IMPROVEMENT OF COLD FLOW PROPERTIES OF BIODIESEL

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Thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

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ABSTRACT

Cold flow properties of biodiesel mean the mechanism of biodiesel properties in winter or cold condition. In this type of condition, biodiesel won't work properly because biodiesel cannot flow easily and will result in engine operational problem and will be more stress-resistant. This research highlights how to improve the cold flow properties of biodiesel which is a major hurdle in cold weather or condition where biodiesel is not working in full efficiency. Thus with my research, it will be a major breakthrough for the usage of biodiesel in any weather no matter cold or warm. Pour point (PP) is defined as the lowest temperature where the biodiesel flows or can be pumped. Pour point can also be described as the lowest temperature at which a fuel performs satisfactorily and beyond this temperature, the fuel stops flowing and starts to freeze. The cloud point (CP) of the fuel is defined as the temperature where crystals become visible forming a hazy or cloudy suspension. Pour point and cloud point are the most important parameters which are involved in determining whether cold flow properties are improved or not. There are many methods used for this purpose such as winterization, fractanation and also biodiesel and petro diesel blending but the method of two types of different biodiesel just been rarely tested. Thus, I came up with this method and tried it using two types of biodiesel which are jatropha oil and palm oil. The FFA (free fatty acid) produced from both of this oil is blended in different proportion and the biodiesel is produced. After the biodiesel is produced, the samples are sent to the GCMS analysis to determine whether biodiesel is produced or not. Then, the cold flow properties are determined for each sample. The pour point, cloud point, density, viscosity and kinematic viscosity were determined. From the results, the main objective of this research is achieved where the blending of two types of biodiesel can improve the cold flow properties of biodiesel. The blended biodiesel have the lower cloud and pour point compared to the unblended biodiesel.

PENAMBAHBAIKAN SIFAT ALIRAN DINGIN BIODIESEL

ABSTRAK

Sifat aliran dingin biodiesel bermakna mekanisme biodiesel hartanah di musim sejuk atau keadaan sejuk. Dalam jenis ini keadaan, biodiesel tidak akan berfungsi dengan betul kerana biodiesel tidak boleh mengalir dengan mudah dan akan menyebabkan masalah enjin operasi dan akan menjadi lebih tahan tekanan. Kajian ini menekankan bagaimana untuk meningkatkan sifat-sifat aliran sejuk biodiesel yang merupakan halangan utama dalam cuaca sejuk atau keadaan di mana biodiesel tidak bekerja dalam kecekapan penuh. Oleh itu, dengan penyelidikan saya, ia akan menjadi satu kejayaan besar bagi penggunaan biodiesel dalam cuaca mana-mana tidak kira sejuk atau panas. Tuangkan tumpah ditakrifkan sebagai suhu terendah di mana aliran biodiesel atau boleh dipam. Tuangkan titik juga boleh digambarkan sebagai suhu terendah di mana bahan api melakukan memuaskan dan di luar suhu ini, bahan api berhenti mengalir dan mula membeku. Titik awan bahan api ditakrifkan sebagai suhu di mana kristal menjadi kelihatan membentuk penggantungan kabur atau mendung. Tuangkan titik dan titik awan adalah parameter yang paling penting yang terlibat dalam menentukan sama ada sifat-sifat aliran sejuk baik atau tidak. Terdapat banyak kaedah yang digunakan untuk tujuan ini seperti ‘winterization’, ‘fractanation’ dan juga pengadunan biodiesel dan petro diesel tetapi kaedah dua jenis biodiesel yang berbeza hanya telah jarang diuji. Oleh itu, saya terfikir dengan kaedah ini dan cuba menggunakan dua jenis biodiesel iaitu jatropha dan kelapa sawit. FFA (asid lemak bebas) yang dihasilkan dari kedua-dua minyak ini dicampur dalam nisbah yang berbeza dan biodiesel dihasilkan. Selepas biodiesel dihasilkan, sampel akan dihantar untuk analisis GCMS untuk menentukan sama ada biodiesel dihasilkan atau tidak. Kemudian, sifat aliran sejuk ditentukan bagi setiap sampel. Titik tumpah, titik awan, ketumpatan, kelikatan dan kelikatan kinematik telah ditentukan. Dari keputusan, objektif utama kajian ini dicapai di mana pengadunan dua jenis biodiesel boleh meningkatkan sifat-sifat aliran sejuk biodiesel. Biodiesel dicampur mempunyai titik tumpah dan awan yang lebih rendah berbanding biodiesel tidak dicampur.

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LIST OF SYMBOLS

^{o}C	Temperature
l	Length
ρ	Density
s	Time (second)
M	Mega
Hz	Hertz
Ml	Milimeter
G	Gram
Wt	Weight Percent

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The production of biodiesel or also known as the mono-alkyl esters of fatty acid is mainly derived from the transesterification of agricultural lipids with a short-chain alcohol. Actually, biodiesel refers to an alternative fuel derived from vegetable oils or animal fats. Due to its environmental benefits, including the fact that it can be manufactured from renewable resources such as vegetable oils and animal fats, there has been considerable interest in developing biodiesel as an alternative fuel. Biodiesel is compatible with compression-ignition or diesel engines. It may be utilized in neat 100% form or in blends with conventional diesel fuel or petrodiesel. Biodiesel has been widely used as an alternative fuel in transportation trucks, farm and other off-road vehicles, automobiles, locomotives, aircraft, power generators, boilers and heaters.

At the present time, biodiesel is being preferred more than the petroleum fuel because of the high oil prices and to limit greenhouse gas emissions. Biodiesel is also safe, non-toxic and biodegradable in water, contains less sulfur and has a high flash point (>130c). Biodiesel is also less polluting than petroleum diesel because combustion of biodiesel produces less carbon monoxide, unburned hydrocarbons and sulfur dioxide. The lubricating effects of the biodiesel also may extend the lifetime of engines.

Biodiesel has its own advantages and disadvantages. For the advantages, as a renewable, clean and domestic fuel source which is produced using a variety of vegetable feedstock, production of this fuel helps multiple industries flourish is addition to being a cleaner burning fuel.

With the ability to run in any unmodified diesel engine, pure bio diesel can also help increase the life of your diesel engine because it leaves no deposits. The life of your diesel engine is increased by bio diesel due to the fact that it is more lubricating than traditional petroleum diesel products. Fuel consumption, ignition, engine power and torque remain unaffected by the use of bio diesel.

Moving to the disadvantages, the performance of biodiesel in cold weather which may compromise its year-round commercial viability in moderate temperature climates. This is because its poor cold flow properties in comparison with fossil-based diesel fuel. The main problem is the crystallization temperature of biodiesel fuel is generally higher than that of fossil-based diesel fuel, so the formation of crystals at relatively high temperatures can plug fuel lines and filters, hence causing problems in fuel pumping and engine performance during winter operation.

1.2 RESEARCH OBJECTIVES

The main objective of this research is to improve the cold-flow properties of biodiesel using the blending of biodiesel method.

1.3 SCOPE OF STUDY

In order to achieve the objective, there are several scope was have been identified

- The FFA will be produced from jatropha and palm oil by saponification.
- The FFA will be blended in different ratio and then biodiesel will be produced through esterification.
- The biodiesel will be tested its viscosity, density, pour point and cloud point.

1.4 PROBLEM STATEMENT

The cold flow properties of biodiesel are a major hurdle in order for the fuel can work efficiently in any weather or condition. An experiment should be conducted to see whether the blending of biodiesel method can improve the cold-flow properties of biodiesel.

CHAPTER 2

LITERATURE REVIEW

2.1 BIODIESEL

At the forefront of the array of alternative energy sources that are being researched and developed today, is biofuel. Having physical and chemical properties that are compatible with its fossil counterpart has placed biodiesel as one of the most suitable alternatives to complement today, and perhaps even replace fossil diesel tomorrow. Its ability to fuel conventional diesel engines with minimum or no modifications, and to form blends with fossil diesel make it the most practical, and feasible alternative energy source to invest in.

There are many ways how biodiesel serves to benefit the environment more than fossil diesel. One major aspect of life cycle assessments is the potential of global warming, expressed as carbon dioxide, CO_2 equivalents. CO_2 is produced during the whole production process of fuels, biological based and fossil based alike.

Due to the positive energy balance of biodiesel and the fact that biodiesel mainly consists of renewable material one could expect a large saving of greenhouse gases compared to fossil fuel. Now, while this remains true in the case of CO_2, certain parties argue that if other greenhouse gases like N_2O and CH_4 are considered, which have higher global warming potential, the advantages of biodiesel are slightly diminished. Even so, the relative savings of greenhouse gases for the use of biodiesel over fossil diesel is 2.7kg of saved CO_2 equivalents for every kg of substituted fossil diesel fuel. Pure biodiesel is also completely free of sulfur and, this inadvertently reduces sulfur dioxide exhaust from diesel engines to virtually zero.

2.2 CHARACTERISTIC OF BIODIESEL

Biodiesel is well known as an alternative fuel for diesel engines that is chemically produced by reacting the virgin or used vegetable oil or animal fats with an alcohol such as methanol in order to accelerate the reaction (Leung et al, 2006). However, it colors cab be varied between golden and dark brown because it depends on the production feedstock. It is practically immiscible with water, has high boiling point and low vapor pressure. Typical methyl ester biodiesel has a flash point of ~150°C (300°F), making it rather non-flammable. Biodiesel has density of ~0.88g/cm3, less than water. Biodiesel that unpolluted with starting material can be regarded as non-toxic. It also has similar viscosity with petro-diesel that produces from petroleum. Moreover, biodiesel is also clean burning diesel fuel replacement made from natural, renewable source, such as new and used vegetable oils or animal fats. It will run in any diesel engine with a little or no modification and can be mixed with regular diesel fuel in any ratio. Biodiesel is non-toxic and biodegradable.

2.3 PROPERTIES OF BIODIESEL

According to M.M. Gui(2008), in the past few years, fossil fuels dominantly petroleum, natural gas and coal have been doing a major role as the leading energy resources all over the world. Even so, all these energy resources are non-renewable and are projected to be depleted in the near future. The situation became worse with the increasing energy usage worldwide due to escalating population growth and economic development. Thus, there is an important need to find a new reliable energy resource that is renewable, environmental friendly and also economically suits as a substitution to the current fossil fuels.

Moreover, recently, biodiesel produced from vegetable oil has been shown to be a potential alternative to replace petroleum-derived diesel oil for diesel engine. He also added that biodiesel has supreme potential as a new and also renewable energy source in the coming future, as a replacement fuel for petroleum-derived diesel and can be used in existing diesel engine without modification. Nowadays, approximately more than 95% of the world biodiesel is manufactured from edible oil which is readily available on large scale from the agricultural industry. Technically, biodiesel is mono alkyl ester derived from oils (plant or animal) which have characteristics exactly to petroleum-derived diesel oil. Until now, about 84% of the world biodiesel production is dominated by rapeseed oil. The remaining part is from sunflower oil (13%), palm oil (1%) and soybean oil and others (2%) (M.M. Gui, 2008). As more than 95% of the biodiesel is done from edible oil, there are a lot of claims that many unwanted problems may rise upon.

By converting edible oils into biodiesel, food resources are basically being converted into automotive fuels. It is also believed that mega-scale production of biodiesel from the edible oils may lead to global imbalance to the food supply and demand market. Lately, environment specialists have started to debate on the bad impact of biodiesel production from edible oil on our mother earth especially deforestation and destruction of the ecosystem. The environmentalists claimed that the escalating of oil crop plantations for biodiesel production on a mega scale has lead to deforestation in many countries such as Malaysia, Indonesia and Brazil and even worse, more and more forest has been cleared for plantation purposes. In addition, the line between food and fuel economies is unsure as both of the fields are fighting for the same oil resources. In other words, biodiesel is competing limited land availability with food industry for plantation of oil crop.

Biodiesel fuel can be easily produced by transesterification process of virtually any triglyceride feedstock. This does includes oil-bearing crops, animal fats, and also not forgotten algal lipids. Nowadays, nevertheless, the controlling feedstocks are the soybean oil in the U.S., rapeseed oil in Europe, and palm oil in Southeast Asia (S. Kent Hoekman, 2012). Animal fats (mainly beef tallow) and used cooking oil (also known as yellow grease) represent important niche markets for biodiesel in many places.

Type of oil	Oil yield (kg oil/ha)	Oil yield (wt%)	Prices (USD/ton)
Non-edible oil			
Jatropha [5,6]	1590	Seed: 35–40, kernel: 50–60	N/A
Rubber seed [7]	80–120	40–50	N/A
Castor [5,9]	1188	53	N/A
Pongamia pinnata [8]	225–2250	30–40	N/A
Sea mango [9]	N/A	54	N/A
Edible oil			
Soybean [5,11]	375	20	684
Palm [5,12]	5000	20	478
Rapeseed [5,13]	1000	37–50	683

Figure 2.1 Oil Yield for Major Non-Edible and Edible Oil Sources
(Source: M.M. Gui, 2008)

The composition for different types of edible and non-edible oils is tabulated in Figure 2.1. It was observed from this table that the most oil composition in both non-edible and edible oils is generally same except for castor oil. The major fatty acids compositions in both the non-edible and edible oils are such as oleic, linoleic, stearic and palmitic acid. The fatty acids in the oils are further categorized into saturated and unsaturated fatty acids.

Saturated fatty acids include stearic, palmitic and dihydroxystearic acid, while the unsaturated include oleic, linoleic, ricinoleic, palmitoleic, linolenic and eicosenoic acid. Castor oil has the most specific composition with approximately 89.5% ricinoleic acid. Ricinoleic acid or known as castor oil acid, an unsaturated fatty acid which is soluble in many major organic solvents. Besides the content of fatty acids in the oil, edible oils such as soybean, rapeseed and palm oil also have valuable nutrients that should not be ignored. For instance, soybean oil has a high content of protein (35–40%), which contains all the essential amino acids that very important for human growth and can promote health at all stages of development (M.M. Gui, 2008).

Fatty acid composition (%)	Molecular formula	Non-edible oil					Edible oil		
		Jatropha [6]	Rubber seed [7]	Castor [14]	*Pongamia pinnata* [8]	Sea mango [9]	Soybean [15]	Palm [16]	Rapeseed [17]
Oleic	$C_{18}H_{34}O_2$	43.1	24.6	3.0	44.5–71.3	54.2	23.0	40.0	64.1
Linoleic	$C_{18}H_{32}O_2$	34.3	39.6	4.2	10.8–18.3	16.3	51.0	10.0	22.3
Palmitic	$C_{16}H_{32}O_2$	14.2	10.2	1.0	3.7–7.9	20.2	10.0	45.0	3.5
Stearic	$C_{18}H_{36}O_2$	6.9	8.7	1.0	2.4–8.9	6.9	4.0	5.0	0.9
Linolenic	$C_{18}H_{30}O_2$	-	16.3	0.3	-	-	7.0	-	-
Eicosenoic	$C_{20}H_{38}O_2$	-	-	0.3	9.5–12.4	-	-	-	-
Ricinoleic	$C_{18}H_{34}O_3$	-	-	89.5	-	-	-	-	-
Dihydroxystearic	$C_{18}H_{36}O_4$	-	-	0.7	-	-	-	-	-
Palmitoleic	$C_{16}H_{30}O_2$	-	-	-	-	-	-	-	0.1
Others	-	1.4	-	-	-	2.4	-	-	9.1

Figure 2.2 Oil composition of various non-edible and edible oil
(Source: M.M. Gui, 2008)

The properties of biodiesel differ accordingly to the fatty acid composition in the feedstock oil which is used to produce biodiesel. The properties of biodiesel have to be different or better than petroleum-derived diesel oil so that it can be used in diesel engine without any transformation. The properties such as flash point, viscosity, cetane number, cloud point, pour point, calorific value, acid value, ash content and cold flow properties. Figure 2.2 highlights some of the major physical and chemical properties of biodiesel produced from different sources oil sources as compared to petroleum-derived diesel oil. Among all of listed in Figure 2.3, cold flow properties (pour point and cloud point) are among the most important or specific properties that are usually looked upon. Cold flow properties basically concern the changes of biodiesel properties such as crystallization, gelling or viscosity increase due to temperature changes that might will affect the operability of the vehicles. These properties are reflected by the values of cloud point and pour point. These properties will be the important factor if the biodiesel produced can be used in cold climate countries. This is important because currently the largest demand of biodiesel is in the European countries. The cold flow properties of biodiesel are obstinate by the types of fatty acid in the feedstock oil. Higher percentage of unsaturated fatty acid in the feedstock oil will lead to biodiesel having better cold flow properties.

Parameters	Non-edible oil				Edible oil			Petroleum-derived diesel
	Jatropha [26]	Rubber seed [7]	Castor [27]	*Pongamia pinnata* [9]	Rapeseed [7]	Palm [28]	Soybean [7]	
Viscosity (Cst) at 40 °C	4.80	5.81	-	4.80	4.50	4.42	4.08	2.60
Specific gravity	-	0.874	0.960	-	0.882	0.860–0.90	0.885	0.850
Calorific value (MJ/kg)	39.23	36.50	39.50	-	37.00	-	39.76	42
Flash Point (°C)	135	130	260	150	170	182	69	68
Cloud point (°C)	-	4	−12	-	−4	15	−2	-
Pour point (°C)	2	-	−32	-	−12	15	−3	−20
Ash content (wt%)	0.012	-	0.020	0.005	-	0.020	-	0.010
Acid value (mg KOH/g)	0.400	0.118	-	0.620	-	0.080	-	-

Figure 2.3 Physical and chemical properties of biodiesel from different oil sources as compared to petroleum-derived diesel
(Source: M.M. Gui, 2008)

2.4 COLD FLOW PROPERTIES OF BIODIESEL

Data in Table 2.1 shows clearly that CP, PP, CFPP and LTFT of biodiesel (FAME) from a lot of lipid feedstocks are generally escalate than corresponding data for petrodiesel. Cold flow properties of biodiesel basically depend solely on fatty acid composition. Straightforward transesterification to biodiesel do not changes the fatty acid composition based in the parent feedstock. Fatty acid compositions happening in several biodiesel feedstocks are summarized in Table 2.2. In the bottom row of this table are shown MP data of the corresponding pure FAME compound.

Table 2.1 Cold flow properties of fatty acid methyl esters (FAME) and petrodiesel fuels

Fuel	CP (°C)	PP (°C)	CFPP (°C)	LTFT (°C)
Canola	0	-9	-7	
Coconut	5	-3		
Corn	-3	-4	-7	
Jatropha	4	3	2	
Olive	-2	-3	-6	
Palm	16	15	12	
Rapeseed, < 5% erucic	-3	-9	-9	
Soybean	0	-2	-2	0
Tallow	17	15	9	20
No. 1 petrodiesel	-31	-46	-42	-27
No. 2 LSD	-16	-27	-18	-14
No. 2 ULSD	-11	-20	-16	

(Source: Robert O. Dunn, 2011)

Table 2.2 Fatty acid composition of biodiesel feedstock lipids and melting points (MP) of corresponding FAME, C12 =Dodecanoic acid; C14 = myristic acid; C16 = palmitic acid; C18 = stearic acid; C18:1 = oleic acid; C18:2 = linoleic acid; C18:3 = linolenic acid; C20:1 = eicosenoic acid; C22:1 = erucic acid.

Oil or Fat	Fatty Acid (mass%)								
	C_{12}	C_{14}	C_{16}	C_{18}	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	$C_{20:1}$	$C_{22:1}$
Canola			3.6	1.5	61.6	21.7	9.6	1.4	0.2
Coconut[a]	45-53	17-21	7-10	2-4	5-10	1-3	≤ 0.2	≤ 9.2	
Corn		≤ 0.3	12-14	1-3	22-32	52-62	≤ 0.9		
Jatropha[b]		0.1	14-15	7	34-45	31-43	0.2		
Olive			10.5	2.6	76.9	7.5			
Palm[c]	0.2	1.1	44.1	4.4	39.0	10.6	0.3		
Rapeseed			4	1	14.8	14.2	9.1	10	45.1
Soybean			2-13	2-6	18-31	49-57	2-11		≤ 0.3
Tallow		3.4	29.5	26	34.9	1.5			
FAME MP (°C)	4.3	18.1	28.5	37.7	-20.2	-43.1	-55.5	-7.8	-3.0

(Source: Robert O. Dunn, 2011)

In contrast, a curvilinear relationship was expressed for CFPP escalating from -12 to +12ºC as ΣSats in biodiesel inclined from 5 to 45 mass% (Hilber et al., 2006). This study also stressed that CFPP of biodiesel extracted from animal fats generally more than 0ºC. Same types of results were obtained by correlating CFPP with respect to ΣSats for mixture of SME and FAME extracted from rapeseed and palm oils (Park et al., 2008). Results indicated a incliner degree of scatter and a sharp negative slope as unsaturated FAME content more than 85%.

2.5 METHODS TO IMPROVE COLD FLOW PROPERTIES OF BIODIESEL

2.5.1 Winterization

The main importance of winterization is to reduce the pour point of biodiesel by bringing down its saturated fatty acid methyl ester components. To make this happen, significant reductions in pour point, some winterization steps are needed to yield of higher than 25–26% and thereby make this technique viable. Besides that, another option is winterizing methyl esters in different solvents. Because of the lower yields of the winterized unblended methyl esters from familiar oils, researchers have initiated to dilute the esters with different type of solvents. Methanol, acetone, chloroform, and hexane have been tested as diluting solvents. Methanol gives the advantage that the winterization may be easily integrated into the industrial biodiesel production facilities. (Lee et al., 1996)

In their standard form, fats and vegetable oils melt at temperatures that makes them valuable for thermal energy storage. Incremental improvements of their heat release characteristics could make way for commercial applications as phase change materials or also known as PCM. PCM and their standard application are one of the most leading technologies for developing greenhouse gas emission concerns (Suppes et al., 2003). Some saturated fatty acid methyl ester components may be helpful for PCM applications.

The main importance of this work are as here: first, the study of the cold flow properties of five different biodiesels obtained from vegetable oils that are soybean, rapeseed, sunflower, palm and peanut oil; and next, the implementation of winterization techniques to get rid of long-chain saturated compounds (i.e., arachidic, behenicand lignoceric acid methyl esters) of peanut biodiesel and improve the cold flow properties.

Basically, winterization is a method for distinguish that fraction of oils with a solidification temperature below a specific cut-off. One technique involves freezing of the oils for a prescribed period at a specific temperature and then decanting of the remaining liquid. Besides that, more energy efficient method is to make tanks of oil to stand outside in cold-temperatures for long periods of time. In either case, the fraction that remains dissolvent is distinguished from the solid thus producing an oil with improved pour and handling qualities. Nevertheless, the rid of such a mega proportion of product would be prohibitive on a bigger scale, as would the time of a week to finish the process. A point blank method for modifying biodiesel feedstocks is to genetically alter the fatty acid profile of oilseeds.

It been suggested that soybean could be altered to yield an oil profile with increased oleic acid (C18:1) and with deduced polyunsaturated and saturated fatty acids. Such an oil would yield biodiesel with escalated oxidative stability and would be helpful (in terms of low-temperature properties) in most weathers. Another possibility would be to several elevated oleic acid (C18:1) with an escalate in stearic acid (C18:0), which would have promote burn qualities (CN, reduced NOx emissions) and oxidative stability but with relatively poor low-temperature properties. Until now, little or no possible progress has been made in genetic modification for the need of creating an oil feedstock especially for biodiesel production.