STUDY ON LOW TEMPERATURE PROPERTIES OF PALM OIL METHYL ESTERS-PETRODIESEL BLENDS

LIM, W H*; OOI, T L* and HONG, H K*

ABSTRACT

*Synergistic properties, especially low temperature properties (*e.g. *pour point and cloud point), can be achieved by blending palm oil methyl esters with petroleum diesel in appropriate ratios. In a preliminary study, appropriate blending of palm oil methyl esters-petrol diesel at 70%-80% palm oil methyl esters led to a decrease in pour point temperature. A decrease in cloud point temperature was also noted at mixtures of 90% palm oil methyl esters with petrol diesel. A similar phenomenon was observed in the viscosity properties of the palm oil methyl esters-petrol diesel mixture. Further improvement in the low temperature properties (*e.g. *pour point temperature) of the palm oil methyl esters-diesel mixtures at 3°C can be achieved by adding 1% of a palm-based additive. However, the blended palm oil methyl esters-petrol diesel fluid resulted in an increase in viscosity. The decrease in low temperature properties (both pour point and cloud point) in the blended palm oil methyl esters-petrol diesel mixtures and in the presence of the additive was suspected to be mainly due to the disruption and changes in the molecular orientation and arrangement on both the palm oil methyl esters and the petrol diesel.*

Keywords: palm oil methyl esters, pour point, cloud point, viscosity, palm-based additive.

Date received: 14 November 2008; **Sent for revision:** 16 January 2009; **Received in final form:** 1 July 2009; **Accepted:** 30 July 2009.

INTRODUCTION

There has been considerable interest in developing biodiesel as an alternative fuel in recent years. This is mainly due to its environmental benefits and being a renewable resource like other vegetable oils (Graboski and McCormick, 1998; Srivastava and Prasad, 2000; Altin *et al*., 2001; da Silva *et al*., 2003; Demirbas, 2007). Recent global shortages in petroleum which were due to various unexpected factors have further increased the awareness of using biodiesel in various fields and applications (Knothe *et al*., 1997; Lois *et al*., 2000; Kalligeros *et al*., 2002). Even though biodiesel exhibits fuel properties comparable to petroleum diesel, the former still needs to overcome several drawbacks (both physical and chemical properties) before it can be used successfully without any limitations just like petroleum diesel (Dunn and Bagby, 1995; Lee *et al*., 1996).

Some of the problems in biodiesel can be overcome by blending biodiesel with petroleum diesel. By using appropriate blend ratios and formulations, synergistic properties and increased engine performance, such as engine torque and power output, can be achieved. In mixing vegetable oil (*e.g.* rapeseed oil) with condensate gas fuel or petroleum diesel, it is possible to obtain improved performance characteristics such as solid point, cloud point and self-ignition point (Dunn, 2002; Semenov, 2003; Altiparmak *et al*., 2007).

Low temperature properties such as cloud point (CP), pour point (PP) and low-temperature filterability (LTFT) have been routinely used to characterize the cold flow operability of both bio- and petroleum-based diesel fuels (Chandler *et al*., 1992; Dunn *et al*., 1996). These parameters are important indicators for fuel quality control specifications, storage, pipeline distribution, and suitability for use in cold conditions.

* Malaysian Palm Oil Board,
P. O. Box 10620,
50720 Kuala Lumpur,
Malaysia.
E-mail: limwen@mpob.gov.my

One of the primary solutions to overcome bulk flow and fuel filter blockage is to incorporate a pour point (PP) additive that will provide impact on the change of the crystal morphology of the fuel. It is known that most fuel additives function by modifying the wax crystals, reducing their size and shape. As a result, it provides a barrier to crystal agglomeration rather than by altering the initial formation of the crystals (Hagemann, 1988; Lewtas *et al*., 1991; Lee *et al*., 1996; Teoh *et al*., 2005).

This article presents some physical properties (*e.g*. CP, PP and viscosity) of blended palm oil methyl ester-petroleum diesel systems (of different formulations). The effect of selected ratios of the blended diesels in the presence of a palm-based additive was also tested using similar methods.

MATERIALS AND METHODS

Materials

Palm oil methyl ester and three different diesel samples (diesel P, S and M) were obtained from local sources. These materials were selected as they are most commonly used and easily obtained in the market. The additive used in this study was palm-based and synthesized in the laboratory of the Malaysian Palm Oil Board (MPOB). Early studies on this compound indicated that it exhibited great potential to be used as a fuel additive (Ooi *et al*., 2005).

Methods

Sample preparation. Samples of different weight percentages of palm oil methyl ester and petroleum diesel were mixed and blended thoroughly prior to any tests (for CP, PP and viscosity). The mixtures started from 10% and gradually increased to 90% with a 10% increment each time of palm oil methyl ester in petroleum diesel. Briefly, palm oil methyl ester was added into petroleum diesel at a low stirring rate at room temperature. The mixtures were stirred continuously for 15 min and left for 30 min to reach equilibrium before they were subjected to any tests.

Selected samples of the blended palm oil methyl ester and petroleum diesel were mixed with different amounts of palm-based additive for further studies. The additive was added into selected blends at 45°C at a low stirring rate for 10 min. The blended diesel containing the additive was equilibrated for 30 min before conducting any tests. A minimum of three replicate measurements were averaged for each experiment.

Microscopic analysis. Polarized light micrographs (PLM) of samples placed against two glass discs were observed under a Leica DMLP microscope equipped with Linkam (THMS 600) for temperature control. The sample was first heated to 40°C and held isothermally for 2 min prior to cooling to the desired temperature (up to -5°C) at a rate of 5°C min^{-1}. Liquid nitrogen was used to cool the system.

Cloud point test. CP is defined as the temperature at which a cloud of wax crystals first appears in a liquid form when the liquid is cooled under certain conditions. The CP test was performed using MPOB test method (MPOB, 2005). Briefly, the samples were heated at 45°C for 15 min and then were left to cool to room temperature. The samples were then immersed into a water bath for further cooling and were continuously stirred until the temperature at which sufficient clouding occurred so as to render the thermometer bulb immersed in the sample was no longer visible.

Pour point test. PP is defined as the lowest temperature at which a liquid can flow. The PP apparatus and procedure adopted were according to the ASTM D 97 standard method (ASTM, 1997). The test apparatus manufactured by Petrolab Corporation (Latham, NY) was used. Test jars, thermometers, corks and rubber rings met ASTM D 97 specifications.

The sample was immersed into the test jar at 0°C or other temperature, as specified in the method. Readings were taken at every 3°C decrease in temperature until the sample totally ceased to flow (with the sample held in a horizontal position for 5 s). A reading of the test thermometer was taken, and 3°C was added to the temperature and recorded as the result, following of the ASTM D 97 method. All measurements were carried out at least twice.

Viscosity test. The viscosities of samples (0.5 ml) were analysed using a Brookfield Programmable Digital Viscometer Model DV-III. The spindle used was CP40. The operating temperature and speed were set at 40.0±0.5°C and 150 rpm, respectively. All the data were recorded, extracted and analysed.

Fatty acid methyl ester composition. The fatty acid compositions of palm oil methyl ester were determined using gas chromatography, with reference to the standard method (AOCS Method, Ce 1-62, 1997). *Table 1* shows the fatty acid compositions.

RESULTS AND DISCUSSION

Cloud Point and Pour Point Analyses

In this investigation, various weight ratios of palm oil methyl ester and three different petroleum diesels were blended to observe the changes in both CP and PP. In general, CP can be defined as the highest temperature used for characterizing cold

TABLE 1. FATTY ACID COMPOSITIONS OF PALM OIL METHYL ESTERS

Sample	Fatty acid composition (%)									
	C8	C10	C12	C14	C16	C18:0	C18:1	C18:2	C18:3	Others
PME	-	-	0.2	1.0	43.9	4.5	39.9	9.6	0.3	0.6

Note: PME – palm oil methyl ester.

flow properties while PP is the lowest temperature. The CP and PP of the original components in *Table 2* show palm oil methyl ester had a relatively higher CP and PP than petroleum diesels.

As indicated in *Figure 1*, the blended palm oil methyl ester and petroleum diesel had a lower PP than palm oil methyl ester and petroleum diesels, except in the case of petroleum diesel M (which had a lower PP only when it was blended with 60%-80% palm oil methyl ester). A significant reduction in PP (to 5°C) was observed especially at a high palm oil methyl ester content of between 60% and 80% w/w. It was also observed that the blends of palm oil methyl ester-petroleum diesel P and palm oil methyl ester-petroleum diesel S exhibited a wider PP range (that was lower than those of the individual components) than that of the blend of palm oil methyl ester-petroleum diesel M.

All blended palm oil methyl ester-petroleum diesel exhibited the lowest CP at 90% palm oil methyl ester and 10% petroleum diesel. Both palm oil methyl ester-petroleum diesel P and palm oil methyl ester-petroleum diesel S blends had a similar trend, exhibiting a broader range of CP which was lower than individual components, *i.e.* between 70% and 90% palm oil methyl ester, than that of palm oil methyl ester-petroleum diesel M (only at 90% palm oil methyl ester). The sudden drop in both CP and PP of palm oil methyl ester with the addition of petroleum diesel (by 10% for CP and up to 20% for PP, respectively) may very well indicate that petroleum diesel was acting as a diluent for palm oil methyl ester. The addition of petroleum diesel will dilute the palm oil methyl ester and form complex mixtures among the aliphatic, aromatic and esters compounds. As a result, a synergistic interaction between palm oil methyl ester and petroleum diesel molecules occurred and this affected the orientation of the molecular arrangement during crystallization (whether at PP or CP temperatures) as the operating temperature decreased. This was further analysed by observing at the microstructure of palm oil methyl ester, S diesel and palm oil methyl ester-S mixture samples using the PLM at -5°C (*Figure 2*). The micrograph of palm oil methyl ester shows agglomerates of sharp crystal and needle shape crystal was formed in S diesel sample. However, significant changes in microstructure of the crystals were noted in the palm oil methyl ester-S mixture sample.

TABLE 2. POUR POINT AND CLOUD POINT OF TEST FLUIDS

Fluid	CP (°C)	PP (°C)
Palm oil methyl esters	10.8	15
Petroleum diesel P	9.1	12
Petroleum diesel S	9.2	12
Petroleum diesel M	9.7	12

Note: CP – cloud point; PP – pour point.

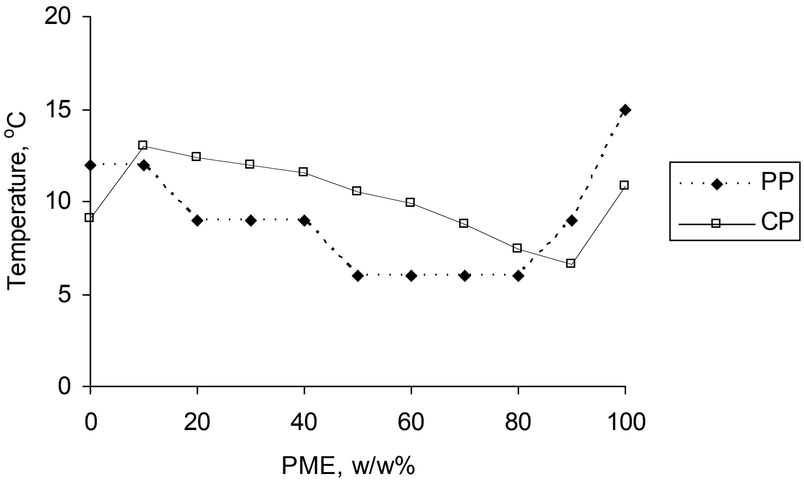
Flow Analysis

Viscosity measurements of the original components are shown in *Table 3*. Among the original components, palm oil methyl ester was the most viscous, followed by petroleum diesel P and petroleum diesel M, with the least viscous being petroleum diesel S.

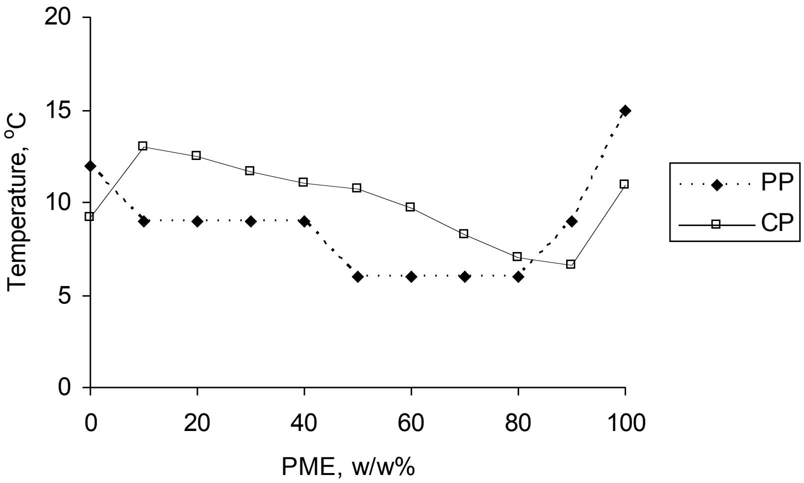
An interesting phenomenon was observed when different weight ratios of palm oil methyl ester and petroleum diesel (P, S and M) were blended. As shown in *Figure 3*, irrespective of the palm oil methyl ester and petroleum diesel weight ratios, palm oil methyl ester-petroleum diesel blends exhibited lower viscosity than their individual components. Blends of palm oil methyl ester-petroleum diesel P exhibited minimum reduction in viscosity, whereas a dramatic decrease in viscosity was observed at high palm oil methyl ester content (50%-80% palm oil methyl ester) with petroleum diesel S. However, an opposite trend was noted in palm oil methyl ester-petroleum diesel M blends in which the viscosities were reduced dramatically at low palm oil methyl ester content. If there was a weak interaction or repulsion among the molecules, the mixtures would have deviated from the sum of the individual interactions according to the ratios of the blends. However, the decrease in viscosity of palm oil methyl ester-petroleum diesel mixtures to lower than the individual components

TABLE 3. VISCOSITY OF TEST FLUIDS

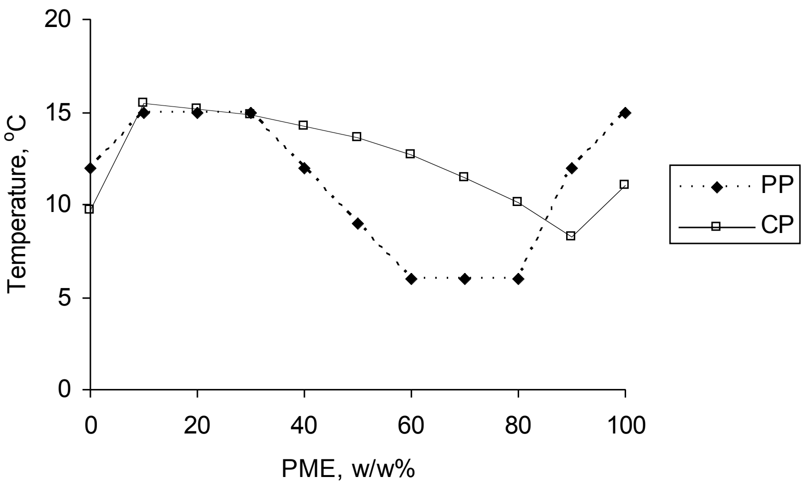
Fluid	Viscosity at 40°C (cP)
Palm oil methyl esters	3.66
Petroleum diesel P	3.62
Petroleum diesel S	3.19
Petroleum diesel M	3.49



(a)



(b)



(c)

Figure 1. Cloud point and pour point of palm oil methyl ester (PME) with different petroleum diesels. (a) Diesel P, (b) diesel S and (c) diesel M.

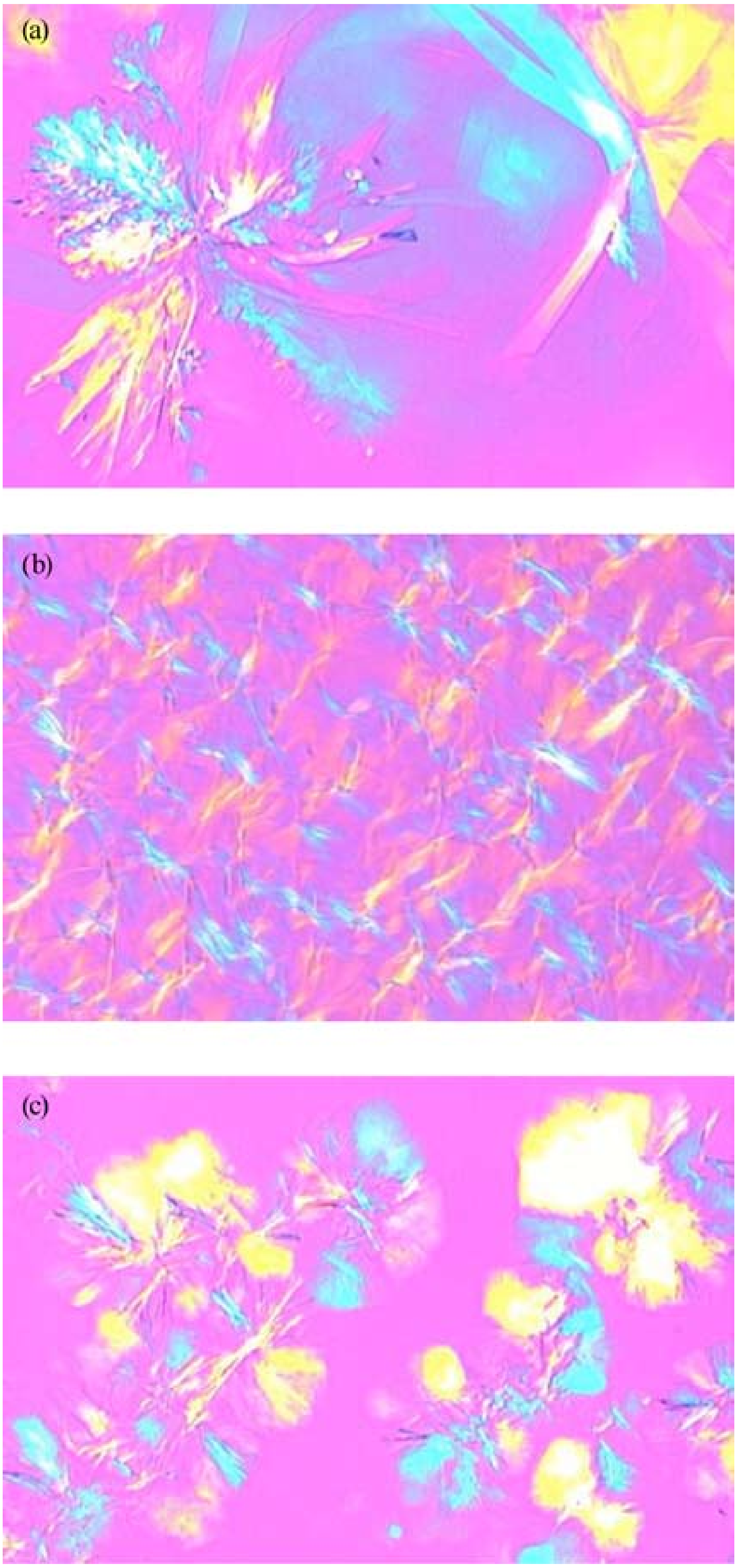


Figure 2. Polarized light micrographs of (a) palm oil methyl esters, (b) S diesel and (c) mixtures of 70% palm oil methyl esters and 30% S petroleum diesel at -10°C to -50°C (20X magnification).

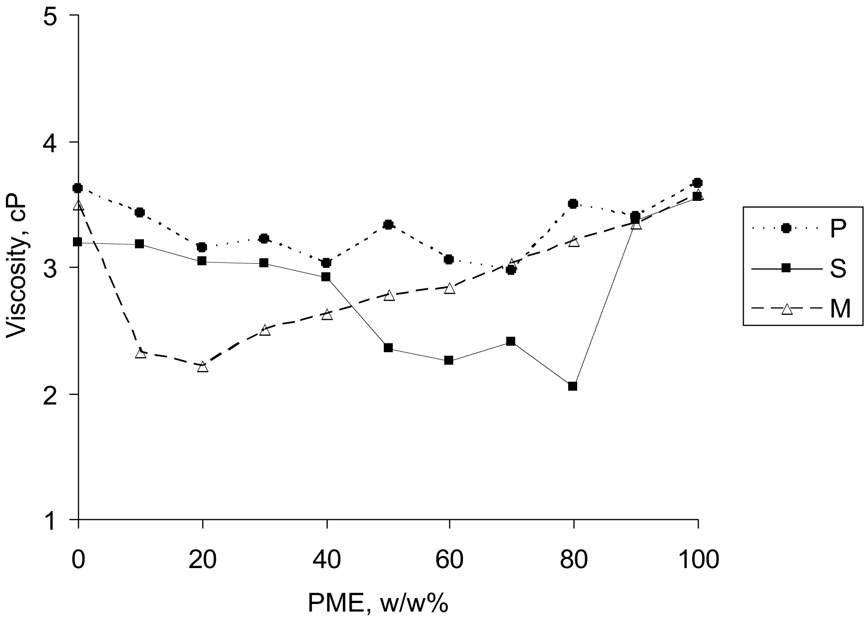


Figure 3. Viscosity of blended palm oil methyl ester (PME) with different petroleum diesels (P, S, and M) at 40°C.

was quite substantial, which suggested that an unfavourable interaction between the molecules as well as dilution factor have affected the behaviour of the blends. The type of additives present in the petroleum diesel (local source) may also play an important part in affecting the viscosity of the palm oil methyl ester-petroleum diesel blends.

Use of an Additive Derived from Palm Oil

From the above experiments on the three different palm oil methyl ester-petroleum diesel (P, S, and M) systems, two weight ratios of 70-30 and 80-20 of palm oil methyl ester-petroleum diesel blends which exhibited the lowest PP values were selected for further studies. A palm-based additive synthesized in our laboratory was added into these blends. As indicated in *Figure 4*, the presence of the additive changed the PP, CP and viscosity of 70-30 weight ratio of palm oil methyl ester-petroleum diesel. The additive lowered the PP of both palm oil methyl ester-petroleum diesel P and S blends from 6°C to 3°C. The PP temperature remained constant even when the additive was increased to 3%. Interestingly, the additive did not seem to have any effect on the palm oil methyl ester-petroleum diesel M blend. The presence of the additive might in a way have affected the arrangement of the crystal packing, which prevented the mixtures from solidification, or allowed the crystals to get effectively bound to the crystal stacks (Teoh *et al*., 2005).

Among the blended palm oil methyl ester-petroleum diesels, the palm oil methyl ester-petroleum diesel M blend had the highest CP, followed by palm oil methyl ester-petroleum diesel P and palm oil methyl ester-petroleum diesel S. However, the presence of the additive further increased the CP temperature by 2°C. The additive used seemed to have the ability to decrease the PP of the blends, but not the CP. Continuous addition of the additive above 1% into the palm oil methyl ester-petroleum diesel blends did not cause any change in the CP (*Figure 4b*). As shown in *Figure 4c*, the presence of additive increased the viscosity of the blended palm oil methyl ester-petroleum diesel. The viscosity of palm oil methyl ester-petroleum diesel blends continued to increase with the increase in additive concentration.

At the 80-20 weight ratio of palm oil methyl ester-petroleum diesels (*Figure 5a*), the presence of the additive did not affect the PP temperature, even when the additive concentration reached 3%. However, the CP of the blended palm oil methyl ester-petroleum diesel decreased slowly as the additive was increased. This indicates that the effectiveness of reducing PP and CP in the presence of the chosen palm-based additive was also dependent on palm oil methyl ester-petroleum diesel ratio. Just as in the 70-30 weight ratio of palm oil methyl ester-petroleum diesel blend, a similar trend in viscosity was observed for the 80-20 weight ratio, as the additive concentration increased to 3%.

CONCLUSION

Blending of palm oil methyl esters with petroleum diesel has the ability to provide synergistic effects on both the PP and viscosity of palm oil methyl ester-petroleum diesel blends. However, a reduction in CP of palm oil methyl ester only occurred in blends having high palm oil methyl ester content. The

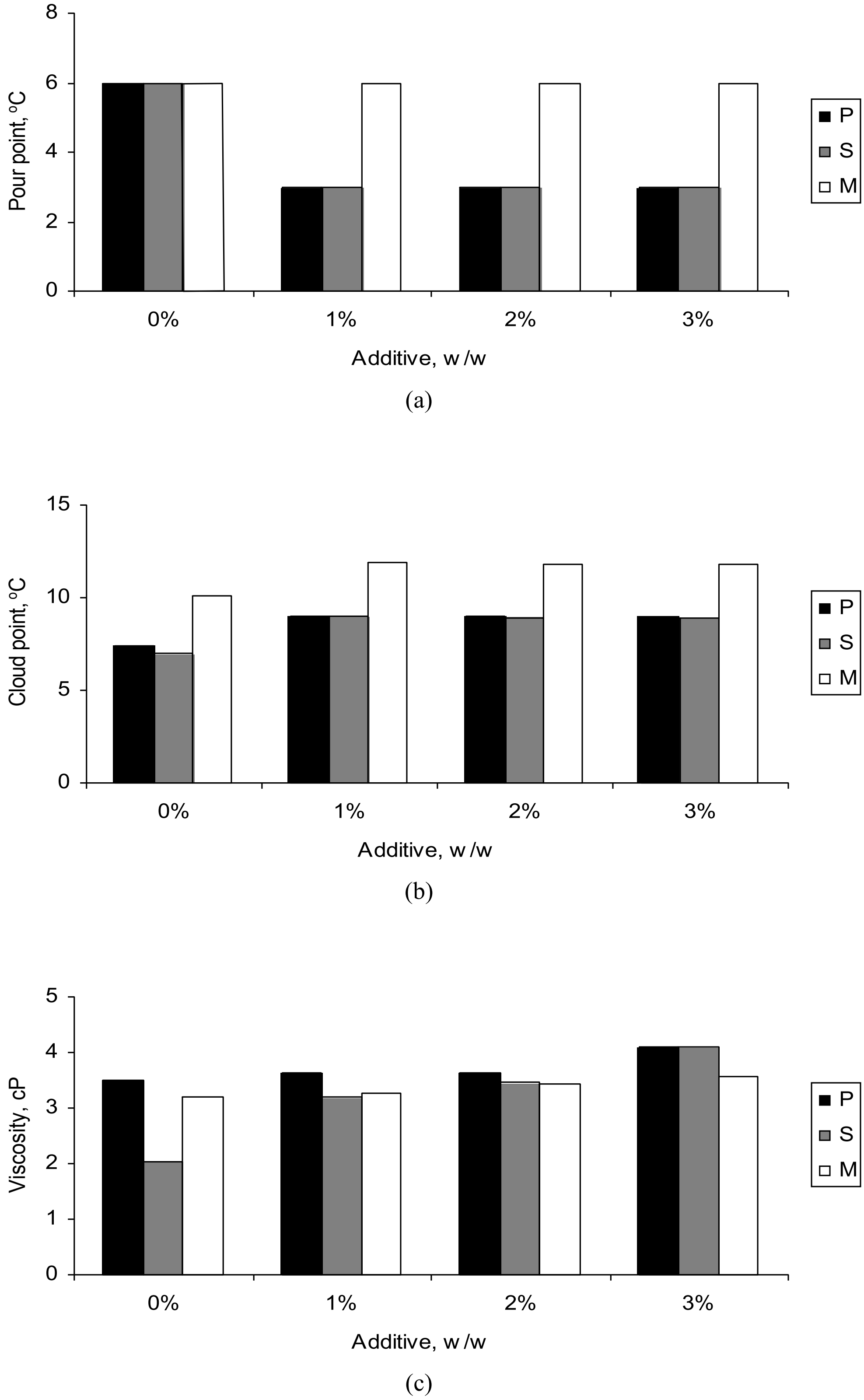
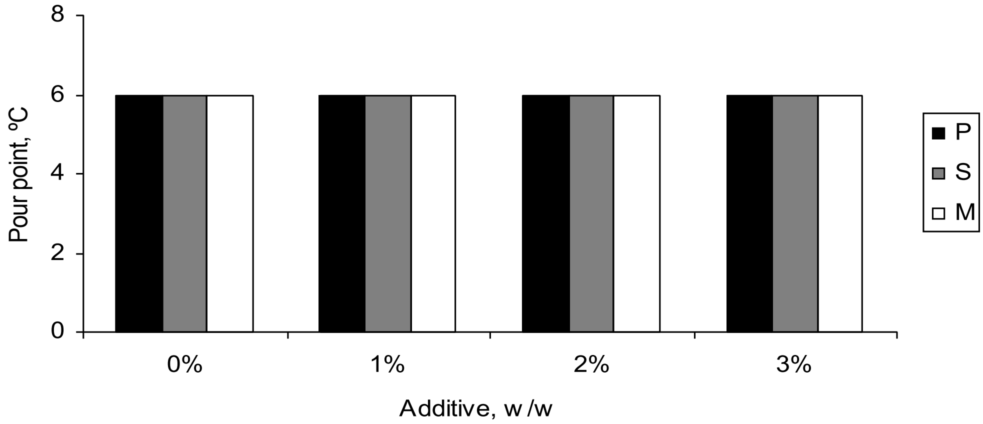
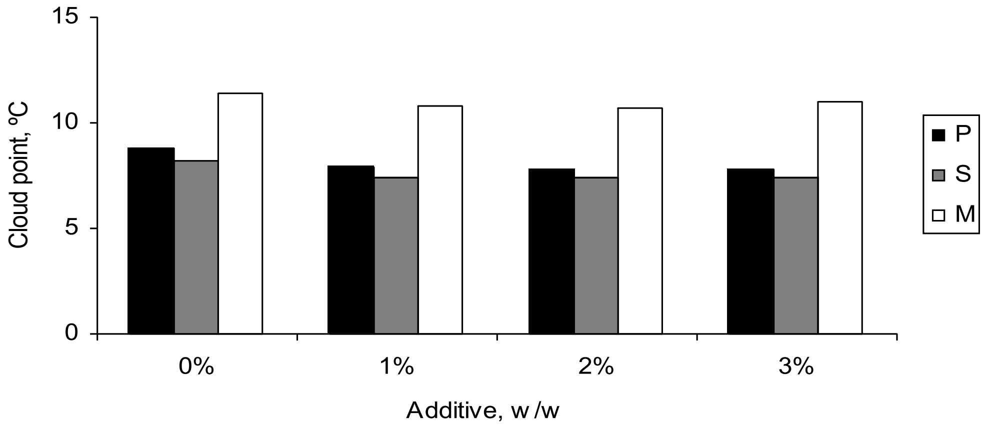


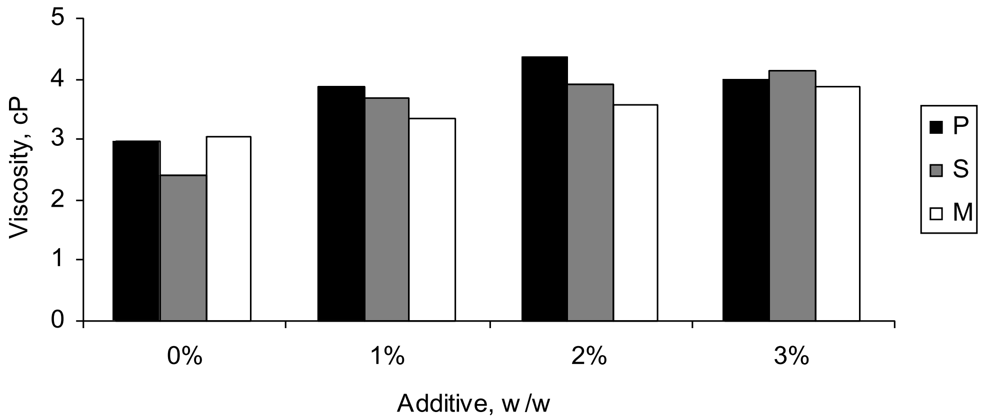
Figure 4. Effect on (a) pour point, (b) cloud point, and (c) viscosity of blend of mixtures of 70% palm oil methyl ester and 30% petroleum diesel (P, S, and M) in the presence of different concentrations of additive.



(a)



(b)



(c)

Figure 5. Effect on (a) pour point, (b) cloud point, and (c) viscosity of blend of mixtures of 80% palm oil methyl ester and 20% petroleum diesel (P, S, and M) in the presence of different concentrations of palm-based additive.

presence of a palm-based additive selected for this study had some profound effects on the PP, CP and viscosity of palm oil methyl ester-petroleum diesel blends. The degree of effects on the blends was also highly dependent on their blending ratios.

ACKNOWLEDGEMENT

The authors would like to thank the Director-General of MPOB for permission to publish this article.

REFERENCES

ALTIPARMAK, D; KESKIN, A; KOCA, A and GÜRÜ, M (2007). Alternative fuel properties of tall oil fatty acid methyl ester-diesel fuel blends. *Biores. Technol*., *98*: 241-246.

ALTIN, R; C¸ETINKAYA, S and YUCESU, H S (2001). The potential of using vegetable oil fuels as fuel for diesel engines. *Energ. Conserv. Mgmt*., *42*: 529-538.

AOCS (1997). *Official Methods and Recommended Practices*. American Oil Chemists' Society, Champaign, IL.

ASTM (1997). Sec. 5 – Petroleun products; lubricants and fossil fuels. *1997 Annual Book of ASTM Standards.* ASTM International, West Consnohocken, P.A.

CHANDLER, I E; HORNECK, F G and BROWN, G I (1992). The effect of cold flow additives on low-temperature operability of diesel fuels. *SAE Technical Paper Series Paper No. 922186*. Society of Automotive Engineers, Warrendale, USA.

DA SILVA, F; PRATA, A S and TEIXEIRA, J R (2003). Technical feasibility assessment of oleic sunflower methyl ester utilisation in diesel bus engines. *Energ. Conserv. Mgmt*., *44*: 2857-2878.

DEMIRBAS, A (2007). Recent developments in biodiesel fuels. *Int. J. Green Energ*., *4*: 15-26.

DUNN, R O (2002). Low-temperature flow properties of vegetable oil/cosolvent blend diesel fuels. *J. Amer. Oil Chem. Soc*., *Vol***.** *79***:** 709-715.

DUNN, R O and BAGBY, M O (1995). Low-temperature properties of triglyceride-based diesel fuels transesterified methyl esters and petroleum middle distillate/ester blends. *J. Amer. Oil Chem. Soc*., *Vol***.** *72***:** 895-904.

DUNN, R O; SHOCKLEY, M W and BAGBY, M O (1996). Improving the low-temperature properties of alternative diesel fuels: Vegetable oil-derived methyl esters. *J. Amer. Oil Chem. Soc*., *Vol. 73*: 1719-1728.

GRABOSKI, M S and McCORMICK, R L (1998). Combustion of fat and vegetable oil derived fuels in diesel engines. *Progr. Energ. Combust. Sci*., *24*: 125-164.

HAGEMANN, J W (1988). Thermal behavior and polymorphism of acyl-glycerides. *Crystallization and Polymorphism of Fats and Fatty Acids* (Garti, N and Sato, K, eds.). Marcel Dekker, Inc., New York, US. p. 9-95.

KALLIGEROS, S; ZANNIKOS, F; STOURNAS, S; LOIS, E; ANASTOPOULOS, G; TEAS, C and SAKELLAROPOULOS, F (2002). An investigation of using biodiesel/marine diesel blends on the performance of a stationary diesel engine. *Biomass Bioenerg*., *24*: 141-149.

KNOTHE, G; DUNN, R O and BAGBY, M O (1997). Biodiesel: The use of vegetable oils and their derivatives as alternative diesel fuels. *Fuels and Chemicals from Biomass* (Saha, B C and Woodward, J, eds.). ACS Symposium Series 666, ACS, Washington, USA. p. 172-208.

LEE, I; JOHNSON, L A and HAMMOND, E G (1996). Reducing the crystallization temperature of biodiesel by winterizing methyl soyate. *J. Amer. Oil Chem. Soc*., *Vol***.** *73*: 631-636.

LEWTAS, K; TACK, R D; BEINY, D H M and MULLIN, J W (1991). Wax crystallisation in diesel fuel: Habit modification and the growth of n-alkane crystals. *Advances in Industrial Crystallization* (Davey, R J and Jones, A G, eds.). Butterworth-Heineman, Oxford, UK. p. 166-179.

LOIS, E; SERDARI, A; FRAGIOUDAKIS, K; KALLIGEROS, S and STOURNAS, S (2000). Impact of using biodiesels of different origin and additives on the performance of a stationary diesel engine. *J. Eng. Gas Turb. Power*, *122*: 624-631.

MPOB (2005). *MPOB Test Methods. A Compendium of Test on Palm Oil Products, Palm Kernel Products, Fatty Acids, Food Related Products and Others*. MPOB, Bangi.

OOI, T L; TEOH, C M; YEONG, S K and AHMAD, S (2005). A new natural based pour point depressant for fatty alkyl esters. *MPOB Information Series No. 279*. MPOB, Bangi.

SEMENOV, V G (2003). Optimization of the composition of binary alternative diesel fuel. *Chem. Technol. Fuels Oils*, *39*: 192-196.

SRIVASTAVA, A and PRASAD, R (2000). Triglycerides-based diesel fuels. *Renew. Sust. Energ. Rev.*, *4*: 111-133.

TEOH, C M; RAMLI, N; OOI, T L; SAID, M and KASIM, Z (2005). Strategies for decreasing the pour point and cloud point of palm oil products. *Eur. J Lipid Sci. Technol.*, *107*: 505-512.

NEW COLUMNS

Interested parties are invited to contribute ideas and comments related to the published articles or on how to improve the overall quality of the journal, so as to make it more presentable and useful to the readers.

Contributors are encouraged to abide by the guidelines stated below:

Guidelines for LETTERS TO EDITOR

A 'Letter to Editor' should be concise. Please include your full name (add a pseudonym, if you like), address, gender and phone number (for reference only). You can send by e-mail, regular mail or fax (603-8922 3564). Personal information of sender will be kept confidential. Send your letter to: Malaysian Palm Oil Board, P.O. 10620, 50720 Kuala Lumpur (Attn: Publication Section) or e-mail us at: pub@mpob.gov.my

Some common guidelines are:

- There will be a very short word limit, which is strictly enforced. A general guideline would be 200-250 words.
- You must not submit the same letter to more than one publication at the same time.
- The letter should refer to a specific article recently published by JOPR.
- There is a strict deadline for responding to a given article. The sooner you respond to specific article, the more likely it is that your letter will be published.

Guidelines for SHORT COMMUNICATIONS

- Short Communications are original short articles which are published with the objective of disseminating technical ideas of the originator without losing time. This will provide researchers with a venue where they can share their most current results and developments in the shortest possible time. The Short Communications, like regular papers will be reviewed by expert reviewers and evaluated by editor. Unlike regular papers, Short Communications will be published within six months of submission.
- Short communications should be prepared in a camera-ready format and limited to 2000 words and not more than four illustrations (*i.e*. Figures and Tables).
- Format: Abstract (~80 words), Keywords, Introduction, Materials and Methods, Results and Discussion, Conclusion and References.
- In order to help expedite the reviewing process, authors are advised to suggest a list of two unbiased potential reviewers to the Editor. Please include their names and e-mail addresses in the submission e-mail. These reviewers should not be related to the author, nor should they be associates or collaborators.