Journal of Industrial Technology 11 (1), 2002, 1-6

SHORT COMMUNICATION

EFFECTS OF MIXED FATTY ALCOHOL/ALKANOL ON THE SOLUBILIZATION OF METHANOL AND ETHANOL IN PALM OIL FOR BIODIESEL

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RINGKASAN: *Solubilisasi metanol dan etanol dalam minyak sawit olein dan minyak sawit merah telah dikaji menggunakan campuran alkohol berlemak/alkanol sebagai pensolubilisasi. Kawasan solubilisasi kemudian ditentukan daripada gambarajah pertigaan. Keputusan menunjukkan solubilisasi metanol dan etanol dalam minyak sawit olein dan minyak sawit merah adalah tinggi dengan kehadiran campuran alkohol berlemak/alkanol. Alkanol seperti dekanol, oktanol dan okta-2-ol membentuk kawasan isotropic yang lebih besar. Urutan keluasan kawasan isotropik dalam kedua-dua sistem adalah butanol < pentanol < heksanol < oktan-2-ol < oktanol < dekanol. Semua larutan isotropik didapati stabil pada 24°C, tetapi pengenapan berlaku pada suhu dibawah 20°C.*

ABSTRACT: Solubilisation of methanol and ethanol in palm olein and red palm oil were studied using mixed fatty alcohol/alkanol as solubiliser. Ternary phase diagrams were constructed to determine the solubilisation (isotropic) regions. Results showed that methanol and ethanol were readily solubilised in palm olein and red palm oil in the presence of mixed fatty alcohol/alkanol. Large isotropic regions were formed with mixtures containing long-chain alkanols (decanol, octanol and octa-2-ol). The order of increasing isotropic region in both fatty alcohol systems was butanol < pentanol < hexanol < octan-2-ol < octanol < decanol. Cold-stability test showed that all isotropic solutions were stable at 24°C, but sedimentation occurred below 20°C.

KEYWORDS: Palm oil, solubilisation, isotropic, fatty alcohol.

INTRODUCTION

Vegetable oil based biofuel has become important due to it being renewable and environmental friendly. Unmodified crude palm oil (CPO) has been tested recently as fuel in diesel engine (Hitam and Salmah, 1995), followed by a successful engine trial on palm fatty methyl esters as diesel fuel (Choo *et al.,* 2000). However, most of the problems encountered were associated with the high viscosity of CPO which interfered with the injection process and led to incomplete combustion. Palm olein (PO) and red palm oil (RPO) are relatively viscous as compared to soybean, sunflower and sesame oils. This characteristic hindered the use of palm oil as diesel fuel. It is therefore of great interest to formulate palm oil products into a stable solution which is more suitable for engine operation. This could be done by solubilization process using short-chain alcohols (as fuel extender) and amphiphiles or co-surfactant (Krawczyk, 1996; Dunn and Bagby, 1994). Solubilization is the preparation of a thermodynamically stable isotropic solution of insoluble or slightly soluble substance (e.g methanol and ethanol) in a given solvent (e.g. triglyceride oil), by the addition of amphiphilic compound (Drew Myer, 1999).

Methanol and ethanol are used as fuel extenders though they are less soluble in vegetable oils. Their solubility can be increased substantially when an amphiphilic compound or cosurfactant such as alkanol is added to the system (Vesala and Rosenholm, 1985; Schwab and Pryde, 1985). Solubilization of methanol and ethanol in triolein, soybean, sesame and sunflower oils using medium and long-chain alkanols (from C_4 - C_{14}) has been extensively investigated (Schwab and Pryde, 1985; Dunn *et al.,* 1992; Schwab *et al.,* 1983). Dunn and Bagby (1994) used mixed amphiphile systems of fatty alcohol/1-alkanol to investigate the solubilization of methanol in triolein and soybean oil. Their results have shown that addition of fatty alcohol/alkanol mixtures dramatically affected the miscibility between methanol and triglyceride oils. The three-component mixtures (oil, methanol and amphiphile) form a clear, homogeneous, one-phase solution, also termed as isotropic solution.

Palm olein and RPO are relatively saturated (iodine-value, IV less than 57) (Choo *et al.,* 1993) compared to soybean (IV 130) and sunflower (IV 136) oils, which are extensively investigated for biodiesel (Schwab and Pryde, 1985; Dunn and Bagby, 1994). We have recently reported solubilizations of methanol and ethanol in palm oil (Dzulkefly *et al.,* 2001a) and red palm oil (Dzulkefly *et al.,* 2001b) using alkanols as solubilizers. The present study is to evaluate the isotropic regions of PO and RPO with methanol and ethanol in the presence of mixed fatty alcohol/alkanol as solubilizers.

MATERIALS AND METHODS

Samples of refined, bleached and deodorized (RBD) PO and RPO were obtained from a local oleochemical company. PO is liquid at room temperature (about 29°C) and is obtained by

fractionation of RBD palm oil. RPO is a refined product of CPO, in which more than 80% (>513 ppm) of the carotene originally present in the CPO is retained in the refined oil (Choo *et al.*, 1993). Alkanols used (*n*-alkanols, unless otherwise stated) were butanol, pentanol, hexanol, octanol, octan-2-ol and decanol. Fatty alcohols were dodecanol (C_{12}-OH) and octadecenol ($C_{18:1}$-OH) and the fuel extenders used were methanol and absolute ethanol. All alkanols, fatty alcohols and the fuel extenders were of high purities (> 99% purity). Solubilization experiments were conducted at 29 ± 1°C in the presence of mixed fatty alcohol/alkanol (1:9, v/v) as solubilizer. A mixture of fatty alcohol, alkanol and PO (0.5 g) was titrated with ethanol until an 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 confirm solubility and allowed to equilibrate in a constant-temperature bath at 29 ± 1°C. The weight ratio of PO to mixed fatty alcohol/alkanol was varied but the total weight was kept constant at 0.5 g. A similar experiment was repeated using 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. A cold-stability test was also performed on the isotropic solutions prepared with compositions corresponding to randomly selected points in the isotropic region.

RESULTS AND DISCUSSION

Figure 1 shows ternary phase diagrams of PO, ethanol with mixed $C_{18:1}$-OH/alkanol (Figure 1A) and mixed C_{12}-OH/alkanol (Figure 1B) systems at 29 ±1°C. The regions on the right of the

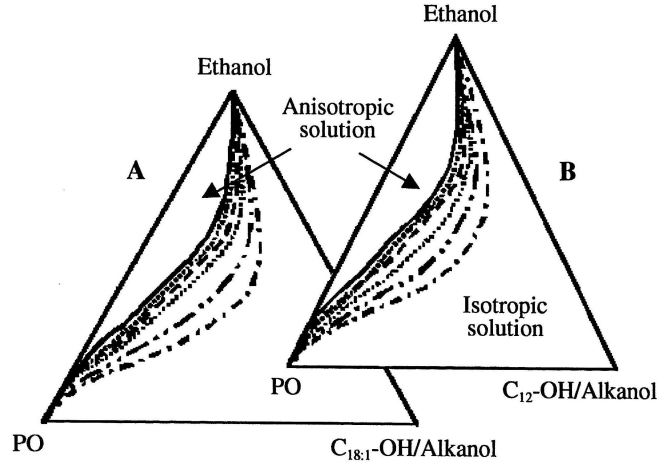

Figure 1: *Ternary phase diagrams of PO with ethanol and mixed fatty alcohol/ alkanol systems at 29 ± 1°C. A: mixed $C_{18:1}$-OH/alkanol; B: mixed C_{12}-OH/alkanol.*
Decanol (———), octanol (.....), octan-2-ol (----------),
hexanol (.....), pentanol (—..—..), butanol (—.—.—)

curves are one-phase (isotropic) solutions, whereas those on the left are two-phase (anisotropic) solutions. Both the $C_{18:1}$-OH/alkanol and C_{12}-OH/alkanol mixed amphiphiles produced large isotropic regions, which curved from ethanol apex towards PO or RPO apex and covered more than half of the phase diagrams. It was noticed that the area of the isotropic region increases by increasing the hydrocarbon chain-length of alkanols irrespective of the fatty alcohol used. The order of increasing isotropic region in both the $C_{18:1}$-OH and C_{12}-OH systems was butanol < pentanol < hexanol < octan-2-ol < octanol < decanol. This phenomenon probably occurred due to the increased stability of the association of component mixture involving long-chain alkanols. The long hydrocarbon-chain (of alkanol) is more soluble in oil than the shorter-chain, as described by Dunn and Bagby (1994). Thus, such associations produce a stable ethanol-in-PO or RPO mixture. The results also showed that the presence of different chain-length fatty alcohol (C_{12}-OH and C_{18}-OH) in the mixture did not affect the area of isotropic region. Based on our previous results (Dzulkefly *et al.*, 2001a, 2001b), the isotropic solution is a monomer solution.

Similar trends were observed when PO was replaced with RPO (Figure 2), except for the RPO/ethanol/C_{12}-OH/alkanol system (Figure 2B). The presence of C_{12}-OH in the system does not favour solubilization of short-chain alkanols, typically butanol and hexanol. Their solubility areas or isotropic regions were very much smaller than those of PO systems. Similarly, when ethanol was replaced with methanol, smaller isotropic regions were formed (Figure 3). The short-chain methanol was less soluble in PO and RPO but the trend of increasing isotropic region remained the same.

This study has shown that the association of PO or RPO with ethanol and mixed fatty alcohol/alkanol occurred readily except for the methanol system. The association led to the formation

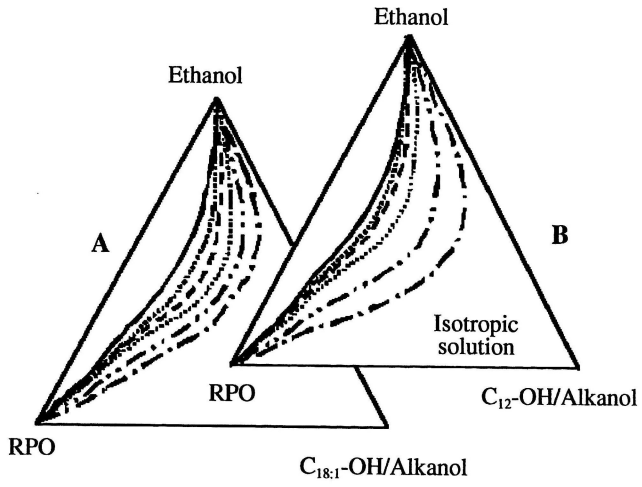

Figure 2: *Ternary phase diagrams of RPO with ethanol and mixed fatty alcahol/alkanol systems at 29 ±1°C. Refer to Figure 1 for legend.*

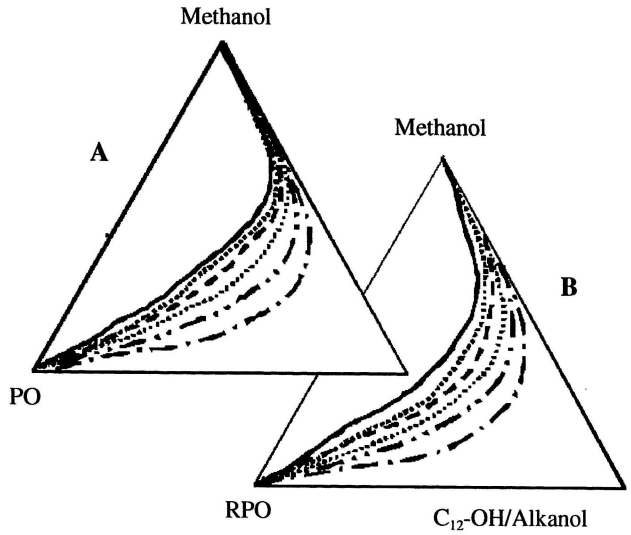

Figure 3: *Ternary phase diagrams of PO and RPO with methanol and mixed fatty alcohol/alkanol systems at 29 ± 1°C. Refer to Figure 1 for legend.*

of large isotropic regions. The size and pattern of isotropic region are not affected by the hydrocarbon chain-length of fatty alcohols. These results indicate that mixing fatty alcohol with alkanol was effective in solubilising ethanol in PO and RPO. Dunn and Bagby (1992) have reported a similar result, where the miscibility between methanol and triglyceride was dramatically increased in the presence of fatty alcohol/1-alkanol amphiphiles and was independent of the fatty alcohol chain-length. Cold-stability test has shown that all the isotropic solutions of PO and RPO were stable at 24°C (bath temperature) for both fatty alcohol systems. The test was performed on solutions prepared with compositions corresponding to the selected points in the isotropic region and was kept in a water bath for 24 hours at the test temperature. However, below 20°C some of the isotropic mixtures were found to be unstable, where more solid particles were precipitated out. This could be due to the crystallization of palm oil.

As a summary, our results suggest that mixtures of fatty alcohol with alkanol of longer chain-length (decanol, octanol and octa-2-ol) are good solubilizers for ethanol in PO and RPO. The isotropic region formed is not affected by the hydrocarbon chain-length of fatty alcohols but increases with the chain-length of alkanols.

ACKNOWLEDGEMENT

The support of this research by the Ministry of Science, Technology, and the Environment Malaysia, under IRPA grant no. 51630, is gratefully acknowledged.

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