# ENHANCEMENT OF COLD STABILITY OF PALM OIL METHYL ESTERS

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**ABSTRACT**

*As with palm oil, palm oil methyl esters (POME) have poor cold stability. This drawback has limited their use in low temperatures. The objectives of this research were to identify some additives suitable for reducing the pour point and cloud point of POME to improve its low temperature performance. Of the additives used, EP produced the most promising results. The biggest reduction in pour point was about 15.0ºC (addition of 2% EP to POME) while the biggest depression in cloud point was about 6.4ºC (addition of 4% EP to POME).*

**Keywords:** palm oil methyl esters, pour point depressant, wax crystal inhibitor, cloud point.

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## INTRODUCTION

Fatty esters are one of the basic oleochemicals, apart from fatty acids, fatty alcohols, fatty amines and glycerol. Methyl esters of vegetable oils and animal fats are useful in a variety of contexts. They are widely used as lubricants in the metalworking industry, carriers for the active ingredients in pesticides, bases for drilling muds and as biodiesel fuels.

However, their relatively high pour points - typically at or above the freezing point of water and poor cold stability have prevented their use in a number of applications.

The use of methyl esters as agricultural adjuvants market is hampered by their poor low temperature properties. Pesticides are usually stored outside in large drums for use. However, in colder climes, they become frozen and require thawing before use.

Diesel and mineral oils have typically been used as the base for drilling muds and fluids. However, their use has raised environmental concerns. Due to the environmental friendliness of methyl esters, they have been alternatively used although not in the colder climes due to their high pour points.

Methyl esters have in the past few years been extensively tested as a substitute for diesel. As previously discussed, the disadvantage of methyl esters is their relatively high pour point, which cause them to solidify in fuel pipes at temperatures at or above the freezing point of water. Thus, it is desirous to produce methyl esters with lower pour points as biodiesel (Majerczak, 2001).

Some of the common methods that have been used to further enhance the use of methyl esters at low temperatures are the addition of additives (known as pour point depressant, wax crystal inhibitor and cold flow improver), blending with diesel, winterization and the use of branched esters. Additives are the preferred method as it is more economical. Therefore, in this paper, an attempt to improve the low temperature properties of palm oil methyl esters is described.

## MATERIALS AND METHODS

### Materials

The additives used in this research were palm-based oligomer EP, palm-based oligomer GP and palm-based oligomer PP. The oligomers were synthesized in the Advanced Oleochemicals Technology Division (AOTD), Malaysian Palm Oil Board.

Initially, the properties of the palm oil methyl esters were characterized - pour point, cloud point, viscosity, fatty acid composition, free fatty acid content and iodine value. The pour point, cloud point and viscosity tests were re-run after each addition of the additives to determine the effectiveness of the additives used.

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### Analyses

***Pour point test.*** The method and apparatus for pour point measurements was based on the ASTM D97 test method.

***Cloud point test.*** The cloud point test was performed using the AOCS Cc 6-25(97) test method.

***Viscosity test.*** The viscosity of the samples was analysed using the Brookfield Programmable Digital Rheometer Model DV-III. Only a small sample (0.5 ml) was needed to run the test. The spindle used was CP40. The temperature and speed were set at 40.0ºC and 150 rpm.

***Other tests.*** The fatty acid composition of the samples was determined using gas-liquid chromatography, with reference to the AOCS Ce 1-62 (97) standard method. The acid value was analysed using the AOCS Cd 3d-63 (97) test method and the iodine value of the samples was determined using the AOCS Cd 1d-92 (reapproved 1997) test method while the differential scanning calorimetry analysis was based on the AOCS Cj 1-94 (97) standard method. Microscopic observations of the samples were made under an Olympus optical microscope AX 70 attached with a Linkam temperature control unit.

## RESULTS AND DISCUSSION

### Characteristic Studies

*Table 1* shows the characteristics and the properties of palm oil methyl esters, (POME).

POME has a relatively high pour point and cloud point - 12.0ºC and 8.8ºC, respectively. The pour point is the lowest temperature at which a sample stops flowing while the cloud point is the temperature at which a cloud of crystals first appears on cooling (Krawczyk, 1996). To enhance the use of POME in temperate countries, especially during winter, it is desirable to incorporate additives to depress the pour and cloud points, preferably to below 0ºC.

POME has an iodine value (I.V.) of 64.9, which is considered quite high. The I.V. of POME was almost the same as the I.V. of super olein (double fractionated palm olein) which usually has a minimum I.V. of 60. Oleins with higher I.V. generally resist crystallization better although this may not always be the case as other factors also influence the cold stability of olein (Siew, 1999; Siew and Ng, 1996).

TABLE 1. CHARACTERISTICS AND PROPERTIES OF PALM OIL METHYL ESTERS (POME)

| Parameter | Reading | Method |
|---|---|---|
| Pour point (ºC) | 12.0 | ASTM D97 |
| Cloud point (ºC) | 8.8 | AOCS Cc 6-25 (97) |
| Viscosity at 40ºC (cP) | 3.8 | |
| Acid value | 0.3 | AOCS Cd 3d-63(97) |
| Iodine value | 64.9 | AOCS Cd 1d-92 (97) |

*Table 2* shows the fatty acid composition of POME. Determination of the fatty acid composition of POME is important in studying its crystallization behaviour.

Siew (1999) reported that the palmitic acid content should be below 35.0%, preferably below 31.0% for palm olein to be stable and remain clear. Thus, POME with about 31.8% palmitic acid content should theoretically have favourable low temperature properties.

### Addition of Additives to POME

After characterizing the POME, three palm-based oligomers - EP, GP and PP were added to determine their effectiveness in reducing the pour point and cloud point of POME.

The effects of EP, GP and PP on POME are shown in *Table 3*.

The performances of the three additives were similar, with EP producing only slightly better results than GP and PP.

### Addition of EP to POME

As EP showed better results, all further studies were conducted with it. *Table 4* shows the effects of adding EP to POME.

Addition of 2% EP caused the most dramatic effect, depressing the pour point by 15.0ºC (from 12.0 to –3.0ºC).

TABLE 2. FATTY ACID COMPOSITION OF PALM OIL METHYL ESTERS (POME)

| Fatty acid composition (%) | | | | | | | |
|---|---|---|---|---|---|---|---|
| C12 | C14 | C16 | C18:0 | C18:1 | C18:2 | C18:3 | Others |
| 0.3 | 0.9 | 31.8 | 4.0 | 47.6 | 14.4 | 0.3 | 0.7 |

TABLE 3. EFFECTS OF ADDITIVES ON PALM OIL METHYL ESTERS (POME)

| Additive | Pour point (°C) | Cloud point (°C) | Viscosity (cP) |
|---|---|---|---|
| POME | 12.0 | 8.8 | 3.75 |
| POME + 1% EP | 6.0 | 4.0 | 3.88 |
| POME + 1% GP | 6.0 | 5.6 | 3.91 |
| POME + 1% PP | 6.0* | 7.0 | 3.66 |

Note: *: Sample solidified at 6.0°C but with a small flow that only stopped at –9.0°C.

TABLE 4. EFFECTS OF ADDING EP TO PALM OIL METHYL ESTERS (POME)

| Sample | Pour point/°C | Cloud point/°C | Viscosity/ cP |
|---|---|---|---|
| POME | 12.0 | 8.8 | 3.75 |
| + 1% EP | 6.0 | 4.0 | 3.88 |
| + 2% EP | -3.0 | 3.9 | 3.99 |
| + 3% EP | 3.0 | 2.6 | 6.17 |
| + 4% EP | 6.0 | 2.4 | 4.36 |
| + 5% EP | 6.0 | 2.7 | 6.52 |

Other concentrations also achieved satisfactory results, reducing the pour point from 12.0°C to 6.0°C, except for 3% EP which lowered the pour point to 3.0°C.

The results were in agreement with the findings of Nielsen (1995) and Siew (2000). Both, in their studies on palm olein, reported the dosage of the additive to be very important. Excessive dosage reduces the anti-crystallizer effect. On the other hand, an insufficient dose will not yield the optimum effect.

For the cloud point, the addition of 4% EP recorded the largest temperature reduction - from 8.8°C to only 2.4°C (a reduction of 6.4°C).

## Solid Fat Content (SFC) and Differential Scanning Calorimetry (DSC)

Both SFC and DSC are important in studying the crystallization behaviour of POME.

*Table 5* shows the SFC of POME with the addition of EP. POME has high SFCs at 0°C and 5°C of 17.7% and 12.0%, respectively. Some solids were still detected at 15°C. The addition of EP significantly reduced the SFC at all temperatures, with the highest reduction recorded at 0°C and 5°C. With 1% EP, the SFC of POME at 0°C was reduced from 17.7% to 13.6% and the SFC at 5°C from 12.0% to only 7.1%.

Generally, the higher the concentration of EP used, the lower was the SFC recorded. However, POME with 2% and 3% EP recorded slight increases in the SFC at 10°C. This could be due to the presence of impurities in the POME.

From the DSC cooling and melting curves of POME, EP at all concentrations decreased the peak temperatures of the curves, with 1% EP addition recording the largest decrease. However, as the concentration of EP increased, there was a slight increase in the peak temperatures.

In addition, the areas of the peaks, which represent the exothermic heat released by the crystallization process, were also slightly changed. The peaks of the curves of POME with EP were all narrower than the peak of the control POME.

## Microscopic Observations

Microscopic observations were done to further assess the effectiveness of EP in improving the low temperature properties of POME. *Figures 1* to *5* show the POME crystals formed with the addition of EP at various concentrations.

From the *Figures*, it was found that addition of EP successfully minimized the POME crystal size. As the concentration of EP increased, the size and intensity of POME crystals formed decreased.

TABLE 5. SOLID FAT CONTENT (wt. %) OF PALM OIL METHYL ESTERS (POME) WITH THE ADDITION OF EP

| Sample | Temperature/°C | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 |
| POME | 17.7 | 12.0 | 3.7 | t | l | - | - |
| POME + 1 % EP | 13.6 | 7.1 | 3.1 | l | - | - | - |
| POME + 2 % EP | 12.8 | 5.4 | 4.3 | l | - | - | - |
| POME + 3 % EP | 12.6 | 4.7 | 4.1 | l | - | - | - |

Notes: l = liquid.
t = trace.

*Figure 1. Crystals of POME without EP (at 20X magnification).*

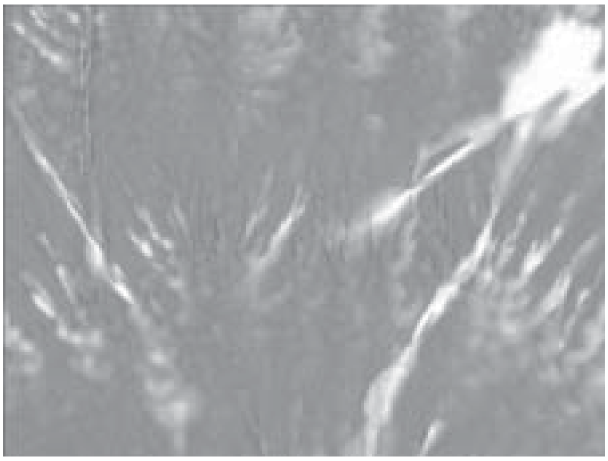

*Figure 2. Crystals of POME + 1% EP (at 20X magnification).*

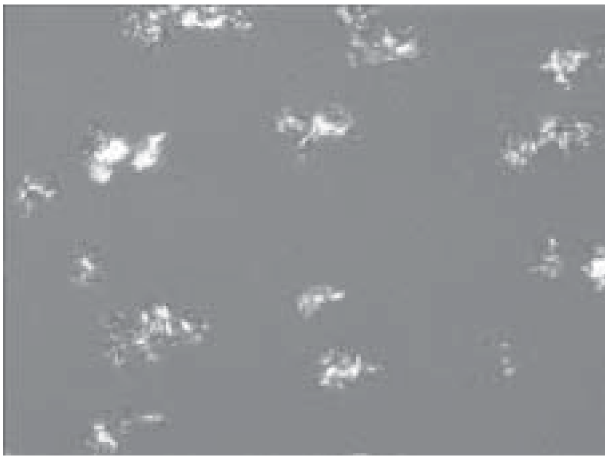

*Figure 3. Crystals of POME + 2% EP (at 20X magnification).*

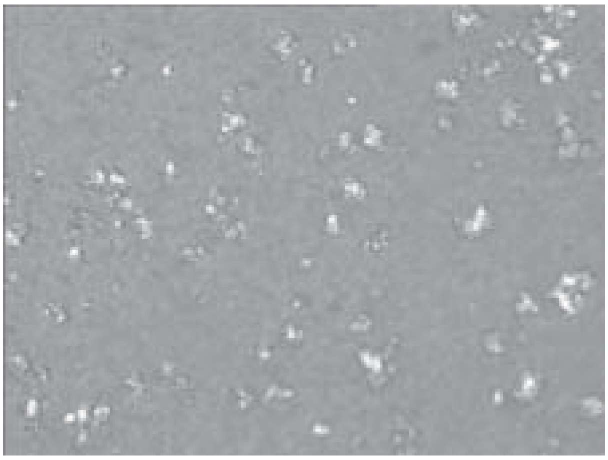

*Figure 4. Crystals of POME + 3% EP (at 20X magnification).*

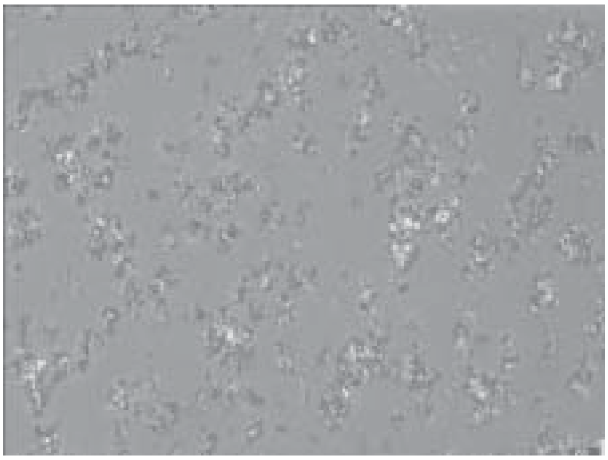

*Figure 5. Crystals of POME + 5% EP (at 20X magnification).*

## CONCLUSION

This study showed that the palm-based oligomer EP, can be used as a pour point and cloud point depressants for POME. The optimum dose to use is about 2% which depressed the pour point and cloud point to -3.0ºC and 3.9ºC , respectively. With the solid fat content reduced to 12.8% (0ºC) , 5.4% (5ºC) and 4.3% (10ºC). Further research should be done on depressing the pour point and cloud point of POME further and on prolonging its storage stability.

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