UREA FRACTIONATION OF USED PALM OIL METHYL ESTERS

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ABSTRACT

Urea has shown a remarkable ability in forming well-defined and easy-to-handle crystalline complexes. In general, the use of urea as a ligand provides efficient separation in fat with a wide variety of straight chain compounds but is not applicable to fat containing branched or cyclic compounds. This study was conducted to investigate the fractionation of used frying oil (palm-based) methyl esters (UFOME) with urea and the separation profile according to their degree of unsaturation. A comparison on the effectiveness of fractionation was made with the increment of the treatment level of urea. The urea was added at different ratios (UFOME: urea, w/w) i.e. *1:0.5, 1:0.75 and 1:1. It was found that the most effective fractionation of the unsaturated methyl esters (ME) was achieved when the treatment level of UFOME: urea was 1:0.75. The unsaturated ME was enriched from 58.81% to 88.03% after the urea fractionation. The enriched unsaturated ME will be a useful feedstock for oleochemicals and other processes requiring high level of unsaturation in their fatty acyl chain.*

Keywords: fractionation, used frying oil methyl esters, urea complexation, unsaturation, separation technique.

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INTRODUCTION

Generally, palm oil contains several saturated fatty acids (lauric, 0.1%; myristic, 0.1%; palmitic, 44%; and stearic, 5%) and unsaturated fatty acids (oleic, 39%; linoleic, 10%; and linolenic, 0.3%). Owing to the very different chemical properties of the saturated and unsaturated fats in palm oil and its derived methyl esters (ME), it is important to separate them as useful raw materials for oleochemicals and other chemical processes.

Recent investigations have shown that it is possible to separate the mixtures of fatty acids or fatty acids ME on the basis of their degree of unsaturation. As the stabilities of urea adduct decrease with the increasing unsaturation, the technique to eliminate saturated fatty acids from monounsaturated and polyunsaturated fatty acids have been well established (Hayes *et al*., 1998; 2000; Wu *et al*., 2008). This technique has potential as a separation technique for free fatty acids as the formation of complexes between urea and linear hydrocarbon templates is a well-known process (Hayes, 2006).

Using this technique, large quantities of ME can be separated without disturbing the unsaturated esters. Furthermore, since it is an irreversible reaction, the reaction can be controlled (Jumat *et al*., 2012). The crystals of the coordinated complexes are extremely stable, thus filtration of crystals does not necessarily need to be conducted at low temperatures. This method has been widely used for fatty acid fractionations, especially for analytical purposes (Chin *et al*., 2010). As palm oil contains about 50% of unsaturated fatty acids which are valuable raw materials for the production of oleochemicals and biochemicals, thus this study

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explored the possibility of separating the saturated and unsaturated components of a palm-based by-product derived from cooking/frying activities, *i.e.* used frying oil (UFO) via urea fractionation, and examined its process efficiency and product quality.

MATERIALS AND METHODS

Materials

The UFO was obtained from a local fast food restaurant and the used frying oil methyl esters (UFOME) was prepared via transesterification. Urea was purchased from R & M Chemicals and all solvents used were of analytical grade.

Methods

Preparation of UFOME. UFO (1005.9 g) was treated with the catalyst, sodium hydroxide (5.47 g, 0.1368 mol) which was first dissolved in 500 ml of methanol. The reaction mixture was stirred and heated to 60°C for 30 min under reflux. Thin-layer chromatography (TLC) was used to monitor the completion of the reaction. After the reaction was completed, the reaction mixture was allowed to cool down. The reaction mixture consisted of two layers; the upper layer (esters) and the lower layer (glycerol). The esters layer was separated from the glycerol layer using a separating funnel. The yellowish esters layer was washed several times with hot distilled water until neutral and vacuumed dry for fuel characterisation (Loh *et al*., 2006).

Analysis. The triglyceride of UFOME was determined by gas chromatography (GC) using published method (Lau *et al*., 2005). A sample of 0.02 g was weighed into a 2-ml GC vial. Then, 1.2 ml of dichloromethane and 0.3 ml of the silylating reagent, N,O-bis(trimethylsilyl) fluoroacetamide with 1% trimethylchlorosilane were pipetted into the vial. The vial was capped tightly and heated at 60°C for 2 hr. The instrument used was a Hewlett-Packard Series II gas chromatograph, model 5890 (Hewlett-Packard, Avondale, PA), equipped with a flame ionization detector (FID) and on-column injector. A BPX 5 fused-silica capillary column (15 m x 0.32 mm) coated with 5% phenyl/95% polysilphenyl-siloxane, with a film thickness of 0.25 μm (SGE, Austin, TX), was used. GC conditions were as follows: injector temperature, 45°C; detector temperature, 370°C; initial oven temperature, 100°C; initial holding time, 16 min; carrier gas (He) flow rate, 2 cm^3 min^{-1}; column pressure, 14.4 psi; injection volume, 1 ml. Quantification of the components was performed using a five-point external standard calibration assay, with R^2 values of >0.09.

The fatty acid compositions of all the UFOME samples were determined according to ISO 5508: Animal and Vegetable Fat and Oil Analysis by Gas-Liquid Chromatography of Methyl Esters of Fatty Acids. Analysis was carried out with a Hewlett Packard 5890 Series II gas chromatograph equipped with a FID and split injector. A fused silica capillary column (60 m x 0.25 mm) coated with a highly polar stationary phase, Supelco SP2340 (0.2 μm) was used with a programmed temperature profile as follows: oven temperature: 185°C, injector temperature: 240°C, detector temperature: 240°C, split ratio: 1:100, carrier gas: helium at 2.0 ml min^{-1}.

Urea complexation. The UFOME (20.0 g) was dissolved in 200 ml of methanol to which urea in three different weight ratios were added (UFOME:urea w/w = 1.0.50, 1:0.75, 1:1). The mixture was warmed (65°C) until all the urea dissolved. The solution was then allowed to cool to 25°C to 30°C with occasional swirling. After a minimum of 4 hr, the materials were filtered through a Buchner funnel to remove the urea complexes. The filtrate was washed twice with methanol (5 ml) saturated with urea and then poured into 120 ml of 1% HCl and extracted alternately with hexane and diethyl ether. The combined organic layers were washed twice with water and the solvent was removed under reduced pressure. The fractionated ME was analysed using GC (Hayes *et al*., 2000). A detailed urea complexation procedure employed by this study is summarised in *Figure 1*.

RESULTS AND DISCUSSION

Preparation of UFOME

The prepared UFOME was analysed using a GC to monitor the ester content and the completion of the transesterification process. The first eluted component was free fatty acid (FFA) with a retention time ranged from 9.0 to 15.0 min, followed by monoglycerides (MAG), 15.5-17.0 min; squalene, 17.2 min; free sterols, 19.0-20.5 min; diglycerides (DAG), 22.5- 25.5 min; and triglycerides (TAG), 28.0 – 38.0 min (*Figure* 2). The chromatogram showed good baseline separation with nine major peaks observed. The relative compositions of the above components are tabulated in *Table 1*.

The UFOME produced was 97.41% pure with the presence of 0.30% FFA, 0.35% MAG, 0.30% DAG, 1.57% TAG, 0.01% squalene and 0.06% sterol. This implied that the conversion of UFO to UFOME via transesterification was good and in accordance with European Standard (EN 14214) stating a desirable conversion of more than 96% for ME to be used as a biofuel. However, these compositions were slightly

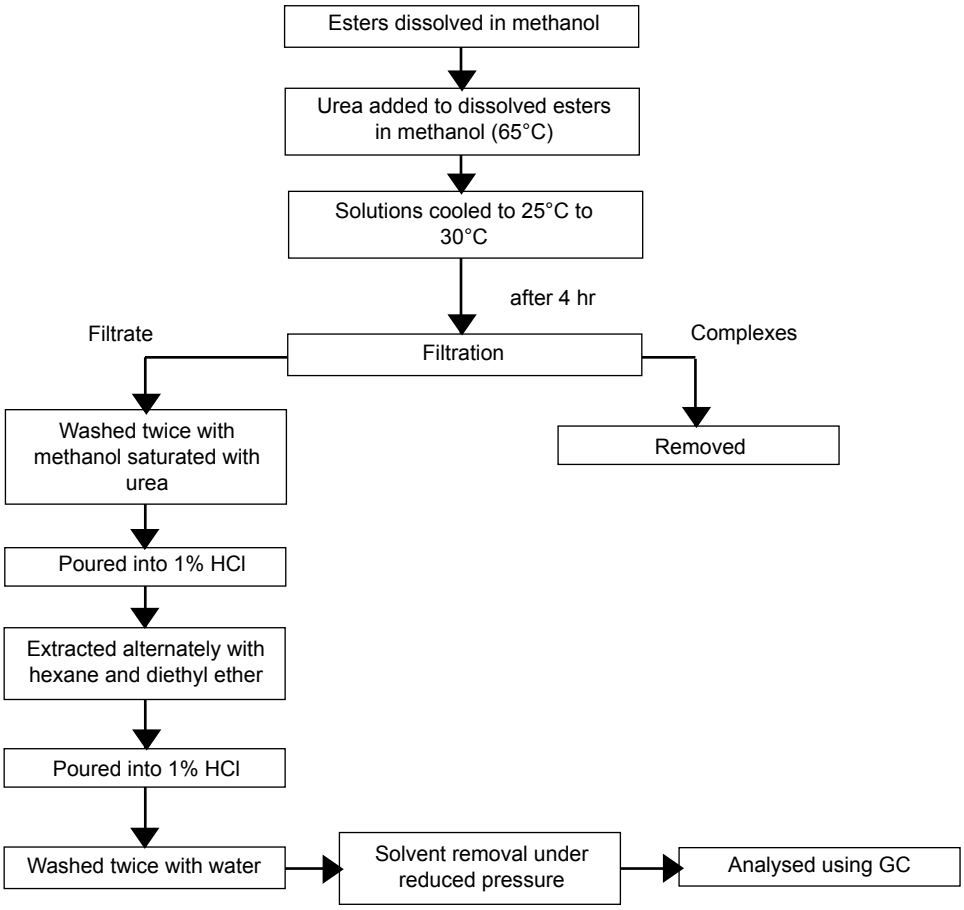


Figure 1. Urea complexation procedure.

TABLE 1. COMPOSITIONS OF USED FRYING OIL METHYL ESTERS (UFOME)

Composition	Purity (%)
Free fatty acid (FFA)	0.30
Esters	97.41
Monoglycerides (MAG)	0.35
Diglycerides (DAG)	0.30
Triglycerides (TAG)	1.57
Squalene	0.01
Sterol	0.06

different from those obtained previously (Loh *et al*., 2006).

Urea Complexation

Basically, urea is used to fractionate fatty acids or esters into groups with different unsaturation. It crystallises in tetragonal structure but forms hexagonal prism when certain aliphatic compound is present. However, some aliphatic compound will stay intact inside the hexagonal prism, hence coordinated with urea to form complexes (Hwang and Liang, 2001).

In this study, the urea was added at different weight ratios, *i.e*. 1:0.5, 1:0.75 and 1:1 (UFOME: urea w/w). The profiles of the fatty acids fractionation in the solution mixtures were compared. The degree of fatty acid fractionation at different ME: urea treatment in increasing order was 1:1.0<1:0.5<1:0.75 (*Figure 3*). In future, more experiments are required to look into controlling the various process parameters such as the effects of FFA amount, filtration temperature, solvent amount, water content in methanol, and repeated urea fractionation with each filtrate, *etc*., to get an optimum urea complexation process employing UFOME.

Different treatment levels of UFOME to urea gave different percentages of the unsaturated and saturated fatty acids. After urea complexation, the unsaturated UFOME increased by 34.1%, 49.7%

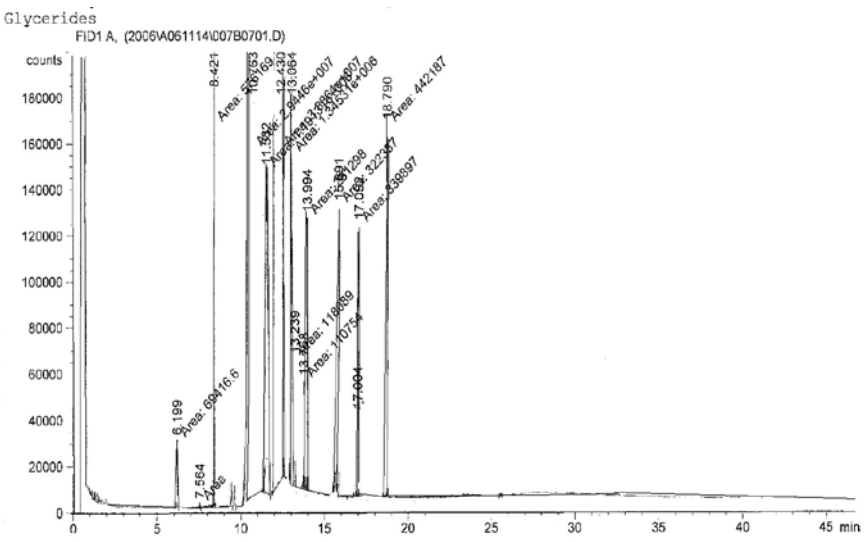
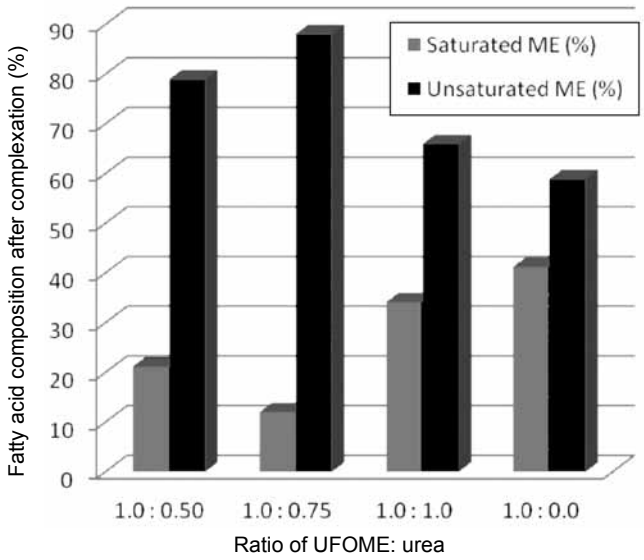


Figure 2. Chromatogram of used frying oil methyl esters (UFOME).

and 12.1% at the UFOME: urea weight ratio of 1:0.5, 1:0.75 and 1:1 respectively (*Figure 3*).

The saturated fatty acids were able to form stable complexes which crystallised more readily than the unsaturated fatty acids. The double bond in unsaturated fatty acids could increase the molecular size, making it unfit to the hexagonal crystal channel, and hence complexation and crystallisation with urea did not take place (Hayes *et al*., 2000). Since the UFOME: urea treatment level at 1: 0.75 provided the highest efficiency in fractionation, it was recommended as the optimum level for urea complexation with UFOME.

The fatty acid compositions which indicate the purity of UFOME before and after urea complexation at UFOME: urea treatment level of 1:0.75 were compared (*Figure 4*). The unsaturated fatty acids namely C18:1 and C18:2 increased from 44.39% to 67.49% and 12.69% to 20.33%, respectively. On the other hand, the saturated fatty acids such as



Note: Percentage increment of the unsaturated UFOME (after urea complexation)
= 100% - percentage of saturated UFOME

$$= 100\% - \frac{\text{weight of urea complexes recovered}}{\text{total weight of UFOME used (before urea complexation)}}$$

Figure 3. The percentage composition of the saturated and unsaturated used frying oil methyl esters (UFOME) before and after urea complexation at different UFOME: urea treatment levels.

C16:0 and C18:0 decreased from 35.65% to 10.56% and 4.48% to 0.21%, respectively. Generally, the formation of the urea complex depends on the degree of unsaturation of fatty acids. Larger fatty acid namely C18:0 has long-chain unbranched molecules that will ease the complexation as it is large enough to coordinate the aliphatic chain by urea. This provides higher tendency to complex and crystallise eventually compared to the relatively smaller molecules such as C16:0, leaving behind the unsaturated fatty acids dominated in the solution. The presence of double bonds in the carbon chain will increase the size of the molecule and will reduce the tendency of the complexation.

The efficiency of urea complexation with UFOME can be assessed by GC (*Figure 5*). In *Figure 5b*, the absence of the saturated ME particularly C16:0 and C18:0 confirmed that these fatty acids were successfully separated via crystallisation using urea.

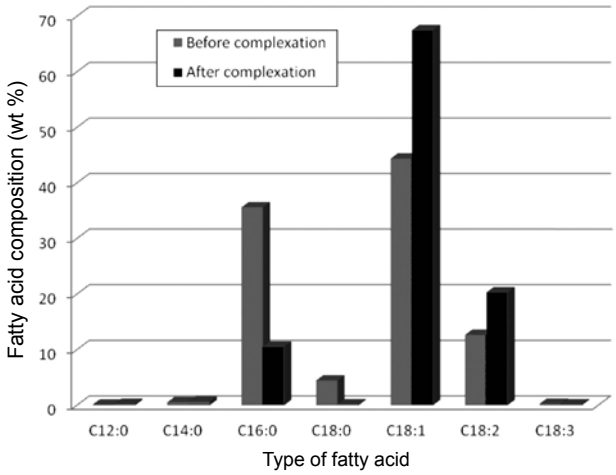


Figure 4. Fatty acid composition of used frying oil methyl ester (UFOME) before and after urea complexation at UFOME: urea treatment level of 1:0.75.

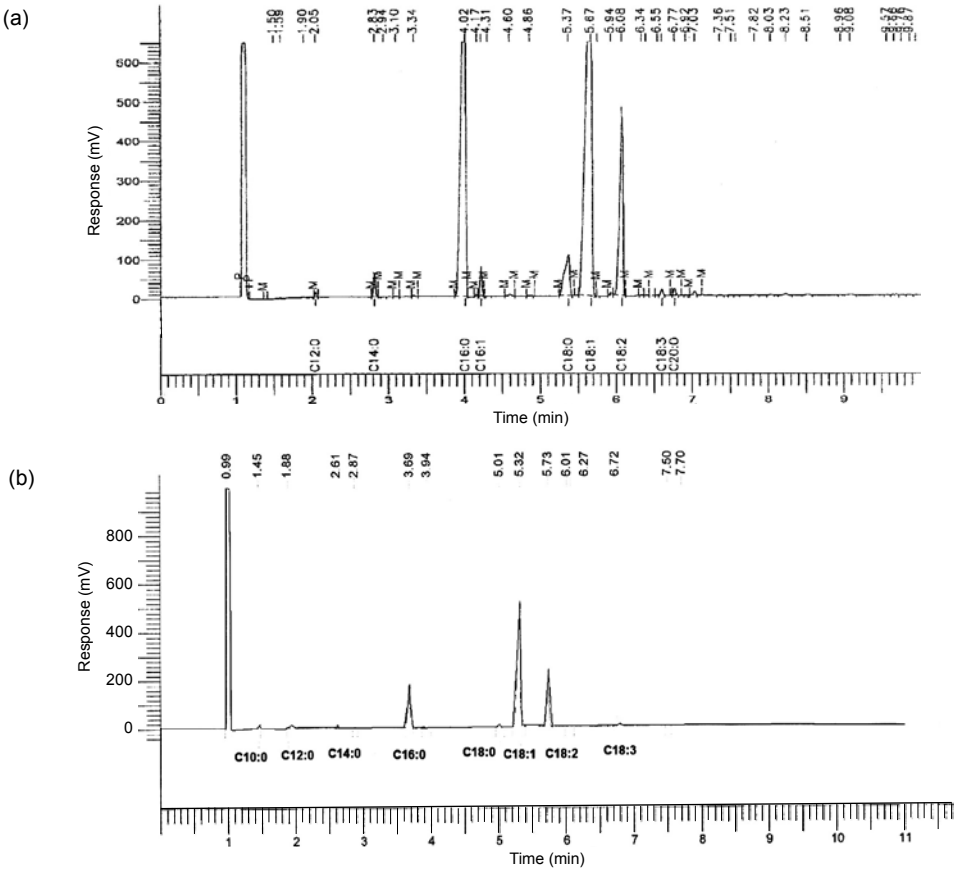


Figure 5. Fatty acid compositions of used frying oil methyl esters (UFOME); (a) before and (b) after urea complexation at UFOME: urea treatment level of 1: 0.75.

CONCLUSION

In this study, urea was found efficient in fractionating UFOME into its respective saturated and unsaturated counterparts. The unsaturated ME was successfully increased from 58.81% to 88.03% using optimum ME: urea treatment level of 1: 0.75. It is recommended that the various control parameters possibly influencing the urea fractionation process be looked into in the future. Nevertheless, the unsaturated UFOME that was separated, concentrated and purified can be used as an intermediate for many processes.

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