Recovery of Oil *via* Acid-Catalyzed Transesterification

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ABSTRACT: The process of preparing oil palm seed for planting generates vast quantities of waste pulp. The pulp (*ca.* 80% oil), for which no use has been found, is indiscriminately dumped because either reprocessing it into a useful product or disposing of it properly is expensive. *In situ* transesterification of the pulp with methanol and ethanol using sulfuric acid as catalyst was carried out on a laboratory scale. Our aim was to develop a process to recover the largely hydrolytically degraded oil (PV, 25–26; FFA, 25–26%) from the pulp. Acid-catalyzed conversions of the oil into alkyl esters were 96–97% for both methanol and ethanol. The accompanying concentrations of FFA, TG, DG, and MG were low. The identities and proportions of FA ester in the alkyl esters reflected the FA content of the palm oil. The values for the esterified products of some fuel properties such as cloud point and viscosity were slightly below the general current specification. However, with optimization of the reaction conditions and simplification of some of the technical aspects, the waste pulp could be a good source of alkyl esters for both oleochemical and fuel applications.

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KEY WORDS: Alkyl esters, oil palm, palm oil, pulp, transesterification.

FAME, known as biodiesel (1), can be used directly or mixed with conventional fuel for diesel engines, and as a heating fuel (2). Biodiesel can be produced by transesterifying a TG with a short-chain alcohol in the presence of a catalyst. Synthesis of biodiesel has been extensively studied. However, most of the vegetable oils used for the production and studies of biodiesel presently are produced for the food market, including palm, rapeseed, sunflower, and soybean oils. This dichotomy may impose a market conflict between biodiesel and edible oils feedstocks, leading to higher biodiesel costs (3,4). Studies on the use of biodiesel in diesel engines have shown great reductions in emissions of sulfur, carbon monoxide, polyaromatics, hydrocarbons, smoke, noise, and particulates (5).

Vegetable oil-based fuels are renewable, biodegradable, and nontoxic. They contribute little to the greenhouse effect because CO_2, a greenhouse gas and the major by-product of biodiesel combustion, is captured by growing plants *via* photosynthesis. However, higher production costs at present offset the multiple environmental advantages of using renewable, less-polluting crop oils and chemicals.

At the Seed Production Division (SPD) of the Nigerian Institute for Oil Palm Research (NIFOR), approximately 9,000 tonnes of palm fruits are processed annually for seeds by soaking and depulping. The pulp (*ca.* 5,400 tonnes), projected to contain 2,100 tonnes of oil, is dumped without further treatment. The rotting mass is both malodorous and unsightly.

This study therefore was undertaken to recover the large quantities of oil in the mesocarp via *in situ* alcoholysis of the pulp. This was with a view to converting waste into wealth and indirectly or directly generating environmental gains.

EXPERIMENTAL PROCEDURES

Chemicals. All the chemicals and reagents used in this experiment were of analytical grade.

Sample collection. Wet pulp samples (about 1 kg each) were collected weekly from SPD, NIFOR (Benin City, Nigeria), dried, and analyzed immediately for a total of 10 wk. Samples of equal weight were taken from the top, middle, and bottom of the pulp heap and blended manually to ensure a fairly uniform distribution of constituents. Moisture and volatiles, oil, and residue of the pulp were determined according to PORIM Test Methods (6).

The wet pulp was dried in an oven at 105°C for 36 h (moisture 5%). The dried oily pulp was allowed to cool to ambient temperature (32°C) and Soxhlet-extracted with *n*-hexane. The extracted oil was immediately analyzed for PV, saponification value (SV), FFA content, density, cloud point (CP), iodine value (IV), and FA composition (FAC) according to an AOCS method (7). The average M.W. of the oil was calculated by multiplying the inverse of the SV by 168,000 (8).

In situ *transesterification*. A 400-g (0.2816 mol of oil) oven-dried, fibrous, solid, sticky, and oily pulp sample was placed in a 1000-mL three-necked flat-bottomed flask equipped with mechanical stirrer, thermometer, and condenser. The pulp was heated to 62°C with stirring in a thermostated oil bath. In a beaker, 316.8 g (9.9 mol) of methanol was mixed with 15 mL of 98.9% sulfuric acid (6.86 wt% relative to the pulp) as catalyst and added to the melted pulp and heated for 12 h at 68°C with stirring. At the end of the reaction, the mixture was vacuum-filtered through a Büchner funnel using Whatman no. 42 filter paper. The filter residue then was washed with 4 × 60 mL methanol.The residue was not oily to the touch after drying at ambient temperature overnight. Hence, it was not reextracted.

The excess methanol was recovered in a rotary evaporator. To the partially desolventized filtrate in a 2000-mL separatory funnel was added 200 mL of distilled water. The re-

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sulting solution was extracted four times with redistilled *n*-hexane. The combined extracts were washed with distilled water, dried over anhydrous sodium sulfate, and concentrated in a rotary evaporator to give the transesterified crude product. The crude alkyl esters were distilled *in vacuo* (0.25 mm Hg, 168°C). The distillate was cooled and redistilled two times under the same conditions stated above.

The distilled (purified) yellow alkyl esters were passed through a micropipette packed with a mixture 1:1 of fuller's earth (Fulmont; Laporte Inorganics, Widness Cheshire, United Kingdom) and silica Gel G (Merck) to yield clear, colorless alkyl esters. These were analyzed on a Shimadzu GC 9A Chromatograph (Shimadzu Scientific Instruments, Columbia, MD) equipped with an FID and a 15 m × 0.53 mm i.d. column (Supelco SPB™; Supelco, Bellefonte, PA). The main parameters were: helium as carrier gas with a flow rate of 8.5 mL/min; injection temperature, 75°C; detector temperature, 350°C; temperature program, 75°C for the first minute, 75–140°C at 24°C/min, 140–330°C at 8°C/min, 330°C for 2 min, 330–345°C at 12°C/min, and 345°C for 12 min.

The alkyl esters were subjected to viscosity (9), CP (10), refractive index (11), and density (12) analyses.

RESULTS AND DISCUSSION

Table 1 shows the oil content reaction conditions for the *in situ* transesterification and average ester yield relative to the percentage of oil content of the palm fruit pulp. Reaction conditions were chosen to ensure maximal alkyl ester yield without regard to process optimization. This objective was achieved. In view of the low solubility of oil in ethanol and methanol, the high relative ester yields (97 and 99%, respectively, for methyl and ethyl esters) may be due to the stepwise dissolution of oil in the alcohol and subsequent transesterification (13). In other words, the respective alcohols performed as solvent and as esterifying agent.

TABLE 1
Oil Content and Reaction Conditions for *in situ* Transesterification, and Average Ester Yield Relative to the Oil Content of the Palm Fruit Pulp

	Methanol[a]	Ethanol[a]
Average oil content (%)	79.88 ± 1.06	79.88 ± 1.06
Molar ratio (alcohol/oil)	35.16:1	35.16:1
Sulfuric acid (mL)	15	15
Temperature (°C)	68	78
Time (h)	12	12
Relative ester yield (%)	97.20 ± 0.21	99.35 ± 0.13

[a] Where given, data represent mean ± SD.

The physicochemical properties of the oil that was Soxhlet-extracted with *n*-hexane from the pulp are shown in Table 2. There was little variation within parameters for the 10 wk. The respective averages of the measured parameters, save saponification and IV, were much higher than those of edible palm oil.

Although the comparatively high values of FFA (Table 2) suggest the occurrence of hydrolysis of the palm fruits during the 7 d prior to depulping, the high PV may be due to oxidation reactions. The FA compositions of the oil extracted from the 10 weekly palm fruit pulp samples are summarized in Table 3. There was relatively little variation in either the type or amount of individual FA. The major components of the TG analyzed were palmitic (42–44%) and oleic (39–40%) acids. These results were in general agreement with earlier reported values (14) and demonstrated that any modifying reactions taking place during the soaking and depulping of the palm fruits did not significantly affect the FA profile of the oil.

Table 4 shows the results of the GC analysis of the purified products obtained *via in situ* transesterification. The purified products generally had 96–97% esters. The average FA composition of the alkyl ester was similar that in the report of Zaizi *et al.* (15) and also was consistent with the statement by Davis Clements (16) that relative FA composition of an oil changes by source but that the component FA do not. That is, the FA component of the alkyl ester, which was produced

TABLE 2
Physicochemical Properties of Oil Recovered by Soxhlet Extraction with *n*-Hexane from the Pulp on a Weekly Basis[a]

		Properties					
Week	Oil yield (%)	FFA (%)	SV (mg/KOH)	PV (meq/kg)	IV	Unsaponifiables (%)	Moisture (%)
1	80.1	26.8	198	26.4	51.1	1.5	0.27
2	78.4	27.4	195	25.4	50.1	1.3	0.26
3	82.0	31.8	193	22.1	51.9	1.4	0.27
4	78.9	26.3	204	22.6	52.3	1.2	0.27
5	81.1	26.0	205	22.6	50.8	1.4	0.25
6	80.0	32.9	192	22.9	52.5	1.4	0.26
7	79.6	27.3	199	26.1	50.9	1.5	0.25
8	78.9	29.4	199	25.0	50.6	1.6	0.27
9	80.0	29.7	193	22.4	52.8	1.4	0.25
10	79.8	29.2	197	25.6	50.2	1.1	0.23
Ave.[b]	79.9 ± 1.1	28.7 ± 2.3	197.5 ± 4.4	24.1 ± 1.7	51.3 ± 1.0	1.4 ± 0.2	0.26 ± 0.01

[a] Values of measured parameters typical of edible crude palm oil: FFA, 2.5%; SV, 190–202; PV, 2.0; IV, 50.1–54.9; unsaponifiable matter, 0.15–0.99; and moisture, 0.25 (18).
[b] Mean ± SD.

TABLE 3
FA Composition (%) of Crude Palm Oil Extracted from the Palm Fruit Using a Soxhlet Extraction and *n*-Hexane

Week	C12	C14	C16:0	C18:0	C18:1	C18:2	C18:31
1	0.20	1.10	44.10	4.12	39.20	10.10	0.21
2	0.25	1.01	44.12	3.90	39.40	10.00	0.20
3	0.23	10.2	44.12	3.70	39.56	10.09	0.23
4	0.19	1.07	43.67	4.32	40.00	10.06	0.40
5	0.24	1.00	42.25	4.50	40.01	10.17	0.42
6	0.22	0.98	44.21	3.79	39.61	10.20	0.40
7	0.21	0.89	44.20	3.80	39.80	10.01	0.32
8	0.21	1.07	41.90	4.56	39.43	10.45	0.36
9	0.21	1.06	42.73	4.51	39.97	10.21	0.40
10	0.24	1.03	42.94	4.50	39.91	10.47	0.42
Ave.[a]	0.22 ± 0.02	1.02 ± 0.02	43.43 ± 0.85	4.17 ± 0.33	39.69 ± 0.27	10.18 ± 0.16	0.37 ± 0.09

[a] Mean ± SD. C12 and C14 refer to all C12 and C14 FA.

from transesterification of the soaked oil palm fruit pulp, is similar to that of a normal processed palm oil.

Table 5 depicts the FA composition of the *in situ* transesterified and purified methyl and ethyl esters from the pulp. Comparison of Tables 3 and 5 indicates that the identities and proportions of FA in the crude oil and esters did not vary much. This indicates that the FA composition of the esters reflects the starting material; the predominant acids in the crude extract still predominate in the esters.

Table 6 presents some physical properties of the esterified product. These properties are closely related to fuel quality of the alkyl esters. These properties, slightly inferior to results reported in Reference 18, fall within the range of general specification of alkyl esters for use as biodiesel.

The study has demonstrated the possibility that large quantities of hitherto unrecovered oil could be converted *via in situ* transesterification to alkyl esters in appreciable percentages. Glycerol is also liberated in the course of the *in situ* transesterification, but its recovery was not attempted in this experiment. Besides increasing the choices of starting materials for biodiesel production, this process may contribute to much-needed zero-waste management in the oil palm industry, which is in accordance with better resource management and sustainable development. The slight inferiority of the alkyl ester produced could be improved by process optimization. These esters could also serve as feedstock for oleochemical applications or in blends.

TABLE 4
Composition of the *in situ* Transesterified and Purified Products[a]

Alcohol	Week	AE	MG	DG	TG	FFA	Total
Methanol	1	97.60	0.75	0.40	0.20	0.90	99.85
	2	97.50	0.55	0.15	0.30	1.00	99.50
	3	96.90	0.45	0.17	0.37	0.85	98.74
	4	97.40	0.52	0.23	0.30	0.88	99.33
	5	96.85	0.43	0.18	0.35	1.00	98.81
	6	96.79	0.55	0.30	0.39	1.01	99.04
	7	97.01	0.42	0.19	0.35	1.00	98.97
	8	96.31	0.41	0.24	0.36	0.98	98.30
	9	96.81	0.46	0.24	0.33	0.97	98.81
	10	96.76	0.59	0.18	0.35	1.00	98.88
Ethanol	1	96.76	0.42	0.32	0.29	1.05	98.84
	2	96.28	0.49	0.29	0.31	0.97	98.81
	3	97.73	0.41	0.26	0.32	1.02	99.74
	4	97.24	0.43	0.25	0.30	0.92	99.14
	5	97.98	0.40	0.28	0.39	1.12	99.17
	6	96.86	0.39	0.27	0.38	1.20	99.10
	7	97.08	0.40	0.27	0.33	0.90	98.98
	8	97.62	0.38	0.22	0.31	0.99	99.52
	9	96.89	0.44	0.32	0.38	1.19	99.22
	10	97.21	0.42	0.35	0.39	0.99	99.36

[a] AE = alkyl esters. Variability of data is: for methanol: AE, 96–99 ± 0.40; MG, 0.51 ± 0.10; DG, 23 ± 0.08; TG, 0.33 ± 0.05; FFA, 0.96 ± 0.06; total, 98.92 ± 0.53; for ethanol: AE, 97.06 ± 0.42; MG, 0.42 ± 0.03; DG, 0.28 ± 0.04; TG, 0.34 ± 0.04; FFA, 1.04 ± 0.10; total, 99.24 ± 0.42.

TABLE 5
FA Composition (%) of *in situ* Transesterified and Purified Methyl and Ethyl Esters[a]

Ester	C12	C14	C16:0	C16:1	C18:0	C18:1	C18:2
Methyl	0.3	0.8	44.3	0.2	5.0	39.1	10.1
Ethyl	0.2	0.8	44.4	0.0	4.7	39.3	9.8

[a] C12 and C14 refer to all C12 and C14 FA.

TABLE 6
Some Physical Properties of the Esterified Products[b]

	Ester		
	Methyl	Ethyl	General specification
Density @ 15°C (g/mL)	0.88	0.79	0.85–0.89
Viscosity @ 40°C (mm^2/s)	4.81	4.68	0.35–5.0
Refractive index	1.4094	1.4249	NA
Cloud point (°C)	+9	+10	NA
Color (visual)	Reddish	Reddish	—
IV	51.1	50.6	50–59

[a] The purest ester was utilized for the above determination. NA, not applicable.
[b] Reference 17, pp. 134–135.

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