Journal of Oil Palm Research Vol. 23 December 2011 p. 1135-1140

PRODUCTION OF DISTILLED BIODIESEL FUELS THROUGH DIRECT ALKALINE TRANSESTERIFICATION OF USED FRYING OIL

LOH SOH KHEANG*; NUR AZREENA IDRIS* and CHOO YUEN MAY*

ABSTRACT

Vegetable oils are the most suitable renewable feedstock for biodiesel production, in particular palm oil which has unique characteristics, stability and attractive price. Besides the fresh vegetable oils, used frying oil (UFO) can also be used to make an equally good product. MPOB has investigated palm olein-derived UFO for biodiesel production since 2001 employing an additional pre-treatment using silica gel prior to transesterification of UFO, which increased the production cost. Alternative approaches focusing on cost improvement are being sought. This study found that direct alkali transesterification (DAT) is possible, preferably with UFO having low free fatty acids (FFA) content. The undistilled methyl esters (ME) produced have comparable physicochemical and fuel properties with an exceptionally better yield, are more stable against oxidation and have higher heat of combustion. The ME conversion exceeded 98% and the UFOME purity was 96.5%. The UFOME produced had properties comparable to petroleum diesel and can be used as a diesel substitute. Distillation of UFOME was conducted to further improve its colour, yielding a novel UFOME (UFOME-DAT distilled). However, while the distilled UFOME had similar fuel properties with those of the undistilled UFOME, its oxidative stability was reduced to an induction period of 4.13 hr, below the compliance level of the European Standard specification EN 14214.

Keywords: used frying oil, palm olein, direct alkali transesterification, used frying oil methyl esters, biodiesel.

Date received: 7 September 2010; **Sent for revision:** 4 October 2010; **Received in final form:** 28 January 2011; **Accepted:** 26 August 2011.

INTRODUCTION

Biodiesel is a renewable, biodegradable and environmentally benign fuel. It is as energy dense as petroleum diesel and so can be used in lieu of the latter without sacrificing engine performance. Thus, it is a feasible solution to the twin problems of fossil fuel depletion and environmental pollution (Refaat, 2009).

Biodiesel, however, costs more than petroleum diesel due to the high cost of its raw materials – mainly vegetable oils (Supple *et al*., 2002; Zhang *et al*., 2003). Therefore, it is necessary to explore the use of cheaper feedstocks, *e.g.*, used frying oil (UFO) which costs only half as much as the fresh oil (Zhang *et al*., 2003; Haas, 2005).

UFO generally has a high content of free fatty acids (FFA) which causes excessive soap formation during the transesterification process to produce the methyl esters (ME), or biodiesel. It is thus necessary to first reduce FFA in UFO to a less problematic content of 5% to improve the efficiency of the process (Loh *et al*., 2006a, b). A pre-treatment has already been developed for this process in 2001, using absorbents to remove the fatty acids as well as other impurities and undesirable products, such as colour pigments (Loh and Choo, 2001; Loh *et al*., 2006a, b, c). However, the pre-treatment is costly, thus, in part obviating the advantage of the cheaper feedstock. MPOB has therefore investigated alternative and more cost-effective ways of doing this, and has discovered that direct

---

* Malaysian Palm Oil Board,
P. O. Box 10620,
50720 Kuala Lumpur,
Malaysia.
E-mail: lohsk@mpob.gov.my

alkaline transesterification (DAT) – a one-process method for converting UFO with FFA not exceeding 5% to biodiesel – is possible.

In this study, DAT was used to produce ME from UFO (UFOME), followed by distillation to obtain a more appropriate yellow colour for the resultant biodiesel. This article addresses both the processing of UFOME by DAT and the fuel quality of the final product.

MATERIALS AND METHODS

Materials

A batch of UFO (100 kg, 100% palm olein) was obtained from a local fast food restaurant. The restaurant discards the oil after continuous frying activities over a week. This used oil appeared like a clear liquid – brownish in colour, moderately viscous, and with about 5% solid settlement (food residues and dust debris) at the bottom. Fresh palm olein frying oil was purchased from a supermarket. Commercial grade sodium hydroxide (NaOH) and methanol were purchased from Merck.

Methods

Physical treatment of UFO. UFO was filtered by water suction to allow food residues and dust debris to settle. The filtrate was used for DAT while the filtrand was discarded.

a. Production of UFOME via DAT (abbreviated as UFOME-DAT).

The transesterification of UFO was adapted from the protocol described by Choo *et al.* (1990). The filtrate of UFO (90 g, FFA 0.95%) was subjected to ME conversion using NaOH (0.5 g, 0.013 M) which was first dissolved in 45 ml methanol before being reacted with the oil for 10 min at a temperature of 65°C (reflux). The yellowish ester layer was washed several times with warm distilled water until neutral, then vacuum-dried to yield crude esters (88 g).

b. Distillation of UFOME-DAT.

The distillation of UFOME-DAT was performed in a round-bottomed, one-neck flask with a temperature controller, and a receiver flask connected to a vacuum gauge and a condenser. A pump connected to the condenser provided a vacuum in the range 1-2 mmHg. The solution was heated gradually under controlled temperature to a maximum of 150°C. The distillates were collected in the receiver flask at a temperature between 60°C and 120°C to yield the distilled light yellow ME (83 g). The distillation was terminated when all distillates were collected.

c. Analyses of physicochemical properties.

FFA, peroxide value (PV), saponification value and iodine value were determined for the fresh palm olein frying oil, UFO and UFOME via MPOB test methods p2.5: 2004, p2.3: 2004, c2.8: 2004 and c2.6: 2004, respectively (MPOB, 2005). All measurements were done in triplicate and only the means were reported. Carotene content was determined via MPOB Test Method p2.6: 2004 using an UV spectrophotometer at 446 nm in 10 mm path length silica cells. Two other properties analysed were based on ASTM test methods: kinematic viscosity at 40°C and 100ºC by an automated multi-range viscometer HVM472 (Walter Herzog, Germany) according to ASTM D445, and density (25ºC) by a digital density meter based on ASTM D 4052. Moisture content was determined by the Karl Fisher method. Oxidative stability via the Rancimat method was measured using a Model 743 Rancimat instrument (Metrohm AG, Switzerland). Samples of 3 g were analysed under a constant airflow of 10 litre hr^{-1} and at a 110ºC temperature of the heating blocks. All determinations of the induction periods were performed in duplicate and only the means were reported. The fatty acid compositions (FAC) of all samples were determined according to ISO 5508: Animal and vegetable fat and oil analysis by gas-liquid chromatography of ME of fatty acids. Analysis was carried out using a Hewlett Packard 5890 Series II gas chromatograph equipped with a flame ionization detector and a 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, 185ºC; injector temperature, 240ºC; detector temperature, 240ºC; split ratio, 1:100; and carrier gas, helium at 2.0 ml min^{-1}. IR spectrum was recorded using a Perkin-Elmer Spectrum One FTIR in the 400-4000 cm^{-1} region. The ^{1}H NMR spectrum was recorded at 25°C on a Bruker ACF 300 MHz spectrometer.

d. Analyses of fuel properties.

The fuel characteristics of all UFOME obtained were measured according to the respective ASTM test methods: kinematic viscosity at 40ºC by an automated multi-range viscometer HVM472 (Walter Herzog, Germany) according to ASTM D445; specific gravity at 15ºC by a digital density meter based on ASTM D 4052; pour point by an automatic pour point measuring apparatus (ISL CPP 97-2 Analyzer) according to ASTM D97; flash point by a Pensky-Martens closed cup tester based on ASTM D93; moisture content was determined by the Karl Fisher method; gross heat of combustion was determined by an automatic bomb calorimeter AC-350 (Leco, USA) according to ASTM D240. All measurements were performed in duplicate and only the means were reported. Oxidative stability via the Rancimat method was measured according to the method described in the previous section (c. Analyses of physicochemical properties).

RESULTS AND DISCUSSION

In a previous study (Loh *et al.*, 2006a), it was established that UFO with high FFA content (10%) had to undergo an adsorption process, *i.e.* pre-treatment with several adsorbents to lower its FFA before subjecting it to transesterification to produce ME with a preferred colour. ME produced in that study is abbreviated as UFOME-T. The oil, without any pre-treatment and with FFA above 5%, can easily form soap with NaOH during transesterification, thus greatly reducing the yield of ME (Loh *et al.*, 2006a, b). In this study, UFO with low FFA content (less than 5%) was subjected to a one-step process, *i.e.* DAT, to produce ME without prior pre-treatment with adsorbents.

The physicochemical properties of fresh palm olein frying oil, UFO and UFOME-DAT were compared (*Table 1*). UFO exhibited poorer properties relative to fresh frying oil in terms of FFA, PV, saponification value and iodine value due to oil deterioration during excessive frying (over a week) (Pantzaris and Ahmad, 1998). The heat, air and moisture to which the oil is exposed lead to polymerisation, oxidation and hydrolysis in the oil (Gebhardt, 1996). As palm olein comprises triglyceride molecules with different reactive sites (*Figure 1*) dependent on their polarity, these reactive sites react differently with the heat, air and moisture present in determining the structure of palm olein after excessive frying. One of the reactive sites – unsaturated fatty acyl chains – is particularly susceptible to oxygen free radical attack, with a high probability of accelerating different chemical reactions like polymerisation and oxidation (Kodali, 1996). This explains why the PV of UFO in particular increased enormously by about 18-fold while the iodine value decreased by two-fold compared to fresh frying oil. Due to oil degradation, the saponifiable substances increased as the ester bonds were easily broken to form soap with an alkali.

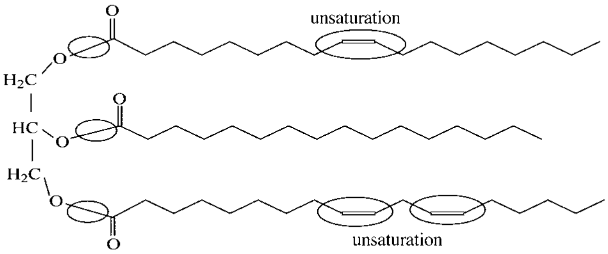

Figure 1. Structure of triglyceride molecule of palm olein and its reactive sites. Left side: glycerol; right side, from top to bottom: oleic acid C18:1, palmitic acid C16:0 and linoleic acid C18:2.

Interestingly, while carotene content and kinematic viscosity reduced greatly, DAT was able to improve FFA content, PV, saponification value and iodine value of UFOME-DAT. It was speculated that some mechanism must have occurred leading to the removal of substances affecting the respective quality parameters in the course of transesterification. Probably, DAT was capable of removing some of the oxidised and/or polymerised materials from the oil through interactive contact with NaOH, methanol and water. Unfortunately, there was not enough evidence to support the

TABLE 1. COMPARISON OF PHYSICOCHEMICAL PROPERTIES OF FRESH PALM OLEIN FRYING OIL, USED FRYING OIL (UFO) AND UNDISTILLED USED FRYING OIL METHYL ESTERS VIA DIRECT ALKALI TRANSESTERIFICATION (UFOME-DAT)

Property	Fresh palm olein frying oil	UFO	UFOME-DAT
Density (g cm^{-3})	0.9101	0.9092	0.8692
Free fatty acids (%)	0.13	0.95	0.18
PV (meq kg^{-1})	2.28	41.32	13.59
Carotene content (ppm)	17.24	15.66	5.13
Moisture content (%)	0.61	1.03	0.05
Saponification value (mg KOH g^{-1} oil)	27.9	130.3	26.5
Iodine value (wijs)	57.72	25.25	65.76
Oxidative stability (hr)	22.57-28.03	24.22-25.06	15.62-20.30
Kinematic viscosity (cSt)			
@ 40°C	43.08	40.18	4.47
@ 100°C	8.63	8.32	1.72

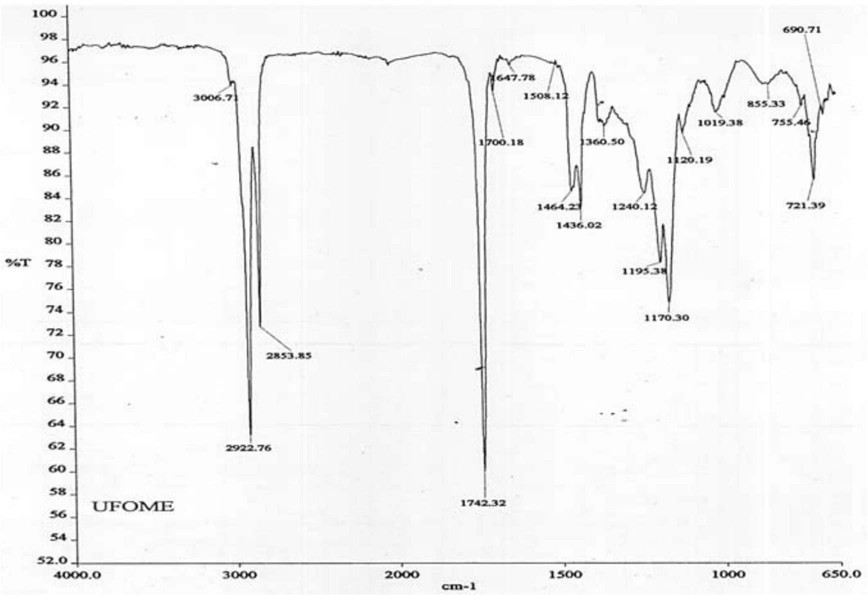

Figure 2. FTIR spectrum of undistilled used frying oil methyl esters via direct alkali transesterification (UFOME-DAT).

TABLE 2. RESULTS OF ^{1}H NMR FOR UNDISTILLED METHYL ESTERS VIA DIRECT ALKALI TRANSESTERIFICATION (UFOME-DAT)

Functionality	Chemical shift (δ)	Integration	Signal	Remarks
$-CH_3$	0.76	1.35	t	Methyl
$-(CH_2)n-$	1.17, 1.50, 1.91	9.22, 0.99, 1.51	m, t, m	Alkyl
$-CH_2CO_2-$	2.16, 2.65	1.03, 0.16	t, t	Methylene adjacent to carbonyl
$-CO_2CH_3$	3.52	1.56	s	Methyl esters
-HC=CH-	5.21	1	m	Unsaturation

hypothesis of an appropriate mechanistic approach on this at the moment.

The IR spectrum (*Figure 2*) of UFOME-DAT reveals that all the typically characteristic stretching vibration bands of the functional groups of a fatty ester, *e.g.* the distinct C=O stretching mode at 1742 cm^{-1} and the C-O-C stretching mode at 1170 cm^{-1}, are indicative of O-coordinated behaviour while the asymmetric stretching modes of CH_3CH_2 at 2923 cm^{-1} and 2854 cm^{-1}, CH bending at 1464 cm^{-1} and C=C rocking at 721 cm^{-1} are diagnostic of the presence of a hydrocarbon chain. Similarly, the ^{1}H NMR (*Table 2*) of UFOME-DAT shows all chemical shifts which are diagnostic of the formation of ME.

Table 3 shows that UFOME-T and UFOME-DAT (undistilled and distilled) have similar fuel properties; in fact UFOME-DAT (undistilled and distilled) have better heat of combustion. Hence, they are comparable to commercial petroleum diesel and can be used as diesel substitutes.

By simply skipping the pre-treatment part and relying only on DAT, the whole process of UFOME production is believed to be more cost-competitive. It is interesting to note the significant finding on the DAT process used in this study – that the carotene presence as an antioxidant in UFO was not totally diminished but indeed was substantially retained during DAT to provide a higher oxidative stability to UFOME-DAT. In contrast, it was noted previously (Loh *et al.*, 2006d) that the adsorbent used to treat UFO was capable of adsorbing almost entirely the carotene present in the oil, thus UFOME-T showed poorer oxidative stability. While UFOME-DAT can be used in its current form, further improvement to its colour appearance by distillation can be considered as has been shown in this study. The distillation of UFOME-DAT conducted in this study has not previously been reported elsewhere. On the other hand, distilled UFOME-DAT exhibited the expected low value in oxidative stability compared to undistilled UFOME-DAT due to the removal of the high-molecular-weight carotene compound during distillation. It is thus proposed that unless undistilled UFOME-DAT has a colour problem unacceptable for use, it should not be distilled prior to its intended use. Alternatively, it is envisaged that distilled UFOME-DAT can be considered as a diesel substitute after addition of some promising antioxidants, something which can be easily accomplished (Loh *et al.*, 2006d).

TABLE 3. COMPARISON OF THE PROPERTIES OF USED FRYING OIL METHYL ESTERS (UFOME) OBTAINED BY DIFFERENT APPROACHES WITH PETROLEUM DIESEL

Characteristic	UFOME-T[b]	UFOME-DAT (undistilled)	UFOME-DAT (distilled)	Petroleum[c] diesel
Physicochemical Properties:				
Free fatty acids (%)	0.10	0.44	0.25	N/A
PV (meq kg^{-1})	8.68	13.59	6.82	N/A
Carotene content (ppm)	0.05	5.13	1.11	N/A
Moisture content (%)	0.05	0.10	0.05	< 0.05
Yield (%)	80.0	98.7	93.9	N/A
Colour (visual)	yellowish	brownish	yellowish	yellow
Glyceride components (%) (MG, DG and TG)[a]	0.9	0.8	0.1	N/A
Others (%) (non-glyceride compositions)	99.1	96.5	99.9	N/A
Fatty acid composition, FAC (wt% as ME)				
Myristic acid	0.8	0.9	0.9	N/A
Palmitic acid	38.2	35.7	42.2	N/A
Stearic acid	5.6	4.5	4.9	N/A
Oleic acid	45.7	44.4	50.7	N/A
Linoleic acid	7.8	12.7	0.3	N/A
Fuel Properties:				
Density (g cm^{-3})	0.8863	0.8692	0.8682	0.8538
Viscosity (cSt) @ 40°C, ASTM D445	4.4	4.5	4.5	4.5
Oxidative stability (hr), DIN EN 14112B	3.40	20.30	4.13	N/A
Pour point (°C), ASTM D97	15.0	12.0	12.0	12.0
Flash point (°C), ASTM D93	192	182	182	93
Gross heat of combustion (kJ kg^{-1}), ASTM D240	37 365	40 068	40 072	45 800d

Note: [a] MG denotes monoglycerides, DG denotes diglycerides, TG denotes triglycerides.

[b] All physicochemical properties of UFOME-T were obtained via analyses conducted in this study. Fuel properties of UFOME-T were retrieved from Loh *et al*. (2006a).

[c] MPOB (2009).

[d] Choo *et al*. (1993).

DAT - direct alkali transesterification.

CONCLUSION

DAT can be used to produce biodiesel fuel from palm-olein based UFO with FFA content less than 5%. In fact, UFOME-DAT has improved fuel characteristics, especially its oxidative stability, due to the presence of carotene unlike UFOME-T from which carotene is removed during pre-treatment. The production of UFOME-DAT eliminates a pre-treatment step using adsorbents, but is only applicable to UFO with low FFA content. Although the distillation process can be used after DAT to produce biodiesel fuel with a more desirable colour, it is not necessarily practical depending on the needs or the intended application of the fuels.

ACKNOWLEDGEMENT

The authors thank the Director-General of MPOB for financial support to carry out this work, and for permission to publish the findings. The technical assistance provided by the staff of the Processing Research Laboratory is also deeply appreciated.

REFERENCES

CHOO, Y M; ONG, A S H; GOH, S H and KHOR, H T (1990). Transesterification of fats and oils. UK patent No. 2188057.

CHOO, Y M; MA, A N and BASIRON, Y (1993). Palm oil methyl esters as fuel: palm diesel. *PORIM Information Series No. 17.*

GEBHARDT, B (1996). Oils and fats in snack foods. *Bailey's Industrial Oil & Fat Products* (Hui, Y H ed.). 5th ed., vol. 3, John Wiley & Sons, New York. p. 407-427.

HAAS, M J (2005). Improving the economics of biodiesel production through the use of low value lipids as feedstocks: vegetable oil soapstock. *Fuel Process. Technol., 86*: 1087-1096.

KODALI, D R (1996). Industrial application of vegetable oils and fats: lubricants. *Proc. of the 1996 PORIM International Palm Oil Congress (Soap & Detergent).* PORIM, Bangi. p. 465-474.

LOH, S K and CHOO, Y M (2001). Esterification of used frying oil and oils recovered from spent bleaching earths. *Viva Report No. 167/2001(34)*. MPOB, Bangi.

LOH, S K; CHENG, S F; CHOO, Y M and MA, A N (2006a). Recovery and conversion of palm-olein-derived used frying oil to methyl esters for biodiesel. *J. Oil Palm Research Vol. 18 No. 1*: 247-252.

LOH, S K; CHENG, S F; CHOO, Y M and MA, A N (2006b). A study of residual oils recovered from spent bleaching earths: their characteristics and applications. *Amer. J. Applied Sciences, 3(10)*: 2063-2067.

LOH, S K; CHOO, Y M; CHENG, S F and MA, A N (2006c). Used frying oil for biodiesel. *Inform, 17(10)*: 623-625.

LOH, S K; CHEW, S M and CHOO, Y M (2006d). Oxidative stability and storage behavior of fatty acid methyl esters (FAME) derived from used palm oil. *J. Amer. Oil Chem. Soc., 83*: 947-952.

MPOB (2009). *Palm Biodiesel - Environmental-friendly Fuel.* MPOB, Bangi.

MPOB (2005). *A Compendium of Test on Palm Oil Products, Palm Kernel Products, Fatty Acids, Food Related Products and Others*. MPOB, Bangi.

PANTZARIS, T P and AHMAD, M J (1998). Deep frying – assessment of palm oil against rapeseed oil/soyabean oil blend. *Palm Oil Technical Bulletin, July-August*: 7-9.

REFAAT, A A (2009). Different techniques for the production of biodiesel from waste vegetable oil. *Int. J. Environ. Sci. Tech., 7 (1)*: 183-213.

SUPPLE, B; HOWARD-HILDIGE, R; GONZAEZ-GOMEZ, E and LEAHY, J J (2002). The effect of steam treating waste cooking oil on the yield of methyl ester. *J. Amer. Oil Chem. Soc., 79*: 175-178.

ZHANG, Y; DUBE, M A; MCLEAN, D D and KATES, M (2003). Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresour. Technol., 89*: 1-16.