

Effects of Alkanols on the Solubilization of Methanol and Ethanol in Red Palm Oil for Biofuel

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Abstract: Solubilizations of methanol and ethanol in crude palm oil (CPO) and red palm oil (RPO) were studied by using different hydrocarbon chain-length alkanols (C₄-C₁₂) as solubilizers. Ternary phase diagrams of oil/methanol/alkanol and oil/ethanol/alkanol were constructed to determine the solubilization (isotropic) region. Results showed that the solubilization of methanol and ethanol is more favourable in unsaturated RPO than in saturated CPO in the presence of long-chain alkanols. The relatively large isotropic regions were formed with long-chain alkanols in both the methanol and ethanol systems. The order of decreasing isotropic regions in both methanol and ethanol systems was dodecanol > decanol > octanol > octan-2-ol > hexanol > pentanol > butanol > *t*-butanol. The branched chain alkanols and mixed oleyl alcohol/alkanol do not promote solubilization. Cold-stability test has shown all isotropic solutions were stable at 24°C for both methanol and ethanol systems. Kinematic viscosity of the selected isotropic solutions increased with the increase in both the chain length and percentage of alkanols. Long-chain alkanols (dodecanol, decanol and octanol) showed a steady increase in kinematic viscosity with increasing alkanol content. Solubilization of RPO/methanol/medium-chain alkanols (butanol, pentanol and hexanol) systems significantly reduced the kinematic viscosity of RPO from 43.7 mm²s⁻¹ to the range allowable for No. 2 diesel fuel (1.9 - 4.1 mm²s⁻¹ at 40.0°C).

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Key words: Solubilization, palm oil, biodiesel, kinematic viscosity, phase diagram

1 Introduction

The issues of environmental awareness and the possible depletion of fossil fuels have attracted interest to a 'green' renewable biofuel, based on vegetable oils. Efforts are under way in many countries to convert vegetable oils to liquid biofuels as a substitute for diesel fuel. Research on fatty acid methyl ester derivatives of vegetable oils and animal fats, termed as biodiesel (1) has progressed rapidly in Europe and in the USA fol-

lowing the energy crisis of the 70s. Fatty acid methyl esters of soybean (2,3), rapeseed (4), sunflower (5), safflower (6) and palm oils (7,8) are among the most extensively investigated biodiesel for internal combustion engines. Other oils studied are corn, cottonseed, peanut, used frying oil and tallows (9). Vegetable oils can be transformed into alternative diesel fuels by either; i) chemical methods such as transesterification reaction with methanol to produce methyl ester derivative, amidation reaction using diethylamine, and pyrolysis to obtain paraffin and olefin; ii) by physical methods such as blending with diesel fuel, using them in a pure (unmodified) form, winterization to remove the more

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saturated high melting glycerides and making microemulsions with alcohols (1); or iii) by enzymatic methods (5). Details of production methods and performances of individual oil related to fuel properties have been reviewed by Srivastava and Prasad (9) and Bhattacharyya and Reddy (10). The main problem encountered with vegetable oils as biodiesel is their relatively high viscosities, ranging between 30 to 40 mm²/s at 38°C (9) or up to 12 times that of no.2 diesel fuel (maximum viscosity allowable is 4.10 mm²/s (11)). The high viscosity of vegetable oils is due to their large molecular mass (three or more times higher than diesel fuel) and their chemical structures. These factors interfere with the injection process that leads to poor fuel atomization and causes incomplete combustion, which resulted in carbon deposition and injector coking. To date, only fatty acid methyl ester (FAME) derivatives of vegetable oils have shown promise result as biodiesel, since their fuel properties are similar to that of diesel fuel. Converting the triglyceride oils to FAME through a transesterification process reduces the molecular weight to one-third that of triglyceride, reduces the viscosity by a factor of eight or between 3.4 to 5.7 mm²/s (close to diesel fuel) and increases the volatility. FAME biodiesels from rapeseed, soybean and palm oils have already on commercial production in European countries (French, Italy, Germany and Austria), the USA and Malaysia respectively (1, 4, 9). However, results on field trials have shown that vegetable oil biodiesel performed satisfactorily in short-term tests, but their long-term performance still remains questionable due to heavy deposition problem and significant engine wear. In spite of this, biodiesel is environmentally friendly because it reduces emission of CO, hydrocarbons and particulate matters (PM), in addition to sulfur-free fuel (12).

Recently, unmodified crude palm oil (CPO) has been tested as a fuel in diesel engines (13), after a successful engine trial on palm fatty methyl esters as diesel fuel (7), but most of the problems encountered were associated with the high viscosity of CPO, especially in the morning, when the oil was solidified. The melting temperature of CPO is about 33 - 39°C, and it easily solidifies at ambient temperature (about 29°C). It is therefore of great interest to formulate CPO and its product, i.e red palm oil (RPO) into a stable solution with sufficiently low viscosity for use as alternative diesel fuel. The viscosity of CPO and RPO could reduce by a solu-

bilization process with short-chain alcohols and amphiphiles or co-surfactant (1, 14).

Methanol and ethanol as fuel extenders are less soluble in vegetable oils. Their solubility can be increased substantially when an amphiphilic compound such as alkanol is added to the system (15, 16). Medium and long-chain alkanols (from C₄ to C₁₄) have been extensively studied as co-surfactants for solubilization of methanol and ethanol in triolein, soybean, sesame and sunflower oils (16-18). Dunn and Bagby (14) used mixed fatty alcohol/alkanol systems to investigate the solubilization of methanol in triolein and soybean oils. These studies showed that the amphiphile or amphiphilic systems used are effective solubilizers for methanol and ethanol in triglyceride oils. The three-components mixtures (oil, methanol and amphiphile) form a clear, homogeneous, one-phase or isotropic solution. Dunn and Bagby (14) have suggested that solubilization in a non-aqueous system proceeds *via* co-solvency rather than a microemulsification process. A microemulsion is formed only when water is added to the solubilized system (16). A nonaqueous microemulsion could also be formed with the amphiphile (alkanol), but under limited conditions (14, 17, 18).

Crude and red palm oils are relatively saturated (iodine-value, IV, less than 57) (19, 20) compared to soybean (IV 130) and sunflower (IV 136) oils. Due to differences in their saturation properties, palm oil products (CPO and RPO) will exhibit different isotropic regions when mixed with fuel extenders and alkanols. Therefore, this study is to evaluate the isotropic regions of CPO and RPO with methanol and ethanol in the presence of alkanols (C₄ to C₁₂) as solubilizers. The kinematic viscosity of selected isotropic solutions is also being investigated to determine the effect of alkanol in the systems.

2 Experiments

2.1 Materials

Two commercial palm oil products, CPO and RPO, were obtained from a local oleochemical company. CPO is semisolid at room temperature (about 29°C) and contains about 500-700 ppm of carotene. RPO is a refined product of CPO, in which more than 80% (> 513 ppm) of the carotene originally presents in the CPO, is retained in the refined oil (20). It is liquid at room temperature with an iodine value of 57. Palm oil

samples were used as received. All alkanols used (*n*-alkanols, otherwise stated) were butanol, *t*-butanol, pentanol, hexanol, octanol, octan-2-ol, decanol, dodecanol and octadecanol (oleyl alcohol). The fuel extenders used were methanol and absolute ethanol. All alkanols and fuel extenders were of high purity (> 99% purity). They were purchased either from Fluka Chemical or Sigma Chemical Company.

2·2 Method

2·2·1 Solubilization experiments

Solubilization of methanol or ethanol in a CPO/alkanol mixture was conducted at $29 \pm 1^\circ\text{C}$. A mixture of CPO/alkanol (0.5 g) in a sample vial was titrated with methanol until a clear isotropic solution was obtained (when a turbid solution changed to a clear transparent solution as judged by visual observation). The mixture was vortexed (Thermolyne 37600 Mixer) for complete mixing, centrifuged at 5000 rpm to confirmed solubility and allowed to equilibrate in a constant-temperature bath at $29 \pm 1^\circ\text{C}$. The weight ratio of CPO to alkanol was varied but the total weight was kept constant at 0.5 g. A similar experiment was then repeated with RPO. A representative triangular phase diagram, depicting phase equilibria was constructed and an isotropic region was assigned. The boundary of an isotropic region was estimated by noting the turbid-to-clear transition.

2·2·2 Viscosity and particle-size measurements

From a ternary diagram, two lines were drawn across the phase diagram from the alkanol apex to meet the oil-methanol axis at 70:30 and 50:50 of oil to methanol ratios (lines A and B in **Fig. 2**). A similar line was drawn for the ethanol system at 70:30 of the oil to ethanol ratio (line C in **Fig. 3**). Isotropic solutions with the compositions corresponding to the selected points on the lines were prepared and the kinematic viscosity of each solution was determined with a calibrated suspended-level viscometer at $29 \pm 1^\circ\text{C}$. The particle size distribution was analyzed by photon correlation spectroscopy (PCS) with a Malvern Zetasizer 5000 Instrument.

3 Results and Discussion

Solubilization is the preparation of a thermodynamically stable isotropic solution of an insoluble or slightly soluble substance (*e.g.* methanol and ethanol) in a given solvent (*e.g.* triglyceride oil), by adding amphiphilic

compounds (*e.g.* alkanol) (21). **Figure 1** shows ternary phase diagrams of CPO/methanol/alkanol and CPO/ethanol/alkanol systems at $29 \pm 1^\circ\text{C}$. The regions on the right of the curves are one-phase (isotropic) solutions, whereas those on the left are two-phase (anisotropic) solutions. The isotropic regions formed in these systems were relatively small. Long-chain alkanols (octanol, octan-2-ol, decanol and dodecanol) only produce isotropic regions, which extended from the methanol or ethanol to alkanol apexes with oil content less than 10%. Medium-chain alkanols (butanol, *t*-butanol, pentanol, hexanol) did not form any isotropic solution. These results indicate that solubilization of methanol and ethanol in CPO is not favourable.

A large isotropic region was obtained when CPO was replaced with liquid RPO. The RPO/ethanol/alkanol system (**Fig. 3**) formed larger isotropic regions than the RPO/methanol/alkanol system (**Fig. 2**). In both systems, the isotropic regions curved from the ethanol or methanol apex towards the RPO apex and expanded to more than half of the phase diagram. The minima of the solubilization curves for some alkanols were 23% (dodecanol), 25% (decanol) and 27% (octanol) in the methanol system (**Fig. 2**). Similarly, in the ethanol system the minima for the same alkanols were found at 14%, 16% and 18% (**Fig. 3**). It was noticed that the area of the isotropic region increases by increasing the

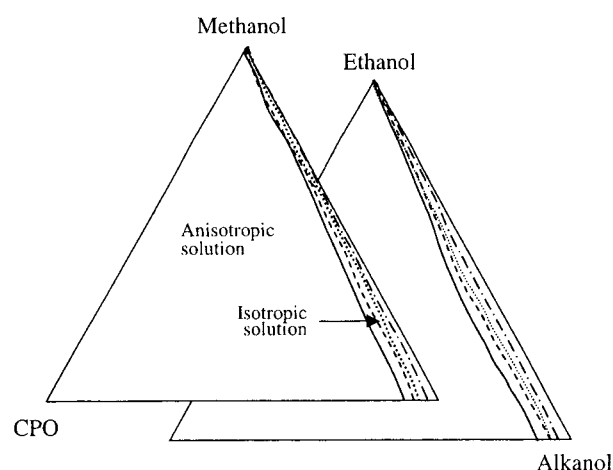


Fig. 1 Ternary Phase Diagrams of CPO/methanol/alkanol and CPO/ethanol/alkanol Systems at $29 \pm 1^\circ\text{C}$. Solubilization is less favourable in saturated CPO that leads to the formation of small isotropic regions (right side of the curve). Dodecanol (—), decanol (----), octanol (.....), octan-2-ol (— · — · —).

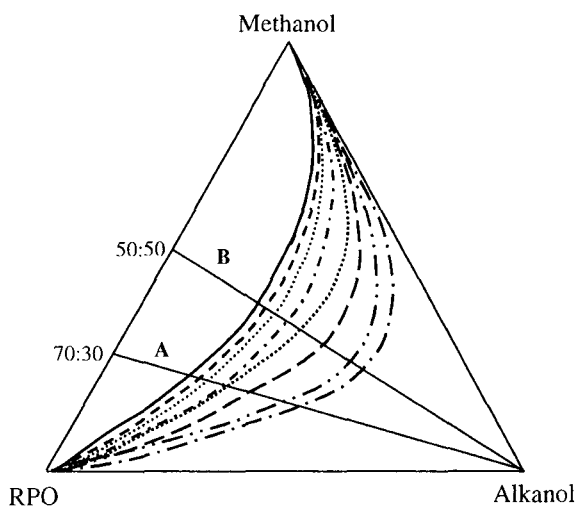


Fig. 2 Ternary Phase Diagram of RPO/methanol/alkanol System Showing Isotropic Regions (right side of the curve) at $29 \pm 1^\circ\text{C}$. Dodecanol (—), decanol (---), octanol (.....), octan-2-ol (-.-.-), hexanol (- - - -), pentanol (- - - - -), butanol (- - - - -) and *t*-butanol (- · - · -).

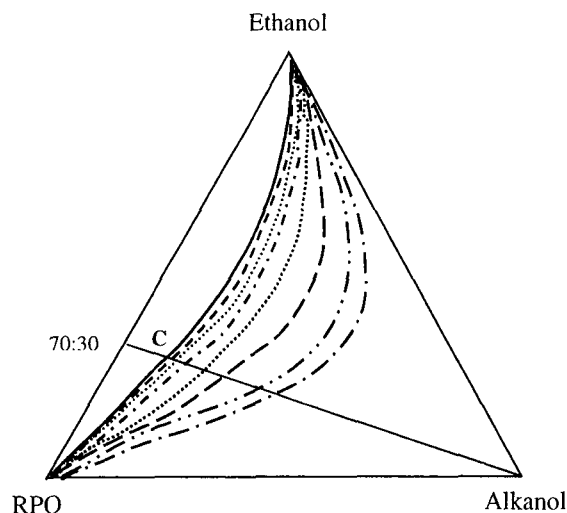


Fig. 3 Ternary Phase Diagram of RPO/ethanol/alkanol System Showing Isotropic Regions at $29 \pm 1^\circ\text{C}$. Refer to Figure 2 for legend.

hydrocarbon chain-length of alkanols. Association of the component mixture involving long-chain alkanols is probably more stable than the medium-chain alkanols, since the long hydrocarbon-chain (of alkanol) is more soluble in oil, as described by Dunn and Bagby (14). Such associations produced stable methanol-in-RPO and ethanol-in-RPO mixtures. The order of decreasing isotropic regions in both methanol and ethanol systems was dodecanol > decanol > octanol > octan-2-ol > hexanol > pentanol > butanol > *t*-butanol. The branched chain alkanols (*t*-butanol and octan-2-ol) do not promote solubilization as compared to the corresponding *n*-alkanols. Their isotropic regions were smaller than their *n*-alkanols counterparts.

This study has shown that the association of palm oil, alkanol, methanol or ethanol to form a homogeneous solution is more favourable in unsaturated RPO than in saturated CPO. Schwab and Pryde (16), and Schwab *et al.* (18) reported a similar result, where large isotropic regions were obtained for highly unsaturated soybean, sunflower and sesame oils. The relatively free movement of the component mixture in the less viscous medium, in unsaturated RPO, might enhance the interactions in the component mixture. These interactions lead to the formation of large isotropic regions. Photon correlation spectroscopy (PCS) measurements show the presence of particles with a diameter of less than 9 nm,

which is smaller than the microemulsion size (the lower limit of microemulsion size is 10 nm) (22). This indicates that no microemulsion is formed in the isotropic solutions. Schwab and Pryde (16) reported a similar result for nonaqueous system of triolein/methanol/2-octanol. Their study had shown that no microemulsion was formed in the system but just a molecular dispersion of triolein and methanol in 2-octanol.

There was no improvement in the solubilization of methanol in RPO when medium-chain alkanols were mixed with oleyl alcohol, (9:1, v/v) (Fig. 4). The size and pattern of the isotropic regions were similar to those of the RPO/methanol/alkanol system (Fig. 2). This suggests that alkanol mixed with oleyl alcohol do not significantly promote the solubility of methanol in RPO.

Cold-stability test has shown that all isotropic solutions are stable at 24°C for both methanol and ethanol systems. The test was performed on solutions prepared with compositions corresponding to the selected points on the lines A, B and C (Figs. 2 and 3) and kept in a water bath for 24 hours at the test temperature. At a lower temperature than 20°C some of the isotropic mixtures were found unstable, where the solid particles were precipitated out.

Figures 5 and 6 show kinematic viscosities at $29 \pm 1^\circ\text{C}$ vs percent alkanol at 70:30 (line A) and 50:50 wt ratios (line B) of mixed RPO/methanol respectively. The kinematic viscosity was dependent on the alkanol

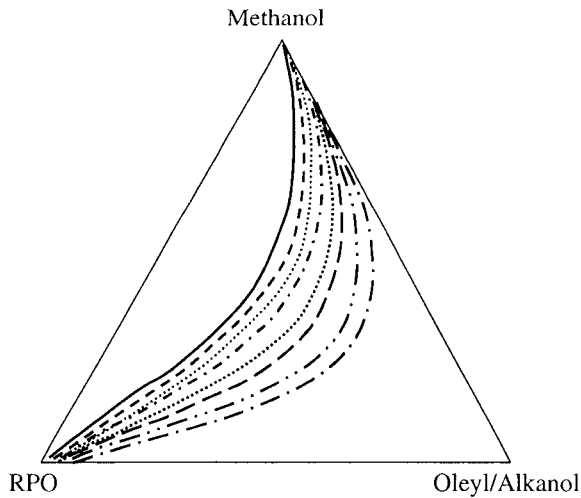


Fig. 4 Ternary Phase Diagram of RPO, Methanol and Mixed Oleyl Alcohol-alkanol (1:9, v/v) System at $29 \pm 1^\circ\text{C}$. No significant change in pattern and size of the isotropic region as compared to RPO/methanol/alkanol system. Refer to Figure 2 for legend.

chain-length and its percentage. Generally, the viscosity was higher for longer chain-length alkanols. Dodecanol had the highest viscosity where the values varied from 9.6 to $13.4 \text{ mm}^2\text{s}^{-1}$ for 70:30 wt ratio (**Fig. 5**) and 7.2 to $13.2 \text{ mm}^2\text{s}^{-1}$ for 50:50 wt ratio (**Fig. 6**). Butanol gave the lowest viscosity in both the 70:30 and 50:50 of RPO/methanol wt ratios. The values varied from 2.7 to $4.8 \text{ mm}^2\text{s}^{-1}$ in both wt ratios. The kinematic viscosity of the solutions containing medium-chain alkanols (butanol, pentanol and hexanol) was slowly decreased with an increasing percentage of alkanol up to 90%, whereas the long-chain alkanols (octanol, decanol and dodecanol) showed a steady increase in kinematic viscosity with increasing alkanol content. As expected, a dilution effect occurs in solutions containing a large amount of medium-chain alkanols. This effect leads to gradual reduction in viscosity as the percentage of alkanol increases. Because long-chain alkanols are viscous an increase in their percentage results in higher viscosity. In addition, the attraction between the long hydrocarbon-chains (tailgroups) of the alkanols and RPO, which might lead to aggregation of the component mixture, also contributes to the increase in viscosity as reported by Dunn and Bagby (14) and Peter *et al.*(23). This resulted in a steady increase in viscosity, as observed in octanol, decanol and dodecanol systems.

At 50:50 wt ratio, no significant change in viscosity

was observed, except that the medium-chain alkanols had a slight increase in viscosity at higher alkanol content (**Fig. 6**). The results also showed that the minimum amount of alkanol to achieve miscibility differs depending on the chain-length of the alkanol. The longer-chain length requires a lesser amount of alkanol to achieve miscibility compared to the shorter chain-length. **Figure 5** shows that a homogeneous mixture of methanol in RPO could be achieved at approximately 26% dodecanol or 42% butanol. Similar phenomena also occurred in an ethanol system as shown in **Fig. 7**. The range of viscosity was slightly higher than in the methanol system. In general, the solubilization process drastically reduced the kinematic viscosity of RPO,

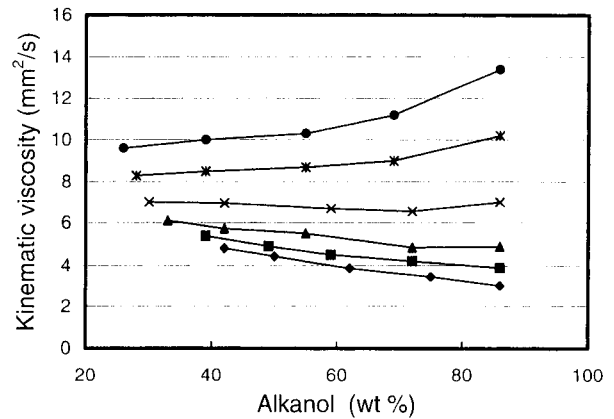


Fig. 5 Kinematic Viscosities of Isotropic Solutions at $29 \pm 1^\circ\text{C}$ for RPO/methanol/alkanol System at Ratio of RPO/methanol of 70:30 wt%. Dodecanol, ●; decanol, *; octanol, ×; hexanol, ▲; pentanol, ■; butanol, ◆.

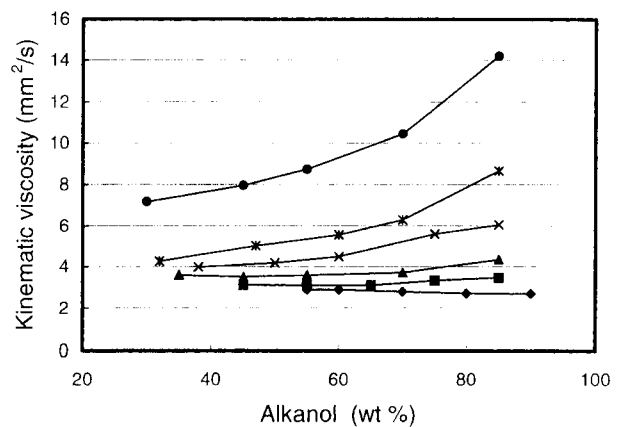


Fig. 6 Kinematic Viscosities of RPO/methanol/alkanol System at $29 \pm 1^\circ\text{C}$ for RPO/methanol Ratio of 50:50 wt%. Refer to Figure 5 for legend.

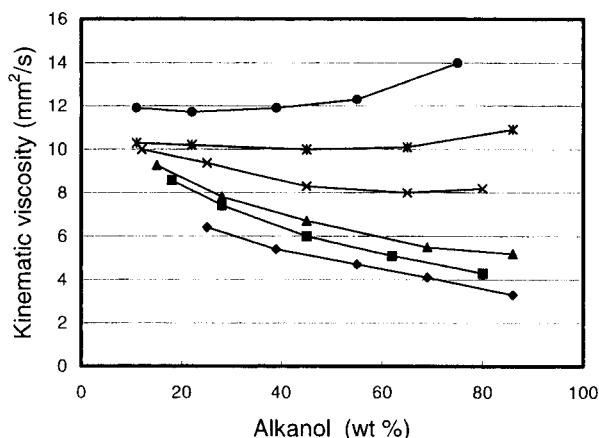


Fig. 7 Kinematic Viscosities of RPO/ethanol/alkanol System at $29 \pm 1^\circ\text{C}$ for RPO/ethanol Ratio of 70:30 wt%. Refer to Figure 5 for legend.

from the initial value, $43.7 \text{ mm}^2\text{s}^{-1}$ (as determined in this study) to well below $15.0 \text{ mm}^2\text{s}^{-1}$. Isotropic solutions of RPO/methanol/medium-chain alkanol gave kinematic viscosities within the range of No. 2 diesel fuel, $1.9 - 4.1 \text{ mm}^2\text{s}^{-1}$ at 40.0°C (the range specified by the American Society for Testing and Material, ASTM) (11).

4 Conclusion

The long-chain alkanols (dodecanol, decanol and octanol) are good solubilizers for methanol and ethanol in RPO but, with respect to viscosity, the medium-chain alkanols (butanol, pentanol and hexanol) are potential solubilizers for the formulation of palm oil based biofuel. The methanol system, on other hand, gives an isotropic solution of much lower kinematic viscosity than the ethanol system, particularly with butanol as a solubilizer.

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