

Liquid Fuels from *Mesua ferrea* L. Seed Oil

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Mesua ferrea L. seed oil consists of triglycerides of linoleic, oleic, palmitic and stearic acids. These acids were pyrolyzed separately in the presence of different amounts of solid sodium carbonate. Pyrolysis experiments revealed that linoleic and oleic acids can be converted to hydrocarbons of a wide range of molecular weights by pyrolyzing them with even 1% by wt of sodium carbonate up to a temperature of 500°C, whereas palmitic and stearic acids can be converted to hydrocarbons only by pyrolyzing them with equivalent amounts or more of sodium carbonate up to a temperature of about 650°C.

The fractions of boiling range 60-320°C of all of the pyrolytic oils were analyzed for their hydrocarbon types by the method of fluorescent indicator adsorption (FIA). The aromatic contents of the pyrolytic oils of linoleic and oleic acids were found to be much higher than those of palmitic and stearic acids. GS and GC-MS analyses of all the saturate fractions indicated mainly normal alkanes with a carbon number range of 6 to 17.

The use of biomass as an alternative source of fuel and chemical feedstocks is attracting increasing interest (1-6). The possibility of using vegetable oils as fuel for diesel engines has also been the subject of recent discussion (7-9). The advantages and disadvantages of vegetable oils as fuel have already been reported elsewhere (10).

Early attempts were made by several workers to produce hydrocarbons from vegetable oils (11-13). Weisz et al. have demonstrated that the use of size- and shape-selective zeolite catalysts of the ZSM-5 type used in the methanol-to-gasoline process can be extended to produce gasoline from glyceride oils such as corn oil, peanut oil and castor oil (14). Lipinsky et al. have shown that steam cracking of fatty acids at temperatures exceeding 500°C yields a mixture of gaseous and liquid products (15). Recently, Konwer and Baruah have reported that when *Mesua ferrea* seeds were pyrolyzed in the presence of about 1% of sodium carbonate up to a temperature of 500°C a black pyrolytic oil was produced that was similar to petroleum crude (16). From the studies of various properties of different fractions of this pyrolytic oil, they have shown that the fraction distilling between the initial boiling point and 140°C may be a substitute for petroleum gasoline whereas the fractions of boiling ranges 140-300°C may readily be used as kerosene and diesel fuel, respectively (17). Therefore, it was of interest to examine the effect of sodium carbonate on the pyrolytic conversion to hydrocarbons of those fatty acids that are the principal constituents of *Mesua ferrea* seed oil. In this paper we report on the identification of some hydrocarbons produced by the fatty acids of *Mesua ferrea* seed oil when they are pyrolyzed separately in the presence of sodium carbonate.

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EXPERIMENTAL

Materials. *Mesua ferrea* seeds used in this study were collected by one of us from the trees on the campus of Assam Agricultural University at Jorhat, India. Linoleic acid (99%), oleic acid (99+%), palmitic acid (99%) and stearic acid (99+%) were obtained from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. Silica gel (grade 923, 100-200 mesh) used for Fluorescent Indicator Absorption (FIA) analysis was also the product of Aldrich Chemical Company, Inc. Dyed gel used for FIA analysis was obtained from UOP Inc., Des Plaines, Illinois. All other chemicals used were of reagent grade.

Methods. A portion of 27.2 g of ground kernels of *Mesua ferrea* seeds was extracted in a Soxhlet apparatus for 24 hr with normal heptane. The solvent was then removed from the extract, and the oil content was found to be 75.1% by wt of the kernel.

The total amount of unsaponifiable materials present in *Mesua ferrea* seed oil was determined by the same method as used by Fedeli et al. (18) for other vegetable oils and was found to be 2.65% by wt of oil.

The fatty acid composition of *Mesua ferrea* seed oil was determined by GC analysis of the methyl esters prepared by the method reported by Hartman et al. (10). The lipids were saponified by boiling in 0.5 M KOH in methanol for 5 min and then transesterified by refluxing in a solution containing 60 ml of methanol, three ml of H₂SO₄ and two g of NH₄Cl. The fatty acid esters were then extracted with petroleum ether. GC was conducted with a Hewlett-Packard Model 5730 chromatograph equipped with a flame ionization detector (FID) and a DB-5 10 m × 0.25 mm i.d. glass capillary column (J&W Scientific, Folsom, California; 5% phenyl-95% methyl-silicone). Operating conditions were: carrier gas (helium) 1.5 ml/min; make-up gas (nitrogen) 2.9 ml/min; column temperature, 150°C; injector temperature, 250°C, and detector temperature, 300°C. Qualitative analysis was effected by using methyl esters of linoleic, oleic, palmitic and stearic acids as standards. The percentages of the methyl esters from the seed oil were calculated from the peak areas obtained from the integrator of the chromatograph. The results of analysis of the fatty acid composition of *Mesua ferrea* seed oil are given in Table 1.

The pyrolysis experiments of the fatty acids and *Mesua ferrea* seed oil were conducted in Pyrex glass

TABLE I

Fatty Acid Composition of Saponifiable Part of *Mesua ferrea* Seed Oil

Acid	Wt % of total
Saturated	
Palmitic (hexadecanoic)	15.9
Stearic (octadecanoic)	9.5
Unsaturated	
Oleic (9-octadecenoic)	52.3
Linoleic (9,12-octadienoic)	22.3

TABLE 2

Pyrolysis of Fatty Acids and *Mesua ferrea* Seed Oil in the Presence of Sodium Carbonate

Acid/oil	Sodium carbonate wt % of acid/oil	Maximum temp (°C)	Yield of pyrolytic oil, wt % of acid/oil	Gas evolved in ml/g of acid/oil	Residue, wt % of acid/oil
Linoleic	1	500	74	95	9.0
Linoleic	20	500	59	108	32.5
Oleic	1	500	73	92	9.5
Oleic	20	500	62.5	105	31.0
Palmitic	20	650	62.5	125	29.5
Stearic	20	650	63	120	29.0
<i>Mesua ferrea</i> seed oil	1	500	66	84	17.5

TABLE 3

Hydrocarbon Type Analysis of the Fractions of the Pyrolytic Oils Distilling Between 60 and 320°C

Pyrolytic oil of	Sodium carbonate, wt % of acid/oil	Aromatics % volume	Olefins % volume	Saturates % volume
Linoleic acid	1	20.4	53.2	26.4
Linoleic acid	20	13.8	62.3	23.9
Oleic acid	1	26.3	50.	23.7
Oleic acid	20	12.6	63.5	23.9
Palmitic acid	20	1.4	75.8	22.8
Stearic acid	20	2.4	75.7	21.9
<i>Mesua ferrea</i> seed oil	1	21.3	46.9	31.8

test tubes of equal size (20cm × 1.25cm i.d.), using a laboratory-scale pyrolyzer manufactured by E. H. Sargent & Co., Chicago, Illinois. The test tubes were provided with quick-fit glass joints in their open ends. The pyrolyzer was equipped with a cylindrical, hollow electric furnace (18 cm × 1.75 cm i.d.) and a temperature recording system.

For each of the pyrolysis experiments a known weight of the sample of a fatty acid or *Mesua ferrea* seed oil was placed in a test tube along with a known weight of solid sodium carbonate, and then the test tube was placed vertically inside the furnace of the pyrolyzer. The top of the test tube was connected to a distillation head which was further connected to a condenser and a receiver provided with a gas outlet tube. Before heating the furnace, the air inside the glass assembly was removed by blowing nitrogen gas through a side tube connected to the distillation head. The nitrogen flow was then stopped and the furnace was heated gradually. The initial rate of heating was about 5°C/min up to 300°C; then it was controlled at about 1°C/min for the higher temperature ranges. The gas evolved in each of the experiments was collected in graduated cylinders over brine. The results of pyrolysis experiments are given in Table 2. All of the pyrolytic oil samples were further distilled separately, and the fractions distilling between 60 and 320°C were collected for hydrocarbon type analysis. The analysis was done by the FIA method (20) and the results are given in Table 3.

After two sets of readings of zone boundaries were made for each of the oil samples, the saturate fractions were isolated by cutting the portions of the analyzer tubes containing the saturates, as indicated by the

nonfluorescent zone observed under ultraviolet light. The cutting was done with a diamond-tipped pencil. The gel was then eluted with methylene chloride and the eluted solutions filtered to remove the silica gel particles. The filtrates were analyzed with a Hewlett-Packard Model 5730 chromatograph, using a 30-m × 0.249-mm i.d. fused silica capillary column. The temperature was programmed from 70-170°C at 4°C/minute. The other operating conditions and the method of identification of the compounds were the same as described above. A typical chromatogram for the saturate fraction of the pyrolytic oil of oleic acid is shown in Figure 1. The results of GLC analysis are summarized in Table 4.

GC-MS data were obtained on a Hewlett-Packard Model 5970 MSD coupled to a GC equipped with a (30m × 0.53mm i.d.) DB5 fused silica column.

RESULTS AND DISCUSSION

The low value of unsaponifiable materials present in *Mesua ferrea* seed oil (2.65%) indicates that the oil consists mainly of triglycerides of fatty acids. From Table 1 it is clear that only linoleic, oleic, palmitic and stearic acids are present in the oil and the total percentage of unsaturated fatty acids is about three times that of the saturated acids. Because these four acids are the principal constituents of *Mesua ferrea* seed oil, we pyrolyzed each of them separately in the presence of different amounts of solid sodium carbonate and analyzed the pyrolytic oils for their hydrocarbon content.

Although there is a rich literature on the pyrolysis of fatty acids and their salts, the use of sodium carbon-

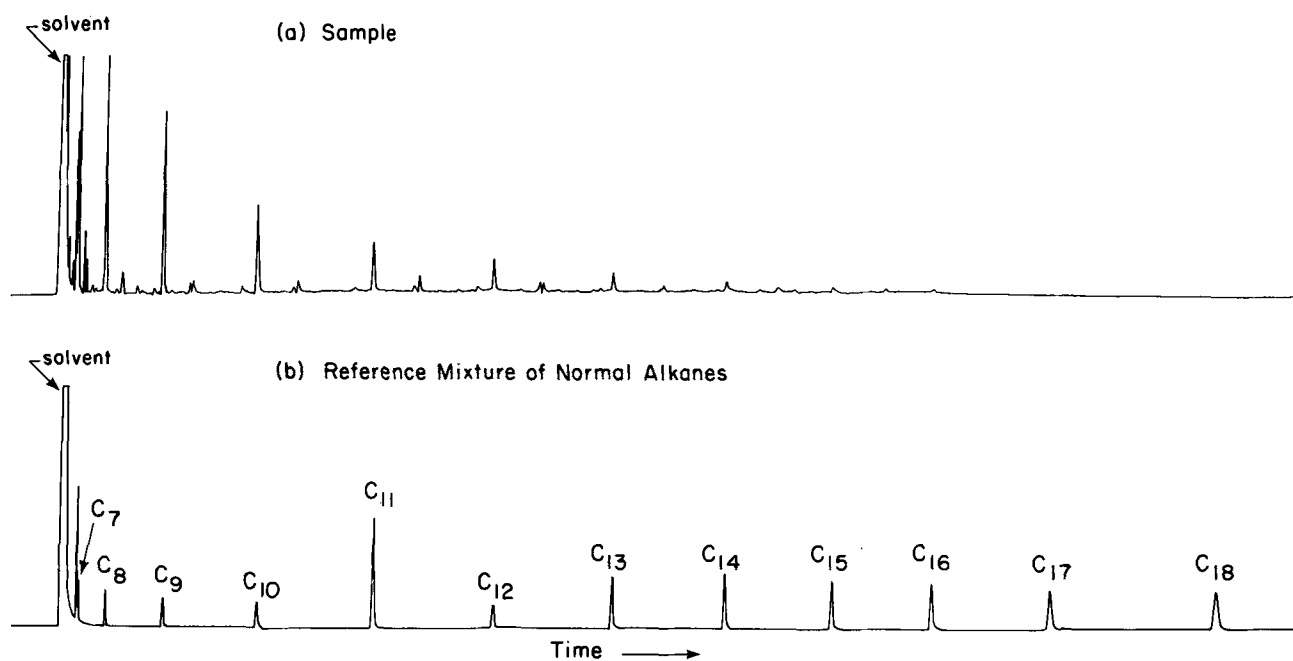
FUELS FROM *MESUA FERREA*

FIG. 1. Gas chromatogram of saturate fraction of pyrolytic oil from oleic acid.

TABLE 4

GC Analysis of the Saturate Fractions of the Pyrolytic Oils of Boiling Range 60–320°C, Obtained from Different Fatty Acids and *Mesua ferrea* Seed Oil

Sample	Wt of sodium carbonate	% Wt of n-alkane of carbon number														% Wt of unidentified compounds
		C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆	C ₁₇	C ₁₈		
Acids																
Linoleic	1	17.6	21.4	16.6	9.8	6.3	4.1	2.5	1.8	1.0	0.5	—	—	—	—	18.4
Linoleic	20	20.5	22.1	16.6	8.6	4.8	2.6	1.6	0.9	—	—	—	—	—	—	22.3
Oleic	1	2.2	17.4	21.1	18.6	4.9	2.5	1.7	0.9	0.7	1.2	0.7	0.6	—	—	27.5
Oleic	20	2.6	19.9	22.2	15.7	4.2	2.3	1.3	0.7	0.6	0.6	0.7	0.4	—	—	28.8
Palmitic	20	3.4	10.0	12.0	14.9	14.2	11.6	8.3	20.5	2.1	2.4	—	—	—	—	0.6
Stearic	20	1.3	7.0	8.6	9.7	10.5	12.5	11.5	9.5	7.2	18.1	1.9	2.0	—	—	0.2
<i>Mesua ferrea</i> seed oil	1	2.3	20.20	9.1	7.8	4.6	4.0	4.6	5.7	7.6	12.2	5.5	6.7	—	—	9.7

ate as a catalyst for the pyrolytic conversion of fatty acids to hydrocarbons has not been reported in the literature that we examined.

From the pyrolysis experiments it has been observed that linoleic and oleic acids can be converted to petroleum-like hydrocarbons with a wide range of molecular weights by pyrolyzing them even in the presence of only 1% by wt of sodium carbonate up to a temperature of 500°C. But when palmitic and stearic acids were pyrolyzed in the presence of 1% by wt of sodium carbonate, most of the fatty acids distilled off and condensed inside the condenser as solid masses. (These products were not analyzed further.) However, when each of these acids was pyrolyzed in the presence of 20% by wt of sodium carbonate, which was slightly more than that equivalent amounts to both the acids, light green pyrolytic oils were obtained within the temperature range of 500–650°C. In these cases, the fatty acids probably first reacted with sodium carbonate to form sodium salts, which further decomposed at higher temperatures to form hydrocarbons. This can be supported by the fact that the formation of salts of fatty

acids by fusing them with anhydrous oxides or carbonates of certain metals is already known (21).

When we pyrolyzed linoleic and oleic acids in the presence of 20% by wt of sodium carbonate, the yields of pyrolytic oils were found to decrease (Table 2). But unlike to decomposition of palmitic and stearic acid with 20% by wt of sodium carbonate, the decomposition of these two acids occurred within the temperature range of 400–500°C.

After completion of the pyrolysis experiments, we added hydrochloric acid to each of the pyrolyzer tubes and carbon dioxide gas evolved, indicating the presence of sodium carbonate in the residues.

After the pyrolytic oil samples were collected, they were further fractionated by distillation, and the fraction distilling between 60 and 320°C was collected for further analysis. Analysis of samples collected from linoleic or oleic acid pyrolyzed in the presence of 1% sodium carbonate showed that aromatic compounds constituted more than 20% (by volume) of this 60–320°C distillate fraction (Table 3). However, when they were pyrolyzed in the presence of 20% by wt of sodium

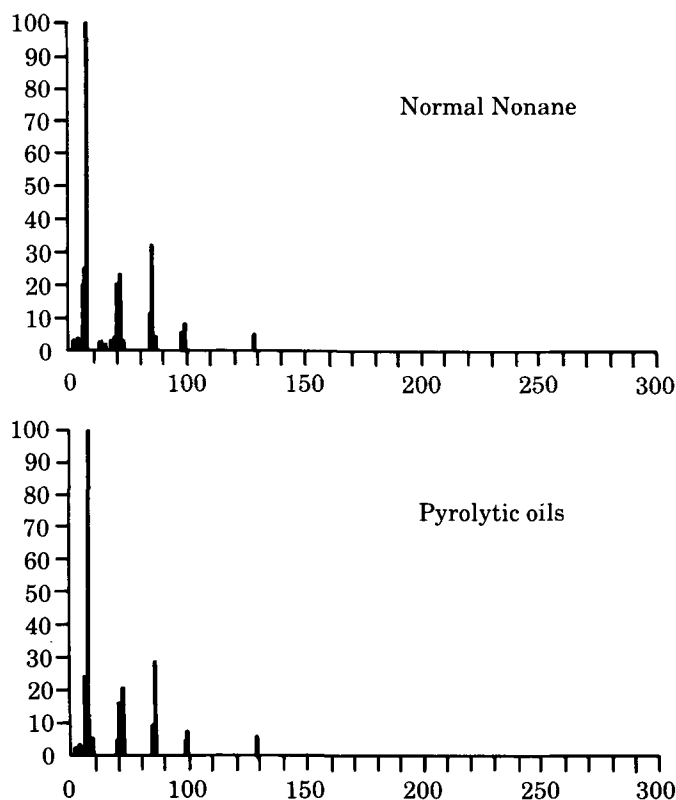


FIG. 2. MS cracking patterns of *n*-nonane and the major C_9 component of the saturate fraction of pyrolytic oil from oleic acid.

carbonate the aromatic contents were found to decrease, whereas the olefin contents increased. On the other hand, palmitic and stearic acids on pyrolysis with 20% by wt of sodium carbonate produced very small percentages of aromatics and large percentages of olefins in the 60-320°C distillate. Earlier workers have also reported that the pyrolysis of calcium stearate produced 76% of cracked distillate which contained 4.4% of aromatic hydrocarbons, 65.1% of olefinic hydrocarbons, 24.8% of naphthenes and paraffins (22). However, the saturate contents of the fractions of all pyrolytic oils were within a comparable range. The increased doses of sodium carbonate in the pyrolysis of linoleic and oleic acids do not seem to have an effect on the relative abundance of saturates. The pyrolysis of *Mesua ferrea* seed oil with 1% of sodium carbonate also produced more than 20% by volume of aromatics in the 60-320°C distillate fraction.

GC analysis of the saturate fractions of boiling range 60-320°C of all the pyrolytic oils (Table 4) reveals that a wide range of *n*-alkanes along with some unidentified compounds were present in these fractions. The saturate fractions of both oleic and stearic acids contained C_6 to C_{17} *n*-alkanes whereas the saturate fractions of linoleic acid contained C_6 to C_{15} *n*-alkanes. But when linoleic acid was pyrolyzed with 20% by wt of sodium carbonate, C_6 to C_{13} *n*-alkanes were found to be present in the saturates. Except linoleic acid, each of the other fatty acids produced *n*-alkanes of carbon numbers up to one less than the carbon

numbers of the original acids. The carbon atom of the carboxyl group splits off as carbonate.

The formation of higher alkanes even in the case of the pyrolysis of linoleic and oleic acids in the presence of sodium carbonate indicates that some saturation reaction also took place.

It has further been observed that the saturate fractions of both linoleic and oleic acids contain more than 50% *n*-alkanes within the carbon number range 6 to 10. The major portions of these saturates were found to be *n*-alkanes, as shown in Figure 1. The emergence times of the major peaks correspond closely to those of normal hydrocarbons in a standard mixture. Confirmation that the components were *n*-alkanes was also obtained from a GC-MS analysis (Figure 2) which shows, for example, the same MS cracking pattern for the C_9 component of the oil as for *n*-nonane.

From a comparison of the results of GC, GC-MS hydrocarbon-type analysis of the pyrolytic oils of linoleic, oleic, palmitic and stearic acids with those of *Mesua ferrea* seed oil (Tables 3 and 4) it is quite clear that the formation of hydrocarbons on pyrolysis of *Mesua ferrea* seed oil with sodium carbonate is due to the decomposition of the fatty acids present. The aromatic hydrocarbons are produced mainly by linoleic and oleic acids.

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