Experimental Study of Additives on Viscosity biodiesel at Low Temperature

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1. Introduction

Biodiesel is an alternative to diesel fuel in diesel engines made from vegetable oils or animal fats by the transesterification process. The viscosity of biodiesel becomes higher at low temperatures due to crystallization or a gel formation which can cause problems in the fuel line. At low temperature, the gel will clog the fuel filter so the fuel injection pump needed more energy or will be failed. Solutions to reduce the viscosity of biodiesel is to add the biodiesel with some additives.

This study is a continuation of the studies that have been conducted by previous researchers. Udomsap, P. e*t al,* (2008) studied a commercial additive, which was mixed with the biodiesel from CPO. The results showed that the use of commercial additives FA 205 with a concentration of 0.5% vol could reduce the pour point of 4°C (from 18°C to 14°C) [5].

Refaat et al, (2008) also have examined the oil-based biodiesel blending cotton (cottonseed oil methyl ester) with four commercial additives consisting of Technol B100 biodiesel cold flow improver, Gunk premium anti-gel diesel fuel, diesel fuel anti Heet -gel, and Howe's diesel treat conditioner and anti-gel, in which the concentration of each mixture was: 0.2; 0.5; 0.75; and 1% vol. Joshi, H. et al, (2008) stated that the Tecnol B100 was the best additive. The results showed that the use of commercial additives Technol B100 biodiesel cold flow improver at a concentration of 0.2; 0.5; and 0.75 vol% could reduce the pour point by 3°C (from 7 °C to 4°C) [5].

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Rohmax Company (in 2010) is a manufacture of commercial additives Viscoplex 10-330 CFI, which was carried out a research using the commercial additives Viscoplex 10-330 CFI and the biodiesel based from palm oil with various concentrations of 0, 0.2, 0.4, 0.6, 0.8, 1, and 1.2% vol. At a concentration of 10-330 Viscoplex of 1% vol could reduce the pour point the by 5°C (from 11°C to 6°C) [4].

Effect of diethyl ether generic mixing additives on biodiesel JME (Jojoba Methyl Ester) with an average concentration: 5, 10 and 15 vol% has been investigated by Selim, M.Y.E. (2009). Generic additive diethyl ether was selected for very low viscosity (diethyl ether kinematic viscosity of 0.32 cSt at 40 °C). The results showed that the viscosity of the mixture add 5% diethyl ether could reduce viscosity of 16.6 cP to 11.3 cP, adding 10% diethyl ether reduced to 7.7 cP and 15% diethyl ether added declined from 16.6 cP viscosity becomes 5.3 cP.

Sivalakshmi, S. et al, (2010) studied the addition of diethyl ether (DEE) to reduce emissions in particular soot, NOx and particulate emissions. The results showed a significant reduction in NOx emissions primarily to the addition of DEE over 10% vol and a slight decrease compared with JOME pure smoke. It has been found that the addition of 15% volume DEE on JOME improved the performance and the emission [4].

2. Experimental Methods

Biodiesel, diethyl ether and Merck Viscoplex 10-330 CFI (Cold Flow Improver) were used to study the viscosity blends. Table 1 shows the specification of the biodiesel.

Table 1. The specification of Biodiesel.

	Specification	
Density at 15°C	kg/m^3	815-870
Kinematic viscosity at 40°C	mm^2/s	2.0-5.0
Cetane number		≥48-45
Flash point 40°C	°C	≥60
Pour point	°C	≤18
Carbon residue	% mass	≤30
Water content	mg/kg	≤50
T90/95	°C	<370
Oxidation stability	g/m^3	-
Sulphur	%m/m	≤0.35
Total acid number	mg-KOH/g	≤0.6
Ash content	% m/m	≤0.01
Sediment	>% m/m	≤0.01
FAME	% m/m	≤10
Particulate	mg/l	-

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The diethyl ether was made by Merck. The diethyl ether specification can be seen on table 2.

Table 2. The specification of diethyl ether.

Specification	
Grade	ACS,ISO,Reag. Ph Eur
Chemical formula	$(C_2H_5)_2O$
HS code	2909 11 00
EC code	200-467-2
Molar mass	74.12 g/mol
Index number EC	603-022-00-4
Number CAS	60-29-7
Ignition temperature	180°C
Solubility	69 g/l (20°C)
Melting point	-116.3°C
Massa molar	74.12 g/mol
Density	0.71 g/cm^3
Boiling point	34.6 °C (1013 kPa)
Vapour pressure	587 kPa (20°C)
Flash point	-40°C
Heating value	8096.32 cal/gr
Kinematic viscosity	0,32 cSt at 40°C

The Cold Flow Improver Viscoplex 10-330 (CFI) is designed to control the formation of wax crystals from various sources of biodiesel feedstock, so it has a very good performance at low temperature. The Viscoplex 10-330 CFI can be used in mixtures with the biodiesel concentration of 0.5% - 1% to increase the cold filter plugging point (CFPP) - (DIN EN 116), pour point (PP) (ASTM D97) and cloud point (CP).

Table 3. The composition of the mixture of biodiesel with diethyl ether and the biodiesel with viscoplex.

Concentration of Generic Additive Diethyl Ether or Viscoplex (%)	Volume of Generic Additive Diethyl Ether or Viscoplex (ml)	Volume of Biodiesel (ml)
0.25	0.04	15.996
0.50	0.08	15.992
0.75	0.12	15.988
1	0.16	15.984
1.25	0.20	15.980

Biodiesel was produced by transesterfication from a mixture of crude palm oil (CPO) and methanol, whereas KOH was as a catalyst. The biodiesel was blended with diethyl ether with the concentration of 0.25%, 0.5%, 0.75%, 1.0% and 1.25%. The Biodiesel was also blended with the

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viscoplex with the concentration the same with the concentration of diethyl ether. The volume of biodiesel, the volume of diethyl ether and the volume of viscoplex can be shown in table 3.

Figure 1. Brookfield DV-III Ultra Rheometer.

The Brookfield DV-III Programmable Rheometer measures fluid parameters of Shear Stress and Viscosity at given Shear Rates. Viscosity is a measure of a fluid's resistance to flow. The principle of operation of the DV-III is to drive a spindle (which is immersed in the test fluid) through a calibrated spring. The viscous drag of the fluid against the spindle is measured by the spring deflection. Spring deflection is measured with a rotary transducer. The measuring range of a DV-III (in centipoise) is determined by the rotational speed of the spindle, the size and shape of the spindle, the container the spindle is rotating in, and the full-scale torque of the calibrated spring.
The specification of the Brookfield III as follows:

- Speed Range: 0-250 RPM, 0.1 RPM increments
- Viscosity Accuracy: ± 1.0% of full-scale range for a specific spindle running at a specific speed.
- Temperature sensing range: - 100°C to 300°C (-148°F to 572°F)
- Temperature accuracy: ± 1.0°C from -100°C to 150°C

  ± 2.0°C from +150°C to 300°C

- Analog Torque Output: 0 - 1 Volt DC (0 - 100% torque)
- Analog Temperature Output: 0 - 4 Volts DC (10mv / °C)

3. Results and discussion

Figure 2 shows the dynamic viscosity as a function of the concentration viscoplex. The unit of the kinematic viscosity is cP (centi Poise) while concentration is a ratio of the volume of viscoplex to the total volume in%. The study was carried out in the range temperature from 282 K up to 318 K and in the range viscoplex concentraion from 0% up to 1.25 %. At first, the viscosity decreases when the concentration decreases and then increases again with the increase in the viscoplex concentration. This case occurs when the temperature is 282 K. Minimum viscoplex viscosity occurs at a concentration of 0.5%. In the range temperature of 283 K and 284 K, the viscosity decreases up to the viscoplex

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concentration of 1.25. Then these characteristics change when the temperature is greater than 284 K. In this case the viscosity rises with increase in the viscoplex concentration. When the viscoplex concentration reaches 0.5%, the viscosity decreases again. This characteristic can be approximated by a polynomial equation [6]. General polynomial equation can be seen in equation 1.

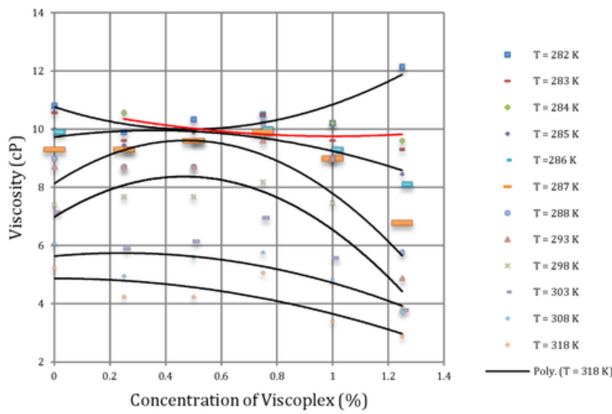

Figure 2. Viscosity blends vs Concentration of Viscoplex.

$$\mu = p_1 C^2 + p_2 C + p_3 \qquad (1)$$

where μ is the dynamic viscosity in cP, C is the volume percentage (vol.%) of the biodiesel blend; p_1, p_2 and p_3 are the adjustable parameters. The adjustable parameter can be seen on table 4. The transition characteristic of biodiesel blends can be be seen in table 4. The changing of p1 indicates the characteristic transistion. The value of p_1 changes from negative to positive value. If the p1 are negative, the each curve of polynomial equation has a maximum viscosity. Whereas the p1 are positive, the polynomial curves have a minimum viscosity.

Figure 3 shows the dynamic viscosity as a function of the diethyl ether concentration. The each polynomial curve is indicated that has a minimum viscosity. Those minimum viscosities occur at the diethyl ether concentration of 0.75 %. The parameter of p_1, p_2 and p_3 can be seen on table 4. The p1 is always positive therefore the each curve has a minimum viscosity.

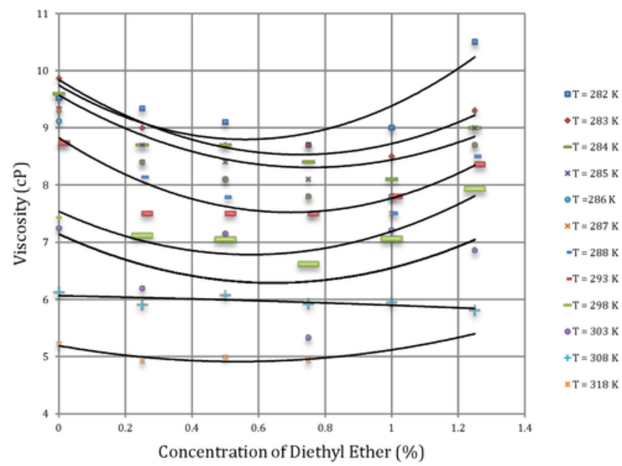

Figure 3. Viscosity blends vs Concentration of Diethyl Ether.

Table 4. The empirical correlation of biodiesel blends at constant temperature.

$\mu = P_1 C^2 + P_2 C + P_3$							
No	T (K)	Diethyl Ether			Viscoplex		
		P_1	P_2	P_3	P_1	P_2	P_3
1	282	3.02	-3.378	9.7416	3.229	-3.1406	10.761
2	283	2.4943	3.6127	9.8399	-0.5314	0.0026	10.208
3	284	2.2143	-3.345	9.5704	-0.3429	0.3943	10.243
4	285	2.604	-3.7946	9.4301	-1.7314	1.2489	9.7364
5	286	2.6543	-3.7967	9.1719	-1.9886	1.5017	9.5657
6	287	3.0171	-4.464	9.3634	-4.5371	4.1651	8.9769
7	288	2.6863	-3.7412	8.8242	-5.5857	5.4027	8.3848
8	293	2.9086	-3.7477	8.57533	-6.5743	6.323	8.1315
9	298	2.2674	-2.617	7.538	- 6.3983	5.9567	6.9821
10	303	2.0566	-2.6491	7.1418	-2.6097	1.3346	6.5794
11	308	0.046	-0.1199	6.0641	-1.789	0.8696	5.6369
12	318	0.96	1.0336	5.1906	-1.22	0.061	4.8688

The study was carried out using a mixture of biodiesel concentration from 0.25 % up to 1.25%. From figures 1 and 2 can be seen that there are two difference characteristics. Biodiesel blends and diethyl ether has a viscosity minimum of around 0.6 %, while a mixture of biodiesel and viscoplex have a maximum of 0.5 %. But viscoplex biodiesel blends have the same characteristics as biodiesel and diethyl ether mixture at low temperatures (less than 284 K), therefore a mixture of biodiesel with diethyl ether selected for a concentration of 0.5% and 0.75%, while the mixture of biodiesel with viscoplex selected for the concentration of 0.5% and 1.25%.

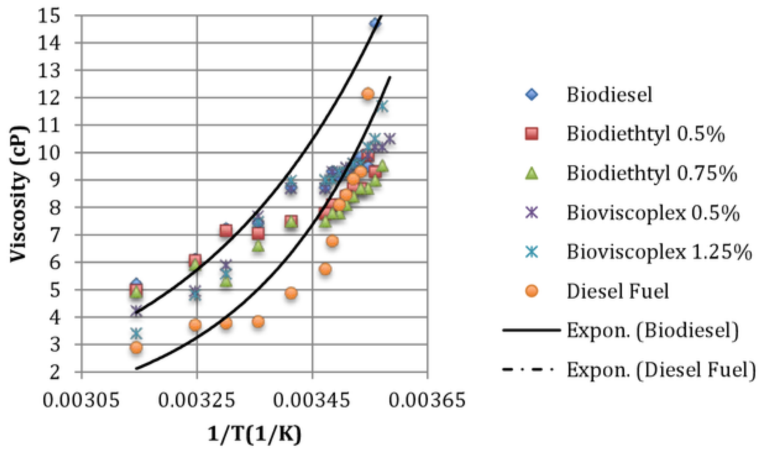

Figure 4. Viscosity of biodiesel blends as function temperature.

The dashed line in Figure 4 shows the trend line for diesel oil and the continous line shows the trendline for biodiesel. When the temperature is above 298 K or less than 0.0345 K^{-1}, all the mixture has a viscosity of biodiesel greater than the diesel fuel viscosity. Even a mixture of biodiesel and diethyl ether has viscosities greater then the pure biodiesel viscosity. But overall viscosity value is still smaller the allowable viscosity of 4.8 cP.

When the temperature is below 298 K or greater than 0.0345 K^{-1}, all the viscosities of the mixture are below the trendline diesel fuel line. The Lowest viscosity of the biodiesel blends and viscoplex occurred at concentrations of 1.25%, while for the biodiesel and diethyl ether mixture occurs at a concentration of 0.75%.

The empirical correlation of biodiesel blends at constant concentration could be written as [6]:

$$\mu = p_1 \exp\left(\frac{p_2}{T}\right) \qquad (2)$$

where μ is the dynamic viscosity in cP, T is the absolut temperature in K of the biodiesel blend, p1and p_2 are the adjustable parameters. The empirical correlation of biodiesel blends at constant concentration can be seen on table 5.

Table 5. The empirical correlation of biodiesel blends at constant concentration.

Concentration of Diethyl Ether (%)	$\mu=p_1\exp(p_2/T)$	
	p_1	p_2
0,25	2.10^{-5}	3807.7
0,5	6.10^{-5}	348,7
0,75	0.0019	2428.4
1,0	8.10^{-6}	4093.6
1,25	7.10^{-6}	4154.3
Concentration of Viscoplex (%)	$\mu=C_1\exp(C_2/T)$	
	C_1	C_2
0,25	9.10^{-6}	4091.1
0,5	0.006	2097.2

0,75	8.10^{-5}	3418.9
1,0	0,0002	3219.1
1,25	0,0003	3003,6

4. Conclusions
The addition of additives into biodiesel can improve the viscosity at low temperatures. In this study was used two kinds additivetive, namely the diethyl ether and the viscoplex (commercial additive). The mixtures have a different character to the change in concentration at a constant temperature. Biodiesel blends and diethyl ether have a minimum viscosity at a concentration of 0.75%, while the mixture of viscosity of biodiesel and viscoplex have maximum at concentration of 0.5%. But mixtures of biodiesel and viscoplex have the same characteristics with the characteristics of biodiesel and diethyl ether mixture at temperatures below 284 K. This mixture has a minimum value at a concentration of 0.5%. This characteristic can be approximated by a polynomial equation: $\mu = p_1 C^2 + p_2 C + p_3$.

The empirical correlation to predict the viscosity of biodiesel blends at various Temperatures, which is characterized by exponential equation. The optimum mixture is at 0.75% for diethyl ether and 0.5% for viscoplex. This characteristic can be approximated by a exponential equation: $\mu = p_1 \exp\left(\frac{p_2}{T}\right)$

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