Investigation on Cold Flow Properties of Biodiesel from Rubber Seed Oil, Palm Oil and its Blending

by

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Dissertation submitted in partial fulfillment of the requirement for the Bachelor of Engineering (Hons) (Chemical Engineering) Final Year Project II

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the Chemical Engineering Programme Universiti Teknologi PETRONAS in partial fulfillment of the requirement for the BACHELOR OF ENGINEERING (Hons) (CHEMICAL ENGINEERING)

Approved by,

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MAY 2012

CERTIFICATION OF ORIGINALITY

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

Muhamad Eaiz Bin Ishak

ABSTRACT

This research aims to discover the effects of mixing two types of biodiesel which are; biodicsel from rubber seed and biodicsel from palm oil, to the cold flow properties of the biodiesel. The cold flow properties had always become the major problem for biodiesel as compared to petroleum based diesel due to its high amount of saturated fatty acid methyl esters (FAMEs) components (Joshi & Pegg, 2007). Both biodiesel are self produces by using optimum conditions available and mixed by desired ratio to discover which ratio of biodiesel from rubber seed and biodiesel from palm oil give the best flow properties. Fresh palm oil obtain from shop is used and it goes through a two step transesterification with 1:6 mole ratio of oil to methanol at 55°C and constantly mixed for 30 minute. 1% KOH by weight is used as catalyst and 70% of mixed KOH methanol solution is used on the first transesterification and the other 30% goes to the next. As for the rubber seed oil, crude palm oil from Vietnam is used and it goes through a series of esterification and transesterification. As for esterification, 1:13 mole ratio of oil to methanol is at 65°C and constantly mixed for 120 minute. This follows with transesterification, with mole ratio of 1:6.5 mole ratio of oil to methanol at 65°C and constantly mixed for 120 minute. The fatty acid methyl ester (FAME) content is analyze before mixed and 7 samples different mixed ratio of both biodiesel are obtain and ready for cold flow properties analysis. The cold flow properties measured are the cloud point and the cold filter plugging point. Other parameters that will be measured during the research are densities, water content, and carbon content of mixture of the two biodiesel. The result shows that the sample which shows the best cold flow properties is sample PO0 which has cloud point of 4.2°C and cold flow plugging point of 0°C.

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CHAPTER 1

1 INTRODUCTION

1.1 BACKGROUND

Biofuels have been gaining recognition as an alternative fuel for diesel engines (Avinash Kumar, 2007). Research had been made which emphasis on developing efficient processes to convert biomass, which is a low-energy density source, to biofuels poses a difficult but attractive pathway to replace petroleum based fuel (Peter, 2002).

Biofuels are derived from biomass, and are renewable either through agricultural processes (i.e. growing corn for ethanol) or biological waste generation (i.e. animal waste products) (Varuvel, Mrad, Tazerout, & Aloui, 2012). One of the well recognized biofuels is biodiesel. Biodiesel is composed of alkyl esters of fatty acids which have a relatively low flash point, a high heating value, as well as density and viscosity comparable to those of petroleum derived diesel (Garcia-Perez, Adams, Goodrum, Das, & Geller, 2010).

However, although biodiesel is a very good solvent, usually it has poorer cold flow properties and lower oxidation stability than petroleum fuels (Garcia-Perez et al., 2010). Biodiesel with high concentration of saturated fatty acids and low melting point unsaturated mono alkyl ester will likely show poor cold flow properties.

The low temperature problems of biodiesel can be improved by several techniques which arc; by blending with conventional diesel fuels, by using additives, by developing branched-chain ester and by adding bulky substitutes to the biodiesel molecules(Garcia-Perez et al., 2010).

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1.2 PROBLEM STATEMENT

As mention earlier, one of the shortcomings of biodiesel is poor cold flow properties compared to petroleum based fuel. It has been found that crystallization or thickening of biodiesel at low temperatures causes fuel starvation and operability problems as solidified materials clog fuel lines and filters, mainly due to its high amount of saturated fatty acid methyl esters (FAMEs) components(Joshi & Pegg, 2007).

Thus, this paper aims to investigate to eliminate this shortcoming by blending with other biodiesel. The two biodiesel used in this research are biodiesel derived from rubber seed oil and from palm oil. This project is significant to country that experience winter, which make the biodiesel, unable to be used due to it poor cold flow properties.

1.3 OBJECTIVE

To study the effect of mixing of two biodiesel which are biodiesel derived from palm oil and biodiesel derived from rubber seed oil to the cold flow properties.

To study the effect of mixing of two biodiesel which are biodiesel derived from palm oil and biodiesel derived from rubber seed oil to the density and specific gravity properties.

To study the effect of mixing of two biodiesel which are biodiesel derived from palm oil and biodiesel derived from rubber seed oil to the carbon content properties.

1.4 SCOPE OF STUDY

This research focuses on cold flow properties of rubber seed oil and palm oil. Cold flow properties are defined by three properties as follow; cloud point, cold filter plugging point (CFPP) and pour point. The main focus of the research is the cloud point and cold filter plugging point. Addition parameters that need to be check during the research are densities, water content, and carbon content of mixture and pure rubber seed oil and palm oil.

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CHAPTER 2

2 LITERATURE REVIEW

2.1 THEORY

Biodiesel is composed of fatty acid methyl esters (FAMEs) and is usually synthesized by transesterifiaction of vegetable oils (triacylglycerols) with low-molecular-weight alcohols (Chen, Huang, Chiang, & Tang, 2012). Biodiesel received a huge attention due to its advantages with its classification as a renewable energy and its biodegradability. Two types of biodiesel used in this research which are biodiesel derived from rubber seed oil and from palm oil.

Biodiesel properties are mainly dependent on the oils or fats used in its production (Coutinho et al., 2010). Biodiesel is much less complex than conventional diesel where it consists of liquid blend of non-toxic, biodegradable fatty acid esters, yellow colored and immiscible with water (Coutinho et al., 2010). Thus, biodiesel gave a poorer cold flow properties compared to petroleum based oil.

Cold flow properties are divided into three parts which are; cloud point, cold filter plugging point and flow point. Cloud point is defined as the temperature of a liquid statement specimen when the smallest observable cluster of wax crystal first appears upon cooling under prescribed conditions (Krishna et al., 2007).

As for Cold Filter Plugging Point (CFPP), it is defined as the temperature at which a fuel will cause a fuel filter to plug due to fuel components which have started to crystallize or gel. Lastly pour point is defined as the lowest temperature where fuel is observed to flow. Cloud point is the most conservative measurement of cold flow properties followed by Cold Filter Plugging Point.

From past research, some of it mentions the properties of both palm oil and rubber seed oil. For palm oil, the characteristic can be seen as in the table follows (Singh & Singh, 2010).

Vegetable oil	Palm
Kinematic viscosity at 38 °C (mm ² /s)	39.6
Cetane No. (°C)	42.0
Heating value (MJ/kg)	-
Cloud point (°C)	31.0
Pour Point (°C)	-
Flash Point ((°C)	267
Density (kg/l)	0.9180
Carbon residue (wt %)	0.23

Table 1 Oil characteristic of Palm

Another table which report on palm oil is as follows. The table summarize on the physical properties of biodiesel of palm oil (Singh & Singh, 2010).

Vegetable oil methyl ester	Palm	Palm b	
Kinematic viscosity (mm ² /s)	5.7 (37.8 °C)	4.3-4.5 (40 °C)	
Cetane No.	62	64.3 - 70	
Lower heating value (MJ/kg)	33.5	32.4	
Cloud point (°C)	13	-	
Pour Point (°C)	-	-	
Flash Point ((°C)	164	-	
Density (kg/l)	0.880	0.872 -0.877 (15 °C)	

Table 2 Physical properties of Biodiesel

The first table of palm oil describes the pre-process palm oil while the latter explain the process palm oil, which in other word, the biodiesel. Meanwhile, as for the rubber seed oil characteristic are as follow. The table below summarize on the properties of rubber seed oil (Ramadhas, Jayaraj, & Muraleedharan, 2005).

Pronerties	Rubber seed oil
Specific gravity	0.91
Viscosity (mm ² /s)	76.4
Flash Point (°C)	198
Calorific value (kJ/kg)	37 500
Saponification value	206
Iodine Value	135.3
Acid value	53

Table 3 Properties of rubber seed oil

Next table that reports on rubber seed oil is as follows. The table shows properties of rubber seed oil methyl ester (Ramadhas, Muralcedharan, & Jayaraj, 2005).

Properties	Rubber seed oil methyl ester
Specific gravity	0.874
Calorific value (MJ/kg)	36.50
Viscosity (mm ² /s) at 40 °C	5.81
Flash Point (°C)	130
Diesel index	43
Cloud point (°C)	4
Pour point (°C)	-8

Table 4 Properties of rubber seed oil methyl ester

The first table of rubber seed oil describes the pre-process rubber seed oil while the latter explain the process rubber seed oil, which in other word, the biodiesel. It can be seen from the tables shown that the cold flow of rubber seed oil is better than palm oil due to it lower cloud point temperature.

CHAPTER 3

3 METHODOLOGY

3.1 RESEARCH METHODOLOGY

Figure 1 show the methodology employed in all phases of this project.



Figure 1 Project Flow Chart

Based on literature review done, the optimum condition to produce biodiesel from palm oil and rubber seed oil are obtain. The optimum conditions for each biodiesel are different from one to another. This is to make sure that the best biodiesel are produces from both raw materials which are the palm oil and the rubber seed oil. The first one to be discussed here is the palm oil. The optimum conditions for each biodiesel are as per stated later.

3.1.1 PALM OIL PREPARATION

Fresh palm oil was bought from local shop which has the acid value of 0.26 mg KOH/g. The palm oil will go through a two step process of transesterification. 500g of oil was heated to 55 °C. 1% KOH was dissolve in appropriate amount of methanol using mol ratio of oil to methanol 1 to 6. 70% of prepared KOH methanol solution was added and the mixture was stirred for 30 minutes before proceed being transferred to separating funnel to settle for 30 minutes.

The bottom layer which consists of glycerol was removed while the upper layer was brought to the second step of transesterification. The upper layer then was heated to 55 °C and the remaining 30% of KOH methanol solution was added. Again, the mixture was stirred for 30 minutes before proceed being transferred to separating funnel to settle for 30 minutes. The bottom layer was removed and the upper layer will go through a series of water washing and drying.

Distill water was used during water washing in order to removed impurities. By using water of approximately 10% by weight of the biodicsel produced, the biodicsel was washed and the water was allowed to settle for 1 hour before the water was discarded. Water wash was repeated until the waste water turned neutral. For drying, anhydrous Na₂SO₄ was used. A total amount of 20% by weight of biodiesel was added to biodiesel produced and stirred constantly for an hour. The mixture was filtered afterwards and the biodiesel is now ready to be mixed.

Feed	Molar ratio	Amount of KOH	Amount of	Reaction	Reaction
	(oil to	methanol solution	KOH catalyst	time	temperature
	methanol)	added in first step (%)	(wt %)	(min)	(°C)
Palm oil	1:6	70	1	60	55

Table 5 Two-steps alkali transesterification process for palm oil



Figure 2 Sequence of producing palm oil biodiesel

3.1.2 RUBBER SEED OIL BIODIESEL PREPARATION

As for rubber seed oil biodiesel, esterification and transesterification process had to be done. The rubber seed oil was taken from crude rubber seed oil available in Vietnam. First, the oil will undergo esterification to lower down its acidity. 500g of oil was heated to 65°C. 10% H₂SO₄ was dissolve in appropriate amount of methanol using mol ratio of oil to methanol 1 to 13. The mixture was added and stirred for 120 minutes before proceed being transferred to separating funnel to settle for a day. The lower layer was removed and the upper layer will proceed to washing. The procedure for washing was the same as previous. After washing, the acid value of the biodiesel was checked. In order to check acid value, titration had to be done. Using adaptation of American Oil Chemists' Society (AOCS) Method Cd 3d-63the acid value of biodiesel was checked. This is important as the alkaline-catalyzed reaction is very sensitive to the content of FFA, which should not exceed a certain limit recommend to avoid deactivation of catalyst, formation of soaps and emulsion.

Acud value =
$$\frac{(A-B) \times N \times 56.11}{W}$$

Where A is the volume titrant used for sample

B is the volume titrant used for blank

N is the normality of KOH = 0.02

W is the weight of sample

When the biodiesel pass the requirement of acid value (below than 2), the biodiesel can proceed to transesterification next. The biodiesel produced during esterification is forward into transesterification and heated to 65 °C. 1.5% KOH was dissolve in appropriate amount of methanol using mol ratio of oil to methanol 1 to 6.5. The mixture was stirred for 120 minutes and the send to separating funnel to settle for a day. The lower layer was discard and the upper layer will undergo series of washing and drying as per describe previously. Then, the biodiesel was ready to be mixed with the biodiesel from palm oil.

Feed	Molar ratio (oil	Amount of H ₂ SO ₄	Reaction time	Reaction
	to methanol)	catalyst (wt %)	(min)	temperature (°C)
Rubber seed oil	1:13	10	120	55

Table 6 Acid esterification process for rubber seed oil

Table 7 Alkali transesterification for rubber seed oil

Feed	Molar ratio (oil	Amount of KOH	Reaction time	Reaction
	to methanol)	catalyst (wt %)	(min)	temperature (°C)
Rubber seed oil	1:6.5	1.5	120	55

3.1.3 GAS CHROMATOGRAPHY ANALYSIS

The biodiesel were sent for analysis using gas chromatography (GC) using model GC-2010 from Shimadzu equipped with flame ionization detector (FID) and capillary column (HT5, Length: 25m. coating thickness: 0.10 μ m, internal diameter: 0.32mm). The analysis was done according to EN ISO 5508 using methyl heptadecanoate and heptanes as solvent. The ester content calculated using following formula:

$$C = \frac{\Sigma A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\%$$

Where ΣA is the total peak area from the methyl ester in C₁₄ to that in C₂₄

 A_{EI} is the peak area corresponding to methyl heptadecanoate C_{EI} is the concentration, in mg/ml, of methyl heptadecanoate used V_{EI} is the volume, in ml of the methyl heptadecanoate used m is the mass, in mg of sample

3.1.4 MIXING OF BIODIESELS

The mixture take place after the ester content value was acceptable (above 95%). The mixture was done by weight percentage and being mixed and stirred constantly for 30 minute at 60°C. The ratio of mixture between the two biodiesel as follows:

Table 8 Rat	o rubber	seed oil	to palm oil
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Sample	1	2	3	4	5	6	7
Biodiesel from rubber	0	20	40	50	60	80	100
seed oil (wt %)							
Biodiesel from palm oil	100	80	60	50	40	20	0
(wt %)							

3.1.5 ANALYSIS STUDY

Cold flow properties was check by using Automated Cloud & Pour Point Analyzer (CPP 5Gs) and Automated Cold Filter Plugging Point Analyzer (FPP 5Gs) to check for the cold flow properties. The CPP 5Gs was used to check for cloud point and pour point wheres the FPP 5Gs was used to check for the cold flow plugging point. These analytical devices were as per standards as for the CPP 5Gs follows ASTM D2500 for cloud point and as for the FPP 5Gs follows the ASTM D6371.

Note that there are other parameters that will be check for all seven samples which are; density, carbon content, and water content. These parameters will be check using their own unique equipment in order to get the value.

3.2 TOOL/EQUIPMENT/SOFTWARE NEEDED

- 3.1.1. Experiment apparatus such as vial, beaker, shaker, etc for experimental work
- 3.1.2. Automated Cloud & Pour Point Analyzer (CPP 5Gs)
- 3.1.3. Automated Cold Filter Plugging Point Analyzer (FPP 5Gs)
- 3.1.4. Density Meters
- 3.1.5. CHNS Analyzer
- 3.1.6. Karl Fisher Titrator
- 3.1.7. Microsoft Excel/Tec plot for plotting data

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CHAPTER 4

4 RESULT AND DISCUSSION

4.1 RESULT

4.1.1 SAMPLE PREPARATION

4.1.1.1 ACID VALUE ANALYSIS AFTER ESTERIFICATION OF RUBBER SEED OIL

Acid values (AV) of vegetable oil were determined according to American Oil Chemists' Society (AOCS) Method Cd 3d-63.

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

Acid Value = $\frac{[(3.4-0.2) \times 0.02 \times 56.11]}{2.048}$ = 1.75 (Requirement value < 2)





Figure 4 Before titration

Figure 5 After titration

The value is lower than requirement. The oil can proceed to transesterification process.

4.1.1.2 DETERMINATION OF ESTER CONTENT

Sample is check using EN ISO 5508 which is to determine the ester content of fatty acid methyl ester (FAME) intended to use as pure biofuel or as a blending component for heating and diesel fuels. Determination of FAME is done by using gas chromatography with internal calibration. The result for both palm oil and rubber seed oil are as follows:

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\%$$



Figure 6 GC FID result for biodiesel palm oil and biodiesel rubber seed oil

Based on the graph from gas chromatography and the calculation method given, the ester content for palm oil and rubber seed oil are as follows:

Table 9 Ester content for biodiesel from rubber seed oil and palm oil

Ester content (%)	
99	
95	
	Ester content (%) 99 95

The ester content is higher than 95%. Thus, the product can now be mixed. And proceed to the next stage which is the analysis.

4.1.2 SAMPLE ANALYSIS

4.1.2.1 COLD FLOW PROPERTIES ANALYSIS

After mixing, all seven samples go through the main analysis which is the cold flow properties using both Automated Cloud & Pour Point Analyzer (CPP 5Gs) and Automated Cold Filter Plugging Point Analyzer (FPP 5Gs) using ASTM standards. The result obtain are as follows:

Sample	PO (wt%)	RSO (wt%)	CP (°C)	CEPP (°C)
PO100	100	0	11.4	
PO80	80	20	8.2	11 7 c
PO60	60	40	6.5	7.5
PO50	50	50	5.0	4.0
PO40	40	60	5.5	2.0
PO20	20	80	5.5	1.0
PO0	0	100	4.3	0,5

Table 10 Result of cold flow properties analysis

Based on table obtain above, this can be simplifies as graph as follows:



Figure 7 Graph of Wt% PO vs. temperature

4.1.3 OTHER PARAMETER ANALYSIS

4.1.3.1 DENSITY ANALYSIS

The densities of all seven samples were check using density meter (Anton Paar DMA 5000 M). The results are as follows:

Sample	PO (wt%)	Density (kg/m3) at 20°C	SG @ 20°C
PO100	100	872.35	0.87393
PO80	80	875.21	0.87681
PO60	60	877.95	0.87955
PO50	50	879.40	0.88100
PO40	40	880.61	0.88220
PO20	20	883.30	0.88491
PO0	0	886.09	0.88770

Table 11 Result of density analysis



Figure 8 Graph of Wt% PO vs. density @ 20°C



Figure 9 Graph of Wt% PO vs. specific gravity @ 20°C

From the graph, the density and specific gravity keep increasing as weight percentage of biodiesel from rubber seed oil increase. This shows that the density of biodiesel from rubber seed oil is higher that density biodiesel from palm oil. However, the density is still in the range of 870~880 kg/m³ which actually a small change only.



Figure 10 Density meter Anton Paar DMA 5000 M

4.1.3.2 WATER CONTENT ANALYSIS

Water content of mixed biodiesel was analysis using ASTM D95 using Mettler Toledo DL 39 (Karl Fischer Coulometer). The result obtain are as follows:

Sample	PO (wt%)	Water content (ppm)
PO100	100	964.825
PO80	80	1154.433
PO60	60	1526.550
PO50	50	1456.025
PO40	40	1780.200
PO20	20	2015.275
PO0	0	1789.350

1	able	12	result	of	water	content	analysis
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Figure 11 Graph of Wt% PO vs. water content

The graph shows the level of water or moisture content in the seven samples. Low moisture content is an important aspect for a biodiesel because it will affect cold flow properties of the sample. The ranges of water level of samples are around 1,000~2000 ppm.



Figure 12 Karl fisher Titrator

4.1.3.3 CARBON CONTENT ANALYSIS

Carbon content of seven samples of biodiesel was analysis using CHNS. The results are as follows:

Sample	PO (wt%)	С	H	N	S
PO100	100	76.65	11.37	0.22	0.00
PO80	80	77.26	10.98	0.21	0.00
PO60	60	77.51	9.45	0.29	0.00
PO50	50	77.08	9.58	0.29	0.00
PO40	40	77.11	9.98	0.29	0.00
PO20	20	77.73	10.59	0.28	0.00
PO0	0	77.43	11.67	0.36	0.00

Table 13 Result of CHNS analysis



Figure 13 Graph of Wt% PO vs. percentage CHNS

From the graph, the carbon content of the seven sample biodiesel are in the range of 76~78% of total component while hydrogen takes around 9~11% of total component. As for nitrogen and sulfur, the content for each of them are around 0%.



Figure 14 CHNS analysis

4.2 **DISCUSSIONS**

Based on the results achieved, there are a few points that could be concluded which are as follows:

4.2.1 EXPERIMENT ACCURACY

Both the result for cloud point of palm oil and rubber seed oil are similar to previous research mention in the literature review. This proves the accuracy of the experiment itself.

Type of biodiesel	Cloud po	int (°C)
	Literature review	Experiment value
Palm oil	13	11.4
(Singh & Singh, 2010)		
Rubber seed oil	4	4.2
(Ramadhas, Muraleedharan,		
& Jayaraj, 2005)		

Table 14 Comparison of literature review and experimental value

4.2.2 COLD FLOW PROPERTIES

Based on the results, the sample which has the best cold flow properties is POO which is pure rubber seed oil. It has cloud point of 4.2 °C and cold flow plugging point of 0 °C. Thus, the minimum temperature in order for this biodiesel to function is 0 °C. Mixing of biodiesel of rubber seed oil into biodiesel of palm oil does has great impact on improving biodiesel but unfortunately, synergy does not take place.

Based on the graph, cold flow properties improve drastically at initial mixing with biodiesel of rubber seed oil. However, as the percentage of rubber seed oil increase, the improvement of cold flow properties gets smaller. In the end, the cold flow properties of pure rubber seed oil are greater that the mixed properties of both biodiesel and pure palm oil biodiesel.

4.2.3 OTHER PROPERTIES

Trends of increasing density and specific gravity as weight percentage of biodiesel from rubber seed oil increase is shown in the result. This proved that the density of biodiesel from rubber seed oil is higher that density biodiesel from palm oil. However, the density is still in the range of 870~880 kg/m³ which thus making this an insignificant change.

A trend of increasing water content is shown as the weight percentage of biodiesel from rubber seed oil increase. This may due to huge water content in biodiesel from rubber seed oil compared to biodiesel from palm oil. This may come from several potential reasons which are as follows:

- The feedstock rubber seed oil itself as it may content a lots of water in it
- The gap duration of production of biodiesel with the analysis is too long making the biodiesel to absorb water from the atmosphere

The carbon content seems to be constant across the seven samples. Only a slight change is observed but the range is still on around 76% to 78%. This shown that the carbon content is similar across the seven samples as all of them are biodiesel.

CHAPTER 5

5 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The cold flow properties of biodiesel improve as the weight percentage of biodiesel from rubber seed oil increase.

Sample PO0 has the best cold flow properties out of the seven sample of mixture between biodiesel from palm oil and biodiesel from rubber seed oil. The cloud point of PO0 is 4.2 °C and the cold flow plugging point is 0 °C, thus making the minimum operating temperature of the biodiesel is 0 °C.

The density and specific gravity increase as the weight percentage of biodiesel from rubber seed oil increase.

The carbon content is constant as the weight percentage of biodiesel from rubber seed oil increase.

5.2 RECOMMENDATION

The cold flow properties problems of biodiesel can be improved by a number of methods, which are (Garcia-Perez et al., 2010).

- by blending with conventional diesel fuels
- by using additives
- by developing branched-chain ester
- by adding bulky substitutes to the biodiesel molecules

The method used in this research was the mixing type but it was a mixing with other type of biodiesel which in this case was the rubber seed oil and palm oil. Thus, the other three options can be consider in order improving the cold flow properties.

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