Solvent Efficiency for Oil Extraction from Spent Bleaching Clay

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ABSTRACT: Various alcohols and hydrocarbons were used as solvents to extract the residual oil in spent bleaching clay from palm oil refining. The content of oil and minor components in the spent clay was >40% by weight. The efficiencies of extraction by the polar alcohols, except for methanol, were higher but with a slower initial rate than the nonpolar hydrocarbons. The free fatty acids contents, the Totox values (anisidine value + 2 × peroxide value), and the color of the alcohol-extracted oil were also higher than that by the hydrocarbons resulting in poorer quality oils. All the extracted oils, irrespective of the solvent used, have poorer quality than crude palm oil. However, for regeneration of the residual spent clay, the polar alcohols should be more suitable as more of the impurities are removed.

Paper no. J9608 in *JAOCS 77,* 1219–1222 (November 2000).

KEY WORDS: Extraction, fatty acids, oil, solvent, spent bleaching clay.

The annual world production of edible oils and fats amounts to >65 million tons, with palm oil constituting more than 20% (1). In the refining of palm oil, bleaching clay dosages of 0.5–1% are generally used. From Malaysia alone, with a production of ~9 million tons of oil in 1999, a total of 70,000 tons of spent bleaching clay is estimated to be generated yearly. Spent bleaching clay contains about 30–40% oil by weight of spent clay, and this constitutes a major loss in oil as well a major cost from the clay since the spent clay is currently disposed untreated. In addition, the use and disposal of the spent bleaching clay is becoming a potential problem in the producing countries because of the rapid growth of the industry and the concomitant rapid increase in the generation of the waste material. Currently, oil-laden spent bleaching clays are mainly disposed of in landfills (2–5) or in waste dumps, as the spent clays are considered nontoxic. Other than the potential leaching of the fatty materials into the water course and the possibility of spontaneous combustion, little is known about the long-term impact on the environment of such a method of disposal.

Whereas efforts to reduce the loss of oil and dosage of clay for the refining process continue, the possibility of recycling the clay has been studied (3,5,6); the first step in recycling is the efficient extraction of the oil. Hexane extraction has been used in the past for the recovery of oil from spent clay (7). However, systematic study on the efficiency of different solvents for the extraction of oil from spent clay from palm oil refining have not been reported. In the research reported here, comparison of various hydrocarbons and polar solvents for oil extraction from spent bleaching clay was made. The yield and quality of the oil extracted using these solvents were evaluated.

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EXPERIMENTAL PROCEDURES

Seven technical grade solvents (R&M Chemicals, Essex, United Kingdom), methanol, ethanol, isopropanol, petroleum ether, pentane, hexane and heptane, were employed in the extraction study using the percolation method (8). Fresh spent bleaching clay samples were collected from a palm oil refiner, Golden Agriculture Pte. Ltd. (Penang, Malaysia). An extraction thimble, lined at the bottom with cotton wool, was partially filled with mixture of a weighed sample of ~6.0 g spent bleaching clay with about 3 g of fine sand to improve the drainage. The mixture was covered with a thin layer of cotton wool to aid solvent distribution. The thimble was then placed in the butt tube and extracted with 50 mL of solvent in the extraction flask, heated with an electric heater adjusted to produce a reflux rate of 150 drops min^{-1}. Timing was started when the first drop of solvent was visible. At regular time intervals, the flask containing the extract was removed and replaced with another containing 50 mL of fresh solvent, and the extraction was continued. A series of extractions at 20 min intervals was made on each sample over a period of 160 min. The solvent in each of the extracts was then vacuum-evaporated until the content came to a constant weight. The residues were weighed to an accuracy of 0.0001 g.

Free fatty acid (FFA), peroxide value (PV) and *p*-anisidine value (AV) were determined by AOCS Official Methods (8).

RESULTS AND DISCUSSION

Oil yield. The combined amount of oils recovered from a sample of spent bleaching clay using the various solvents (Table 1) shows that the total oil yields in terms of the percentage of grams of oil extracted per gram of spent clay obtained by the polar solvents ethanol and isopropanol were

TABLE 1
Oil Yield, Free Fatty Acids (FFA), Peroxide Value (PV), *p*-Anisidine Value (AV), and Totox Value of Solvent-Extracted Oils[a]

Solvent	Oil yield (%)	FFA (%)	Peroxide value	*p*-Anisidine value	Totox value[b]
Methanol	24.4	17.25	—	39.40	39.40
Ethanol	42.4	10.90	—	39.00	39.00
Isopropanol	44.2	8.70	—	39.16	39.16
Petroleum ether	36.6	8.03	2.12	28.87	33.10
Pentane	38.0	8.46	0.59	27.48	28.66
Hexane	37.7	8.11	0.32	28.80	29.44
Heptane	37.6	7.96	0.26	25.50	26.00
Crude palm oil	—	3.76	0.82	35.74	37.38

[a]Values in the table are averages of duplicate determinations.
[b]Totox value = 2PV + AV.

higher than the nonpolar solvents by about 7%. In general, the color of the polar solvent-extracted oils was darker than those extracted with nonpolar solvents. The increased quantity of polar components extracted using the polar solvents undoubtedly includes minor components present in the crude oils, such as phosphatides, fatty acids, and sterols as well as other oxidized, hydrolyzed, and polymerized products from reactions catalyzed by the acidic clay. For example, the methanol extract contained 67.9 ppm of phospholipids, as compared with 2.4 ppm in the hexane extract (9) as well as much higher fatty acids concentrations and Totox value (AV + 2PV). It is obvious that although isopropanol and ethanol are more efficient solvents than the nonpolar polar solvents, the oils extracted have lower quality. Furthermore, the recoveries of the alcohols for reuse are more energy demanding as their latent heats of vaporization are much higher than those of the hydrocarbons. They also form constant-boiling mixtures with water, leading to difficulty in their recovery. However, a cleaner clay in terms of lower amounts of impurities retained is obtainable.

The efficiencies of oil extraction were comparable among the nonpolar solvents. This result is similar to that for the extraction of cottonseed, for which the efficiencies with *n*-pentane and *n*-hexane were comparable but that for *n*-heptane was lower (10).

Extraction rate. The oil extraction rates of different solvents are shown in Figure 1. The oil yield increased rapidly initially, reaching a plateau after less than 40 min for the nonpolar solvents. Essentially 97–98% of the recoverable oil with the particular solvent could be recovered within the first 60 min. For isopropanol and the ethanol, the oil yields were low for the first 20 min, then increased to near maximal yields after ~100 min. By using methanol as the extractant, the yield was low even after 160 min owing to lower oil solubility in this solvent. The color of the extracted oil was dark, indicating the more polar components were efficiently extracted.

FFA yield. The accumulated FFA extracted using the different solvents are shown in Figure 2. Essentially all of the FFA (95–97%) could be recovered within the first 60 min, with most of these extracted after 20 min for the hydrocarbons and methanol. The extractions were slower with isopropanol and ethanol, with most of the acids extracted only after 40 min.

The figure shows that oil extracted with methanol contained the highest FFA, followed by the ethanol and iso-

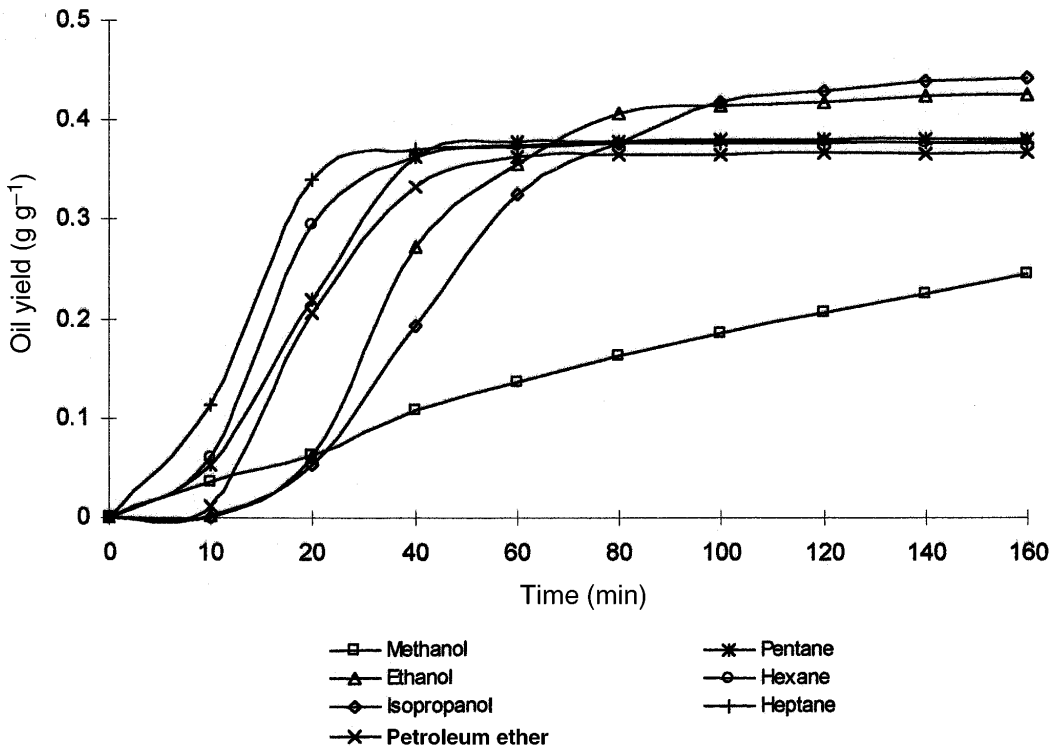

FIG. 1. Cumulative yield of oil extracted per gram of spent clay at different extractions time.

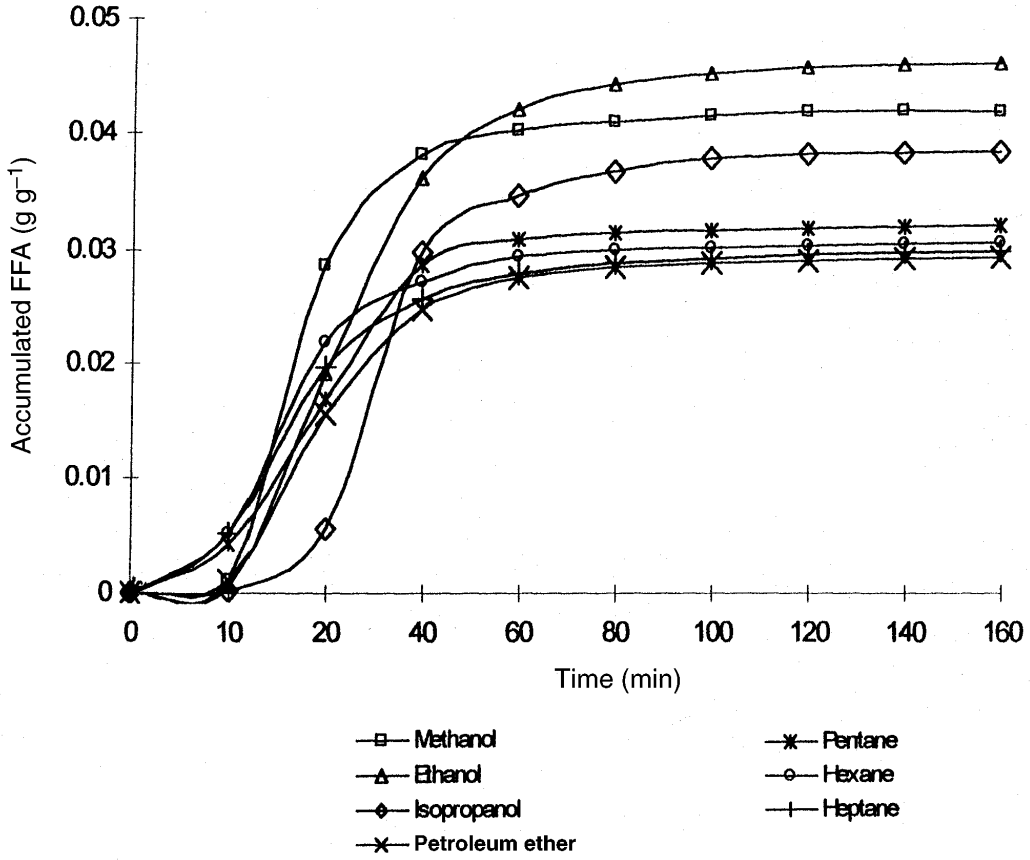

FIG. 2. Cumulative amount of free fatty acids (FFA) extracted per gram of spent clay as a function of extraction time.

propanol. The nonpolar solvent extracts yielded FFA values of about 8%, whereas polar solvents gave higher FFA values (Table 1). This is understandable as the FFA are polar molecules. The exceptionally high FFA content in the methanol extract was evidently due to the lesser amount of oil being extracted.

Crude palm oil (CPO) contains 3–5% FFA (11). The FFA content of all the recovered oils was higher than CPO. This increase in FFA values is attributable to the hydrolysis of some of the triglycerides, catalyzed by the acidic sites of the bleaching clay. Increases in the FFA content of the recovered oils have similarly been observed in the recovered soy oil (12).

PV, AV, and Totox value. PV is a measure of the initial degradation of the oil. In the oxidation of oil by a chain reaction, hydroperoxides are first formed, followed by the peroxides, and finally aldehydes, ketones, and acids. From Table 1, the PV of nonpolar solvent-extracted oils, except for petroleum ether, are lower than CPO, suggesting that these solvents were not efficient in extracting the hydroperoxides adsorbed on the clay surfaces. The PV of the polar solvent-extracted oils could not be determined because of the very dark color.

AV measures the secondary oxidation products of aldehydes and ketones. The AV of the polar solvent-extracted oils was higher than that using nonpolar solvents and CPO. It showed that the polar solvents are better extractants of secondary oxidation products compared to nonpolar solvents.

The total content of primary and secondary products of oxidation were determined from the Totox value. The Totox values of nonpolar solvent-extracted oils are lower than that of CPO, which in turn are lower than that of the polar solvent-extracted oils even without taking into account the PV from the polar solvents. This is evidently due to the better extraction capability of the polar solvents for the polar oxidation products. The results raise the prospect of setting up a two-stage extraction process using a nonpolar solvent to obtain a cleaner oil and a polar solvent to remove the FFA and other impurities. A two-stage process will likely incur higher costs in capital investment, operation, and solvent recovery. However, the cost may be offset by the cleaner oil and cleaner clay obtainable, if the cleaner clay is to be activated for reuse.

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[Received May 4, 2000; accepted July 31, 2000]