RECOVERY AND CONVERSION OF PALM OLEIN-DERIVED USED FRYING OIL TO METHYL ESTERS FOR BIODIESEL

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ABSTRACT

Frying oils (both vegetable oils and animal fats) degrade with use, and beyond the limits, the excessive free fatty acids (FFA), peroxide value (PV) and polar components preclude their further use in food applications, unless they can be purified by very effective adsorbent systems. In this study, four adsorbents: silica gel, activated carbon, aluminium oxide and acid-activated spent bleaching earth were used to reduce some of the poor quality parameters of the oils. Although pre-treatment of used frying oils with these adsorbents could improve the oil quality to a certain extent, the oils could only be used for non-food applications. The FFA and PV of the treated oils subjected to the above adsorbent treatment, were reduced as follows: 33.3% and 65.1%, 6.5% and 7.8%, 30.2% and 20.8%, and 11.8% and 46.9% respectively, and silica gel was found to be the most effective adsorbent. The treated used frying oil was converted into methyl esters as biodiesel. The methyl esters obtained had comparable fuel properties as petroleum diesel. Hence, it can be used as a diesel substitute.

Keywords: used frying oil, palm olein, pre-treatment, adsorbent, used frying oil methyl esters.

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INTRODUCTION

It is estimated that some 20 million tonnes of oils and fats are used for frying around the world, with industrial frying the major user of frying oil. Industrial frying oil requires oils and fats of good quality and nutritive value. Palm oil meets these requirements as it has no unpleasant room odour, a high resistance to oxidation and high content of nutrients from its fatty acid composition, and does not polymerize easily.

In frying, the hot oil serves as a heat exchange medium by which heat is transferred to the food being fried. However, frying eventually leads to darkening of the oil, and palm oil is no exception. This is due to the oil degradation - the heat, air and moisture to which the oil is exposed to lead to its polymerization, oxidation and hydrolysis (Gebhardt, 1996). The oil darkens from formation of polar materials such as phenolic minor components, oxidation products and colour compounds (Subramanian *et al.*, 2000). The indicators of poor oil quality include elevated free fatty acids (FFA), high total polar materials (TPM), change of colour, high foaming property, low smoke point, low iodine value and increased viscosity. TPM is by far the most reliable quality parameter for acceptability of the oil for frying - a value of 25%-27% indicates that the oil is no longer acceptable for health reasons (Pantzaris and Ahmad, 1998).

An estimated 50 000 t of used frying oils, both vegetable oils and animal fats are disposed off yearly in Malaysia without treatment as wastes. This creates a negative impact on the environment. The wastes can be used if they are purified.

Hoover (1966) first purified used frying oil by removing its FFA by magnesium oxide adsorption. Yuki and Hirose (1974) also investigated FFA removal and reported aluminium hydroxide gel to perform the most effectively. Usuki (1993) improved the colour and stability of used frying oil using adsorbents such as zeolite, activated carbon, activated clay, aluminium hydroxide gel, oyster shell, ceramic plate and calcium oxide. In these reports, not all the degradation products in the used oils were examined.

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Processing used frying oils through membrane technology improved their TPM contents (Subramanian *et al.*, 2000; Miyagi *et al.*, 2001). Recycling used frying oil using adsorbents, such as silica gel, magnesium oxide, aluminium hydroxide gel and activated clay, has been studied in detail (McNeill *et al.*, 1986; Lin and Reynolds, 1998; 2001; Maskan and Bagci, 2003; Miyagi and Nakajima, 2003) for improving the quality parameters such as TPM, oxidation products, polymerization, FFA, colour and oil stability. Silica gel was reported to be the most effective adsorbent in reducing FFA, TPM, oxidation products, viscosity and oil decolorization, without altering the chemistry and stability of the recovered oil (Miyagi and Nakajima, 2003).

There have been several attempts to convert used frying oil to biodiesel (Nye *et al.*, 1983; Mittelbach and Tritthart, 1988) via transesterification in acidic and basic conditions without having to purify the oils beforehand. However, the fatty acid alkyl esters formed were of poor quality and yield, and therefore not economically feasible for use. As the used frying oil was used directly without any purification, the yield of methyl esters was poor from formation of soap by the high FFA content. In order to first improve the oil quality for processing into methyl esters, pre-treatment is necessary. This paper describes a simple pre-treatment of used frying oil using cheap adsorbent and the production of methyl esters from the oil.

MATERIALS AND METHODS

Materials

Used frying oil was obtained from local fast food restaurants. The cooking oil in Malaysia is mainly palm olein. Silica gel, activated carbon, aluminium oxide, concentrated hydrochloric acid (37%) and sodium hydroxide were purchased from Merck. Spent bleaching earth was obtained from a palm oil refinery. The earth was de-oiled by solvent extraction and the de-oiled earth treated with a small quantity (4:1 w/v earth: acid) of concentrated hydrochloric acid (37%), dried in an oven at 100° C- 200° C for a week and used as adsorbent to treat the used frying oil.

Methods

Pre-treatment of used frying oil. The used frying oil was dissolved in hexane (1:3 w/v oil: hexane) and then mixed separately with selected adsorbents (silica gel, activated carbon, aluminium oxide, acid-activated spent bleaching earth) in 1:1 w/w oil-in-

hexane: adsorbent. The mixture was stirred at room temperature for 30 min, and then allowed to settle. The mixture was vacuum filtered through sintered glass, transferred to a round bottom flask and vacuumed dry to remove the solvent and water. The pre-treated oil was analysed for FFA content and peroxide value (PV) before conversion to methyl esters.

Preparation of methyl esters. The pre-treated used frying oil (90 g) were subjected to methyl esters conversion using sodium hydroxide (1 g, 0.025 M) which was first dissolved in 45 ml methanol before being reacted with the oil for 30 min under reflux. The yellowish ester layer was washed several times with distilled water until neutral and vacuumed dry for fuel characterization (Choo *et al.*, 1993).

Analyses. FFA and PV were determined for the used frying oil before and after adsorbent treatment via PORIM Test Method p2.5 and PORIM Test Method p2.3. The measurements were done in triplicate and only the means reported. The percentage improvement in FFA and PV for each adsorbent treatment was calculated as:

[FFA or PV (before pre-treatment) – FFA or PV (after pre-treatment)] ------ x 100 %

FFA or PV (before pre-treatment)

Viscosity was measured using an Automated Multi Range Viscometer HVM472 (Walter Herzog, Germany) at 40°C. All the measurements were performed in duplicate and only the means reported.

The oxidative stability was measured using the Model 743 Rancimat (Metrohm AG, Switzerland). Samples of 3 g were analysed under a constant airflow of 10 litres hr¹ and 110°C temperature of the heating blocks. All determinations of the induction period were performed in duplicate and only the means reported.

The fatty acid compositions of all the 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 flame ionization detector 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 μ m) 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.

RESULTS AND DISCUSSION

Pre-Treatment of Used Frying Oil

In this study, the adsorbents used were silica gel, activated carbon, aluminium oxide and acid activated spent bleaching earth. Silica gel was the most effective adsorbent for the pre-treatment of used frying oil. The FFA and PV of the pre-treated used frying oil are shown in *Table 1* with silica gel giving the highest percentage reduction in both the parameters. A similar result was found previously by Miyagi and Nakajima (2003) in improving used frying oil by adsorption with silica gel, magnesium oxide, aluminium hydroxide gel and activated clay.

The effectiveness of the adsorbents in pretreatment of the used frying oil was reflected in the percentage improvement (PI) value (Miyagi and Nakajima, 2003) which compares the quality of the oil before and after pre-treatment, regardless of the oil recovery. Silica gel and aluminium oxide decreased the FFA the most (PI = 33% and 30%, respectively), whereas activated carbon and acid-activated spent bleaching earth were not so effective (PI = 6% and 12%, respectively). Although aluminium oxide showed a comparable ability to reduce the FFA content, its reduction of oxidation products, such as peroxides, was low (PI = 21%) compared to silica gel (PI = 65%).

The simple pre-treatment by silica gel (Loh *et al.*, 2003; Loh and Choo, 2003) sufficed to improve the oil quality for methyl esters conversion. The pre-treatment yielded 75% of a light yellow oil, having effectively discolor it. The characteristics of the used frying oil after pre-treatment by silica gel are shown in *Table 2*. As the used frying oil before and after silica

TABLE 1. PROPERTIES AND PERCENTAGE IMPROVEMENT (PI) OF USED FRYING OIL WITH SILICA GEL, ACTIVATED CARBON, ALUMINIUM OXIDE AND ACID-ACTIVATED SPENT BLEACHING EARTH

Adsorbent	FFA ^a , F ₁ (%)	PI (FFA) (%)	\mathbf{PV}^{a} , \mathbf{P}_{1} (meq kg ⁻¹)	PI (PV) (%)
Silica gel	6.2	33.3	1.8	65.1
Activated carbon	8.7	6.5	4.0	7.8
Aluminium oxide	6.5	30.2	3.5	20.8
Acid-activated spent bleaching earth	8.3	11.8	2.5	46.9

Notes: a FFA and PV were measured in triplicate and only the means reported.

FFA of fresh frying oil = 0.039%

 $F_0 = FFA$ of used frying oil before pre-treatment = 9.3%

 $F_1 = FFA$ of used frying oil after pre-treatment

 $PI(FFA) = F_0 - F_1 / F_0 \times 100\%$

PV of fresh frying oil = 0.46 meq kg⁻¹

 $P_0 = PV$ of used frying oil before pre-treatment = 4.3 meq kg⁻¹

 $P_1 = PV$ of used frying oil after pre-treatment

 $PI(PV) = P_0 - P_1 / P_0 \times 100\%$

TABLE 2. CHARACTERISTICS OF USED FRYING OIL BEFORE AND AFTER PRE-TREATMENT BY SILICA GEL

Characteristic	Before pre-treatment	After pre-treatment
Density (g cm ⁻³)	0.8989	0.8726
FFA (%)	9.3	6.2
P.V. (meq kg ⁻¹)	4.3	1.8
Viscosity (cSt) @ 40°C, ASTM D445	46.5	29.2
Oxidative stability (hr), DIN EN 14112 B	23.81	3.86
Glyceride components (%) (MG, DG and TG)ª	56.5	73.8
Others (%) (non-glyceride compositions)	43.5	25.0
Fatty acid composition, (FAC) (wt% as methyl esters)		
C14:0	1.3	0.9
C16:0	38.5	39.2
C18:0	5.6	5.3
C18:1	45.7	46.4
C18:2	8.8	8.1

Note: ^aMG – monoglycerides, DG – diglycerides, TG – triglycerides.

gel pre-treatment had similar fatty acid compositions (FAC), it is concluded that the silica gel did not alter the chemical composition of the oil.

The viscosity of used frying oil after silica gel pretreatment was greatly reduced. The increase in viscosity of frying oil is mainly caused by the formation of polymers (Paul and Mittal, 1997). Fresh frying oil has a viscosity of 39.6 cSt at 40°C, and used frying oil before pre-treatment 46.5 cSt at 40°C, while the pre-treated used frying oil was 29.2 cSt at 40°C, indicating a great reduction in its contents of polymers and degradation products. The Rancimat stability is an important indicator of the acceptability of methyl esters as biodiesel. The methyl esters must have an induction period (IP) of at least 6 hr (pr EN 14112) to be used as automotive diesel (pr EN 14214). Although the used frying oil was almost as stable (IP = 24 hr) as fresh frying oil (IP = 28 hr), the silica gel pre-treated used frying oil had a very poor oxidative stability (IP = 3.9 hr). This was probably due to almost all its antioxidants being absorbed by the silica gel. Fortunately, the unstable methyl esters (IP=3.4 hr) produced could be easily stabilized by additives (Loh et al., unpublished data).

Conversion of Used Frying Oil to Methyl Esters

Although the used frying oil regenerated by Miyagi and Nakajima (2003) could be recycled, the pre-treated used frying oil in this study had too high FFA to be used again in food applications. Nevertheless, it can be used in non-food applications, such as for conversion to methyl esters as biofuel.

The base catalyst (NaOH) alone sufficed to convert the pre-treated used frying oil to methyl esters due to the reduced FFA after silica gel pretreatment. For oil with considerately higher FFA, an additional esterification step is needed to first convert the FFA to methyl esters before the base catalyst is applied to convert the triglycerides. The conversion of triglycerides and remaining FFA of the pre-treated used frying oil to methyl esters using NaOH yielded 80% methyl esters weight-for-weight.

The composition of the raw methyl esters made from the pre-treated used frying oil is shown in Table 3. The product was 99% pure with 1% monoglycerides and diglycerides based on GC analysis. It had a FAC similar to that in the used frying oil after silica gel pre-treatment. Thus, the reaction to methyl esters did not affect the FAC of the used frying oil.

TABLE 3. COMPOSITION OF RAW METHYL ESTERS MADE FROM PRE-TREATED USED FRYING OIL

Composition	Purity (%)
Esters	99.1
Monoglycerides	0.7
Diglycerides	0.2
Triglycerides	0.0
Fatty acid composition, FAC	C (wt% as methyl esters)
C14:0	0.8
C16:0	38.2
C18:0	5.6
C18:1	47.5
C18:2	7.8

Fuel Characterization

The methyl esters made from the pre-treated used frying oil was analysed for its fuel properties (Table 4). It was found to be comparable to petroleum diesel and fresh palm oil methyl esters as biodiesel. Its

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Property	Used frying oil methyl esters	Crude palm oil methyl esters ^a (palm diesel)	Petroleum diesel
Density at 25°C (kg litre ⁻¹)	0.8863	0.8700	0.8310
Viscosity @ 40°C ASTM D445 (cSt)	4.4	4.5	4.0
Sulphur content (wt %) IP 242	0.04	0.04	0.10 15.0
Pour point (°C) ASTM D97	15.0	16.0	
Flash point (°C) ASTM D93	192	174	98
Gross heat of combustion ASTM D240 (kJ kg ⁻¹)	37365	40135	45800

Note: ^aChoo et al. (1993).

viscosity and low temperature fluidity were similar to those of fresh palm oil methyl esters and petroleum diesel. However, its higher flash point would make it a safer fuel. Thus, the pre-treated used frying oil methyl esters can be a diesel substitute. The sulphur content and calorific value of the pretreated used frying oil methyl esters obtained were similar to those of methyl esters produced by Mittelbach and Tritthart (1988) from used frying oil from restaurants and households in Austria without purification.

CONCLUSION

Used frying oil (mainly palm olein), after pretreatment with silica gel, is a suitable feedstock for conversion to methyl esters by catalytic reaction using NaOH. The methyl esters produced have fuel properties comparable to those of petroleum diesel. Thus, it can be a diesel substitute for unmodified diesel engines.

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