

A Study of Residual Oils Recovered from Spent Bleaching Earth: Their Characteristics and Applications

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Abstract: This study described the extraction of residual oils of spent bleaching earth (SBE) from palm oil refining industry, the properties and applications of residual oils obtained there from. Residual oils of SBE (acid-activated, WAC and neutral, NC) were recovered *via* solvent and supercritical-fluid (SC-CO₂) extraction. The yields of residual oils recovered from WAC were higher than those from NC using solvent and SC-CO₂ extraction respectively. Both the residual oils recovered from WAC and NC had fatty acids composition (FAC) similar to that of crude palm oil. These oils exhibited poor qualities in terms of free fatty acids (FFA) content and peroxide value (PV). As the residual oils had very high FFA value (more than 10%), they were no longer suitable for food applications. Alternatively, these oils can be converted to their respective methyl esters for biofuel and other non-food applications as they were thermally and chemically stable with induction period of up to 29 h in Rancimat test. The methyl esters conversion *via* esterification and transesterification gave optimum yields of more than 80%. The methyl esters obtained have comparable fuel properties as petroleum diesel; hence, they can be used as diesel substitute.

Key words: Residual oil, spent bleaching earth, extraction, methyl esters, biodiesel

INTRODUCTION

Pre-treatment of crude palm oil in refinery which involves degumming and bleaching generates plenty of spent bleaching earth (SBE). It is estimated that about 600,000 metric tones or more of bleaching earth are utilized worldwide in the refining process based on the worldwide production of more than 60 million tones of oils^[1]. The SBE serves as by-product, which contains high percentage of oil^[2]. Disposal of SBE by incineration, inclusion in animal feeds, land filling method or concrete manufacturing is generally practiced. Large quantity of SBE is disposed off in landfills, causing fire and pollution hazards due to the substantial oil content in the earth. The oil in SBE would be wasted if it were not recovered and causes loss of oil in the long run.

The oil was commonly recovered by solvent extraction^[2-7]. Depending on the applications of the extracted oil, several non-polar or polar solvents can be considered as extracting medium. Polar solvents such as acetone, methylethyl ketone, methylene chloride, perchloroethylene, isopropyl alcohol, chloroform extract polar components, coloured bodies together with the oil from SBE while non-polar solvents such as petroleum benzene, petroleum ether, toluene, xylene, hexane, flugen extract the non-polar fractions mainly triglycerides as well as other useful non-polar components. The type of solvent used and the method of oil extraction could determine the quality of the

extracted oil from SBE. Theoretically non-polar solvent such as hexane allows the use of extracted oil in foods. To obtain oil with better quality, the extraction has to be carried out on fresh SBE and under nitrogen protection.

Aqueous extraction was another inexpensive method to recover oil that retained in SBE. The types of aqueous extraction were steam blowing through SBE, circulating hot water through the cake, boiling of SBE in water containing soda and salt. The quality of oil recovered was poor and only suitable for technical purpose.

The oil was also recovered *via* supercritical-fluid extraction^[8]. Extraction of SBE *via* supercritical fluid technology is a clean and environmental friendly technology, utilising non-hazardous carbon dioxide (SC-CO₂) as solvent for extraction of oil. Overall good quality of oil can be recovered by this method.

The loss of oils in SBE is a cause for concern from the palm oil industry as the oil can be used for industrial purposes. The oil retained in SBE should be recovered and re-used as raw materials for industrial applications to save cost in the oil processing industry. One possible approach is to convert the oil into fatty acid alkyl esters. There existed a process to treat SBE in organic (alcohol) phase at high temperature (110-270°C) and moderate pressure to simultaneously recover the oil and convert it into alkyl esters of C1 to C8 carbon atoms^[1]. The oil was converted *in situ* to alkyl esters using methanol and used as oleochemical

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feedstock. The alkyl esters especially methyl esters are very useful ingredients for non-food applications.

In this study, the residual oil of SBE was recovered by solvent extraction and supercritical-fluid extraction and the oil was then converted to methyl esters of C14 to C18 using an modified approach from the established process^[9,10] designated for conversion of methyl esters from pure palm oil.

MATERIALS AND METHODS

Materials: Two types of spent bleaching earth (SBE), i.e. acid-activated, WAC and neutral, NC were obtained from Malaysian local palm oil refinery. All solvents used were of analytical grades: hexane, methanol, ethanol, petroleum ether were purchased from Merck, Germany. The catalysts used for conversion of residual oil to methyl esters i.e. sulphonated ion exchange (RH resin) and sodium hydroxide (NaOH) were purchased commercially.

Solvent extraction of residual oil from SBE (reflux condition): The SBE (WAC) (800 g) was packed in a thimber inside a soxhlet extractor. Hexane (3 L) was poured into a 5 L round bottom flask as extracting medium. The extraction was continued for 2 days until the extracted hexane was colourless. Removal of hexane under reduced pressure left a yellow residual oil (30%), which was then subjected to esterification process. The residual oil of SBE (NC) was obtained in a similar manner to give 21% of yellow residual oil. The percentage yield of residual oil recovered from SBE (WAC & NC) was based on the weight of SBE used for the extraction process.

Solvent extraction of residual oil from SBE (room temperature): The SBE (WAC & NC) (800 g) was soaked at room temperature (30°C) separately with hexane (3 L) in two 5 L flasks for 2 days. The mixture was stirred at regular interval. At the end of extraction, hexane was removed under reduced pressure to give residual oil yields of 29% for WAC and 20% for NC.

Supercritical fluid (SC-CO₂) extraction of residual oil from SBE: The same amounts of SBE (WAC & NC) as above were subjected to SC-CO₂ extraction. The oil yields were 27% for WAC and 20% for NC.

Esterification/transesterification of residual oil of SBE (WAC)^[10]: Residual oil of WAC with free fatty acids (FFA) of 11.45% (200 g) and RH resin (20 g) were mixed with methanol (100 mL) in a round bottom flask. The reaction mixture was refluxed for 3 hours at 80°C, filtered by suction and the residue resin was rinsed several times with methanol/petroleum ether b.p. 60-80°C to remove any oil trapped in the resin. The

filtrate was pumped dry before subjected to the transesterification process.

The resin-treated WAC residual oil (FFA 1.5%, 193 g), methanol (96 mL) and NaOH (0.031M) were refluxed in a round bottom flask at 80°C for 30 minutes. At the end of reaction, the reaction mixture was left settling in a separating funnel. The upper layer containing methyl esters/methanol was separated from the lower layer containing glycerol/methanol. The esters layer was washed excessively with water and pumped dry for fuel characterization. The yield of methyl esters obtained was 84%.

Esterification/transesterification of residual oil of SBE (NC)^[10]: Residual oil of NC (FFA 12.6%, 200 g) and RH resin (20 g) were mixed with methanol (100 mL) in a round bottom flask. The reaction mixture was refluxed for 3 hours at 80°C, filtered by suction and the residue resin was rinsed several times with methanol/petroleum ether b.p. 60-80°C to remove any oil trapped in the resin. The filtrate was pumped dry before subjected to the transesterification process.

The resin-treated NC residual oil (FFA 0.4%, 195 g), methanol (99 mL) and NaOH (0.026M) were refluxed in a round bottom flask at 80°C for 10 minutes. At the end of reaction, the reaction mixture was left settling in a separating funnel. The upper layer containing methyl esters/methanol was separated from the lower layer containing glycerol/methanol. The esters layer was washed excessively with water and pumped dry for fuel characterization. The yield of methyl esters obtained was 82%.

Analysis: The physicochemical characteristics of the residual oil from SBE such as FFA, peroxide value (PV), phosphorus, iron, copper, carotene content and total vitamin E were determined *via* PORIM Test Methods (1995)^[11]. All the above measurements were done in triplicate and the mean values were reported.

The fatty acid compositions (FAC) were determined using gas-liquid chromatography, with reference to the AOCS Ce 1-62 (97)^[12] standard method. The reaction mixture of methyl esters were conducted using gas chromatography (GC) with a BPX 5 capillary column with programmed temperature as follow; oven temperature: 100°C, initial temperature: 100°C, final temperature: 350°C, injector temperature: 254°C, detector temperature: 360°C, rate: 10°C min⁻¹, carrier gas: Helium at 2.0 mL min⁻¹.

Viscosity measurements of the methyl esters were performed using Automated Multi Range Viscometer HVM472 (Walter Herzog, Germany) at 40°C according to ASTM^[13] test method D445. All measurements of viscosity were performed in duplicate and the mean values were reported. The pour point measurements were performed using an automatic pour point/cloud

point measuring apparatus (ISL CPP 97-2 Analyzer) according to ASTM test method D97. The density measurements were conducted using a digital density meter according to ASTM test method D4052. Petronas Research & Scientific Services Sdn. Bhd. Malaysia performed the rest of the measurement for fuel characteristics of methyl esters.

The oxidative stability of methyl esters was performed using the Model 743 Rancimat (Metrohm AG, Switzerland). Samples of 3g were analyzed under constant airflow of 10 L/h and the temperature of the heating blocks at 110°C. All determinations of induction periods were performed in duplicate and the mean values were reported.

RESULTS AND DISCUSSION

The residual oils obtained from different types of SBE were characterized. Residual oils recovered from SBE *via* SC-CO₂ extraction were light yellow in color whereas with hexane, the oils were darker in color for both types of SBE used. It is interesting to find that no iron and copper was detected in the residual oils recovered *via* SC-CO₂. This observation reveals that the residual oils recovered by SC-CO₂ have less impurity. Table 1 shows the better quality of the residual oils recovered *via* SC-CO₂ than oils recovered *via* hexane by lower PV value and total phosphorus content. The FFA values of residual oils remain the same for both types of extraction method used.

It was found that the recovery of residual oils from SBE (WAC) was higher than that of SBE (NC) *via* both solvent and SC-CO₂ extractions respectively. This might be due to the higher capacity of oil retention by SBE (WAC) during the physical refining process. Extraction of SBE by solvent at both room temperature and elevated temperature (reflux condition) gave comparable yields of residual oils. The percentage yields of residual oils recovered in this study were comparable to that reported by other workers^[1,6] corresponding to 20 up to 40% of residual oil yields.

The extraction of SBE by both the extraction methods yielded residual oils with FAC that corresponded fully with the expected values for crude palm oil. The insignificant difference in the FAC between crude palm oil and the residual oil of SBE confirms that the refining process has no effect on the fatty acid or triglyceride composition of the oil and the bleaching earth does not alter the chemical properties of the oil.

Conversion of residual oil of SBE to methyl esters:

Due to the high FFA content of residual oils recovered from both types of SBE, their applications in foods are limited. However, these residual oils can be used in non-food applications such as converting them to methyl esters as biofuels. Other possible applications include bio-lubricants, grease, plasticisers, detergents,

agricultural chemicals, emulsifiers, soap, candle and other oleochemicals.

For this study, the residual oils exhibited FFA of 11.5 and 12.6%. To get rid of the high FFA in oil, the esterification step using RH resin (preferably 10% by weight i.e. ratio of oil to RH resin 10:1) must be accomplished to convert most of the FFA in oil to methyl esters^[9,10]. This could avoid formation of soap that gave complication during the transesterification process, which convert the triglycerides to methyl esters. The conversion of triglycerides and remaining FFA (less than 5%) to methyl esters using small quantity of NaOH was more than 98% (monitored by GC). Table 2 shows the composition of methyl esters derived from residual oils of SBE (WAC and NC).

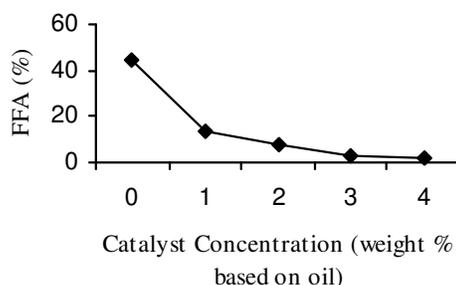


Fig. 1: Correlation of FFA and catalyst concentration in the esterification process. Reaction time: 3 hrs

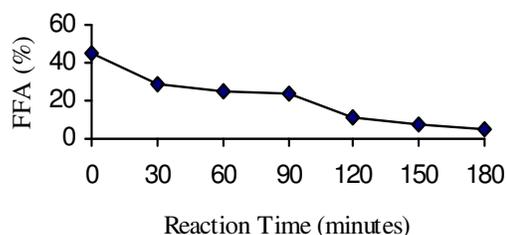


Fig. 2: Correlation of FFA and reaction time in the esterification process. Ratio of oil to catalyst: 10:3

When the FFA of residual oils increased to 44.8% due to the exposure of the earth to air for a couple of months, the conversion of the residual oils to their corresponding methyl esters could still be possible. However, the amount of RH resin used and reaction time for the esterification process could be different. Investigation was done to find the optimum condition for the conversion of residual oil with 44.8% of FFA content. To determine the optimum treat level of RH resin required, the esterification time was fixed at three hours and the amount of RH resin used varied from 1 wt% to 4 wt% based on the amount of residual oil used for esterification. A small quantity of reaction mixture was taken and checked on its FFA content at the end of the reaction. It was found that the ratio of oil to RH resin most effectively used to reduce FFA to below 5%

Table 1: Characteristics of residual oils of SBE (WAC & NC)

Characteristics of residual oil	Solvent extraction		SC-CO ₂ extraction	
	WAC	NC	WAC	NC
FFA (%)	11.5	12.6	11.5	12.6
PV (meq/kg)	3.1	3.4	2.8	2.2
Phosphorus (ppm)	19.3	18.7	18.1	15.8
Fe (ppm)	0.22	1.24	N.D ^a	N.D
Cu (ppm)	0.32	0.38	N.D	N.D
Carotene Content				
β-Carotene (ppm)	3	6	7	7
Total Vitamin E (ppm)	0	0	0	38.8
Fatty Acid Composition, FAC (wt% as methyl esters)				
C14:0	1.1	1.0	1.2	1.3
C16:0	45.2	44.4	44.5	43.6
C18:0	4.9	4.7	5.1	4.9
C18:1	37.9	39.4	38.6	39.7
C18:2	10.9	10.5	10.6	10.5
Oil Recovery (%)	30	21	27	20

Note: ^a Not detected

Table 2: Composition of methyl esters derived from residual oils of SBE

Composition	WAC Methyl Esters (%)	NC Methyl Esters (%)
Esters	99.5	98.9
Monoglycerides	0.45	1.00
Diglycerides	0.05	0.10
Triglycerides	0.00	0.00
Fatty Acid Composition, FAC (wt% as methyl esters)		
C14:0	0.9	0.8
C16:0	44.8	43.8
C18:0	5.1	4.9
C18:1	38.6	39.3
C18:2	10.6	11.2

Table 3: Fuel properties of methyl esters derived from residual oils of SBE

Properties	WAC Methyl Esters	NC Methyl Esters	Malaysian Diesel
Density at 25°C (kg/L)	0.9051	0.8853	0.8310
ASTM D4052			
Viscosity @ 40°C (cSt)	3.7	3.7	4.0
ASTM D445			
Sulfur Content (wt%)	0.04	0.04	0.10
IP 242			
Pour Point (°C)	16	15	15
ASTM D97			
Flash Point (°C)	172	164	98
ASTM D93			
Gross Heat of Combustion (kJ/kg)	38,080	39,470	45,800
ASTM D240			

is 10:3 as shown in Fig. 1. Using this optimum ratio, the esterification process was monitored to find the optimum reaction time required to lower FFA to below 5%. A small quantity of reaction mixture was taken at half an hour time interval and checked on its FFA content. Fig. 2 shows the subsequent reduction trend of FFA of residual oil from 44.8 to 5.6%.

Fuel characterisation: Table 3 shows the fuel properties of methyl esters derived from residual oils of SBE. From the results, it is shown that the methyl esters obtained have comparable fuel properties as petroleum diesel. Hence, these methyl esters may be used as a diesel substitute.

The methyl esters obtained have relatively high induction periods; i.e. 14.6 hours for WAC methyl esters and 29.4 hours for NC methyl esters, determined *via* Rancimat test (pr EN 14112)^[14] at 120°C. The Rancimat stability test determines the acceptance of methyl esters as biodiesel; a minimum of 6 hours is required for the methyl esters to be used as automotive diesel fuel. The Rancimat results thus indicate that the methyl esters derived from residual oil of SBE are of good thermal stability and within the acceptable range for use as a biodiesel.

CONCLUSION

The study shows that solvent and SC-CO₂ extractions could quantitatively recover the residual oils of SBE. The residual oils with various concentration of FFA content can be converted to methyl esters for non-food applications and as diesel substitute.

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