The Effect of Steam Treating Waste Cooking Oil on the Yield of Methyl Ester

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ABSTRACT: The effect of steam injection and sedimentation treatment of waste cooking oil on the quality of TG, to be used as a raw material for the production of biodiesel, was investigated. The effect of steam treatment was evaluated in terms of a number of physical and chemical characteristics. Significant decreases in the moisture, FFA, and PV, as well as increased energy value, were observed. GC analysis of the treated materials demonstrated little change in either the overall composition of the oils or the iodine value. The decreases in moisture from 1.4 to 0.4% and in FFA from 6.27 to 4.28% were found to correlate strongly with an increase in yield of ester from 67.5 to 83.5%.

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KEY WORDS: Biodiesel, effect of steam treatment, ester yield, waste cooking oil.

Biodiesel is the name applied to renewable fuels, manufactured by the alcoholysis or transesterification of vegetable oils or animal fats with methanol, that are used as a substitute for or as an additive to mineral diesel. The methyl ester produced using methanol and a basic catalyst is the major source of biodiesel available for compression ignition engines, as its properties closely resemble those of No. 2 mineral diesel. The European Union (EU) has set an objective of 5% of transport fuels to be produced from renewable resources by 2005, of which a substantial portion is expected to be biodiesel (1).

Primarily owing to the competition with the food industry for available land as well as the price support mechanisms within the EU at present for vegetable oil, it is necessary to look at alternative sources of raw material in order for biodiesel production to become more economical (2). Waste cooking oil (WCO) offers some promise as an alternative low-cost biodiesel feedstock whose availability is not affected by EU land-use policies. Based on estimates from seven countries, a total of about 0.4 Mt is collected within the EU, mainly from the catering industry, while the amount that could be collected is estimated to be considerably higher, possibly from 0.7 to 1 Mt. Its price is variable, but in general is approximately half that of virgin oil (3). More recently the detection of dioxins in WCO used in animal feed rations, its primary market, has focused attention on this material and caused a major reappraisal of its use (4). At present, the use of waste oil in animal feeds has been voluntarily terminated in about half of the EU states.

Biodiesel quality is directly related to the quality of the raw oil. During heating of vegetable oils for frying purposes, thermal, oxidative, or hydrolytic reactions can cause chemical changes (5). The compounds formed depend on the composition of both the oil and the food being fried. The chemical and physical changes induced in the frying fat are influenced by a number of frying parameters, with high temperature, long frying times, and metal contaminants favoring extensive decomposition of the oil. The design and type of the fryer (pan deep-fat batch, or deep-fat continuous) are also important; oxidation of the oil will occur faster at large surface-to-volume ratios. Other factors of concern are turnover rate of the oil, the heating pattern (continuous or intermittent), and whether antioxidants are present (6). It has been proposed that the starting material should meet certain specifications (7). The TG should have an acid value less than 1 and should be substantially anhydrous. As little as 0.3% water in the reaction mixture reduces glycerol yield by consuming catalyst; addition of extra catalyst compensates for higher acidity but results in soaps that interfere with the separation of glycerol. Other investigators have stressed the importance of using reasonably dry oil, substantially free of fatty acids.

The products of decomposition cause a deterioration in oil quality, which can lead to reduced yield of methyl ester during biodiesel production and the formation of unwanted products. WCO requires refining prior to esterification. The objective of this study was to investigate a process for recycling WCO to determine to what extent recycling improved oil quality and contributed to improved yield of methyl ester.

MATERIALS AND METHODS

The refining process. The refining process examined in this study involved steam injection followed by filtration to remove unwanted solids and reduction of the moisture content. WCO contains about 20% waste by volume owing to large solids (food, papers, etc.), smaller-sized solids, which have become suspended within the oil, and water that will gradually settle out.

The WCO was passed through a series of sieves ranging in aperture from 5 to 1 mm, which remove the unwanted solids. The first sieve that the oil encountered was a very coarse grade, with each subsequent sieve being of an increasingly finer grade as the oil quality gradually improved. Oil that has a sufficiently low viscosity at room temperature passed through the sieves relatively quickly, whereas steam

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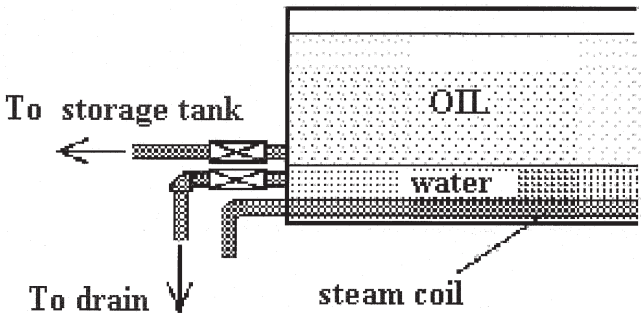


SCHEME 1

was applied to the solid fats, heating them to 65°C to allow filtration. Melting the fats also aided the release of trapped water and other contaminants.

The oil passed through the sieves into a tank fitted with two valves positioned one above the other. The liquid was left to settle in the tank for a period of time to allow water and adventitious particles to sediment (Scheme 1). The longer the settlement time, the better the separation, but the viscosity of the oil also increased as it cooled.

After settling, the water and any suspended solids were drained, and the refined oil was placed in storage. This constituted the first treatment stage (T1). Alternatively, the oil was reheated (65°C) by steam injection into the tank followed by a second cycle of sedimentation and settling before the refined oil was stored (T2).

Materials. Raw and refined WCO (T1 and T2) were obtained from Bolton RVO Ltd. (Castledermot, Co Kildare, Ireland). Two batches were selected on the basis of being derived from two different suppliers of virgin oil. The chemicals used for the analysis and transesterification were supplied by Merck (Darmstadt, Germany), Aldrich (St. Louis, MO), BDH (Poole, United Kingdom), and Riedel de Haen (Salze, Germany). GC standards for FAME were obtained from Sigma-Aldrich (Poole, United Kingdom).

Transesterification of the WCO with methanol was carried out in 500-mL round-bottomed flasks equipped with magnetic stirrer and thermometer. About 400 g of WCO was added and heated to 60°C, and the appropriate amount of alcohol (86.8 g) and dissolved catalyst, 1% w/w KOH, was then added. The reaction mixture was stirred vigorously for 1 h, after which the mixture was transferred to a separating funnel, and the glycerol was allowed to settle for a minimum of 4 h. After draining off the glycerol, the resulting methyl ester was transferred to a clean separating funnel and washed gently with 100 mL of distilled water to remove any soaps that may have formed, and allowed to separate. The resulting weight of ester was used to calculate yield.

GC analysis suggested that oleic acid was the dominant component in the oils, so the biodiesel yield was calculated using the initial amount of olein as the basis for the theoretical yield. From the reaction:

$$3 \text{ mol } CH_3OH + 1 \text{ mol TG} \rightarrow 3 \text{ mol methyl ester} + 1 \text{ mol glycerol} \quad [1]$$

For TG (olein) where molecular weight = 885 g/mol, the mass = 400 g, and number of moles = 400/885 = 0.452. For methanol, where molecular weight = 32 g/mol, the number of moles = 0.452 × 6 = 2.712 (6:1 molar ratio); mass of methanol = 2.712 × 32 = 86.8 g; density of methanol = 0.75 g/mL; volume of methanol = 86.6/0.75 = 115.7 mL. For the theoretical yield for a biodiesel molecular weight equaling 296 g/mol (oleic acid methyl ester), the yield is: number of moles = 0.452 × 3 = 1.356; and theoretical mass of biodiesel = 1.356 × 296 = 401.35 g. For the actual yield, where the mass of biodiesel = X g, the % yield = X/40.35 × 100.

Analyses. Moisture content was obtained by a Karl Fischer titration using a Metrohm autotitrator. Density of the oils was determined by bringing a tared 100-mL volumetric flask to the mark with oil at 20°C and noting the weight on a calibrated analytical balance. The kinematic viscosity was measured using a Schott Gerate Ubbelohde capillary viscometer.

The acid values of the oils were determined in accordance with IUPAC Standard Method 2.201 (8), the peroxide value in accordance with IUPAC Standard Method 2.501, the saponification number according to IUPAC Standard Method 2.202, the unsaponifable matter in accordance with IUPAC Standard Method 2.401, and the iodine value in accordance IUPAC Standard Method 2.205 (8). Iodine values were also calculated from the FAME profile according to AOCS Official Method Cd 1c-85 (9). The energy value was measured using a bomb calorimeter according to ASTM Standard Method 2015-91 (10). Elemental analysis of carbon, hydrogen, nitrogen, and sulfur contents was carried out by the Microanalytical Laboratory in University College Dublin, Ireland.

Thermogravimetric analysis was carried out on a TA (Du Pont 920) instrument, with samples (~20 mg), heated at 10ºC/min to 900ºC in a continuous N_2 stream. GC analysis was carried out on the FAME of the oil. About 30 mg of FAME was weighed out into a 10-mL volumetric flask that was made up to the mark with dichloromethane. A 1.0-µL aliquot of this solution was injected onto the GC. A Zebron ZB-wax column (Phenomenex, Macclesfield, United Kingdom) (30 m length × 0.53 mm internal diameter) was used in a Hewlett-Packard model HP 5980 series II chromatograph equipped with a flame-ionization detector and integrator. The injector and detector temperatures were set at 300ºC, and the carrier gas was nitrogen (5 mL/min). The initial oven temperature was 170ºC and was held for 3 min and then programmed from 170 to 230ºC at 3ºC/min and held at 230ºC for 20 min. Standards of FAME were used to identify the FAME in the sample. Fatty acid composition was calculated as percentage of the total fatty acids present in the sample determined from the peak areas.

RESULTS AND DISCUSSION

For the two batches used in this study, the yields of refined oil were 83.3 and 80.7% by volume, respectively, for batches 1 and 2. The effect of the treatment process on WCO is shown in Table 1. A progressive decrease in the physical and chemical parameters associated with oil deterioration was observed

TABLE 1
Effect of Treatment on Physical and Chemical Properties of Waste Cooking Oil

	Batch 1 raw	Batch 1 T1	Batch 1 T2	Batch 2 Raw	Batch 2 T1	Batch 2 T2
Moisture content (%)	1.1	0.5	0.4	1.4	0.6	0.4
Density (kg/m^3)	0.937	0.925	0.921	0.939	0.929	0.922
Kinematic viscosity (mm^2/s)	190.2	130.1	85.3	201.3	110.2	70.1
Acid value	5.3	4.4	3.9	6.3	4.9	4.3
Iodine value	104.3	103.7	105.2	115.3	117.2	116.2
PV (meq/kg)	5.6	5.3	4.6	6.3	5.7	4.4
Saponification number	204.3	194.2	184.2	195.1	194.3	193.9
Unsaponifiable matter (%w/w)	3.9	2.7	1.9	4.9	3.0	2.1
Energy value (kJ/g)	37.2	38.8	38.6	37.9	38.3	39.1

TABLE 2
Elemental Analysis of Treated Oils

% (wt)	C	H$_2$	N$_2$	S	O$_2$
Batch 1 raw	77.25	11.37	0.14	0	11.23
Batch 1 T1	77.09	12.08	0	0	10.83
Batch 1 T2	76.84	11.72	0	0	11.44
Batch 2 raw	75.73	11.74	0	0	12.52
Batch 2 T1	77.10	12.12	0	0	10.78
Batch 2 T2	77.26	11.87	0	0	10.87

for the two batches as a function of treatment. This included a reduction in moisture content, which corresponds with a similar reduction in the FFA and unsaponifable material that may be of a hydrophilic nature and whose presence may increase the percentage of bound moisture. The liquefaction of the fats may also have freed bound water that had become trapped during the cooling process. There was a significant change in the physical properties of the oil (e.g., density and kinematic viscosity) with treatment. This is a further indication of removal of the products of oxidation, i.e., oligomers and polymers, which contribute to an increase in viscosity when used in cooking.

A significant alteration in the chemical characteristics of the oils was also observed with progressive decreases in both acid value and PV with treatment stages. This corresponded with the removal of the FFA and hydroperoxides, the primary products of oxidation, during the treatment process. There was no change in the iodine value, so the degree of unsaturation remained unchanged. The saponification value is a measure of the mean molecular weight of the constituent FA. There was a slight decrease in the saponification values for both oils when treated, indicating a slight drop in the mean molecular weight of the oils, which may be related to the decrease in acid value. Unsaponifable matter includes lipids of natural origin such as sterols, higher aliphatic alcohols, pigments, and hydrocarbons as well as any foreign organic matter (6). Unsaponifable matter may be a useful test of oil purity. For both batches, the level of unsaponifiables decreased with the treatment process, indicating an improvement in oil quality as treatment was applied. The energy value increased with treatment.

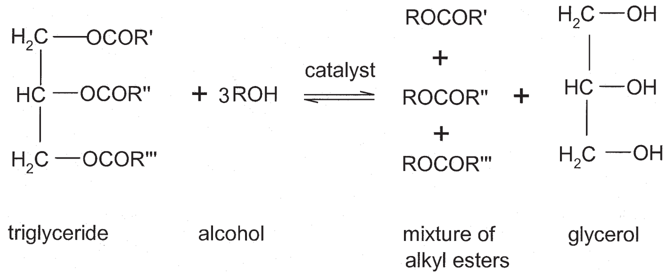
Table 2 contains the elemental analysis for both batches after each treatment stage; oxygen was determined by difference. There was very little change in elemental composition with batch 1, whereas batch 2 showed an incremental decrease in oxygen with corresponding increased carbon content, indicating that the more polar hydroperoxide species and water were removed.

Table 3 shows the GC analyses of the raw and treated oils. The iodine value was also calculated from the FAME analysis, and the results compared well with those from the wet chemical determinations (Wijs method). Although there were slight differences between the two batches, with batch 1 having a greater amount of C18:1 and batch 2 having a larger proportion of C18:2 and C18:3, the FA profile for the oils did not change dramatically as a result of processing (Table 3). This is a good indication that the nonlipid impurities are preferentially removed.

In the alcoholysis or transesterification of vegetable oils, TG reacts with an alcohol in the presence of a catalyst, producing a mixture of fatty acid alkyl esters and glycerol (Scheme 2) (11). In this investigation, methanol was used, and the yields of methyl ester obtained using a methanol to oil ratio of 6:1, 1% KOH, and a temperature of 60ºC are presented in Figure 1. The effect of centrifuging the oil at 1000 rpm for 15 min at room temperature is also reported for comparison. The

TABLE 3
GC Analysis of Treated Oils

FAME (%)	Batch 1 raw	Batch 1 T1	Batch 1 T2	Batch 2 Raw	Batch 2 T1	Batch 2 T2
C12:0	0.03	0.05	0.03	0.05	0.04	0.04
C14:0	0.16	0.16	0.18	0.16	0.14	0.15
C16:0	8.32	8.49	8.41	6.90	7.10	7.10
C16: 1	0.35	0.28	0.56	0.51	0.50	0.45
C18:0	2.94	2.05	2.40	2.92	2.24	2.24
C18: l	60.15	60.42	58.48	58.81	59.34	59.44
C18: 2	18.42	18.59	19.84	20.51	20.64	20.71
C18: 3	6.78	6.93	7.01	8.18	8.37	8.19
C20:0	0.65	0.51	0.39	0.60	0.57	0.55
C20: 1	1.46	1.11	0.99	1.32	0.92	0.97
C22:0	0.41	0.69	0.78	0.02	0.03	N/D
C22: 1	0.29	0.67	0.89	0.09	0.15	0.17
Iodine value	103.0	103.9	104.9	116.1	116.9	116.7



SCHEME 2

temperature of 60°C was chosen because alkaline alcoholysis of vegetable oil is frequently conducted near the boiling point of the alcohol, which for methanol is 65°C (12).

The molar ratio of alcohol to vegetable oil is one of the most important variables affecting the yield of ester in transesterification reactions. The theoretical stoichiometric ratio is 3:1, but a higher proportion of methanol is required if the reaction is to provide high yields of product in a reasonable time. In the ethanolysis of peanut oil, Freedman *et al.* (13) found that a 6:1 molar ratio liberated significantly more (from 77 to 95%) glycerol than 3:1 molar ratio. When this work was extended to refined oils—soybean, sunflower, peanut, and cottonseed oil—the highest conversions to esters were observed at 6:1 molar ratio (14). Several other researchers have found this to be the most suitable ratio in transesterification studies (7,15,16).

Figure 1 shows that there was a significant and progressive improvement in the yield of biodiesel with treatment stages. In the case of batch 2 oil, the yield increased from 67.6% for the untreated oil to 83.4% for oil having undergone two treatment cycles. Further improvements in yield can be achieved as a result of centrifugation. The increased yield can be related to a reduced free acid content with treatment (Table 1).

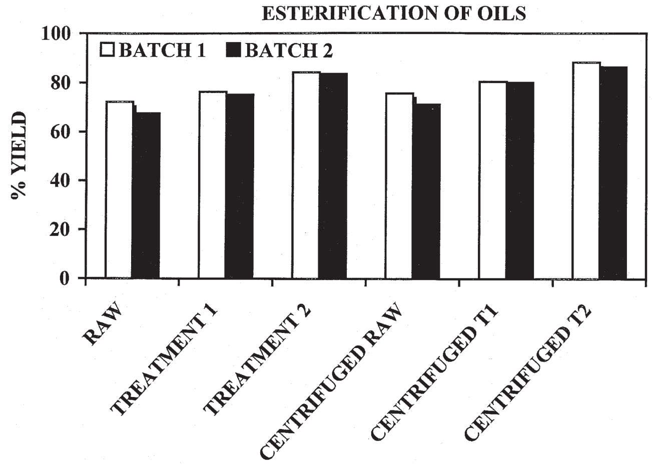


FIG. 1. The effect of steam treatment and centrifuging on yield of methyl ester.

High acid values favor the formation of soaps, which reduce ester yield and make separation of the glycerol and methyl ester more difficult. Steam treatment of WCO reduced the moisture and FFA levels significantly but not below suggested levels (7,12) of an FFA value of 1 and an oil that is moisture free, conditions that are required so as to optimize yield; nevertheless, a considerable improvement in yield of ester resulted. The decrease in moisture content from 1.4 to 0.4%, and FFA from 6.27 to 4.28%, corresponds with increased yield of ester from 67.5 to 83.5%.

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