Catalytic Conversion of *Hevea brasiliensis* and *Virola sebifera* Oils to Hydrocarbon Fuels

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Catalytic hydrocracking of *Hevea brasiliensis* (Seringa) and *Virola sebifera* (Ucuuba) oils was carried out in the presence of a $NiMo/Al_2O_3$ catalyst sulfidized *in situ* with elemental sulfur at 360°C. The initial pressure of hydrogen was 140 bars. Conversions of nearly 100% of the vegetable oils were achieved. The compositions of the liquid fuels were studied in detail by gas chromatography/mass spectrometry. The main products were found to be alkanes, cycloalkanes, aromatics and carboxylic acids.

KEY WORDS: Catalyst, fuels, gas chromatography/mass spectrometry, hydrocracking, vegetable oils.

The interest in biomass as a renewable source for the production of fuels or useful chemicals is increasing (1–7). One of the most promising ways for producing liquid fuels is the direct extraction of vegetable oils from plants, followed by catalytic upgrading (8–19). Detailed studies on the chemical composition of the resulting liquid fuels have not been conducted, due to the complexity of the mixtures or to lack of available analytical methods (3,5,8,20).

Two vegetable oils were extracted from native plants common in northern Brazil—*Hevea brasiliensis* (Willd. ex Adr. Juss.) Muell. Arg. (Seringa, rubber tree) and *Virola sebifera* Aublet (Ucuuba). These two vegetable oils were selected for their different degrees of saturation and also to study the effect of oil composition on the nature of the liquid obtained after catalytic decomposition of the initial vegetable oil. The present work reports the gas chromatography/mass spectrometry (GC/MS) analysis of the liquid fuels.

TABLE 1

Physicochemical Properties of Seringa and Ucuuba Oils

Properties	Seringa	Ucuuba
Refractive index[a]	1.458 (40°C)	1.4511 (50°C)
Viscosity[a]	20.7 (40°C)	34.95 (50°C)
Acid value[b] (mg/g)	36.2	8.31
Peroxide value[b] (meq/g)	180.3	7.0
Unsaponifiable materials[c] (%)	2.7	6.0
Saponification value[b]	209	230
Phosphorus[d] (ppm)	12	47
Sulfur[d] (ppm)	8	<200
Chlorine[d] (ppm)	<8	<100

[a]Determined by the method of Assuncao *et al.* (21).
[b]Determined by the AOCS Official Method (22).
[c]Determined by the method of Maxwell and Schwartz (23).
[d]Determined by Centre National de la Recherche Scientifique (CNRS).
[a,b,c]Determined in the Laboratory of Departamento de Quimica da Universidade Federal do Para, Belém, Brazil.

TABLE 2

Fatty Acid Composition of Seringa and Ucuuba Oils (100 % Basis)[a]

Component	Seringa	Ucuuba
Lauric	—	16.5
Myristic	—	71.0
Palmitic	6.2	6.5
Stearic	10.0	0.6
Palmitoleic	3.1	0.3
Oleic	20.8	4.5
Linoleic	42.3	0.6
Linolenic	17.6	—

[a]Composition was determined by GC/MS analysis of the methyl esters prepared by the method reported by Khan and Scheinmann (24).

EXPERIMENTAL PROCEDURES

Samples. Seringa (*Hevea brasiliensis*) seeds and Ucuuba (*Virola sebifera*) kernels were both collected in the state of Para in northern Brazil. Seeds and kernels were oven-dried to constant weight. The dried materials were extracted exhaustively in a Soxhlet apparatus with n-hexane. The extracted oil content was found to be 43 wt % for seringa seed and 69 wt % for ucuuba dried ground kernel. Physicochemical properties and chemical compositions of these oils are presented in Tables 1 and 2, respectively. The seringa seeds used in this study came from seeds unsuitable for planting. Thus, their low quality can be the cause of the high acid and peroxide values reported in Table 1.

Catalysts. Hydrocracking reactions were carried out over a mixed oxide [NiMo] supported on alumina, provided by IFP (Institut Français du Pétrole) and sulfidized *in situ.* The composition of the catalyst precursor was 12.7 wt % MoO_3 and 2.7 wt % NiO.

Hydrocracking of vegetable oils. Experiments were carried out in a 50-cm^3 microclave from Autoclave Engineering (maximum temperature 450°C, maximum pressure 250 bars, Burton Corblin, Noisy-le-Grand, France) equipped with a magnetic stirrer. The stirrer speed was kept constant at 440 rpm and temperature control was ±5°C. For these batch hydrocrackings, 12 g of vegetable oil, 240 mg of the catalyst precursor $NiMo/Al_2O_3$ (2 wt % related to oil) and 210 mg of elemental sulfur were introduced into the vessel, and the whole system was connected to the apparatus by a flange nut. An o-ring insured tightness. Hydrogen was introduced into the microclave and the total pressure was controlled by a digital tachimeter. The system was purged three times with hydrogen to purge the air. The initial hydrogen pressure at room temperature was set at 140 bars before heating. The heating rate was 300°C h^{-1} and the final temperature of the system (360°C) was maintained for two hours before cooling. At this final temperature, the total pressure was about 200 bars.

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The amount of gases in the autoclave was determined, and the liquid product was weighed. The conversion was calculated from the difference between the weight of the feed and that of the gross products (gases, hydrocarbons, acids and water). The small balance difference was attributed to possible formation of coke and to experimental losses. The conversion of vegetable oils could be considered complete.

Analyses. Gases were analyzed with an Intersmat IGC 12M gas chromatograph equipped with a thermal conductivity detector and an R-Porapak column (2 m × 1/8″; Delsi, Suresne, France) at 50°C. Hydrogen was used as the carrier gas. The liquid phase was analyzed by both gas chromatography (GC) and GC/MS.

Hydrocarbons. Quantitative chromatograms were obtained on an HP-5790 instrument with FID, equipped with a fused silica capillary column (Hewlett-Packard, Palo Alto, CA; 12 m × 0.20 mm i.d., "crosslinked dimethyl silicone"). H_2 was the carrier gas (1 mL/min). The temperature profile was 2 min at 31°C, then a linear increase of the temperature, 5°C min^{-1} to 200°C (30 min).

Detailed analysis of the cracked samples was carried out on an HP-5971A mass spectrometer coupled to a GC HP 5890A (Hewlett-Packard) equipped with an "ultra-2 HP" column [25 m × 0.33 mm i.d., phase (0.17 mm) methyl silicone 5% phenyl]. The carrier gas was He with an inlet pressure of 5 psi. A splitless mode was used. The temperature profile of the column was 2 min at 40°C, a linear increase of 5°C min^{-1} to 100°C (6 min), then a linear increase of 10°C min^{-1} to 200°C (6 min) and finally a linear increase of 15°C min^{-1} to 300°C (17 min).

Identification of the compounds involved a library search program and a visual comparison with already published mass spectra (25–27). Assignment of various compounds was also made on the basis of the retention times and mass spectra of authentic samples and of the mass spectra of homologous products. The fragmentometry method was used in the case of overlapping of components.

Carboxylic acids. The total acidity of the liquid fuel was determined by titration with a 0.1M KOH/EtOH solution. Individual quantitation of each acid was made by gas chromatography on a capillary column (nicol-grafted silicone, 30 m × 0.53 mm i.d., Supelco, Bellefonte, PA). The carrier gas was He (24 mL/min), and the temperature profile was 5 min at 70°C, then a linear increase of 10°C min^{-1} until 220°C (40 min).

RESULTS AND DISCUSSION

The low value of unsaponifiable materials present in *Hevea brasiliensis* seed oil (Table 1) indicates that the oil mainly consisted of triglycerides of fatty acids. From Table 2 it is clear that only oleic, linoleic, linolenic, palmitoleic, palmitic and stearic acids were present in the oil, and the total percentage of unsaturated fatty acids was about five times that of saturated acids. On the other hand, the value of unsaponifiable materials (Table 1) present in *Virola sebifera* kernel oil was about two times that of seringa seed oil, and it mainly consisted of lauric and myristic acids (Table 2). The total percentage of saturated fatty acids was about seventeen times that of the unsaturated acids. Oils with different degrees of saturation and chainlengths can be expected to provide different compositions of the resulting liquid fuels.

TABLE 3

Product Yields After Hydrocracking of Seringa and Ucuuba Oils

Product	Seringa	Ucuuba
	(wt % of feed)	
Gas	8.7	14.5
Alkanes	50.1	68.2
Cycloalkanes	24.8	6.6
Aromatics	8.0	0.4
Acids	0.85	2.7
Phenols	—	0.7
Unidentified compounds	0.25	1.4
Water	5.0	4.0
Coke + losses	2.3	1.5
Total	100	100

TABLE 4

Analysis of Gaseous Products

Compound	Seringa	Ucuuba
	(wt % of gas phases)	
CO	11.5	15
CO_2	66	62
CH_4	0.9	2
C_2H_6	3.4	2
C_3H_8	7.2	5
C_4H_{10}	11	14
Total	100	100

Decomposition of triglycerides into acids, ketenes and acrolein was originally proposed by Chang and Wan (20), and was later confirmed by Greensfelder *et al.* (28) and Gusmao (10). Acrolein and ketenes are very reactive under the present experimental conditions. Brodzki *et al.* (29) have shown that the primary products of this decomposition were quickly transformed into carboxylic acids and C_1, C_2, C_3, R-CH_3, R-C_2H_5 hydrocarbons. In this work all these compounds and new ones were clearly evidenced.

The yields obtained from the hydrocracking of the seringa and ucuuba oils are reported in Table 3. The hydrocracking products consisted of a gas fraction and a liquid fraction. The liquid fraction consisted of an aqueous phase and an organic phase. The gas yield was 60 wt % lower for seringa oil than for ucuuba.

The gas fraction (Table 4) mainly consisted of CO_2 and CO with 20 wt % of C_1 to C_4 hydrocarbons for both oils. The formation of CO_2, CO (Table 4) and water (Table 3) resulted from decomposition of acrolein and ketene primarily formed as intermediates and from decarboxylation, decarbonylation and hydrogenation reactions of the acids. These reactions are confirmed by the high amount of water for both oils and by the presence of C_{17} and C_{18} (seringa) or C_{14} and C_{13} (ucuuba) hydrocarbons in the products (Table 5). Gusmao (10) reported similar reactions for soybean oil in the presence of a Ni/SiO_2 catalyst.

The organic phase consisted mainly of the following classes of compounds—alkanes, cycloalkanes, aromatics, phenols and carboxylic acids. These compounds and their amounts are listed in Table 3. Large differences in com-

TABLE 5

GC/MS Analysis of Alkanes

Compound	Seringa	Ucuuba
	(wt % of feed)	
n-Hexane	0.09	0.12
n-Heptane	0.11	0.16
n-Octane	0.12	0.12
n-Nonane	0.23	0.15
n-Decane	0.30	0.20
n-Undecane	0.39	4.80
n-Dodecane	0.35	3.60
n-Tridecane	0.32	24.30
n-Tetradecane	0.30	19.74
n-Pentadecane	3.10	3.30
n-Hexadecane	4.40	2.77
n-Heptadecane	16.0	3.26
n-Octadecane	21.0	3.12
n-Nonadecane	1.0	0.56
n-Eicosane	0.67	0.48
n-Heineicosane	0.22	0.16
Branched	1.55	1.36
Total	50.1	68.2

position appear between the two products. The totals of identified hydrocarbons (alkanes, cycloalkanes aromatics) obtained from hydrocracking of seringa and ucuuba oils were 83 wt % and 75 wt %, respectively. Alkanes represent 50 wt % and 68 wt % of the seringa and ucuuba oils, respectively. Alkane distributions are reported in Table 5. The formation of higher alkanes (C_{18} and C_{17}) in the hydrocracking of both oils in the presence of sulfidized $NiMo/Al_2O_3$ indicates that double bond hydrogenation took place. The presence in the products of a high amount of C_{17} and C_{18} (seringa) or C_{13} and C_{14} (ucuuba) hydrocarbons resulted from two kinds of reactions. These were decarboxylation and decarbonylation (C_{17} and C_{13}), or reduction of the carboxylic group (C_{18} and C_{14}) as previously shown (29). The low amounts of short-chain hydrocarbons present in the hydrocracking products show that chain cleavage was not significant at this temperature. Each of the two oils mainly produced n-alkanes with equal carbon numbers or one carbon less than the original acids.

Cycloalkane contents from the seringa and ucuuba hydrocrackings were 24.8 and 6.6 wt %, respectively. Aromatic hydrocarbon contents of the hydrocracking products were low for the ucuuba oil (0.4 wt %) and higher (8 wt %) for the seringa oil. Distributions of cycloalkanes and aromatics are reported in Tables 6 and 7, respectively. The cycloalkanes and aromatics are mono- or disubstituted and the side chains have a saturated aliphatic structure.

According to Gusmao *et al.* (12), in similar experiments, soybean oil was hydrogenated between 225 and 260°C (this hydrogenation was complete) and transformed at 360°C into a mixture of linear and saturated hydrocarbons in the presence of a presulphidized $NiMo/Al_2O_3$

TABLE 6

GC/MS Analysis of Cycloalkanes

Compound	Number of carbon atoms in aliphatic side chains	M	Number of compounds		Wt % of feed	
			Seringa	Ucuuba	Seringa	Ucuuba
Cyclohexane or Cyclopentane	3 4	126	—	2	—	0.19
Cyclohexane or Cyclopentane	5 6	154	—	2	—	0.25
Cyclohexane or Cyclopentane	6 7	168	2	2	0.07	0.31
Cyclohexane or Cyclopentane	7 8	182	3	6	0.2	2.14
Cyclohexane or Cyclopentane	8 9	196	—	8	—	1.71
Cyclohexane or Cyclopentane	9 10	210	4	2	0.25	0.15
Cyclohexane or Cyclopentane	10 11	224	5	2	0.54	0.12
Cyclohexane or Cyclopentane	11 12	238	8	6	9.62	1.14
Cyclohexane or Cyclopentane	12 13	252	10	3	12.36	0.35
Cyclohexane or Cyclopentane	13 14	266	4	1	0.92	0.16
Cyclohexane or Cyclopentane	14 15	280	6	1	0.84	0.08
Total					24.8	6.6

TABLE 7

GC/MS Analysis of Benzene Compounds with Aliphatic Side Chains

Number of carbon atoms in aliphatic side chains	M	Number of compounds		Wt % of feed	
		Seringa	Ucuuba	Seringa	Ucuuba
2	106	1	—	0.02	—
3	120	1	1	0.03	0.047
4	134	1	—	0.07	—
5	148	1	—	0.26	—
6	162	1	—	0.08	—
7	176	1	1	0.22	0.12
8	190	1	—	0.13	—
9	204	2	—	0.25	—
11	232	4	—	4.05	—
12	246	3	1	2.89	0.073
13	260	—	1	—	0.08
14	274	—	1	—	0.08
Total				8.0	0.4

TABLE 8

GC/MS Analysis of Phenolic Compounds with Aliphatic Side Chains in Hydrocracked Ucuuba Oil

Number of carbon atoms in aliphatic side chains	Number of compounds	Wt % of feed
3	1	0.24
8	1	0.16
9	1	0.10
10	1	0.05
11	1	0.15
Total		0.7

catalyst. On the other hand, a NiMo/Al_2O_3 catalyst sulphidized *in situ* was active in the hydrogenation, at temperatures below 300°C, of unsaturates initially present in the vegetable oils. Under these experimental conditions the hydrogenation was not complete. Consequently, this partial hydrogenation could permit the formation of cyclic structures, mainly in the more unsaturated vegetable oils. The presence of cycloalkanes and aromatics, mainly in the hydrocracking products of an highly unsaturated oil, indicates that ring formation may occur with the assistance of existing double bonds. To show that fatty acids are precursors of the cycloalkanes and aromatics, pure fatty acids (99.5%) like stearic, oleic and linoleic acids were hydrocracked under the same conditions. The formation of cycloalkanes and aromatics was proven (30).

The phenol contents were lower and detected only in the case of ucuuba oil (0.7 wt %). The distribution of phenols is reported in Table 8. Scharmann *et al.* (31) have shown that cyclization of linoleic acid produced ortho-dodecyl phenol as a secondary product. In the present study, the occurrence of this reaction is doubtful. Phenols were observed only in ucuuba oil and not with many other vegetable oils studied previously (30). Therefore, it can be assumed that phenolic precursors were present in ucuuba oil.

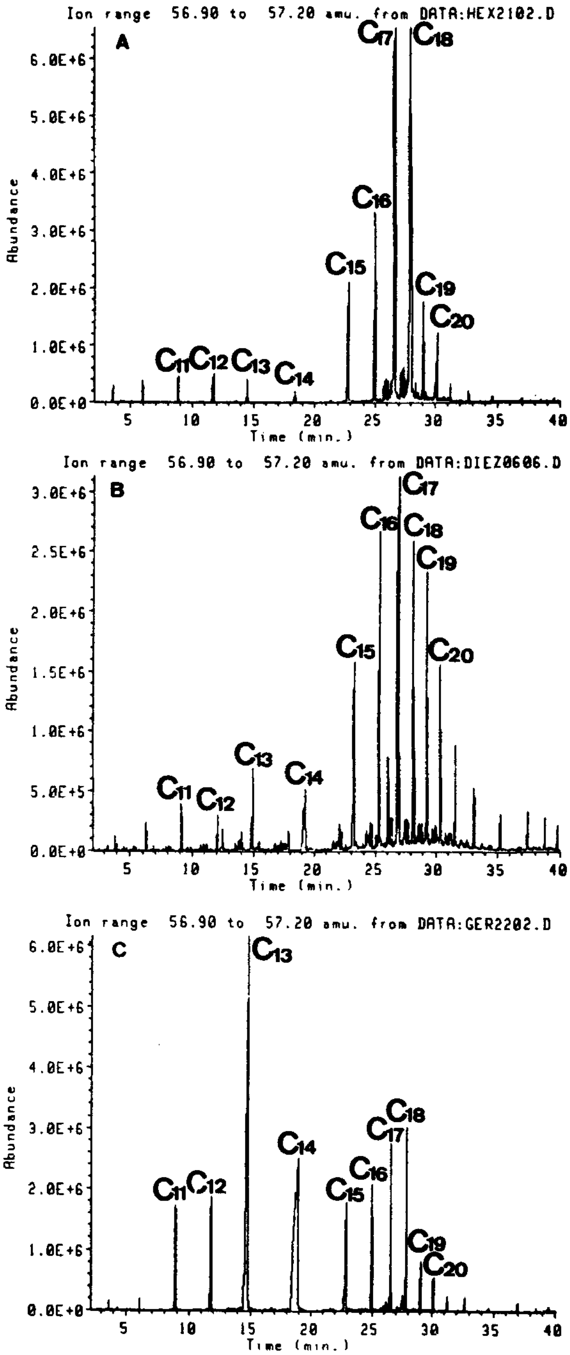

FIG. 1. Ion fragment chromatograms of hydrocracked seringa (A) and ucuuba (C) oils and of a commercial diesel fuel (B).

As previously shown, the liquid fuels from both seringa and ucuuba oils contain more than 75 wt % hydrocarbons. Overlapping of components in the gas chromatograms was resolved by using the fragmentometry technique. Figure 1 compares the alkanes obtained from the seringa and ucuuba oils with a commercial diesel fuel. Comparison is done by selecting the 57 ion fragment characteristic of the alkane family. Both oils and diesel are qualitatively similar, but the components differ quantitatively.

Figure 2 presents the same 57 ion fragment chro-

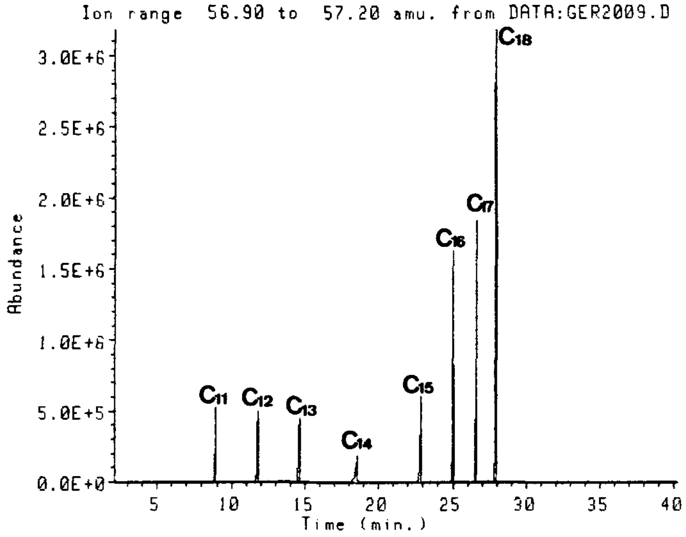

FIG. 2. Ion fragment chromatogram of a standard mixture of n-alkanes.

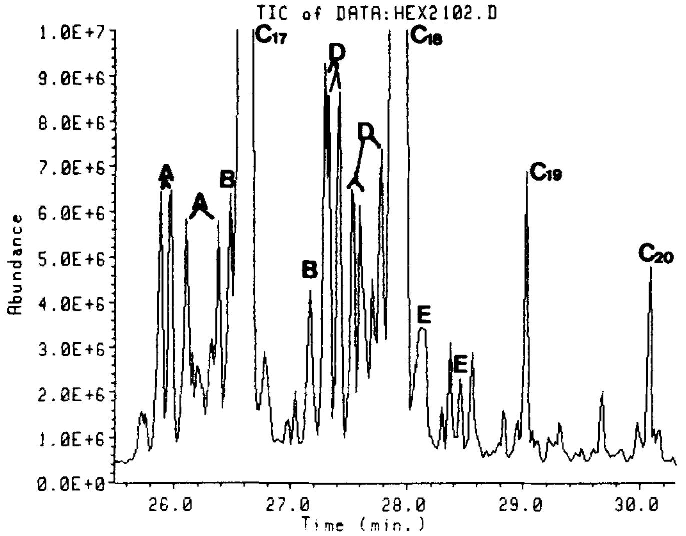

FIG. 3. Total ion current (TIC) of a hydrocracked seringa oil (retention time window between 25 to 30 min). A, Cycloalkanes, molecular weight, 238 (see Table 6), B, benzene compounds, molecular weight, 232 (see Table 7); D, cycloalkanes, molecular weight, 252 (see Table 6); and E, benzene compounds, molecular weight, 246 (see Table 7).

matogram of a standard mixture of n-alkanes. From the retention times it can be deduced that the main hydrocarbons in Figure 1 are n-alkanes. Mass spectra of the main n-alkanes were finally obtained to confirm the nature of these compounds. Aromatics and cycloalkanes were also particularly well detected in the liquid products obtained from seringa oil hydrocracking. This can be seen (Fig. 3) on the total ionic current (TIC) chromatogram of such a liquid fuel at retention times between 25 and 30 min.

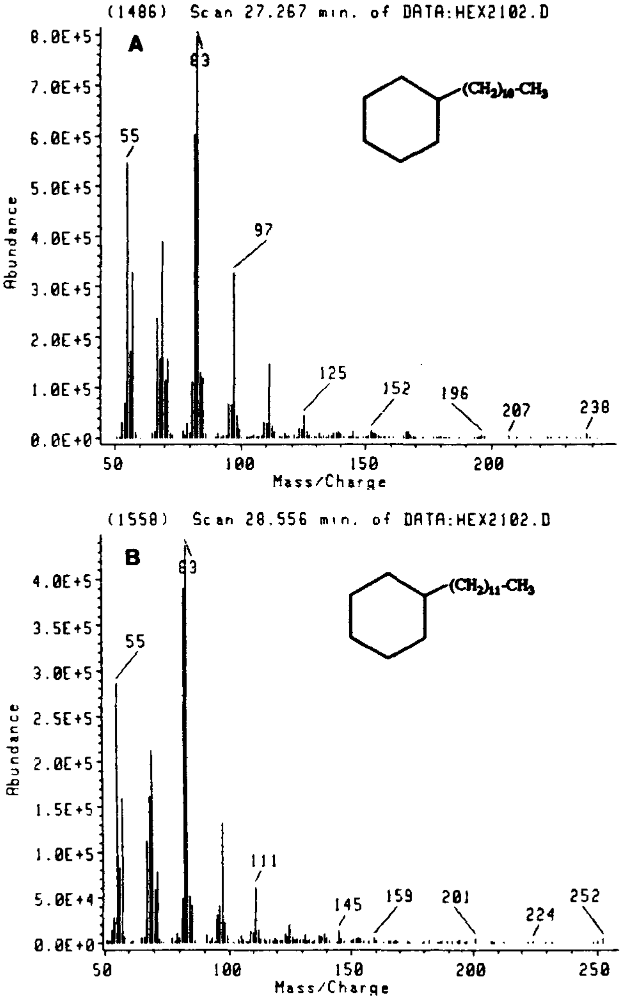

FIG. 4. Example of MS of the cycloalkanes of molecular weights 238 (A) and 252 (B), present in liquid fuels obtained after hydrocracking of seringa and ucuuba oils.

Again the fragmentometry method permitted resolution of the problem of overlapping of components. Cycloalkanes (molecular weights, 238 and 252) and benzene compounds (molecular weights, 232 and 246) are clearly evidenced on Figure 3 in the case of the liquid fuel from the seringa oil. Figures 4 and 5 show, as examples, the corresponding mass spectra of four of these compounds. Several spectra (every second) were registered during one TIC peak and could be studied separately to detect any overlapping of components.

Carboxylic acids accounted for 0.85 and 2.7 wt % in the liquid fuels from seringa and ucuuba oils, respectively. The main acids were stearic and palmitic in the case of seringa oil, and lauric and myristic in the case of ucuuba oil. Unsaturated acids were not detected in either liquid. The higher acidity observed in the products obtained from hydrocracking of ucuuba oil in comparison with the acidity of the products from seringa oil can be explained by the higher amounts of unsaponified materials and other impurities (Table 1) present in ucuuba oil, and which are able to deactivate the catalysts.

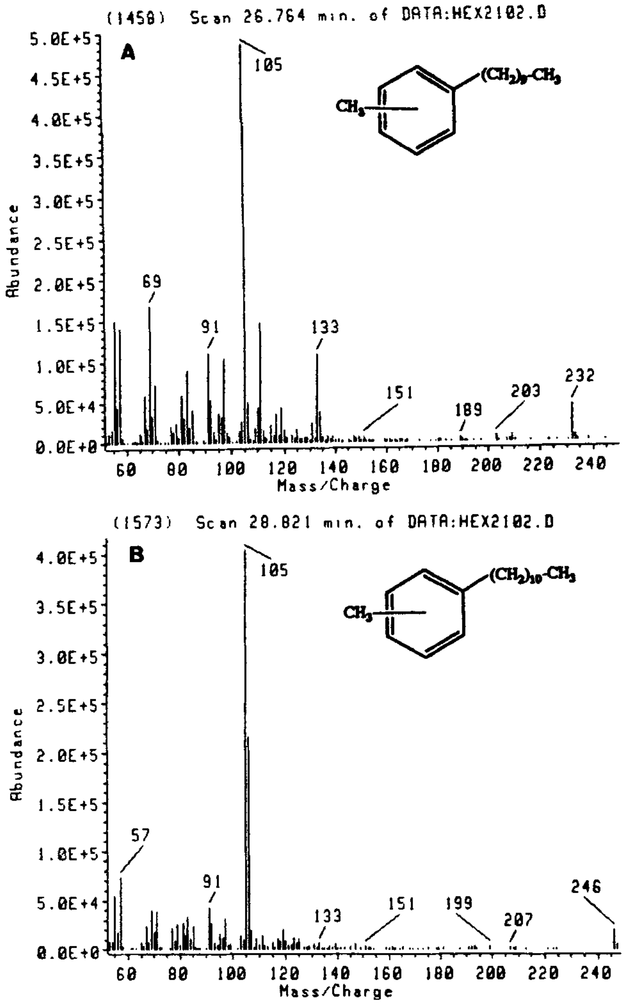

FIG. 5. Example of MS of the benzene compounds of molecular weights 232 (A) and 246 (B), present in liquid fuels obtained after hydrocracking of seringa and ucuuba oils.

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