and the damaged seeds are removed. The seeds are cleaned, de-shelled and dried in an oven. The seeds are ground to power using a grinder before extracting the oil. The extraction of oil is then carried out by soxhlet extraction using hexane. The major toxic compounds in *Jatropha* plants are curcin and purgative which are dominantly found in seeds, fruits and sap [24]. This makes it a non-edible vegetable oil.

2.6 Acidity and Free Fatty Acids

In biodiesel production, one of the key vital issues is acidity of the oil. The amount of catalyst used is heavily dependent on the acidity of the oil, which is expressed in terms of percentage of free fatty acids (FFA). Basic catalysts become ineffective partially due to the consumption by neutralization [16]. Alkaline catalysts are deactivated by high FFA. Formation of emulsion and gels due to addition of excess amount of alkaline increases viscosity thus causes a drop in ester yield. High FFA deactivates alkaline catalysts and the addition of excess amount of alkaline leads to emulsion and gels, which in return increases viscosity and causes loss to ester yield. Soap is produced when FFA reacts with alkaline catalyst. This prevents an effective separation of ester and glycerol. The best method reported by several researchers is a two-step transesterification process in the biodiesel production from non-edible oil which usually contains high FFA.

2.7 Low Temperature Properties

Another vital attribute of biodiesel is the low temperature properties. Generally, low temperature properties are denoted by the change of biodiesel properties such as crystallization or increase in viscosity due to temperature fluctuations. The variety in low temperature properties of biodiesel is crucial for fuel in which it is highly dependent on the climate and seasonal conditions of the region of use. As the largest demand of biodiesel is in the European region, biodiesel produced should be able to cater to the needs of the European market. Low temperature properties are associated with the crystallization temperature due to high concentrations of saturated long-chain fatty acids. Operability problems such as plugged filters and fuel lines are encountered due to crystallization at low temperature [25]. Biodiesel produced from oils such as cottonseed oil and poultry fats suffer from extremely poor cold flow properties because of their high saturated fatty acid content [15].

Cold flow properties of diesel fuel are usually characterized by the following three temperature measures: cloud point (CP) at which crystallization begins, cold-filter plugging point (CFPP) at which fuel starts to plug a fuel filter and pour point (PP) at which fuel no longer pours. Specifically, CFPP is indicated at the temperature at which the biodiesel ceases to flow through a 45 microns mesh filter within 60 seconds or fails to return into the test jar.

The cloud point of biodiesel is relatively higher than fossil fuel and biodiesel has a 15-40 °C higher pour point than fossil fuel [22]. This, biodiesel begins to gel at crystallization temperatures, and it can clog filters or eventually become so thick that it cannot be pumped from the fuel tank to the engine [30]. For example, Palm biodiesel will have a CFPP of around 10 °C, in strong contrast to the CFPP of a rapeseed biodiesel of around -10 °C [33].

Approaches for improving the low temperature operability of biodiesel include blending with petrodiesel [5], transesterification with long- or branched-chain alcohols [30], crystallization fractionation [30] and treatment with commercial petro-diesel cold flow improver (CFI) additives [30]. However, CFI additives designed for petro-diesel are rarely as effective when used in biodiesel [13]. CFPP improvers are available commercially, but their effect depends very much on the origins of the biodiesels in which they are used. For examples, an additive that works well for RME does not have the same effect for a biodiesel that was derived from PME. If multiple feedstocks are processed for a biodiesel blend, the improver needs to be fully effective for all of the biodiesel types, and this is hard to accomplish. CFPP improvers that are on the market today work well for a single source biodiesel, but the manufacturers of these additives are still looking for the suitable formulations to cover a blend of biodiesels originating from multiple feedstock.

Several authors have published different works to improve the low-temperature properties of biodiesel by the usage of different additives for their convenient handling and usage at different climate conditions. Joshi et al. [13] improved the low temperature operability, kinematic viscosity and acid value of poultry fat methyl esters with addition of ethanol, isopropanol and butanol. They observed that the blends of ethanol in poultry fat methyl esters afforded the least viscous mixtures, whereas isopropanol and butanol blends were progressively more viscous, but still within specifications contained in ASTM D6751 and EN 14214.

Torres et al. [25] tested the effect of renewable fatty acids derivatives. The usefulness of fatty acid derivatives as biodiesel additives has been tested through optical microscopy and CFPP analysis of biodiesel blends. The strategy of using of oleates and linoleates derivatives or epoxide formation and subsequent ring-opening reaction offers a more adequate way for the synthesis of biodiesel additives.

Sarin et al. [25] experimented the effect of blending Jatropha and Palm biodiesel. The blending of 20% Palm in Jatropha biodiesel increases cloud point by 2 °C, pour point by 3 °C and CFPP by 1 °C. Jatropha-Palm (60:40) blend was tested for low temperature properties and found to exhibit cloud point of 10 °C, pour point of 12 °C and CFPP of 5°C. Thus, blending of Palm biodiesel in Jatropha biodiesel exhibits additive response in cold flow properties.

Echim et al. [8] concluded the usage of CFI reduced the CFPP of individual biodiesel samples with 2 °C to 11 °C or allowed higher percentage of saturated feedstock to be blended with traditional feedstock. The best depressant effect on samples showed Viscoplex 10-305 for Soybean methyl ester (SME) and rapeseed methyl ester (PME) with CFPP reduction of 3 °C and 11 °C respectively and Viscoplex 10-530 for Palm oil methyl ester (PME) and tallow methyl ester (TME) samples with reduction of 5 °C and 2 °C respectively.

Chen et al. [4] tested the influence of three cold improvers- olefin- ester copolymers (OECF), ethylene vinyl acetate copolymer (EACP) and polymethyl acrylate (PMA) on Soybean biodiesel. The results indicated that the ability of cold flow improvers differed in improving the cold flow properties of Soybean biodiesel, of which OECF was the best candidate, significantly reduced pour point and CFPP. It functioned by inhibiting the wax crystals from growing to a larger size and provided a barrier to crystal agglomeration at low temperatures, thus, improving the cold flow properties of Soybean biodiesel.

Joshi et al. [15] improved the cold flow properties of cottonseed oil and poultry fat upon addition of ethyl levulinate (ethyl 4-oxopentanoate). The influence of ethyl levulinate on acid value, induction period, kinematic viscosity and flash point was determined.

2.8 Oxidation Stability

Oxidation stability, one of the main attributes of biodiesel, is defined as the presence of dissolved oxygen or active oxygen species which to a great extent increases the oxidation possibility of the fuel and lowers the temperature at which degradation happens [10]. Almost in all biodiesel fuel considerable amounts of esters of oleic, linoleic or linolenic acids are present and the tendency of increasing stability is linolenic < linoleic < oleic. These esters go through auto-oxidation at varied rates based on the number and position of the double bonds and results in formation of a series of by-products, such as acids, esters, aldehydes, ketones, lactones, etc. As the oxidation progresses, the fatty acid methyl esters usually form a radical next to the double bond. This radical rapidly binds with the oxygen in the air, which is a biradical. This forms peroxide radical. The fast radical destruction cycle begins hereafter. This peroxide radical instantaneously forms a new radical from the fatty acid methyl ester, which in turn binds with oxygen in the air. Then the destructive radical auto-oxidation cycle begins. During this oxidation process, up to 100 new radicals are formed rapidly from one single radical, where decomposition takes place at an exponentially rapid rate and results in formation of a series of by-products [11]. These species created during the oxidation process effects the fuel, eventually leading to deterioration. Finally the oil spoils and became rancid very fast [23].

2.9 Transesterification of Vegetable Oils

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, yielding a mixture of fatty acids alkyl esters and glycerol as the by-product. The entire process is a sequence of three successive and reversible reactions, in which di- and monoglycerides are formed as intermediates [24]. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of alcohol. However, an excess of alcohol is used to increase the yields of alkyl esters and to permit effective phase separation from the glycerol formed. Figure 1 below details the transesterification of vegetable oils.

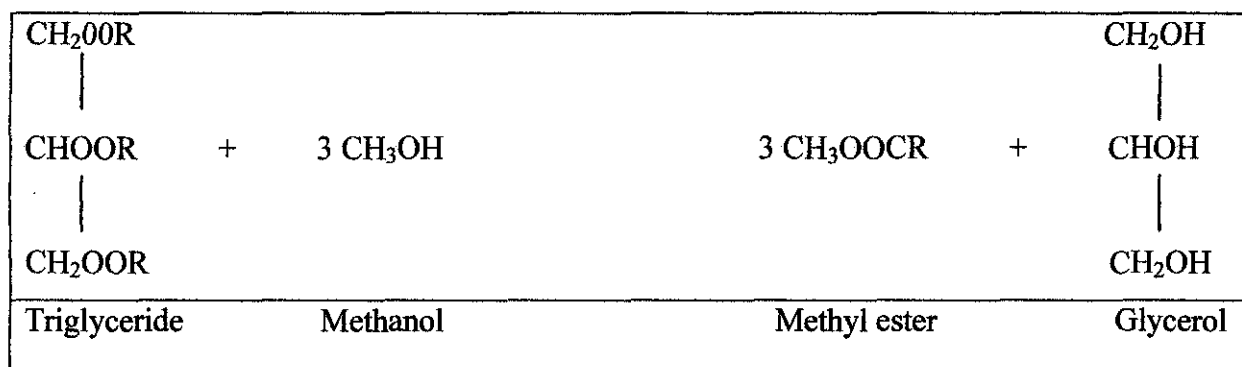


Figure 1: Structure of triglycerides and principle of the transesterification reaction (shown for methyl esters; R = (CH₂)_x CH₃ or unsaturated rests according to the fatty acids)

Many of the researchers have used acid-catalyzed transesterification over alkali-catalyzed process due to the following concerns:

Table 1: Comparison between Acid-catalyzed and Alkali-catalyzed Process

Acid-Catalyzed Process	Alkali- Catalyzed Process
Low yield of FAME	High yield of FAME
Slow temperature above 100 °C, more than 3 hours to complete conversion	Fast, less corrosive than acidic compounds
Excess of alcohol favors the formation of products but also makes the recovery of glycerol difficult	Excess of alcohol favors the formation of products

2.10 Experimental Strategies and Standard Specifications

The primary objective of the study was to evaluate pure biodiesel, Soybean oil methyl ester (SOME), Palm oil methyl ester (POME) and Jatropha oil methyl ester (JOME) along with its blends, at varied compositions as potential biodiesel fuel. Using standard methods low temperature properties, oxidation stability, water content and density were determined. It was further compared to ASTM D6751, EN 14214 and MS123:2008 standards to produce a noble solution.

CHAPTER 3

METHODOLOGY

3.1 Material and Apparatus

The following is the list of material and apparatus that would be required throughout the entire course of research:

3.1.1 Material

- **Oil:**
 - Jatropha Curcas L. oil from Bionas Malaysia and Eco Energy Solutions.
 - Soybean oil from SOCMA Trading (M) Sdn. Bhd.
 - Palm biodiesel from Platinum Energy Sdn. Bhd.
- **Alcohol:**
 - Methanol (Merck, 99.99% purity)
 - Isopropanol (EMSURE, 99.8% purity)
 - Toluene (EMSURE, 99.9% purity)
- **By-product:** Purified glycerol
- **Catalyst:**
 - Sulphuric acid (Merck)
 - Sodium methoxide (Sodium methylate solution, Merck, 30% solution in Methanol for synthesis)
- **Drying agent:** Anhydrous sodium sulfate (99% assay, by ionsensitive electrode)
- **Others:**
 - Phenolphthalein

3.1.2 Apparatus

- 3- necked round bottomed flask
- Reflux condenser
- Thermometer
- Hot plate with magnetic stirrer
- Separating funnel
- Microburet
- Pycnometer
- Rotary Evaporator
- Metrohm 831 Karl-Fischer Coulometer (Reagent: AG-H Hydranal)
- Metrohm 873 Biodiesel Rancimat Instrument
- 7890A Gas Chromatograph (Agilent Technology Inc., USA)
- CPP 5Gs Cold Point/ Pour Point Analyzer
- FPP 5Gs Cold Filter Plugging Point Analyzer
- CLA 5, Fully automatic Flash Point Tester, Petrotest Instruments GmbH and Co.
- SHATOX SX-100K PORTABLE OCTANE ANALYZER with RS-232 interface

3.2 Research Methodology

3.2.1 Material Procurement

Prior to beginning of experiment, procurement was done to purchase/search for the materials required throughout the entire course of research. Means of procurement include online survey, inquiry from regular supplies and assistance from research officers.

3.2.2 Experimental Setup

Figure 2 displays the experimental setup for transesterification and pre-esterification process for edible and non-edible oil. The apparatus required were 3-necked round bottomed flask, thermometer, beaker and hot plate with magnetic stirrer.



Figure 2: Experimental Setup for Pre-esterification and Tranesterification

3.2.3 Determination of Acid Value

In biodiesel production, one of the key vital issues is acidity of the oil. The acidity of the oil is expressed in terms of percentage of free fatty acids (FFA). Acid value has a significant effect on fuel aging. Alkaline catalysts are deactivated by high FFA. Formation of emulsion and gels due to addition of excess amount of alkaline increases viscosity thus causes a drop in ester yield. High FFA deactivates alkaline catalysts and the addition of excess amount of alkaline leads to emulsion and gels, which in return increases viscosity and causes loss to ester yield. Soap is produced when FFA reacts with alkaline catalyst. This prevents an effective separation of ester and glycerol. American Oil Chemists' Society (AOCS) Method Cd 3d-63 was used to determine the acid value of oil and biodiesel. Gas chromatography analysis is performed to investigate the constituents and composition in the neat biodiesel compounds.

Table 2: Expected Observation Before and After Titration for Acid Value Determination

Before Titration	After Titration
Observation: Clear transparent solution	Observation: Purple solution

3.3 Pre-treatment and Transesterification

3.3.1 Pre-esterification Procedure for Non-edible Oil

Acid-catalyzed pre-treatment of CJO with an initial acid value (AV) of 24.02 mg KOH g oil⁻¹ is accomplished in a 500mL three-necked round bottom flask that is connected to a reflux condenser and a mechanical stirrer set to 1200 rpm, and heated with a water bath to control the reaction temperature. Initially, CJO (188.00g, 250 mL) and methanol (88 mL, 35 vol%) are prepared in a flask, followed by drop-wise addition of sulphuric acid (conc., 1.0 vol%) [33]. The contents are heated at reflux for 4 hours. Upon cooling to room temperature, the phases are separated.

The esterification products are separated in a separating funnel to obtain the upper oil layer, which is then washed with ionized water several times until the pH of washing water is close to 7.0. The resultant pre-esterification oil is dried by anhydrous sodium sulphate before subsequent transesterification.

3.3.2 Transesterification Procedure for Edible and Non-edible Oils

200g of pre-treated *Jatropha* oil is taken in a three-necked round-bottomed flask. A water cooled condenser and a thermometer with cork are connected to the top and side of the round bottomed flask, respectively. Meanwhile, the oil is warmed by placing the round-bottomed flask in the water bath which is maintained at a temperature of 60 °C. The required amount of methanol (6:1 mol ratio) and catalyst, sodium methoxide, NaOCH₃ (1.0 wt%) are added into the oil for vigorous mixing by means of a mechanical stirrer fixed into the flask. The required temperature is maintained throughout the reaction time (90 min) and the reacted mixture is then, poured into a separating funnel. The mixture is allowed to separate and settle overnight by gravity settling into a clear, golden liquid biodiesel on the top with the light brown glycerol at the bottom.

The next day, the glycerol is drained off from the separating funnel, leaving the biodiesel/ester at the top. Of the two separated phases; the upper phase consist of methyl esters with small amount of impurities such as residual alcohol, glycerol and partial glycerides, while the lower is the glycerol. The upper methyl esters layer collected is further purified by distilling residual methanol at 800 °C (external bath temperature). Some traces of impurities such as remaining catalyst, residual methanol and glycerol are removed by consecutive rinses with distilled water. Residual water is then removed by drying esters with anhydrous sodium sulphate, Na₂SO₄, followed by filtration [24]. These procedures are repeated for Soybean oil.

3.3.3 Product Analysis

Analysis of biodiesel (fatty acid methyl esters, FAME) for fatty acid profile determination is performed with a 7890A gas chromatograph (Agilent Technology Inc., USA), equipped with a BP-X5 (SGE) capillary columns (30 m x 0.25 mm x 0.25 mm) and a flame ionization detector. The column temperature is programmed at: initial temperature 100°C, kept 3 minutes, and then at a rate of 20°C/min up to 170°C, kept 10 minutes, followed up to 260°C. Helium is used as the carrier gas. The injector temperature is programmed at 280°C. Approximately 0.1 mL of the sample is diluted in 1 mL of solvent (hexane) and a sample volume of 0.1 µL is injected into the column. The identification of the peaks is archived by retention times by means of comparing them with authentic standards analyzed under the same conditions. Soybean oil methyl ester (SOME) and Jatropha oil methyl ester (JOME) are examined, respectively. Testing method is in conformance to EN 14103.

3.3.4 Product Characterization and Properties of Biodiesel

Density

The density of the methyl ester is calculated using a pycnometer (25 mL) at an ambient temperature, 20°C. Jatropha and Soybean methyl ester are tested respectively.

Water Content

The water content of the neat biodiesel is measured by Metrohm 831 Karl-Fischer Coulometer (Reagent: AG-H Hydranal) in conformance to the testing method of ISO 12937. Soybean and Jatropha methyl ester were tested respectively. Only a few drops of sample are required for each run of testing.

Pour Point and Cloud Point

The major attributes for the determination of low temperature properties for biodiesel are cloud point and pour point. Both are measured in conformance to ASTM D97 and D2500 test methods respectively. Cloud point is expressed up to one decimal place and pour point is denoted by multiple of 3°C, either positive or negative. Neat biodiesel of Jatropha and Soybean and its blends are tested with CPP 5Gs Cold Point/ Pour Point Analyzer.

Cold Filter Plugging Point

Cold filter plugging point determines the operability in the engine at low and moderate climates condition. This is in conformance to EN 116 testing method using FPP 5Gs Cold Filter Plugging Point Analyzer. Sample size amounts to 45 mL.

Oxidation Stability

Oxidation stability at 110°C is tested on Metrohm 873 Biodiesel Rancimat Instrument in conformance to EN 14112 testing method. Oxidation stability is expressed in terms of induction time or induction period. Sample size amounts to 2.8 g for each run. Each sample is analyzed under conditions of constant airflow of 10 L/h passing through the fuel. The vapors released during the oxidation process, together with the air, are passed into a vessel containing 50 mL of water, which has been distilled and contains an electrode for measuring the conductivity. The electrode in the vessel is connected to a measuring and recording device for measuring the conductivity. The samples are held at 110°C heating block temperature, with a temperature correction factor DT set to 0.7°C.

Iodine Value

Iodine value is tested in conformance to EN 14111 via gas chromatography (mass-spectrum), calculated from methyl ester composition. It is expressed in terms of g iodine per 100 g of sample.

Table 3: Calculation of Iodine Value From Methyl Ester Composition

Methyl Ester of the Following Acids	Factor
Myristic (C14:0)	0.3
Palmitic (C16:0)	4.0
Palmitoleic (C16:1)	1.1
Stearic (C18:0)	2.0
Oleic (C18:1)	60.5
Linoleic (C18:2)	9.4
Linoleic (C18:3)	0.4
Eicosanoic (C20:0)	0.4
Eicosanoic (C20:1)	0.7
Docosanoic (C22:0)	0.7
Docosenoic (C22:1)	1.1

Calorific Value

Calorific value is tested using IKA C5000 Bomb Calorimeter. Sample size amounts from 0.5 to 1 g for each run.

Flash Point

Flash point is tested in conformance to testing method of ISO 2592 and ASTM D92 using CLA 5, Fully automatic Flash Point Tester, Petrotest Instruments GmbH and Co.

Cetane Number

Cetane number is tested as per ASTM D-613 and EN ISO 5165 with SHATOX SX-100K PORTABLE OCTANE ANALYZER with RS-232 interface.

3.3.5 Blending of Biodiesel

Blending of biodiesel is conducted in a 3-necked round bottomed flask with thermometer and hot plate with magnetic stirrer. The stirring intensity is set at 1200 rpm and temperature is kept constant at 55 °C for 30 minutes. Blending proportions are done as such:

Table 4: Blending Proportions of Biodiesel

No.	Proportion of Non-edible and Edible oil (% vol. fraction)			Proportion of Biodiesel (% vol. fraction)	PETRONAS Dynamic Diesel (% vol. fraction)
	Jatropha ME	Soybean ME	Palm ME		
1	100	0	-	100	-
2	80	20	-	100	-
3	60	40	-	100	-
4	40	60	-	100	-
5	20	80	-	100	-
6	0	100	-	100	-
7	5	-	95	100	-
8	10	-	90	100	-
9	20	-	80	100	-
10	40	-	60	100	-
11	60	-	40	100	-
12	ND	ND	-	5	95
13	ND	-	ND	5	95
14	-	-	100	5	95

*ND denotes proportion identified as noble design.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Calculations

4.1.1 Pre-treatment

Volume of Jatropha oil	=	250 mL (\approx 188.00 g)
Volume of Methanol (35 vol%)	=	35 vol% x Volume of Jatropha oil
	=	88 mL
Volume of catalyst (sulphuric acid)	=	1 vol% x Volume of Jatropha oil
	=	2.50 mL

4.1.2 Determination of Acid Value

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

where

A denotes volume titrant used for sample (mL)

B denotes volume titrant used for blank (mL)

N denotes normality of KOH (0.02 M)

W denotes weight of sample (2 g)

Determination of Acid Value after Acid Pre-treatment on Edible Oil (Jatropha)

Table 5: Determination of Acid Value for Pre-treated Jatropha Oil

Run	Testing Method	Acid Value (mg KOH/g oil)	% Free Fatty Acids (% FFA)
1	EN 14104	1.32	0.66
2	EN 14104	1.00	0.5
Average		1.16	0.58

Determination of Acid Value on Neat Biodiesel (Soybean and Jatropha) after Transesterification

Table 6: Determination of Acid Value for Neat Biodiesel

Biodiesel	Testing Method	Acid Value (mg KOH/g oil)	% Free Fatty Acids (% FFA)
Jatropha	EN 14104	0.11	0.055
Soybean	EN 14104	0.05	0.025
Palm	EN 14104	0.46	0.230

4.1.3 Transesterification on Jatropha and Soybean Oil

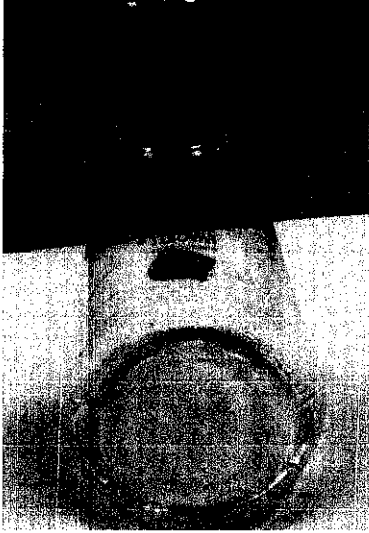
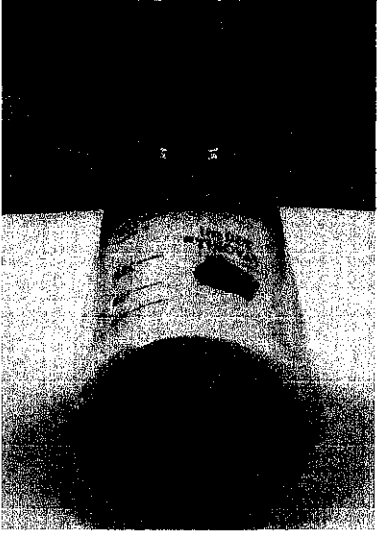
Mass of Jatropha oil = 200 g
 Molecular weight of Jatropha oil¹³ = 870 g/mol
 Mole of Jatropha = 0.23 mol
 Mole of Methanol = 0.23 mol x 6
 = 1.38 mol
 Mass of Methanol = 1.38 mol x 32.04 g/mol
 = 44.22 g
 Mass of catalyst (sodium methoxide) = 1 wt% x Mass of Jatropha oil
 = 2.00 g

 Mass of Soybean oil = 200 g
 Molecular weight of Jatropha oil¹³ = 876 g/mol
 Mole of Jatropha = 0.23 mol
 Mole of Methanol = 1.38 mol
 Mass of Methanol = 44.22 g
 Mass of catalyst (sodium methoxide) = 1 wt% x Mass of Jatropha oil
 = 2.00 g

4.2 Experimental Proceedings

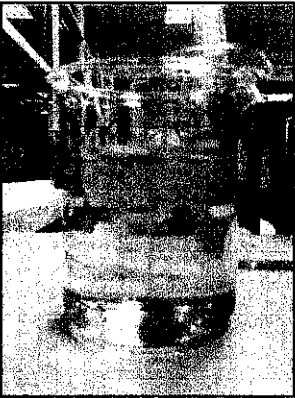
4.2.1 Determination of Acid Value

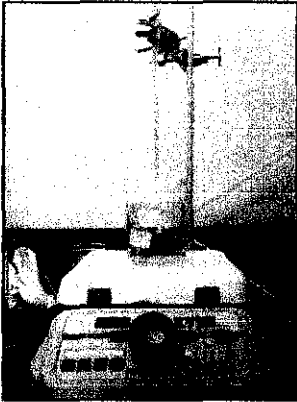
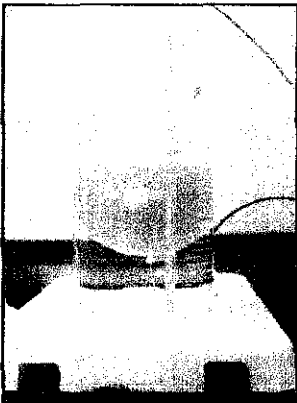
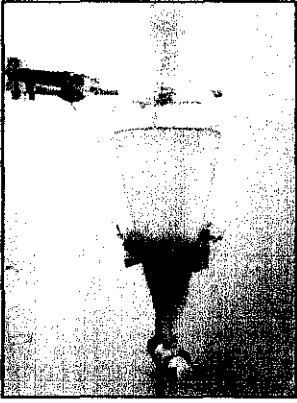
Table 7: Observation Before and After Titration for Acid Value Determination

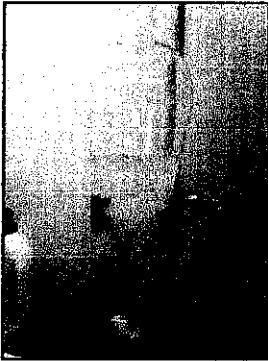
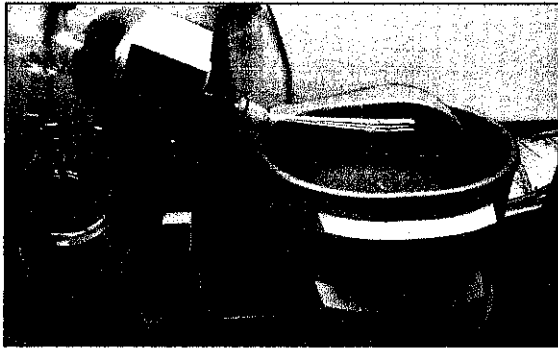


Before Titration	After Titration
 <p data-bbox="158 1131 672 1171">Observation: Clear transparent solution</p>	 <p data-bbox="816 1131 1262 1171">Observation: Purple clear solution</p>

4.2.2 Transesterification

Table 8: Observation for Transesterification

Step	Observation
Preparation of 200 g oil	

<p>Pre-heating of Soybean oil to 60 °C</p>	
<p>Addition of methanol and catalyst (sodium methoxide) into pre-heated Soybean oil. Transesterification process was set to run for 90 minutes at 1200 rpm</p>	
<p>The oil was then poured into a separating funnel to enable separation of methyl ester at the top and glycerol (by-product at the bottom of the funnel</p>	

<p>Washing of methyl ester with warm de-ionized water (50°C)</p>	
<p>Separation in rotary evaporator to remove traces of methanol at 70°C heating bath and rotation intensity of 80 rpm</p>	
<p>Addition of anhydrous sodium sulphate and oil was then left for an hour under the fume hood. Filtration via filter paper to remove anhydrous sodium sulphate from biodiesel.</p>	
<p>Neat biodiesel produced</p>	

4.3 Discussion

Table 9: Fatty Acids Composition of Jatropha and Soybean Methyl Ester

Fatty Acid Profile	Jatropha^A	Jatropha^B	Soybean
Myristic (C14/0)	0.06	-	0.04
Palmitic (C16/0)	16.42	16.31	8.43
Palmitoleic (C16/1)	1.20	0.89	0.06
Margaric (C17/0)	0.12	-	0.06
Stearic (C18/0)	9.30	9.89	3.31
Oleic (C18/1)	38.46	37.33	31.70
Linoleic (C18/2)	34.09	35.58	54.94
Linolenic (C18/3)	-	-	0.67
Arachidic (C20/0)	0.26	-	0.24
Eicosenoic (C20/1)	0.10	-	-
Behenic (C22/0)	-	-	0.26
Lignoceric (C24/0)	-	-	0.08
Gondoic	-	-	0.21
Saturated	26.16	26.20	12.42
Monounsaturated	39.75	38.22	31.97
Polyunsaturated	34.09	35.58	55.60

* Superscript A denotes crude Jatropha oil feedstock from Eco Energy Solutions

* Superscript B denotes crude Jatropha oil feedstock from Bionas

* Soybean oil from SOCMA Trading (M) Sdn. Bhd.

Table 9 depicts the fatty acid (FA) compositions of SOME and JOME. Linoleic, oleic, Palmitic and stearic acids were the main components of SOME with contribution present at 54.94, 31.70, 8.43 and 3.31%, respectively. Minor constituents included linolenic (0.67%), behenic (0.26%), arachidic (0.24%), gondoic (0.21%), lignoceric (0.08%), Palmitoleic (0.06%), margaric (0.06%) and myristic acid (0.04%) also identified. Soybean oil methyl ester was characterized by a high percentage of unsaturated fatty acids (87.58%), followed by saturated fatty acids (12.42%) constituting the remaining.

In Table 9, superscript A denotes *Jatropha* from Eco Energy Solutions and B denotes *Jatropha* from BIONAS. The major fatty acids in JOME^A were oleic, linoleic, Palmitic and stearic fatty acid. Oleic acid showed the highest percentage of composition of 38.46% followed by linoleic acid with 34.09%. Palmitic and stearic contributed 16.42% and 9.30%, respectively. Other fatty acid composition included Palmitoleic (1.20%). The content of unsaturated fatty acids was 73.84%, with saturated fatty acids (26.16%) constituting the remaining. The major fatty acids in JOME^B were oleic, linoleic, Palmitic and stearic fatty acid. Oleic acid showed the highest percentage of composition of 37.33% followed by linoleic acid with 35.58%. Palmitic and stearic contributed 16.31% and 9.89%, respectively. Other fatty acid composition included Palmitoleic (0.89%). The content of unsaturated fatty acids was 73.8%, with saturated fatty acids (26.2%) constituting the remaining. These results are in accordance with previous reports on the FA profile of JOME and SOME [27, 28, 29, 30] as per Table 10. In general, JOME contained lesser unsaturated fatty acids (73.8%) compared to SOME (87.58%). As a comparison, two samples of JOME from different producers were tested and proven to be of close comparison.

Table 10: Fatty Acid Profile in Comparison with Previous Reports

Fatty Acid Profile	Jatropha ^A	Jatropha ^B	[3]	[21]	Soybean	[17]	[12]
Myristic (C14/0)	0.06	-	0.1	-	0.04	-	-
Palmitic (C16/0)	16.42	16.31	14.96	13.77	8.43	2.3-11	7-11
Palmitoleic (C16/1)	1.20	0.89	-	-	0.06	-	-
Margaric (C17/0)	0.12	-	-	-	0.06	-	-
Stearic (C18/0)	9.30	9.89	3.85	6.77	3.31	2.4-6	3-6
Oleic (C18/1)	38.46	37.33	32.49	41.68	31.70	22-30.8	22-34
Linoleic (C18/2)	34.09	35.58	47.43	35.55	54.94	49-53	50-60
Linolenic (C18/3)	-	-	-	-	0.67	-	-
Arachidic (C20/0)	0.26	-	-	-	0.24	-	-
Eicosenoic (C20/1)	0.10	-	-	-	-	-	-
Behenic (C22/0)	-	-	-	-	0.26	-	-
Lignoceric (C24/0)	-	-	-	-	0.08	-	-
Gondoic	-	-	-	-	0.21	-	-

Other physico-chemical properties were tested in conformance to their specific testing methods as per Table 11. Transesterification would not be occurring effectively with FFA content exceeding 3% [24]. Jatropha and Soybean methyl ester recorded acid value of 0.11 and 0.05 mg KOH/g-oil respectively in compliance to ASTM 6751 (D-664) and EN 14104. Maximum allowable limit for acid value is 0.5 mg KOH/g-oil. On the other hand, both Jatropha and Soybean methyl ester recorded no sulphur in the oil, complying to the maximum allowable limit of 10 mg/kg (ppm) under EN 14214 and MS 123:2008. Water content for Jatropha and Soybean methyl ester were determined to be 148.1 ppm and 139.4 ppm respectively, in compliance to the ASTM D2709, EN ISO 12937 and MS 123:2008 with maximum allowable limit of 500 mg/kg (ppm). Oxidation stability at 110°C for Jatropha and Soybean methyl esters were measured to be 7.63/8.84 hours and 4.45 hours respectively as per EN 14112 testing method. The minimum specification for oxidation stability is 3 hours for ASTM 6751 and 6 hours for MS 123:2008 and EN 14214. Neat Jatropha biodiesel complied with all the specifications but Soybean methyl ester did not comply with MS 123:2008 and EN 14214 as expected.

Table 11: Physico-chemical Properties of Biodiesel

Property	Unit	ASTM 6751			EN 14214			MS 123:2008		JOME	SOME
		Test Method	Min.	Max.	Test Method	Min.	Max.	Min.	Max.		
Cetane Number	-	D-613	47	-	EN ISO 5165	51	-	51	-	74	74.8
Sulphur Content	mg/kg	D-5453	-	-	-	-	10	-	10	0	0
Water Content	mg/kg	D-2709	-	500	EN ISO 12937	-	-	-	500	148.1	139.4
Oxidation Stability at 110°C	hrs	N.A.	3	-	EN 14112	6	-	6	-	7.63-8.84	4.55
Density at 15°C	kg/m ³	D-4052	-	-	EN ISO 3675	860	900	860	900	882.46	887.94
Iodine Value	g iodine/100 g	-	-	-	EN 14111	110	-	120	-	93	113
Acid Value	mg KOH/g	D-664	-	0.5	EN 14104	-	0.5	-	0.5	0.11	0.05
Linolenic Methyl Ester	% (m/m)	-	-	-	EN 14103	-	12	-	12	0	1.31
Polyunsaturated Methyl Ester (?4 double bonds)	% (m/m)	-	-	-	EN 14103	-	1	-	1	0	0
Cold Filter Plugging Point	°C	D-6371	-	-	EN 116	5	-20	-	15	-0.1	-6
Cloud Point	°C	D-2500	-	-	EN ISO 3015	-	-	-	18	4	1
Pour Point	°C	D-97	-	-	EN ISO 3016	-	-	-	15	3	-3
Calorific Value	MJ/kg	-	-	-	-	-	-	-	-	39.71	39.58
Flash Point	°C	D-92	130	-	EN ISO 2592	120	-	120	-	122	140

Densities for Jatropha and Soybean methyl ester were tested to be 882.46 kg/m³ and 887.94 kg/m³ as per ASTM D-4052 and EN ISO 3675. The requirement range for EN 14214 and MS 123:2008 for density is between 860 to 900 kg/m³. As per testing method of EN 14111, iodine value was determined for Jatropha and Soybean methyl ester at 93 and 113 respectively. The minimum allowable boundary is 110 and 120 respectively for EN14214 and MS 123:2008. Linolenic methyl ester as per testing method of EN 14103 was identified to be 0 and 1.31 for Jatropha and Soybean methyl ester respectively, complying with the maximum allowable limit of 12 for EN 14214 and MS 123:2008. Polyunsaturated methyl ester (≥ 4 double bonds) for Jatropha and Soybean methyl ester recorded no presence of such fatty acid profile as per testing method of EN 14103, complying with the maximum allowable limit of 1 for EN 14214 and MS 123:2008. Calorific values for Jatropha and Soybean methyl ester were 39.71 MJ/kg and 39.58 MJ/kg respectively. Flash point of Jatropha and Soybean methyl ester were tested to be at 122 °C and 140 °C respectively, in compliance with testing methods of D-92 and EN ISO 2592. The maximum allowable limit for flash point is 120 °C for MS 123:2008 and EN 14214 and 130°C for ASTM 6751.

4.3.1 Oxidation Stability

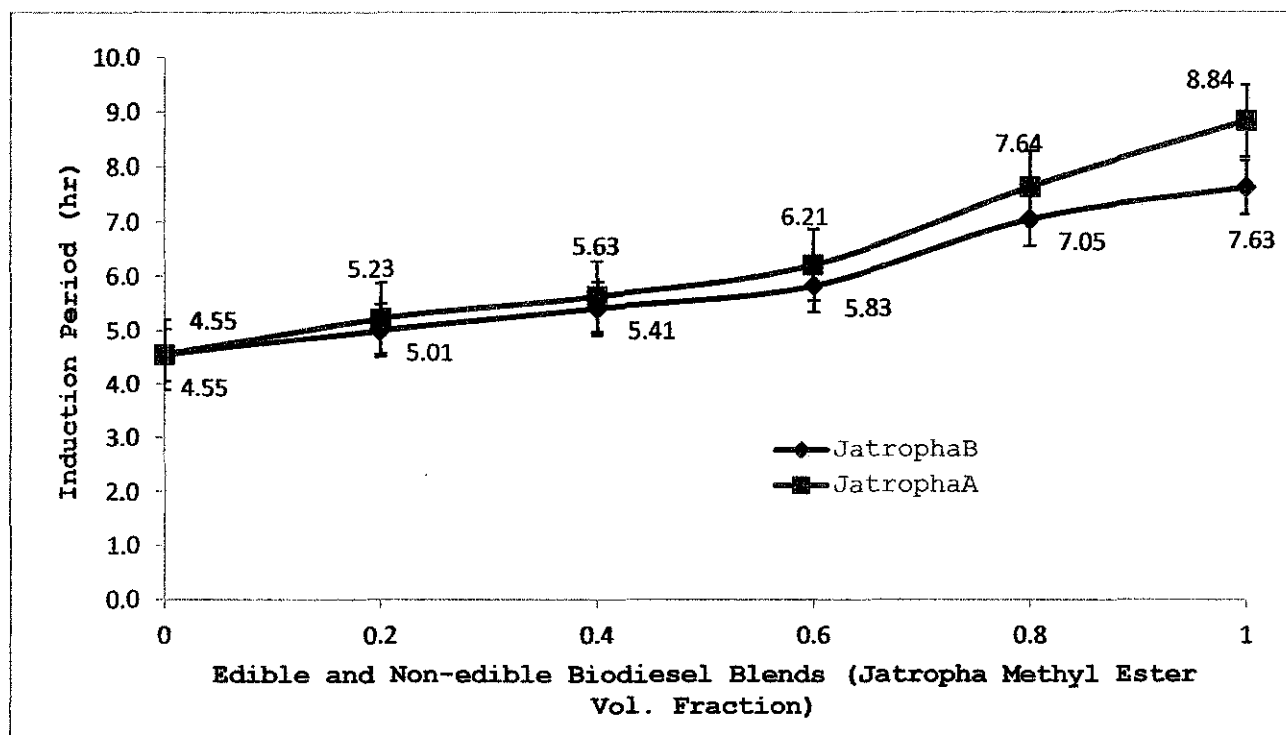


Figure 3: Oxidation Stability of Jatropha and Soybean Methyl Ester Blends

Oxidation stability is a matter of interest as it cannot be kept beyond a period. For best usage, standardization and quality assurance, neat biodiesel has to be stored well to maintain its properties and stability. The Rancimat method (EN 14112) is listed as the oxidative stability specification in ASTM D6751 and EN 14214. A minimum induction period (IP, 100°C) of 3 h is required for ASTM D6751; whereas a more severe limit of 6 h or greater is denoted in EN 14214 [2]. Although, recent researchers have found it possible to meet desired specifications by using antioxidants, it is worth mentioning that these chemicals are costly. So, the current study was undertaken to blend SOME with JOME. Before laying out the results, it is best to understand the concept behind the oxidation stability determination using the Rancimat method. This test is based on the increase of the conductivity of deionized water contained in a reservoir, which holds the volatile acids released during the propagative oxidation of fatty materials [24]. Based on the graphs obtained through Rancimat method in the end of each test, it indicates the end of the induction period when the conductivity begins to increase rapidly. This sudden increase is caused by the dissociation of volatile carboxylic acids produced during the oxidation process and retained in the water. When the conductivity of this measuring solution is recorded constantly, an oxidation curve is illustrated whose point of reflection is known as the induction; this provides the good characteristic value for the oxidation stability [23]. The time that elapses until the secondary oxidation products are detected, and known as the induction period.

It was observed from Figure 3, that as the proportion of Jatropha increases, oxidation stability also increases. For neat biodiesel, Soybean and Jatropha recorded an IP of 4.55 h and 7.63/8.84 h, respectively. It should be noted that Soybean yielded an IP of 5.00 h [20] and 3.80 h [23] in previous studies. So, the IP obtained in the present study is within the range. As for Jatropha, the IP obtained in the current test is close to the results obtained in [34] with an IP of 8 h. The blends were tested at proportions of (SOME:JOME::20:80), (SOME:JOME::40:60), (SOME:JOME::60:40) and (SOME:JOME::80:20), each yielding an IP of 7.05/7.64 h, 5.83/6.21 h, 5.41/5.63 h and 5.01/5.23 h, respectively. Meeting the more stringent specification, ASTM D6751, only blends of 80% of Jatropha and 20% of Soybean conforms. Nevertheless, the objective of the study, which is to reduce the dependency on edible oil, is met.

The cause for good stability is associated to the resistance to auto-oxidation, in the existence of high fraction of saturated fatty acids. Unsaturated and polyunsaturated fatty acids are significantly more reactive to oxidation than saturated compounds. The reason for this is that the unsaturated fatty acid chains contain the most reactive sites which are particularly vulnerable to the free radical attack [16]. The rate of auto-oxidation of fatty acid methyl esters (FAME) is influenced by the presence of double bonds that are separated by allylic methylene positions (AMP) with bis-allylic methylene positions (BAMP) being even more prone to oxidation. The reason polyunsaturated fatty acids are particularly vulnerable to auto-oxidation is due to the presence of BAMP [20]. In this report, JOME displays (Refer Table 9) a lower content (34.09/35.58%) of polyunsaturated compounds as compared to SOME (55.60%). So, it is evident that JOME would exhibit a better oxidative stability as compared to SOME, and blends with higher proportion of JOME would improve the fuel properties.

However, FA profile alone cannot explain the high oxidation stability of JOME as compared to SOME. Eventually, natural anti-oxidants (e.g. Vitamin E) contained in vegetable oil can also restrain the oxidative reaction leading to degradation of the product itself. Though these anti-oxidants are naturally occurring, it's worth noting that the amount of natural anti-oxidants can be strongly affected by the production process of the biodiesel and by the refining process of the parent oil [16]. Hence, with the use of refined Soybean oil in the present study, the induction period is significantly lower than other reports [20]. Besides, water content and acid values may also influence significantly to the disparity in IP obtained through this report as compared to others, though small [34].

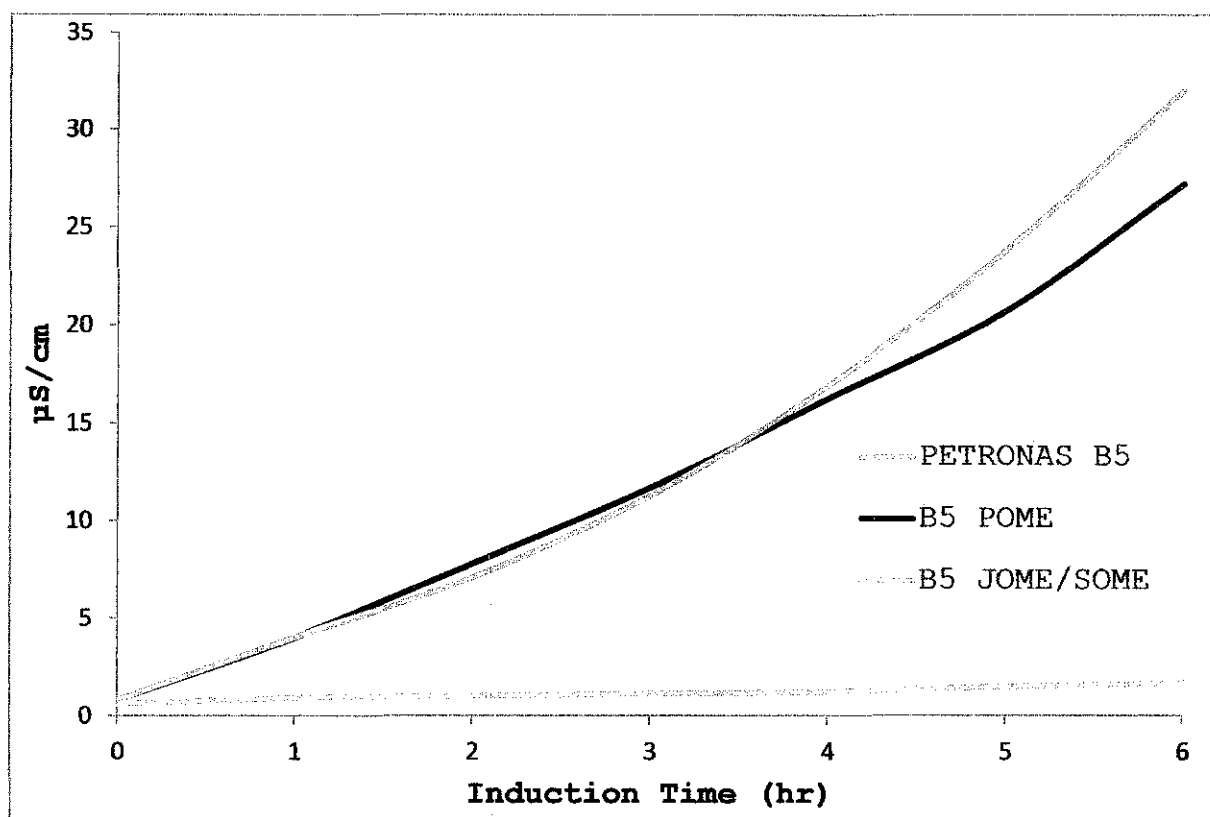


Figure 4: Relative Oxidation Stability at 6 hours

The conduct of experiment was further enhanced to meet the industrial application by blending with fossil fuel to produce B5 blends. The noble design of 80 vol% Jatropha and 20 vol% Soybean methyl ester was then blended at 5 vol% with 95 vol% PETRONAS Dynamic Diesel and denoted as B5 JOME/SOME as per Figure 4. Palm methyl ester was also blended at 5 vol% with 95 vol% of PETRONAS Dynamic Diesel and denoted as B5 POME. The reason of producing B5 POME was to create an untreated B5 blend as PETRONAS is currently using 5 vol% Palm methyl ester biodiesel in their fossil fuel, named as PETRONAS B5 Dynamic Diesel. Commercial product of PETRONAS B5 Dynamic Diesel contains additives with remains as trade secret as a competitive advantage among the competitors. Thus, blending B5 POME creates an equivalent comparison as untreated PETRONAS B5 Dynamic Diesel without antioxidants. As per Figure 4, it clearly showed that PETRONAS B5 Dynamic Diesel has the most stable progression up to 6 hours. The more steady the line of progression, the better the oxidation stability of fossil fuel/biodiesel. As expected, PETRONAS B5 Dynamic Diesel portrays the best results in oxidation stability due to its

antioxidants. B5 POME depicts a better character in oxidation stability as compared to B5 JOME/SOME. Palm methyl ester has an oxidation stability of 10 hours, meanwhile the blend of JOME/SOME has an oxidation stability of 7.05/7.64 hours. This clearly shows that the blend of B5 POME has a better advantage as compared to the noble design. However, as depicted in Figure 4, the line of progression of B5 POME and B5 JOME/SOME are comparable and do not show much differences between the two lines.

4.3.2 Low Temperature Properties

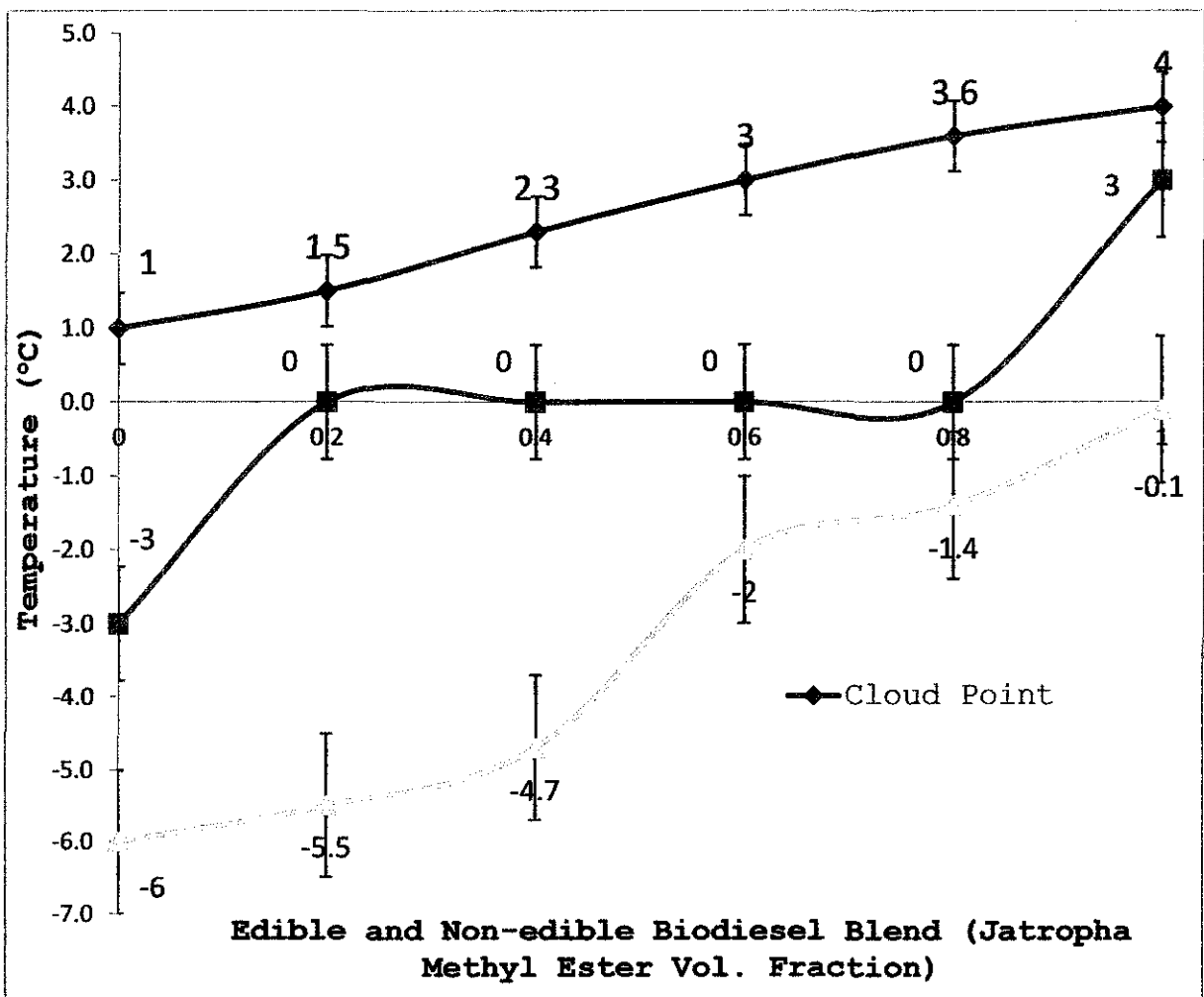


Figure 5: Low Temperature Properties for Jatropha and Soybean Methyl Ester Blends

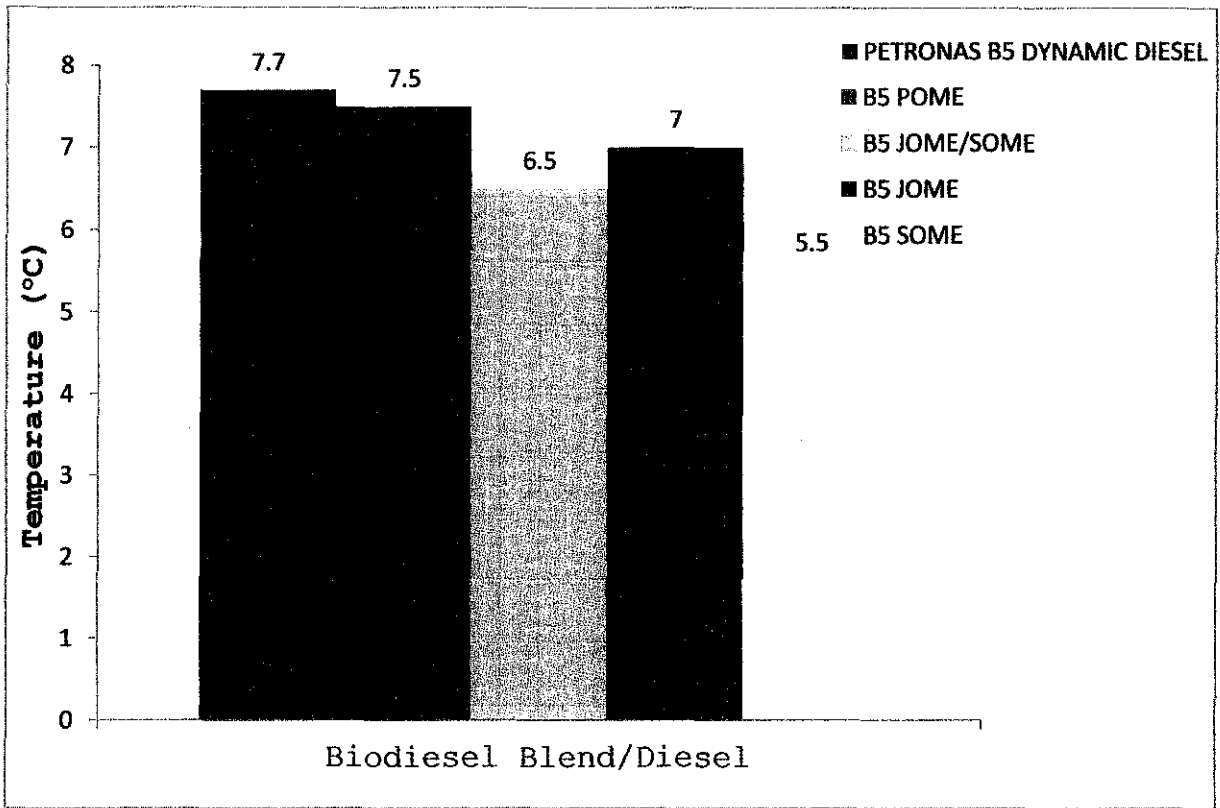


Figure 6: Cold Filter Plugging Point of B5 Admixtures

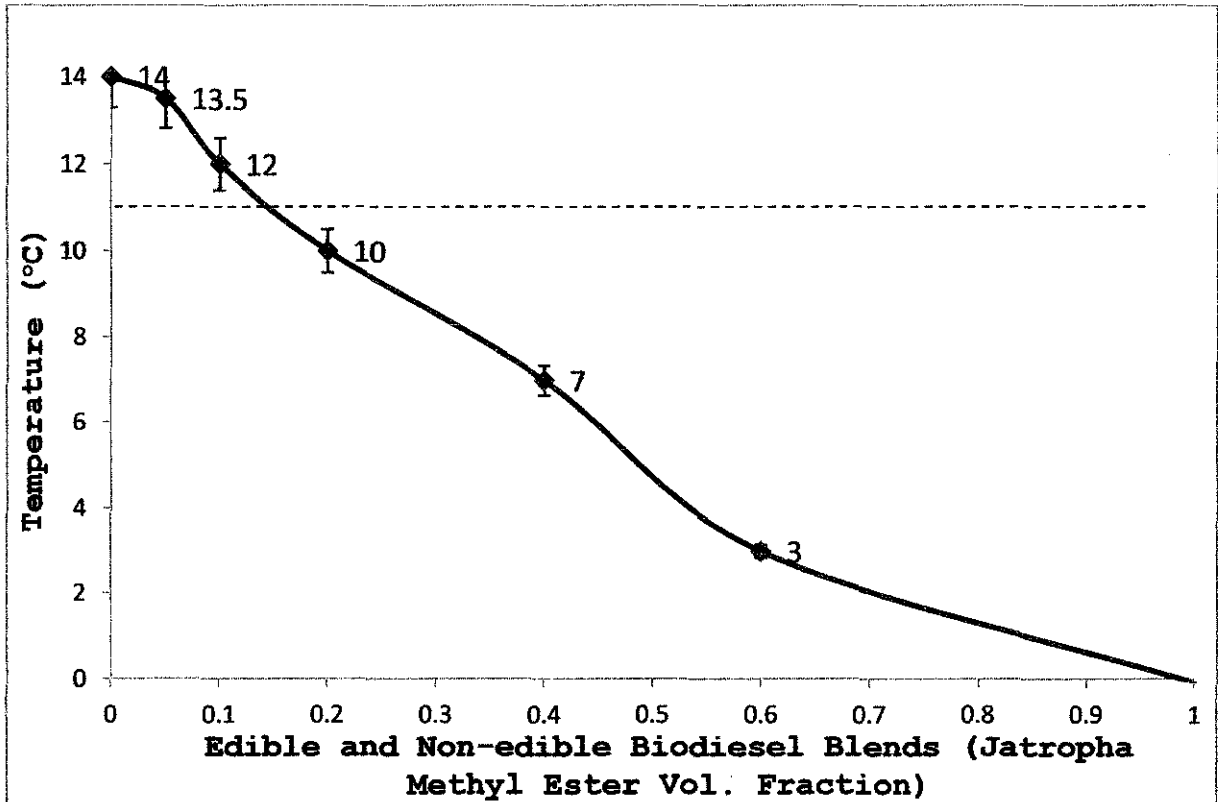


Figure 7: Cold Filter Plugging Point of Jatropha and Palm Methyl Ester Blends

At low temperatures, biodiesel is deemed less appropriate for usage as compared to petro-diesel. Static tests are carried out to identify first wax and non-flow temperatures for the fuel. The low temperature properties were evaluated in terms of cloud point (CP), pour point (PP) and cold filter plugging point [29]. As seen in Figure 5, SOME provided CP, PP and CFPP values of 1°C, -3°C and -6°C, respectively. The values obtained for JOME were 4°C (CP), 3°C (PP) and 0°C (CFPP), respectively. It is notable that the results obtained for SOME in previous reports [19, 24] are almost comparable with the current report. For comparison, a previous study reported the low temperature properties for Jatropha, the CP as 4°C [28] and PP as 2°C [29] closely conforming to the current study. The blends of biodiesel were examined to study the effect of both edible and non-edible oil methyl esters on each other. As per results shown in Figure 5, the blending of 20% Soybean (edible oil) has significantly reduced the cloud point of JOME to 3.6°C, pour point to 0.0°C and cold filter plugging point to -1.4 °C. The increasing fraction of edible oil methyl ester (SOME) in the blends has gradually reduced the overall low temperature properties. It is proven that Soybean oil methyl esters exhibit better low temperature properties as compared to Jatropha. With the blending of Soybean biodiesel in Jatropha biodiesel, we could exhibit improved cloud and pour point properties.

To further add on commercial value, the signature blend of JOME:SOME at 80:20 ratio was blended with PETRONAS Dynamic diesel to produce B5 fuel. A comparison chart as seen in Figure 6 illustrates a better CFPP achieved through the signature blend compared to PETRONAS B5 Dynamic Diesel and a control factor of B5 Palm Methyl Ester (5 vol% Palm, 95 vol% PETRONAS Dynamic diesel). B5 JOME/SOME (5 vol% JOME/SOME admixture, 95 vol% PETRONAS Dynamic Diesel) recorded CFPP of 6.5 °C and PETRONAS Dynamic Diesel recorded CFPP of 7.7 °C. B5 POME (5 vol% Palm Methyl Ester, 95 vol% PETRONAS Dynamic Diesel) recorded CFPP of 7.5 °C and comparable as to CFPP of PETRONAS B5 Dynamic Diesel. Control factors of B5 JOME (5 vol% Jatropha Methyl Ester, 95 vol% PETRONAS Dynamic Diesel) and B5 SOME (5 vol% Soybean Methyl Ester, 95 vol% PETRONAS Dynamic Diesel) were plotted to show the comparison between these two plots at 7 °C and 5.5 °C respectively with B5 JOME/SOME.

On the other hand, the blending of 20% *Jatropha* (non-edible oil) has significantly improved the low temperature properties of POME by 9.5°C (CFPP) as shown in Figure 7. Industrial expectation on CFPP is set at 11 °C based on Platinum Energy. Pure Palm methyl ester recorded CFPP of 14 °C. Based on Malaysian Standard for Diesel Fuel (MS123:2008), the recorded maximum CFPP is 15 °C as per Table 11. For CP and PP, the maximum allowable limits according to MS 123:2008 are 18 °C and 15 °C respectively. Thus, results achieved in this report conform to the standard.

The enhanced low temperature properties of SOME versus JOME may be attributed to its lower content of saturated fatty acids, 12.42% and 26.20%, respectively. Based on previous reports, it has been determined that small levels of saturated FAME have an inconsistent influence on low temperature properties of biodiesel as a result of their higher melting points [27, 28, 29]. Higher content of polyunsaturated fatty acids also contribute considerably to the increasing number of double bond content. It should be noted that melting point decreases significantly in the presence of double bond, as indicated by the melting point of methyl esters of stearic (C18:0; 37.7°C), oleic (C18:1; -20.2°C), linoleic (C18:2; -43.1°C), and linolenic (C18:3; -57°C) acids [12]. Further proven by, the fact that SOME contains higher amount of polyunsaturated FAME (55.60%) as compared to JOME (35.58%).

CONCLUSION AND RECOMMENDATION

Soybean biodiesel, when blended with Jatropha methyl ester produces a composition having efficient and improved low temperature property. Jatropha biodiesel when added to Palm biodiesel has significantly improved the low temperature property while maintaining the oxidation stability within the industry range. Food versus fuel, the current heated argument could be overcome with this optimum mixture, thus, reducing dependability over edible oil. Soybean biodiesel exhibits good low temperature properties, whereas, Jatropha biodiesel has poor low temperature properties. Whereas, when compared to Palm biodiesel, Jatropha has a better low temperature property. With the blend of these esters, an additive effect could be achieved.

The contents of fatty acids in both biodiesel, in view of saturated and unsaturated have extensively contributed to the difference in two vital and critical properties of FAME. A signature design of 80% Jatropha (non-edible oil) and 20% Soybean biodiesel (edible oil), 80% Palm (edible oil) and 20% Jatropha (non-edible oil) conforming to standards set by ASTM D6751, EN 14214 and MS123:1993 can be optimum mix with enhanced oxidation stability and low temperature property in USA, Europe and Asia regions.

Further recommendation for this study would be to run full properties analysis on the noble design of Jatropha/Soybean methyl ester and Jatropha/Palm methyl ester enlisted in ASTM 6751, EN 14214 and MS 123:2008.

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APPENDIX I
GANTT CHART

No.	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project Work Commences															
2	Submission of Progress Report								■							
3	Project Work Commences															
4	Pre-SEDEX											■				
5	Submission of Draft Report												■			
6	Submission of Dissertation													■		
7	Submission of Technical Paper													■		
8	Oral Presentation														■	
9	Submission of Project Dissertation															■

APPENDIX II
OXIDATION STABILITY

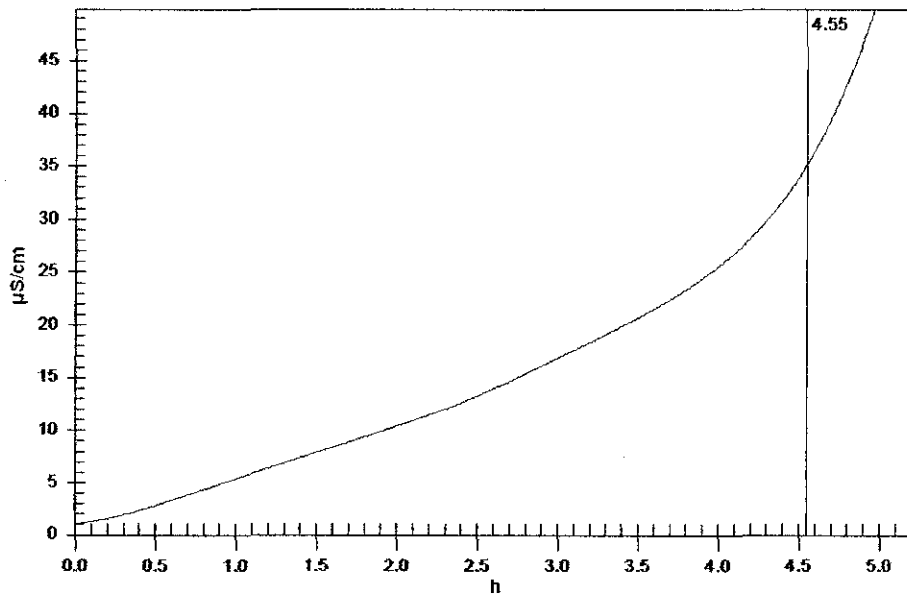


Figure I: Oxidation Stability for Pure Soybean Methyl Ester

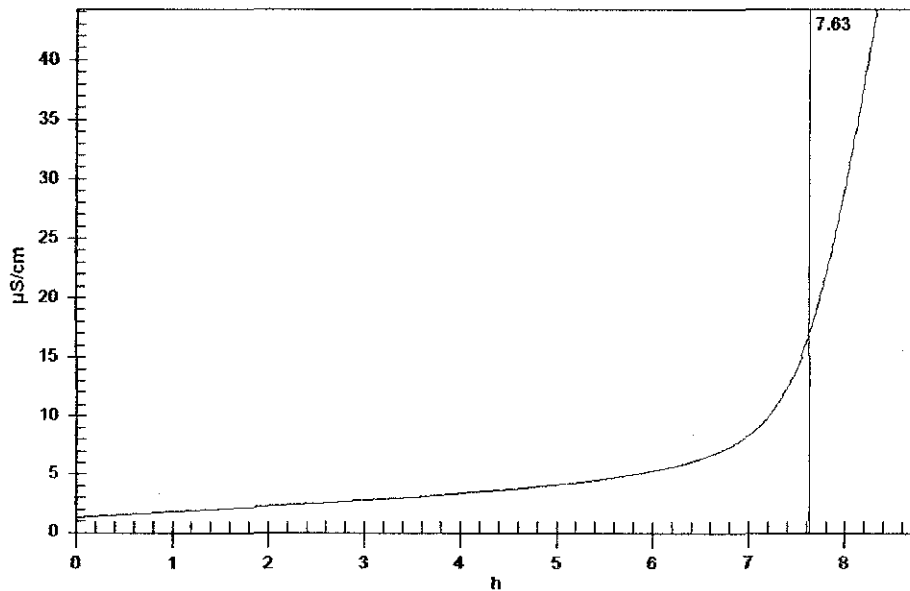


Figure II(a): Oxidation Stability for Jatropha Methyl Ester (Bionas)

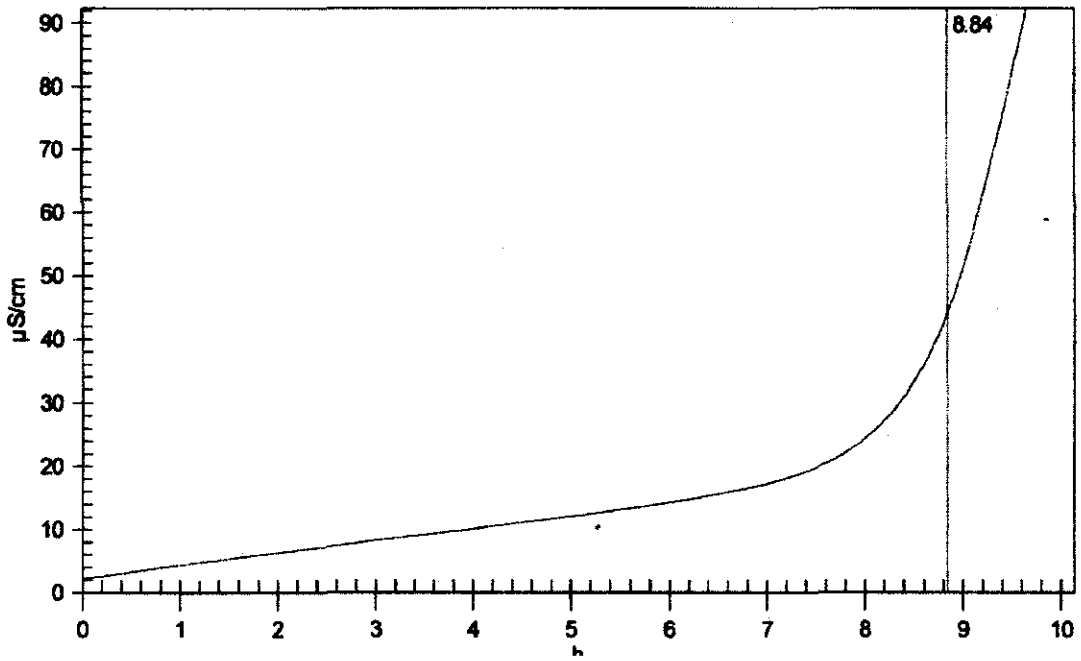


Figure II(b): Oxidation Stability for Jatropa Methyl Ester (Eco Energy Solutions)

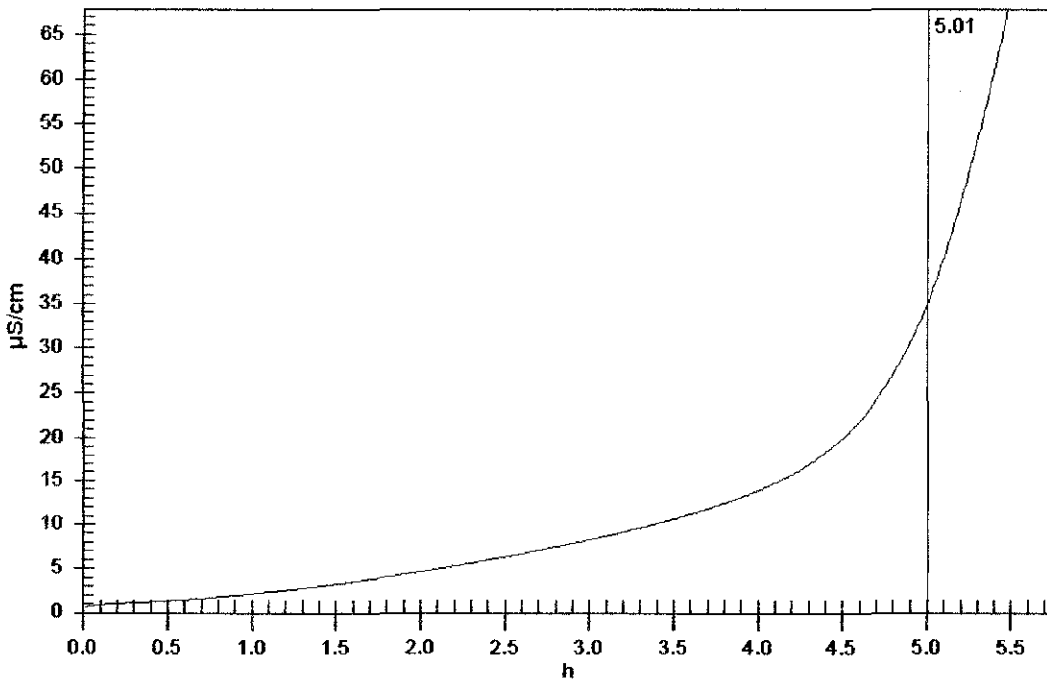


Figure III: Oxidation Stability for Biodiesel Blend (80% Soybean)

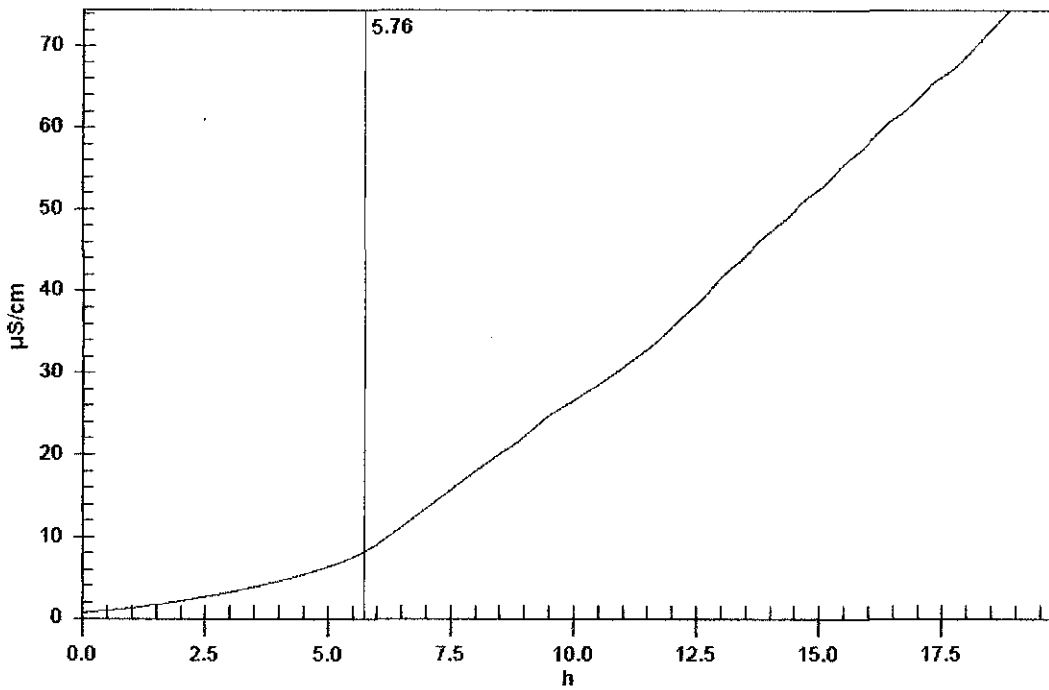


Figure IV: Oxidation Stability for Biodiesel Blend (60% Soybean)

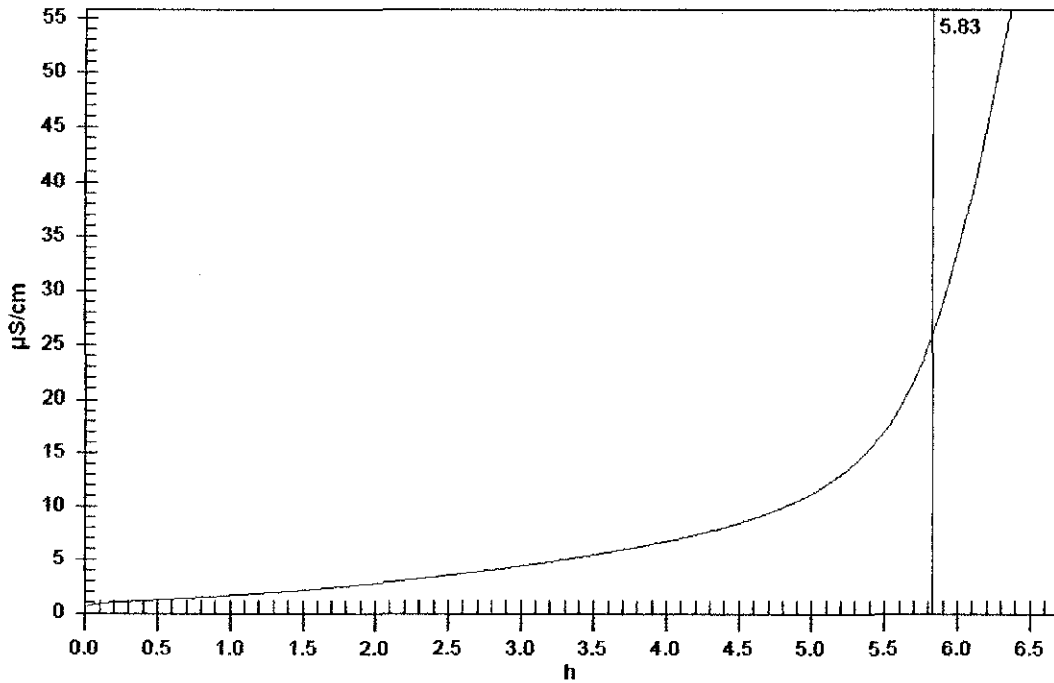


Figure V: Oxidation Stability for Biodiesel Blend (40% Soybean)

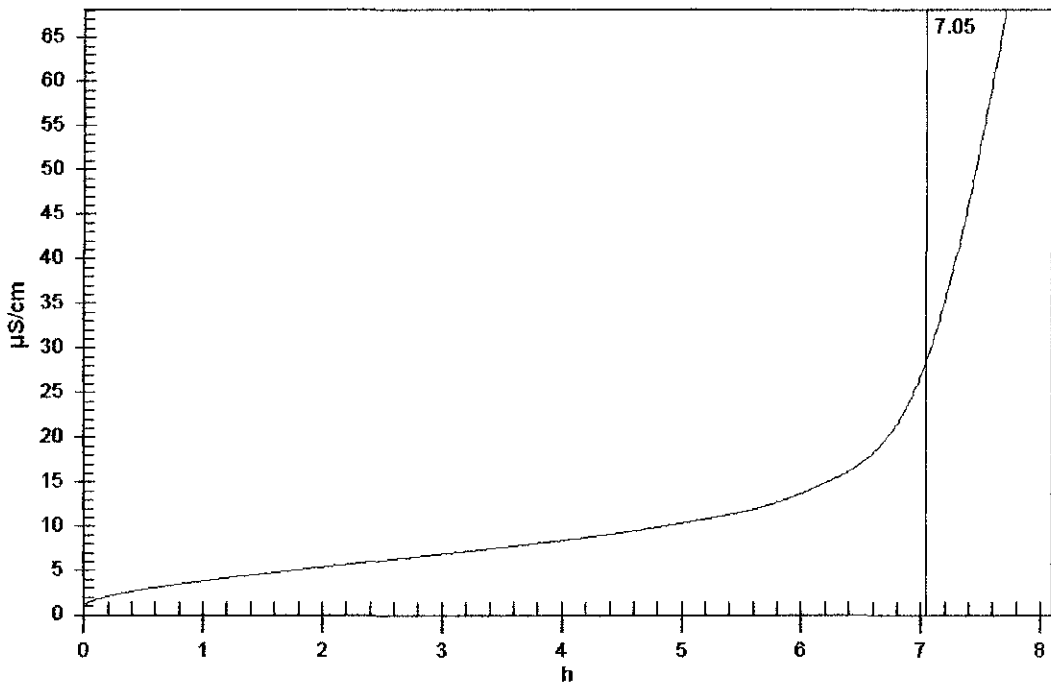


Figure VI: Oxidation Stability for Biodiesel Blend (20% Soybean)

APPENDIX III

GAS CHROMATOGRAPHY ANALYSIS

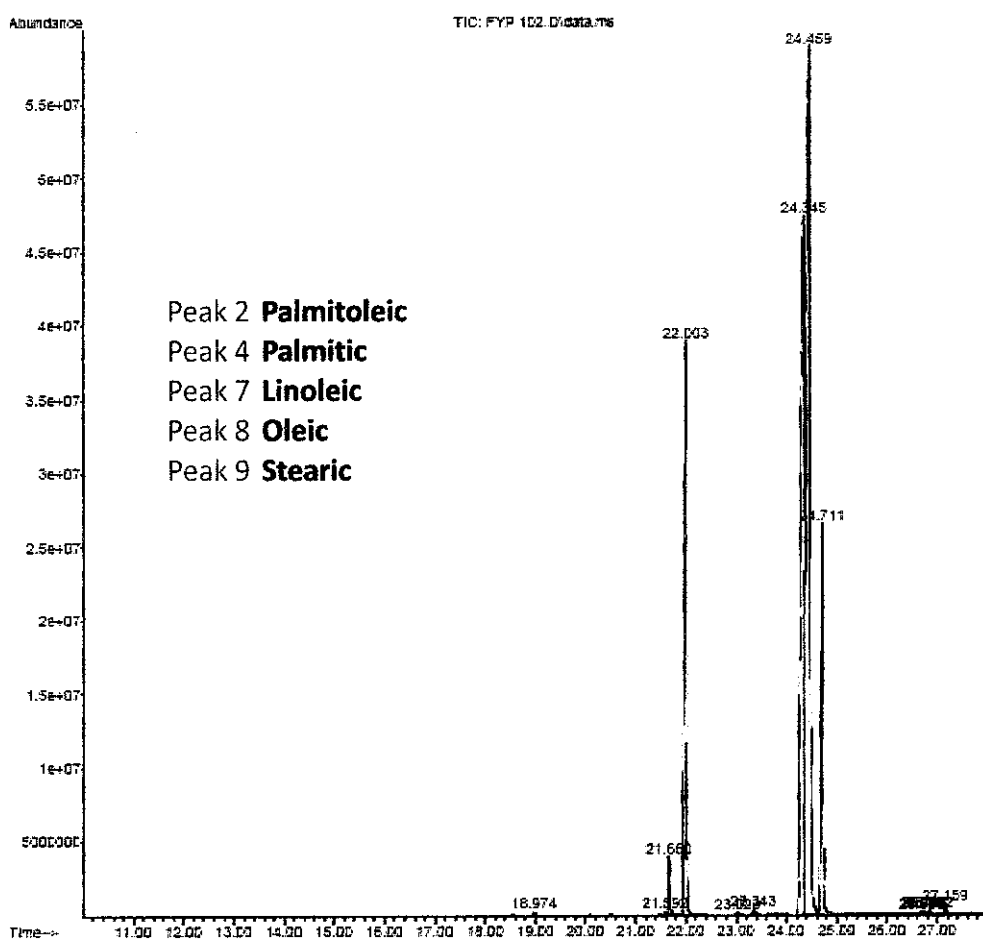


Figure VII: Gas Chromatography for Jatropha Methyl Ester

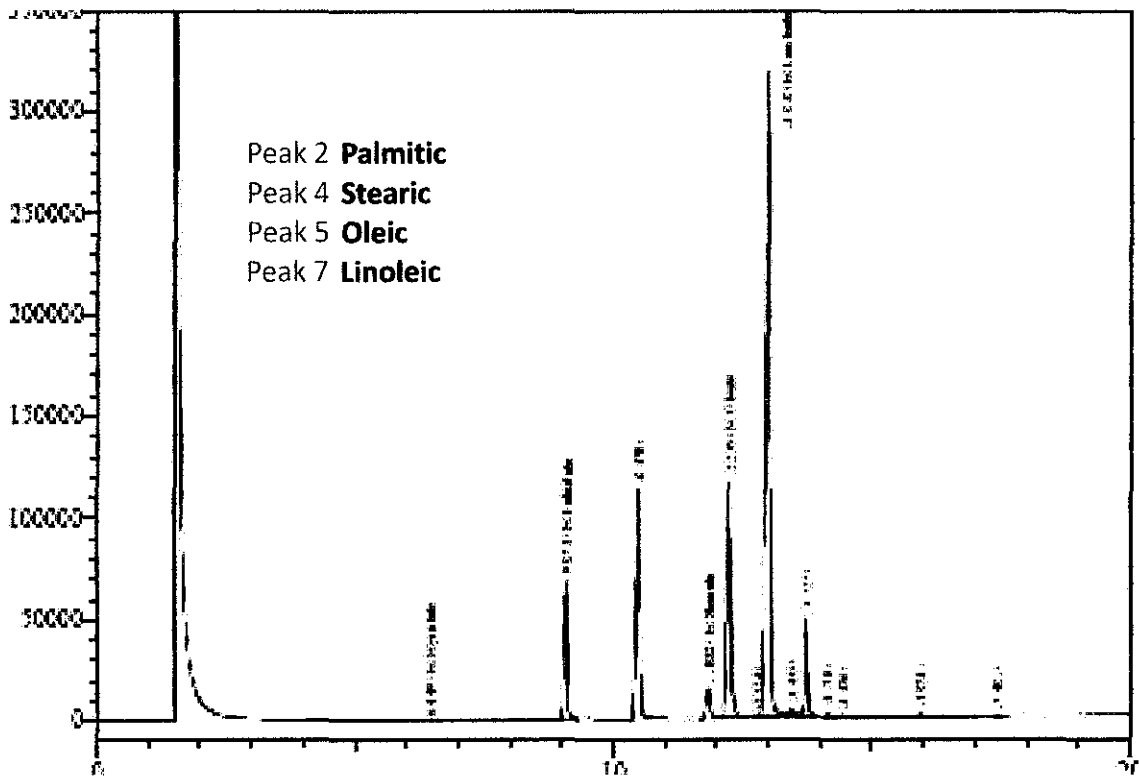


Figure VIII: Gas Chromatography for Soybean Methyl Ester