# *In Situ* Trans-Esterification of Residual Oils in Spent Bleaching Clays from Vegetable Oil Refineries

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**Abstract:** Spent bleaching clays (SBCs) from vegetable oil refineries are industrial wastes. The clays contain large amount of oils (20-25%), which are good feedstock for biodiesels. Non-thermal *in situ* trans-methylation and trans-ethylation of oils in the SBC from rice bran oil (RBO), crude palm oil (CPO) and palm kernel oil (PKO) are rapid and can be accomplished in minutes with an alkaline catalyst. Thus, the process may possibly be used for large scale preparation of ethyl biodiesel.

## INTRODUCTION

Biodiesel has been widely accepted for use in high speed diesel engine in many countries. Therefore, the growth in biodiesel production worldwide would lead to the development of novel processes that are more rapid, cost-effective and more efficient [1]. However, the major raw materials used for biodiesel production are vegetable oils and animal fats. Types of fats and oils used depend very much on the availability and they vary from country to country. Although palm oil can be produced domestically and it is the main raw material for the commercial biodiesels in Thailand, the supply is still far below the total demand for food and biodiesel. Spent bleaching clays (SBCs) from vegetable oil refineries, which have large amount of adsorbed oil would be a good source for biodiesel. Boey *et al.* [2] reported that SBC of crude palm oil (CPO) contained about 24 and 27% when extracted with petroleum ether and ethyl methyl ketone, respectively. An approximately the same percentage of extractable oil was reported by Huang and Chang [2] for SBC of soybean oil. The amount of oil was 21% when extracted with *n*-hexane and a higher percentage could be obtained when methanol, ethanol or polar compounds were used as the solvent but the extracted oil contained higher amount of pigments and polar and phosphorous compounds. Consequently, separation and purification of biodiesel was difficult. About 31 - 36% residual cotton seed in SBC was reported by Ali *et al.* [3]. However, higher amount of residual oils (40%) in SBC of soybean, palm and rapeseed oils were reported

by Lara Pizarro and Park [4] and lower amount (16.0%) of residual palm kernel oil (PKO) was reported by Aladetuyi *et al.* [5].

The maximum yield of biodiesel (98.5 %) from residual cotton seed oil on SBC was reported by Ali *et al.* [3]. The conditions were NaOCH$_3$ (1.00 %), methanol-oil (6:1) at 65 °C and stirring intensity (650 rpm) for 120 min. *In situ* trans-methylation was carried out by Boey *et al.* [6] with the aid of ultrasound with either petroleum ether or ethyl methylketone as a co-solvent. The mixture was sonicated at 55 °C for 2h. Optimal conditions were: 2.67wt% KOH, methanol to oil mass ratio of 5.9:1 and 1:1 mass ratio of co-solvent. Although with the relatively high amount of catalyst, trans-methylation process gave approximately 60 wt% of methyl esters for the ethyl methyl ketoneas the co-solvent and 75 wt% of methyl esters for the petroleum ether as the co-solvent. Huang and Chang [2], on the other hand, prepared biodiesel from SBC by a two-step process. Conversion of the residual oil adsorbed in SBC into methyl esters was 84.5 to 90.1%.

Studies on animal fats, Cunha Jr. *et al.* [7] reported that 96.25% conversion could be obtained with the alcohol to oil molar ratio 8:1 and KOH 0.88% at 70 °C. Although higher yield was obtained at 70 °C, they recommended lower temperature because lower soap formation and better phase separation. However, trans-esterification can proceed satisfactorily at room temperature [8, 9]. Bouaid *et al.* [8] showed that the best results for laboratory scale trans-ethylation reactions was 32 °C with 5:1 ethanol to oil molar ratio and 1.5% of KOH for high erucic acid *brassica carinata* (91.3%), and high oleic acid sunflower oils (97.5%) while the optimum condition for low erucic acid *brassica carinata* oil was 20 °C with 6:1 ethanol to oil

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molar ratio and 1.5% of KOH (98.3% yield). A comparative study on the production of methyl and ethyl biodiesel from cotton seed oil, Fernandes *et al.* [10] found that the yields of methyl and ethyl biodiesels were 91.5% and 88.5%, respectively.

Zhou [11] studied on the ethanolysis of sunflower oil at 23 °C using 1.4% mass of KOH (with respect to oil). Equilibrium was reached in 5 to 10 min for ethanol to oil molar ratios of 20, 25 and 30 and at 60 °C, equilibrium was reached in 2 min. The yield of biodiesel from methanol, ethanol and butanol, for reaction at 23 °C, were 99.4, 98.6 and 95.7%, respectively.

Literature on *in situ* trans-esterification of SBCs was relatively rare and the biodiesel yields were low comparing to biodiesel from the extracted oils. Thus, the objective of this study is to investigate trans-esterification, especially the *in situ* trans-ethylation of SBC of different sources.

## MATERIALS AND METHODS

SBCs of CPO, rice bran oil (RBO) and PKO were gifts of Surin refinery, Siam oil refinery and Lamsung Co. Ltd (Thailand). Solvents were analytical grade and mobile phases were HPLC grade from Lab Scan (Bangkok (Thailand).

### Extraction and Determination of Oil in SBCs

The residual oil in SBC was determined by partial extraction method as described by Lilitchan *et al.* [12]. Two sample tubes contained 5 and 10g of SBCs were mixed with 20 mL each of a solvent (ethyl acetate, dichloromethane and ethanol). The tubes were capped and vigorously shaken on a vortex mixer for 1 min. The clays were allowed to settle. Two milliliters aliquots were taken from the clear liquids, evaporated to dryness under a stream of nitrogen. The dry residues were weighed and calculated for their equilibrium constant (K), which in turn was used for calculation for total oil in the SBCs.

### Conventional Trans-Methylation

Trans-methylation of the extracted oils from SBCs was carried out by dissolving 100 mg of the extracted oil in 3 mL toluene and 1 mL of 1.0% methanolic NaOH and vigorously shaking on a vortex mixer for 1-2 min. One tenth mL of glacial acetic was then added to stop the reaction. The product was washed once with 2 mL of 2% $Na_2CO_3$ and once with 2 mL of distilled water. The upper layer was transferred to another test tube,

dried over anhydrous $Na_2SO_4$ and kept for HPLC and GC analysis.

### *In Situ* Trans-Ethylation

Ten milliliters of 1.0% ethanolic NaOH was added to 5g of SBC. The mixture was vigorously shaken on a vortex mixer for 1-2 min. The reaction was stopped by adding 0.5 mL glacial acetic acid. The clear solution was filtered through a 0.45 membrane filter, washed once with 2 mL of 2% $Na_2CO_3$ and once with 2 mL of distilled water and dried over anhydrous $Na_2SO_4$. The trans-ethylated products were analyzed by HPLC and GC.

### *In Situ* Trans-Methylation

*In situ* trans-methylation was carried out similar to the *in situ* trans-ethylation as described above. Because methanol is poor solvent for oils, toluene was added to help dissolving the oil. The amounts of toluene added were reported in the text.

### High-Performance Liquid Chromatography (HPLC)

The HPLC system consisted of a Waters model 515 pump (Waters Associate, Milford, MA01757, USA.) equipped with a Rheodyne model 7125 six-port injector (Cotati, CA, USA), an evaporative light scattering detector (ELSD) model 55 from SEDEX (Sedere, Alfortville, France). A 100Å Phenogel column (300 x 7.8mm i.d.) obtained from Phenomenex (Phenomenex, Inc., Torrance, CA) was used to check the purity of oils and reaction products. Sample and reference were prepared in toluene and analyzed on the Phenogel column with0.15% (v/v) acetic acid in toluene as the mobile phase at 1.0 ml/min flow rate[13]. The ELSD drift tube was set at 40°C and the $N_2$ flow through the nebulizer was set at two bars. Peaks were identified by comparison with reference standards.

### Gas Chromatography

GC analysis was carried out on a Shimadzu gas chromatograph model 2010 (Shimadzu Corp., Japan) equipped with an FID and a split-splitless injector. An Rtx-2330 (90% biscyanopropyl, 10% cyanopropylphenyl polysiloxane) capillary column (30 m x 0.25 mm i.d. x 0.25 µm film thickness) was obtained from Restex International (Bellefonte, PA, USA). The chromatographic conditions were as follows: helium carrier gas flow, 2 ml/min; nitrogen makeup gas flow, 30 ml/min; detector/injector temperature, 250°C; split ratio, about 50: 1.

Fatty acid identification was performed by its ECL value without reference standard according to Krisnangkura *et al.* [14] with the four column coefficients (a =−7.169, b = −0.596, c = 1007 and d, = 401.3) reported by Sansa-ard *et al.* [15].

## RESULTS

### Extraction of Residual Oils in SBCs and Characteristic of the Oils

All the oils in SBCs were very soluble in both ethyl acetate and dichloromethane. Twenty milliliters of the solvents could completely extract all the free triglyceride in 10g of SBC. This is simply rationalized from the amount of oil extracted into the solvent. With 20 mL solvent, the amount of oil from 10g of SBC was exactly twice that of the 5g of the clay. Thus the adsorption constant (K) cannot be determined for ethyl acetate and dichloromethane. On the other hand, ethanol was also a good solvent, but not as good as ethyl acetate or dichloromethane. The amount of oil extracted from 5g of the SBC was more concentrate than oil extracted from 10 g of SBC. The K values were 0.318 for all types of SBCs. The oil contents of SBCs from RBO, CPO and PKO are summarized in Table **1**. The extracted oils have different color, light brown, dark brown and pale yellow for RBO, CPO and PKO, respectively. The color reflexes pigment in the oils.

HPLC analysis on a 100 Å Phenogel (Figure **1**) shows a small peak eluted right after the main triglyceride (TG) for RBO and CPO, respectively. The retention time is the same as $\beta$-carotene and $\gamma$-oryzanol. HPLC chromatogram of PKO does not have this peak but there are many small peaks eluted at longer retention times. Composition and tentative identification of the oils by comparison of their retention times with the references are summarized in Table **2**. RBO had very high pigment but low free fatty acid (FFA), while CPO had high pigment and FFA. PKO had no pigment but had other unidentified compounds.

The slightly different amount of oils trapped in the SBCs might be due to the different technologies used for oil filtration or due to the difference in viscosities of the oils. However, the difference in compositions, especially the impurities in different oils may be ascribed to the different process of refineries. RBO is chemically refined and FFA is removed by alkaline in the neutralization step. Accordingly, FFA in the subsequent step, including bleaching step, would be very low (0.75%). On the other hand, palm oil is refined by physical refining process, where FFA was removed in the final deodorization step. Thus, large amount of FFA (10.9%) was trapped in the SBC together with the oil. However, degumming and bleaching were separated into two steps. Thus, phospholipids in the clay were negleable. The very high amount of FFA in the SBC of CPO might reflect the FFA in the oil as well as the freshness of the fruit being processed. PKO was refined by physical process but degumming and bleaching were combined into one step. The SBC of

**Table 1:   Oils Extracted from SBCs (N=3)**

| Solvents | Refinery | | |
|---|---|---|---|
|  | **RBO** | **CPO** | **PKO** |
| Ethyl acetate | 25.2±0.70% | 23.1±0.4% | 21.4±0.8% |
| Dichloromethane | 22.2±0.03% | 24.1±0.7% | 19.5±0.6% |
| Ethanol (K[1]) | 0.318 | 0.318 | 0.318 |

[1]K is partition coefficient.

**Table 2:   Composition of RBO and CPO and PKO from SBCs Extracted with Dichloromethane**

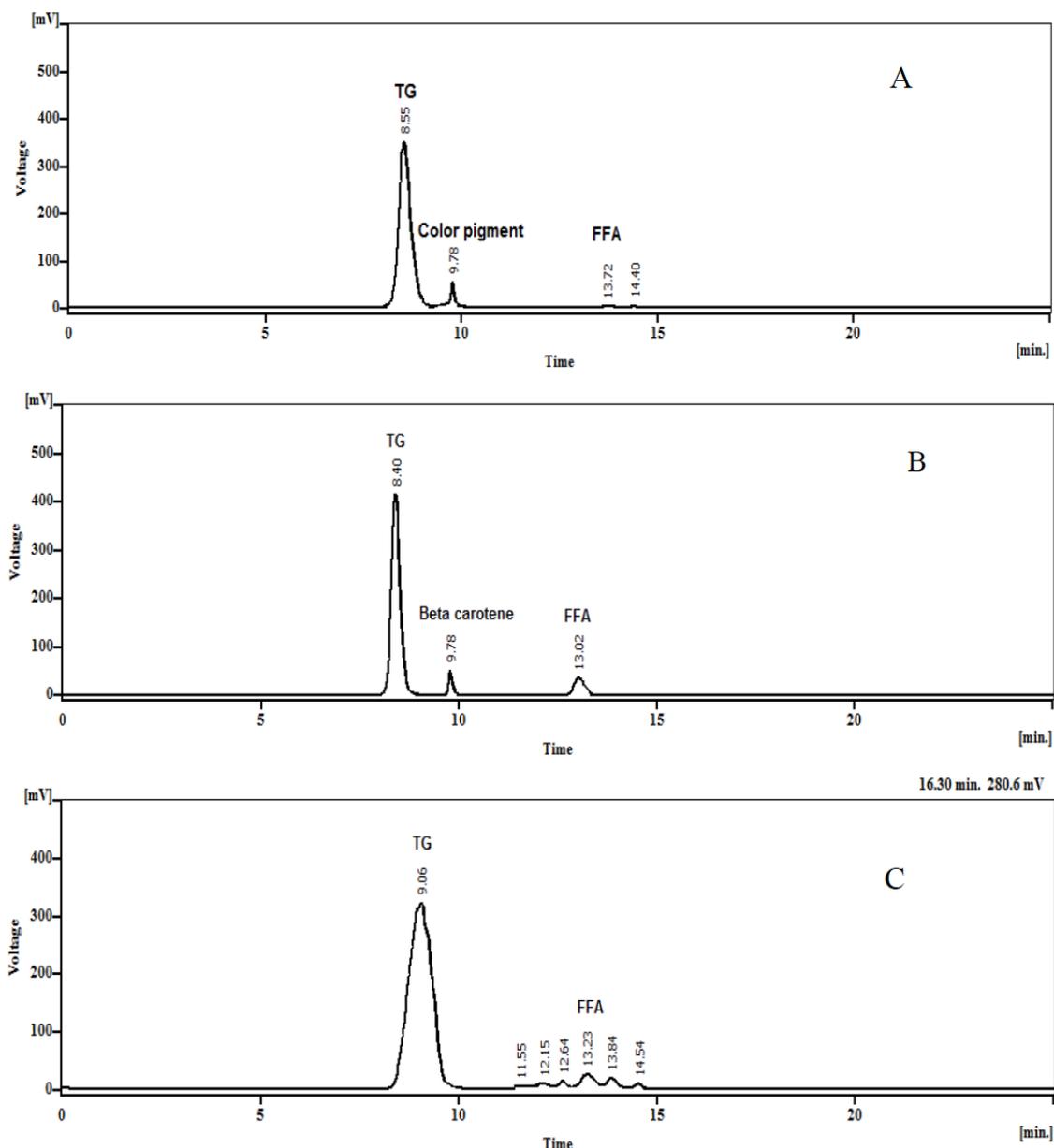| Composition | SBCs (%) | | |
|---|---|---|---|
|  | **RBO** | **CPO** | **PKO** |
| TG | 92.75 | 79.1 | 88.3 |
| Pigment | 6.5 | 7.1 | - |
| DG | - | 2.5 |  |
| FFA | 0.75 | 10.9 | 5.0 |
| Unknown | - | - | 6.7 |

**Figure 1:** HPLC chromatogram of oils extracted from SBCs of RBO (**A**), CPO (**B**) and PKO (**C**) eluted from Phenogel 100 Å column with toluene containing 0.15% (v/v) acetic acid.

PKO contained large amount of both FFA (5.0%) and other impurities.

Ethyl acetate could extract 21 to 25%of oil, which was slightly higher than dichloromethane (20 to 24%) in all clays. However, ethyl acetate is highly flammable, thus scale up the oil extraction with this solvent must be very careful. On the other hand, dichloromethane is non-flammable and it is not allowed for use in food processing, thus it maybe suitable for industrial application. The oil content in the clays was quite high compared to oil bearing material used for biodiesel production. Rice bran, palm fruit and soybean contain 18-25%, 45-50% and 18-20% of oils, respectively [16].

Fatty acid compositions of SBCs of RBO, CPO and PKO are summarized in Table **3**. The SBCs contained slightly higher saturated or higher melting fatty acids than the refined oils. It is speculated that the solid fats are possibly selectively retained on the SBCs or they are more viscous and consequently hard to pass through the filter press. However, the higher saturated fatty acid content would increase the cetane index of the biodiesel [17].

**Conventional Trans-Methylation**

Figure **2** shows trans-methylation of SBCs of RBO, CPO and PKO. Complete trans-methylation was

**Table 3: Fatty Acid Compositions of Oils Extracted from SBCs Compared to the Refined Oils**

| Fatty acid (Cz:m)[1] | RBO | | CPO | | PKO | |
|---|---|---|---|---|---|---|
| | SBC | Refined | SBC | Refined [18] | SBC | Refined [19] |
| $C_{8:0}$ | - | - | - | - | 1.35 | 0.68 |
| $C_{10:0}$ | - | - | - | - | 3.93 | 3.39 |
| $C_{12:0}$ | - | - | - | 0.35 | 47.27 | 51.31 |
| $C_{14:0}$ | - | - | 0.89 | 1.08 | 21.23 | 16.08 |
| $C_{16:0}$ | 23.89 | 20.82 | 47.62 | 43.79 | 11.60 | 7.06 |
| $C_{18:0}$ | 2.35 | 1.99 | 4.96 | 4.42 | 3.49 | 2.02 |
| $C_{18:1}$ | 49.34 | 45.69 | 38.33 | 39.9 | 8.88 | 12.62 |
| $C_{18:2}$ | 23.66 | 29.93 | 8.19 | 9.59 | 2.24 | 2.84 |
| $C_{18:3}$ | 0.67 | 0.67 | - | 0.17 | - | 2.72 |
| $C_{20:0}$ | 0.59 | 0.89 | - | 0.38 | - | 0.82 |

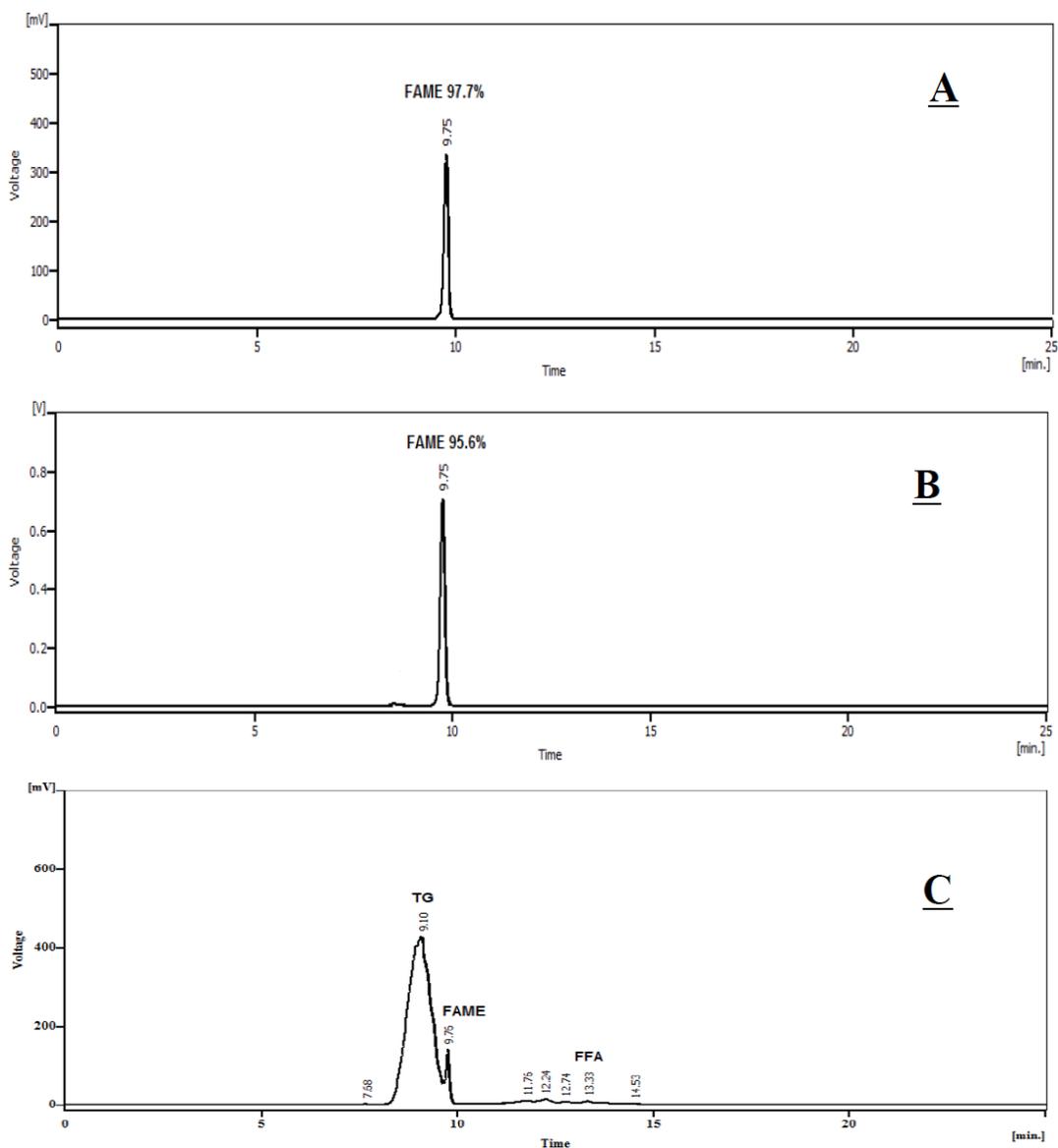[1]z=carbon numbers of fatty acid; m = number of double bonds.



**Figure 2:** Trans-esterification products of oils extracted from SBCs of RBO (**A**), CPO (**B**) and PKO (**C**). See Figure **1** for chromatographic conditions.
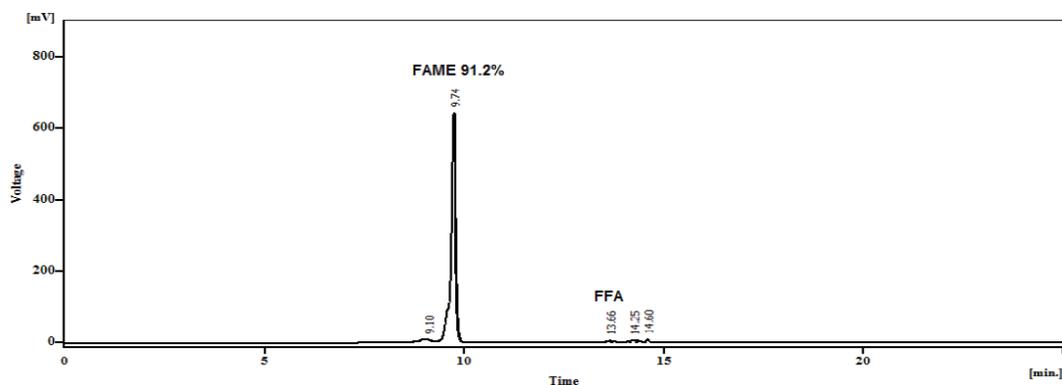
**Figure 3:** Trans-esterification products of oils extracted from SBC of CPO by conventional heat with 1% NaOH for 30 min at 60 °C. See Figure **1** for chromatographic conditions.

observed for RBO and CPO, while PKO conversion was only 4% by conventional heat at 60 °C for 10 min. The HPLC chromatogram of PKO (Figure **2C**) shows that there are many impurities in the SBC of PKO. The PKO refining process is slightly different from CPO and RBO. The gum (mostly phospholipids) from the acid degumming step (PKO processing) was not removed while the bleaching clay was added to decolorize the oil. Therefore, all the gum was trapped in the SBC. In addition, Table **2** shows that there are about 5.0% FFA and 6.7% unknown compounds in the SBC of PKO. Although the impurities in the SBC of PKO were not characterized, trans-methylation could be complete by adding more NaOH catalyst (2.0%) or prolong the reaction to 30 min at 60 °C (Figure **3**).

Also, the HPLC chromatogram in Figure **3** shows that all the impurities are disappeared except the FFA and the main biodiesel peak, suggesting that all the impurities might be the fatty acid base lipids and could be converted to biodiesel.

### *In Situ* Trans-Esterification

*In Situ* trans-methylation of 5g of SBC of CPO with 10 mL of 1.0% methanolic NaOH at room temperature

was not complete. Only 13.2% conversion was observed at 1 min. When 10 mL of toluene was added as a co-solvent, percent conversion was increase up to only 18%. Therefore, the conditions were not suitable for *in situ* trans-methylation of SBC. Hence, 20 mL of 1% methanolic NaOH and 10 mL of toluene were used as the trans-methylation media for 5g of SBC. Percent conversion was increased to 98.9% (Figure **4**) in 1 min. This can be simply explained as the increment in molar ratio of methanol to oil and higher available amount of NaOH for catalysis. In addition, the miscibility between methanol and oil in the presence of toluene as the co-solvent may also play an important role in accelerating the reaction. Without the co-solvent, surface contact between methanol and oil is limited to the extent of agitation. On the contrary, a homogeneous single phase is obtained for methanol and oil in the presence of toluene. Thus, surface contact between methanol and oil is infinity. Interaction between the two reactants is at maximum and limited by their actual concentrations. Therefore, trans-methylation was greatly enhanced and was complete in 1 min. However, the main disadvantage of co-solvent aided in trans-methylation is the removal of co-solvent, which does not only increase the complexity but also increase an
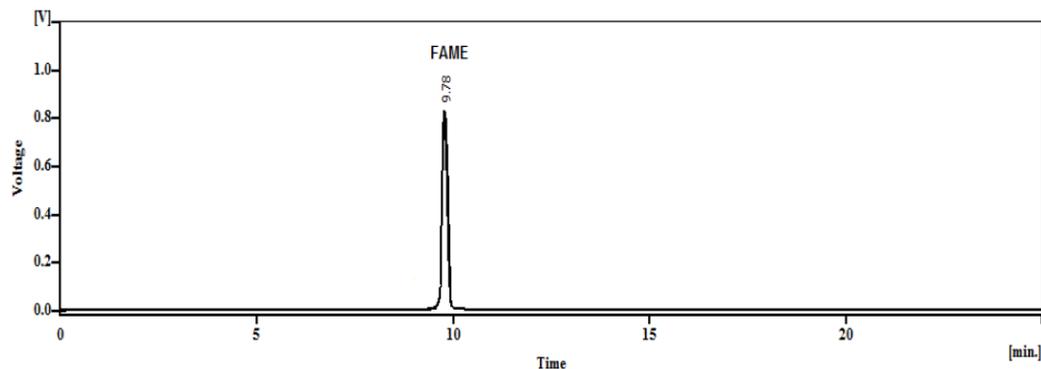


**Figure 4:** *In situ* trans-methylation of SBC of 5g of CPO at room temperature with 20 mL of 1% methanolic NaOH+ 10 mL toluene for 1 min. See Figure **1** for chromatographic conditions.

additional cost to the process. When these conditions were applied to RBO and PKO, yields of biodiesel were 97.7% and 2%, respectively. The peculiar result of PKO was possibly due to the presence of alkaline consuming impurities as mentioned above. The hypothesis was tested by increasing the NaOH to 2%, conversion was increased to 97.0%.

Ethanol has a greater power in dissolving the oil than methanol, while it is miscible with biodiesel at room temperature [20]. *In situ* trans-ethylation of 5g SBC of CPO with 10 mL of 1.0% ethanolic NaOH was not complete in 1 min. on a vortex mixer. About 81% of fatty acid ethyl ester (FAEE) was found together with 11 % of TG and other intermediates in the reaction products. When the volume of ethanolic NaOH was increased to 20 mL, trans-ethylation was 98.6% complete within 1 min with 0.7% of unconverted TG as shown in Table **4**.

**Table 4: Trans-Ethylation of 5g SBC of RBO with Different Volume of 1% Ethanolic NaOH.**

| Lipid compound | 10 mL | 20 mL |
|---|---|---|
| TG | 11.7 | 0.7 |
| FAEE | 81.1 | 98.6 |
| FFA | 0.7 | 1.0 |
| MG | 1.7 | - |
| DG | 4.1 | - |

Trans-ethylation of CPO showed similar trend as RBO. Trans-ethylation of CPO was about 99% complete in 1 min with 20 mL ethanolic NaOH, but PKO gave only about 3% conversion. As it was pointed out earlier that PKO had larger amount of alkaline consuming impurities, higher amount of NaOH catalyst was required. It was found that 20 mL of 2% ethanolic

NaOH was suitable for 98% conversion of PKO in the SBC to biodiesel.

## Fuel Properties

Fuel properties of the biodiesel products were estimated from their fatty acid compositions and are summarized in Table **5**.

## DISCUSSION

Generally, high FFA oils are not directly trans-esterified to biodiesel by alkaline catalysis. FFA does not only consume the alkaline hydroxide in the neutralization step, but the soap (a good emulsifier) also tends to complicate the biodiesel separation from alcohol. Therefore, FFA in the oil is reduced either by esterification with alcohol with an acid catalyst or washing with alkaline hydroxide. Lertsathapornsuk *et al.* [26] combined the alkaline washing and trans-esterification into one step to prepare biodiesel from high FFA waste frying palm oil. In this study, neutralization of FFA and trans-esterication of oil in SBC were combined. For 5g of SBC of 24.1% of CPO (Table **1**), there is 0.49 mmol of FFA (Table **2** and MW 268 from Table **3**), but 5 mmol of NaOH was added to the reaction. Therefore, there was 0.9% of NaOH left as catalyst for trans-esterification. Therefore, prior to carry out trans-esterification, detailed analysis of contaminants in the SBC is essential. The rapid reaction of trans-ethylation might possibly due to the very high molar ratio of ethanol to oil (approximately 100). Usually, the alcohol to oil molar ratio is between 6 and 15, but these ratio cannot be attained due to the solid clay, unless additional solvent is added for the extraction of the biodiesel entrapped in the clay.

Also, an interesting result was observed in Table **4** as well as several chromatograms (Figures **2-4**). The

**Table 5: Fuel (B100) Properties of Biodiesels from Various SBCs**

| Fuel properties | EN14214 | SBC | | |
|---|---|---|---|---|
| | | RBO | CPO | PKO |
| IV (g $I_2$/100 g) [21] | 120 max | 85 | 47 | 11 |
| SN [21] | - | 194 | 198 | 241 |
| HG (MJ/kg) [22] | - | 39.7 | 39.6 | 38.27 |
| Viscosity (mm$^2$/s), 40$^{\circ}$C [23] | 3.5 -5.0 | 4.35 | 4.37 | 3.01 |
| CN [17] | 51 min | 55 | 63 | 67 |
| Viscosity (cP), 40$^{\circ}$C | | 3.75 | 3.75 | 2.59 |
| Density (g/cc) [24] | 0.860 - 0.900 | 0.888 | 0.883 | 0.877 |
| Surface tension (mN/m$^2$) [25] | - | 29.66 | 29.16 | 28.06 |

amounts of FFA in the reaction products are very much lower than the starting oils, especially the oil containing high FFA. The clay could remove sodium soap, but the mechanism of removal might not be established in this study. It might be a simple adsorption or the sodium soap form a semi-solid gel with alcohol and co precipitate with the clay.

SBC is an industrial waste from vegetable oil refinery. It contains very high amount of absorbed oil. The oil can be easily extracted with methylene chloride or ethyl acetate and trans-esterified to methyl or ethyl biodiesel. *In situ* trans-ethylation of the clay to ethyl biodiesel is very practical. In this study, a 99% conversion of the oil to ethyl biodiesel can be done within 1 min. However, for commercial process, optimization must be done to lower the processing cost by lowering the amount of catalyst or alcohol (volume) to SBC (weight) ratio. Thus, reaction time would be longer and external heat must be applied to shorten the reaction time. Fatty acid composition of the absorbed oil was very similar to the crude oil, but the adsorbed oil contains higher amount of saturated fatty acids than the crude oil. This may be due to the higher melting point or pour point of the saturated fatty acid than the unsaturated fatty acid, allowing it to retain more on the clay. However, selective adsorption cannot be ruled out. Normally, biodiesel from saturated fatty acid has higher cetane index than unsaturated fatty acid of the same carbon atom [17]. Therefore, oil from SBC is better than the neat oil for preparation of biodiesel.

*In situ* trans-methylation of oil in the SBC is more difficult than trans-ethylation because of the lower solubility of the oil in methanol than in ethanol. This can be overcome by the addition of a co-solvent. With toluene as a co-solvent, reaction time can be shortened to that of trans-ethylation, but the major drawback is the removal or recovering of the co-solvent, which is an additional processing cost. Also, it must be kept in mind that different SBC contained different impurities. These impurities generally reacted or consumed catalyst. Thus additional amount of catalyst should be added to keep the strength of the catalyst in the required range. One percent of the catalyst would be sufficient to convert oil in SBC from alkaline refining process to biodiesel in one minute at room temperature.

## ACKNOWLEDGEMENT

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