Continuous Transmethylation of Palm Oil in an Organic Solvent

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Palm oil was transmethylated continuously at 70°C in an organic solvent with sodium methoxide as a catalyst. The optimum ratio of toluene to palm oil is 1:1 (v/v). When the methanol-to-oil molar ratio was 13:1, transmethylation was 96% complete within 60 seconds. At higher molar ratio (17:1), transmethylation was 99% complete in 15 seconds. For lower molar ratios of methanol-to-oil (9:1 and 5.8:1), yields of palm oil methyl ester (POME) were 84 and 58%, respectively. Benzene was also a good solvent for transmethylation, but the yield of POME was slightly lower than toluene. Tetrahydrofuran did not accelerate transmethylation.

KEY WORDS: **Palm oil, palm oil methyl ester, transmethylation, vegetable oil.**

Vegetable oils and their methyl esters have long been considered as potential alternative fuels for diesel engines (1–3), but research and development are relatively slow. This may be partly due to renewed availability of the more economical petroleum-derived fuels. Vegetable oil methyl esters (VOMEs) have certain advantages over neat vegetable oils. Viscosities of VOMEs are significantly lower than the oils (4–6), thereby reducing droplet size upon injection into the cylinder and facilitating combustion (6). Cetane indices (7) and gross heat of combustion per unit weight (8) of VOMEs are slightly higher than for the oils. VOMEs have less tendency to polymerize three-dimensionally than the oils (6). Thus, transesterification of vegetable oils has been reinvested by numerous investigators (9–11). Formo (12) has reported that transmethylations proceed rapidly in the presence of alkaline catalysts and that reactions are about 4,000 times faster than those catalyzed by the same amount of HCl. Freedman *et al.* (9) found that transmethylation, with alkaline catalysts, is 99% complete within one hour at 60°C or higher when the molar ratio of methanol-to-oil is 6:1. Heterogeneous catalytic transmethylation requires drastic conditions and longer time periods (10). Continuous transmethylation also has been reported (11). In this paper, we report a rapid continuous transmethylation in the presence of a mutual solvent for methanol and palm oil.

EXPERIMENTAL PROCEDURES

Materials. Refined palm oil was obtained from Palmco (Bangkok, Thailand). Benzene, toluene and methanol (technical grade) were redistilled before use. Water content of methanol was checked by gas-liquid chromatography on a Porapak Q column with thermal conductivity detector. A stoichiometric amount of sodium metal (Aldrich, Madison, WI) was added and methanol was redistilled. Tetrahydrofuran (high-performance liquid chromatography grade) was obtained from J.T. Baker (Phillipburg, NJ). Sodium methoxide (30%) in methanol was obtained from Fluka A.G. (Buchs, Switzerland). Monostearin and distearin were purchased from Sigma Chemical Co. (St. Louis, MO). Palm oil methyl ester (POME) was prepared in our laboratory by alkali-catalyzed transmethylation in a large excess of methanol. POME purity was determined by HPLC.

Transmethylation. Transmethylation of palm oil was carried out in a continuous stainless steel reactor as shown in Figure 1. The two HPLC pumps (Waters Model 510 and 6000 A) were used to deliver 0.5% methanolic sodium methoxide in reservoir A and solvent-diluted palm oil in reservoir B. They were mixed at a three-way connector, E prior to entering into the stainless steel reactor. Total flow and percent A and B were controlled by a gradient controller C (Waters model 680, Waters Associates, Milford, MA). The reactor coil was immersed in a homemade water bath, set at 70°C. Two reactors (2 mL and 40 mL) were used in this study. These two reactors in combination with different flow rates, from 0.5 to 8 mL per min, would give the desired residence time for transmethylation.

High-performance liquid chromatography (HPLC). The HPLC method of Christopoulou and Perkins (13), with a slight modification, was used for the separation and quantitation of palm oil and POME. The HPLC system consists of a Waters Model 6000 A pump, a Rheodyne 7125 valve injector, a Waters model 401 differential refractive index detector and a Zonan and Kipp M8 two-channel recorder. Only one Phenogel 100Å column (Phenomenex, Torrance, CA) was used. The column is 30 × 0.78 ID, pack-

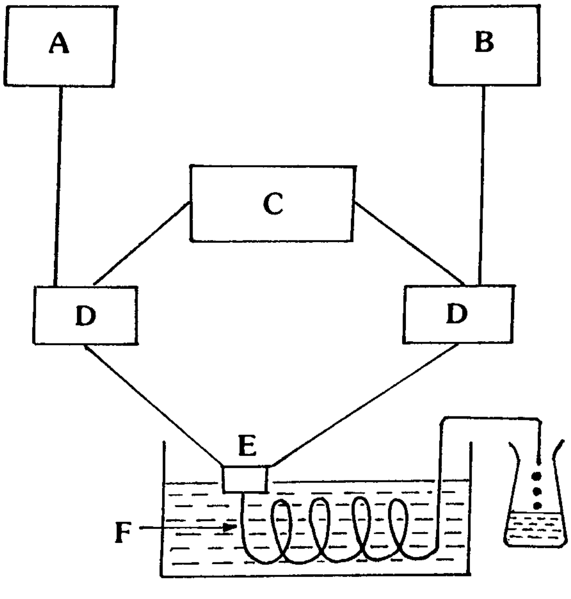

FIG. 1. Schematic diagram of continuous transmethylation of palm oil. A, reservoir containing 0.5% sodium methoxide in methanol; B, reservoir containing solvent-diluted palm oil; C, pump controller (Waters Model 680); D, HPLC pump; E, tee connector; and F, reactor coil.

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ed with styrene/divinyl benzene copolymer beads with a particle size of 10 μM. The column is protected with a Waters column guard packed with silica.

RESULTS AND DISCUSSION

Separation and quantitation. Palm oil, 1,2-distearoyl glycerol, 1-stearoyl glycerol and POME are completely separated, as shown in Figure 2. We found that the silica column guard has a beneficial effect on the separation of diglyceride and palm oil. Without the silica column guard, there is only partial separation of these two components. Because mono- and diglycerides of palm oil were not available and their refractive index detector responses may be different from mono- and distearin (13), they were not quantitated. Transmethylation was followed by disappearance of palm oil and formation of POME.

Transmethylation without solvent. Freedman *et al.* (9) reported that transmethylation of vegetable oil, with alkaline catalysts, is 99% complete within one hour at 60°C when the molar ratio of alcohol-to-oil is 6:1. When these conditions are used in a continuous reactor (1.0 mm ID × 50 meters), the yield of POME never exceeds 50%. This may be due to separation of the two reactants, methanol and palm oil, because there is not any mechanical means to help mix the two reactants. They are only partially mixed at the three-way connector.

Transmethylation in toluene. Toluene is a good solvent for vegetable oil and miscible with methanol. Thus, it is expected that toluene may help mix methanol and oil in the reactor and promote transmethylation. Figure 3 shows that transmethylation is rapid and gives high POME. At a ratio of toluene-to-oil of 1:1 (v/v) and alcohol-to-oil molar ratios of 5.8:1, 9:1, 13:1 and 17:1, yields of POME were 57%, 87%, 96% and 99%, respectively. An 86% yield is observed in 15 seconds (with a molar ratio of 13:1) and the yield of POME increases to 90% and 96% in 30 and 60 seconds, respectively. The yield subsequently decreases slightly to 95%. The difference is within experimental error, but lower yield of POME was observed consistently in other experiments at longer residence time, or more correctly, at lower flow rate. We believe that at a lower flow rate, the pressure at the mixing tee is lower and mixing of the two reactants is less efficient. The effect is more pronounced when the alcohol-to-oil molar ratio is lower (Fig. 3). At a molar ratio of 17:1, reaction is 98% complete within 15 seconds.

When the toluene-to-oil ratio is increased to 2:1 (v/v), a comparable rate of transmethylation and yield of POME are obtained (Fig. 4). But when the toluene-to-oil ratio

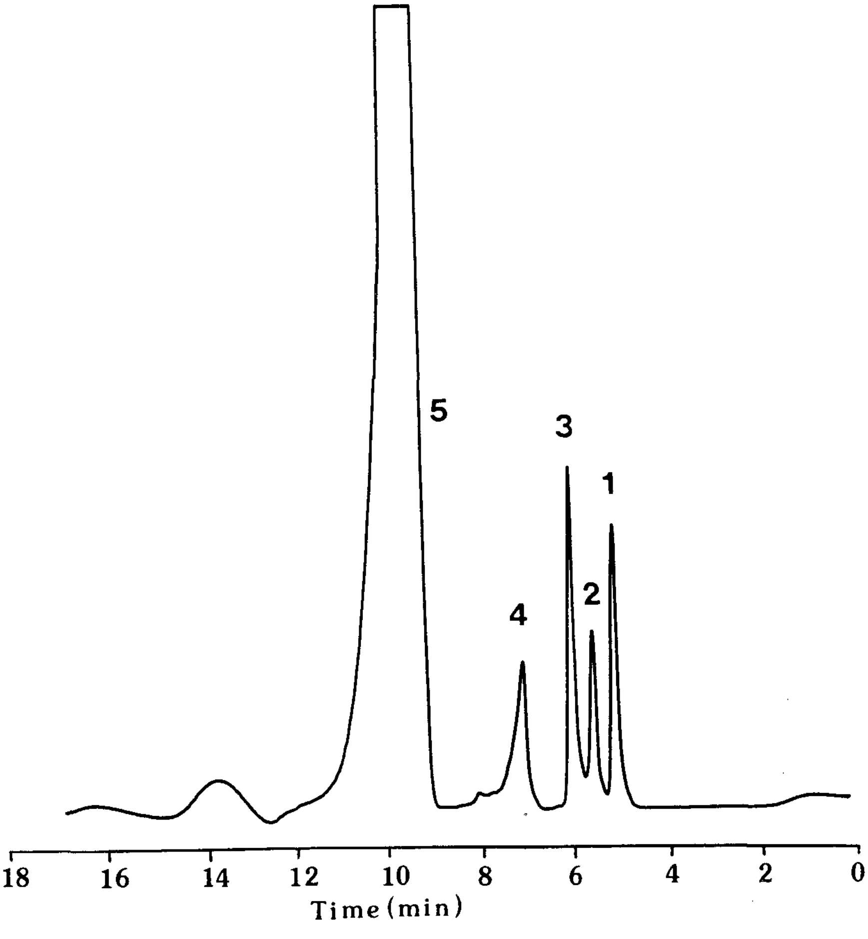

FIG. 2. Size-exclusion liquid chromatogram of reference compounds: 1, palm oil; 2, distearin; 3, palm oil methyl ester; 4, monostearin; and 5, methanol.

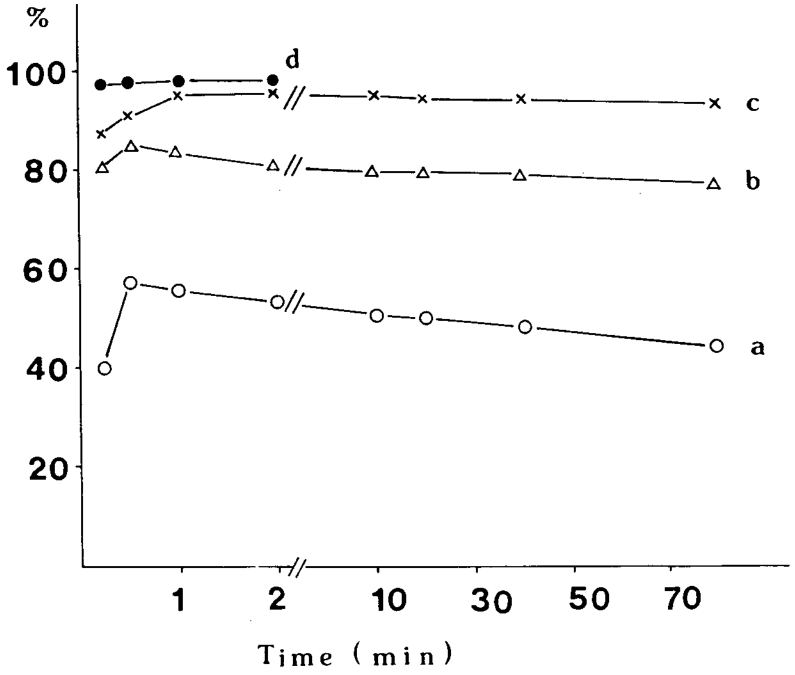

FIG. 3. Transmethylation of palm oil in toluene with toluene-to-oil ratio of 1:1 (v/v) and methanol-to-oil molar ratio: a, 5.8:1; b, 9:1; c, 13:1; and d, 17:1.

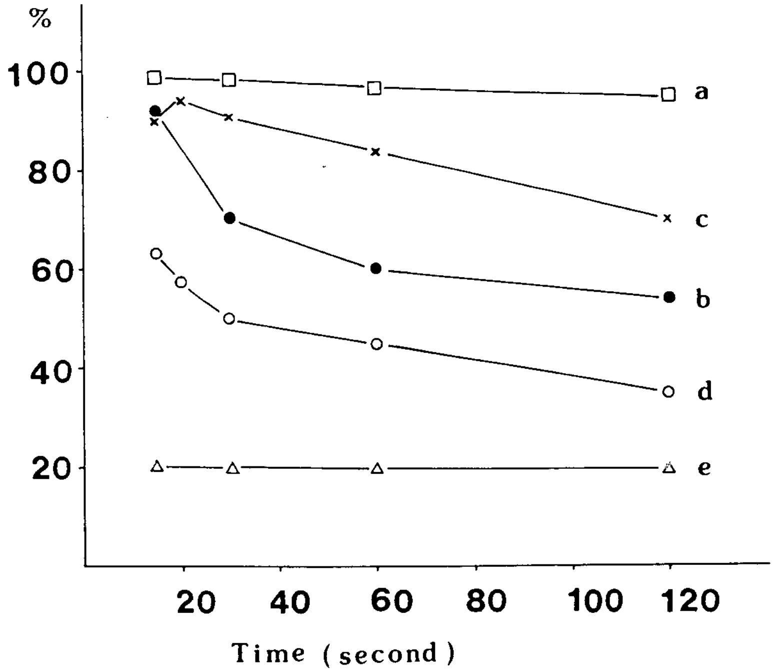

FIG. 4. Transmethylation of palm oil: a, toluene-to-oil ratio 2:1 (v/v) and methanol-to-oil molar ratio 10:1; b, toluene-to-oil ratio 1:2 (v/v) and methanol-to-oil molar ratio 13.5:1; c, benzene-to-oil ratio 1:1 (v/v) and methanol-to-oil molar ratio 13:1; d, benzene-to-oil ratio 1:1 (v/v) and methanol-to-oil molar ratio 5.8:1; e, tetrahydrofuran ratio 1:1 (v/v) and methanol-to-oil molar ratio 13:1.

is reduced to 1:2, the yield of POME is reduced (Fig. 4).

Transmethylation in other solvents. Benzene is not as good as toluene in promoting transmethylation. Figure 4 shows that at methanol-to-oil molar ratios of 5.8:1 and 13:1, and a benzene-to-oil ratio of 1:1 (v/v), the highest yields are 63 and 94%, respectively. Transmethylation in benzene is very rapid but yield of POME is low, especially at lower flow rates (or longer residence time). It is observed that glycerol formed in the presence of benzene precipitates slower and much less than in toluene. Glycerol in solution helps drive the equilibrium back to the left, thereby lowering the yield of POME.

Although tetrahydrofuran is a good mutual solvent for oil and methanol, transmethylation is unsatisfactory. About 20% POME is obtained in the first two minutes, and the solvent was not investigated further. Glycerol formed in tetrahydrofuran remains in solution and does not separate.

Based on results of this investigation, toluene is the most promising solvent in promoting transmethylation. Reaction proceeds rapidly without a mechanical agitator, thus a reactor can be easily designed and scaled up.

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