



Diesel-like fuel obtained by pyrolysis of vegetable oils

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Abstract

The pyrolysis reactions of soybean, palm tree, and castor oils were studied. The pyrolytic products were analyzed by CG-FID, CG-MS, and FTIR, showing the formation of olefins, paraffins, carboxylic acids, and aldehydes. The adequate choice of distillation temperature (DT) ranges made it possible to isolate fuels with physical–chemical properties comparable to those specified for petroleum based fuels. The catalytic upgrading of the soybean pyrolytic fuel over HZSM-5 zeolite at 400 °C was also studied and has shown a partial deoxygenation of the pyrolytic products.

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1. Introduction

Due to economical, social, and ecological reasons, several studies have been done in order to obtain alternative fuel sources. In this respect, fermentation, transesterification, and pyrolysis of biomass, industrial, and domestic wastes, have been proposed as alternative solutions for the increasing of energy demand and environmental awareness. Among these different approaches, pyrolysis seems to be a simple and efficient method for fuel production. For example plastics [1], industrial and automotive waste oils [2], wood pyrolysis oils [3],

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fresh and waste fats and vegetal oils [4–9], etc. have been proposed as pyrolysis raw material to produce gasoline and diesel like fuels.

The pyrolysis of different triglycerides was used for fuel supply in different countries during the First and Second World Wars. For instance, a Tung oil pyrolysis batch system was used in China as a hydrocarbon supply during World War II [4]. These hydrocarbons were used as raw materials for gasoline and diesel-like fuel production in a cracking system similar to the petroleum process now used. Since then several studies on vegetal oil pyrolysis as an alternative method to obtain chemicals and fuels have been reported in the literature [5–9]. Pyrolysis, assisted by solid catalysts, has also been reported and it was recognized that the product selectivity is strongly affected by the presence and the nature of heterogeneous catalysts, as well as the presence of water steam and gas feed [10–12].

Studies of pyrolysis carried out in the absence of a catalyst were done using oil from Soybean [5], Palm tree [6], Babassu [6], Pequi [6], Macauba [7,8], and Canola [9] as raw material. In these works, the characterization of pyrolysis gas and liquid products were reported and some reactions pathways were proposed. The formation of linear and cyclic paraffins and olefins, aldehydes, ketones, and carboxylic acids were observed during thermal decomposition [5–9]. The direct thermal cracking of soybean oil in a distillation apparatus was also studied and the fuel properties of the liquid product fractions were characterized [5]. Indeed, it was observed that this product has low viscosity and a high cetane number compared to pure vegetable Soybean oil. The cetane number of pyrolyzed Soybean oil is enhanced from 37.9 to 43 and the viscosity is reduced from 32.6 to 10.2 cSt at 38 °C, but it still exceeds the specified value of 7.5 cSt for diesel fuel. It is worth while to mention that despite of ≈ 10 wt.% of carboxylic acid content (average acid number of ≈ 132), the liquid fuel obtained give an acceptable copper corrosion value [5].

We wish to report here a study upon Soybean oil, Palm tree oil (*Elaeis* sp.), and Castor oil (*Ricinus communis*) as raw materials for liquid fuel preparation by a pyrolysis reaction. After this reaction, the liquid product was separated into different distillation temperature (DT) range fractions. The different fractions were characterized by FTIR, gas chromatography, and ASTM methods. A tandem deoxygenating reaction of the pyrolysis product over HZMS-5 catalyst was also investigated.

The ultimate aim is the substitution of petroleum derived diesel in isolated communities of Brazilian Savannah and Amazonian rainforest regions. These communities are difficult of access and are located far-away from the centers of diesel production. They are strongly dependent on diesel fuel for economical production, transport, and electricity. However, these communities have a large potential for native or cultivar vegetable oil production, especially for the oils investigated here.

2. Experimental

2.1. General procedures

The pyrolysis products were analyzed by gas chromatography, FTIR, and ASTM standard methods for Cetane number (ASTM D613), distillation (ASTM D86), viscosity (ASTM D445), density (ASTM D4052), and sulfur content (ASTM D4294) of petroleum fuels.

Table 1
Vegetal oil composition [13]

Vegetal oil	Fat acid (wt.%)					
	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Ricinoleic
Soybean	14	4	24	52	6	–
Palm tree	35	6	44	15	–	–
Castor	2	3	5	2	–	88

Gas chromatography analysis were carried out on a Shimadzu GC-17A chromatograph equipped with a FID detector and a polydimethylsiloxane column (CBPI PONA-M50-042) 30 m, 0.25 mm i.d. and film thickness of 0.2 μm , working between 80 and 180 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$, and on a Shimadzu GC-17A chromatograph equipped with a mass spectrometer detector Shimadzu GCMS-QP5050 using an identical column. The FTIR spectra were obtained on a Bruker Equinox 55 from a thin liquid film over a NaCl window. The FTIR spectra correspond to the sum of 64 scans at a 4 cm^{-1} spectral resolution. Refined Soybean oil, Palm oil (*Elaeis* sp.), and Castor oil (*R. communis*) were obtained from commercial sources and used without further purification. The vegetable oil compositions are displayed in Table 1. H-ZMS5 zeolite was obtained from Aldrich and activated by heating at 400 $^{\circ}\text{C}$ under vacuum for 12 h before using.

2.2. Pyrolysis experiments

Pyrolysis experiments were carried out at temperatures ranging from 350 to 400 $^{\circ}\text{C}$ using the bench home-made 5 L stainless still batch unit shown in Fig. 1A. The vegetable oil (2 l) was introduced in the pyrolysis reactor (1 of Fig. 1A) and then heated by an external electric resistance. The temperature was measured at two sites using calibrated thermocouples (see 2 and 3 in Fig. 1A). When the temperature inside the reactor achieved 350 $^{\circ}\text{C}$, the vegetable oil was pyrolyzed, vaporized and a vapor feed left the reactor by the upper side at temperatures ranging from 200 to 250 $^{\circ}\text{C}$. Then the vaporous feed enters a water cooled heat exchanger (4 of Fig. 1A). As a result, two liquid fractions were obtained in the collector (5 of Fig. 1A): an aqueous fraction and an organic fraction. These fractions were separated by decantation and the organic phase was distilled using standard laboratory techniques. The

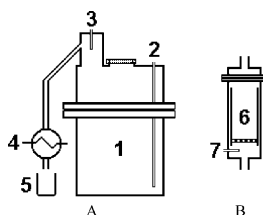


Fig. 1. (A) Bench home-made 5 L stainless still batch unit used for vegetal oils pyrolysis experiments; (B) catalytic pyrolysis product deoxygenating reactor. (1) Pyrolysis reactor; (2), (3), and (7) thermocouple probe; (4) heat exchanger; (5) liquid collector; (6) fritted bottom glass tube.

distillates were separated into four fractions with different distillation temperature ranges: (a) $DT < 80\text{ }^{\circ}\text{C}$; (b) $80\text{ }^{\circ}\text{C} \leq DT < 140\text{ }^{\circ}\text{C}$; (c) $140\text{ }^{\circ}\text{C} \leq DT < 200\text{ }^{\circ}\text{C}$; (d) $200\text{ }^{\circ}\text{C} \leq DT$ (heavy fraction). The different fractions were weighed and the heavy one was analyzed by gas chromatography, FTIR, and ASTM standard methods for petroleum fuels as above described. Alternatively, the vapor feed was forced into the catalytic deoxygenating reactor shown in Fig. 1B, which was placed between the pyrolysis reactor (1 of Fig. 1A) and the heat exchanger (3 of Fig. 1A). In this reactor, the pyrolysis products passed through a 2 cm H-ZMS5 zeolite plug bedded in a fritted bottom glass tube (5 of Fig. 1B). Note that this deoxygenating reactor was heated by an external electric resistance in order to maintain the vapor feed at approximately $400\text{ }^{\circ}\text{C}$.

3. Results and discussion

3.1. Pyrolysis reaction

The three investigated vegetable oils have shown that the vapor feeds begin to leave the reactor when temperatures higher than $350\text{ }^{\circ}\text{C}$ were achieved. At end of the reaction the vapor feed stopped and small amounts of a highly viscous oil (up to 2 wt.% of the vegetal oil) remained in the reactor. The vapor feed passes through a heat exchanger and the collected phases are separated and distilled as described in Section 2. Table 2 summarizes the results obtained for the three raw materials investigated in this work. These results show that the soybean and castor oils present a similar behavior considering the pyrolysis temperature range and the DT fractions yields. On the other hand, palm oil reacts in a lower temperature range with a higher yield in the heavy fraction. This different behavior may be due to differences in the oil composition, as shown in Table 1, especially for the high saturated-alkyl chain content of the palm tree oil.

3.2. Fractions characterization

The four different DT fractions obtained for the three vegetable oils were characterized by FTIR and gas chromatography (CG-FID and CG-MS). Fig. 2 shows the CG-FID chromatograms of the four DT fractions obtained by thermal cracking of the three different vegetable oils. The chromatographic profiles of the four DT fractions (see Fig. 2A and B) obtained for soybean and palm three oils are very similar, albeit the different cracking behavior observed for these oils. On the other hand, the chromatographic profiles obtained for

Table 2
Results obtained for the four different raw materials used

Vegetable oil	Pyrolysis temperature range ($^{\circ}\text{C}$)	Distillation temperature fraction ($^{\circ}\text{C}$) yield (wt.%)			
		<80	80–140	140–200	>200
Soybean	350–400	10	15	15	60
Palm	330–380	7	9	9	75
Castor	350–400	10	10	20	60

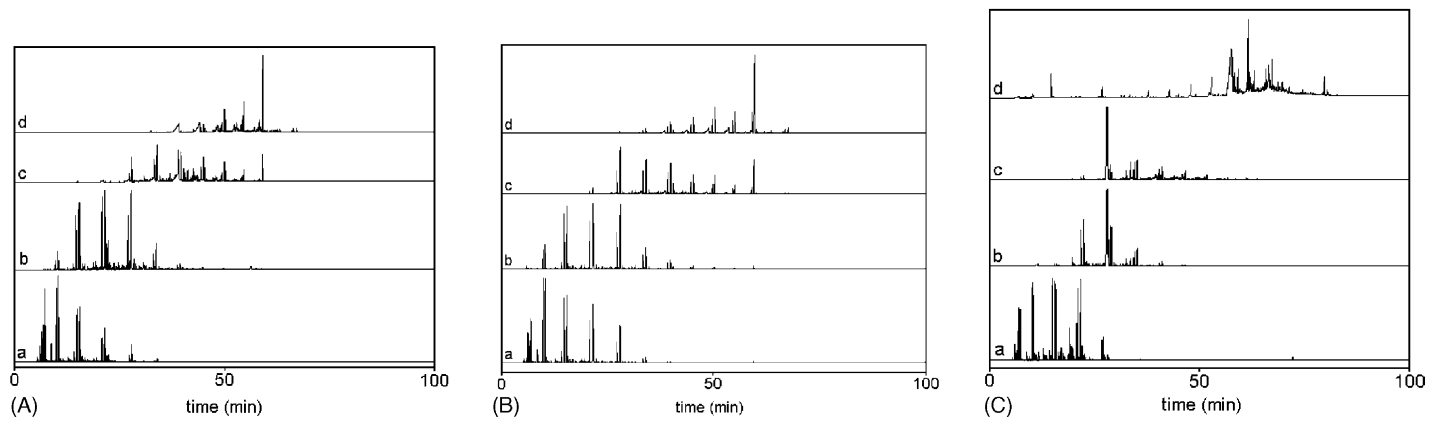


Fig. 2. Gas chromatograms for the four distillation temperature range fractions: (a) $DT < 80^{\circ}\text{C}$; (b) $80^{\circ}\text{C} \leq DT < 140^{\circ}\text{C}$; (c) $140^{\circ}\text{C} \leq DT < 200^{\circ}\text{C}$; (d) $200^{\circ}\text{C} \leq DT$; of the products obtained in the pyrolysis of soybean oil (A), palm tree oil (B), and castor oil (C).

castor oil pyrolysis products are quite different, especially for the heavy fraction as can be seen from Fig. 2C. Indeed, the heavy fraction components present, at the same conditions, higher retention times than those observed for the equivalent fractions of soybean and palm tree oil pyrolysis.

In order to identify the pyrolysis products a CG–MS analysis was carried out. Among the classes of compounds formed, hydrocarbons and oxygenated organic compounds such as alkanes, alkenes, alkadienes, and carboxylic acids were identified. Contrary to what was reported in the literature for soybean oil pyrolysis [5], no aromatic product was detected. Fig. 3 displays a selected region of the chromatogram obtained for the heavy fraction from palm tree oil pyrolysis. The peak assignment was done by comparison with the Wiley Library CLASS-5000 (6th Edition) with more than 95% similarity.

Fig. 4 shows the chromatograms for the heavy fractions obtained in the pyrolysis of the different vegetable oils. These results show that the obtained product mixtures corresponding to the soybean and palm tree fractions have similar chain distribution, from 11 to 15

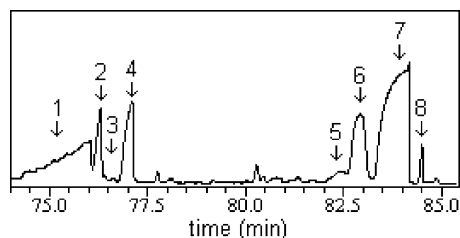


Fig. 3. Selected region of the CG–MS chromatogram for the heavy fraction product obtained in the pyrolysis of palm tree oil: (1) C_9COOH ; (2) $n-C_{14}H_{28}$; (3) $C_{14}H_{30}$; (4) $n-C_{14}H_{30}$; (5) $C_{15}H_{30}$; (6) $C_{15}H_{30}$; (7) $C_{15}H_{32}$; (8) $C_{16}H_{32}$.

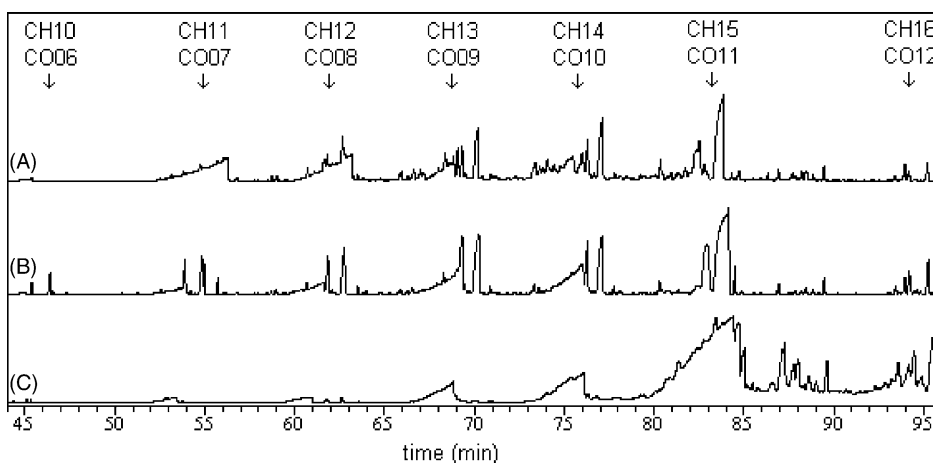


Fig. 4. Gas chromatograms for the heavy fractions obtained in the pyrolysis of soybean oil (A), palm tree oil (B), and castor oil (C).

carbons for hydrocarbons, and from 7 to 11 carbons for carboxylic acids. On the other hand, the results obtained for castor oil (Fig. 4C) show that the mixture contains products with longer chains, most of them corresponding to hydrocarbons possessing 15–16 carbons, and carboxylic acids with 11–12 carbons. This behavior is in agreement with that observed in the CG-FID analysis.

Fig. 5 shows the normalized FTIR spectra obtained for the four different DT fractions from the pyrolysis product of the three vegetable oils. Each spectrum was normalized by the intensity of the absorption band centered at 2930 cm^{-1} (the strongest band). Characteristic vibrational modes are observed at 3080 cm^{-1} (CH stretching, olefinic), $2850\text{--}2980\text{ cm}^{-1}$ (CH stretching, aliphatic), 1710 cm^{-1} (C=O stretching), and 1642 cm^{-1} (C=C stretching, olefinic). These features are observed in all temperature ranges and for all investigated oils. The products of castor oil cracking present some absorption features that are not observed in the other two oil cracking products, e.g. the absorption at 2713 cm^{-1} that is characteristic of aldehydes. A very broad absorption centered at 3430 cm^{-1} is observed in the spectra of Fig. 5 (castor oil) for two distilled fractions. This feature may be assigned to a carboxylic acid that is not present in the cracking products of the other two vegetable oils. It is also observed that for distillation temperatures above $80\text{ }^{\circ}\text{C}$, a broad feature emerges covering the $2800\text{--}3200\text{ cm}^{-1}$ simultaneously to the appearance of absorptions at 1285 and 1240 cm^{-1} characterizing the presence of carboxylic acids. It is worth mentioning that no vibrational feature, characteristic of aromatic compounds, was observed in the FTIR spectra, which is in good agreement with what was observed in the chromatography studies.

3.3. Fuel properties

The main diesel fuel properties specified in Brazil were determined for the heavy fractions obtained from the three different vegetable oils and are shown in Table 3. For comparison purposes, Table 3 also displays the specified values for the petroleum based fuel. The results show that the soybean and palm oils derived fuel present acceptable values for the studied properties when compared to the specified values for the petroleum based fuel. A previous report on pyrolyzed soybean oil derived fuel [5] presents different values for viscosity (ASTM D445 Viscosity of $10.21\text{ mm}^2/\text{s}$), Acid number (132) and

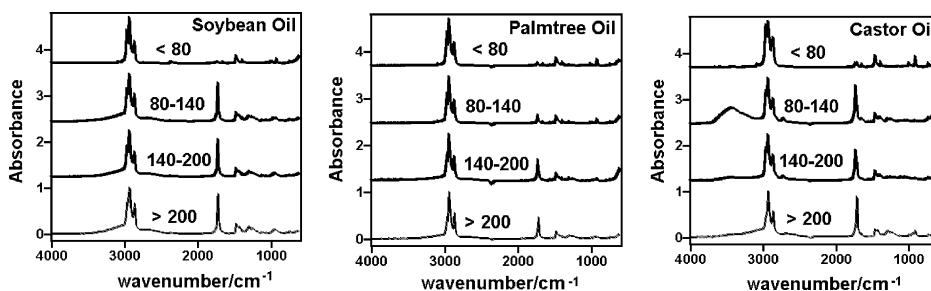


Fig. 5. Normalized FTIR spectra for the four distillation temperature range fractions of the products obtained in the pyrolysis of indicated vegetable oils.

Table 3

Values for the main diesel fuel properties specified in Brazil and acid number determined for the heavy fractions obtained from the three different vegetable oils

Physical–chemical property	Vegetable oil			Brazilian diesel fuel specification	ASTM method
	Soybean	Palm	Castor		
Density at 20 °C (kg/m ³)	844.0	818.4	882.3	820–880	D1298 D4052
Viscosity at 40 °C, cSt (mm ² /s)	3.5	2.7	3.7	2.5–5.5	D445
Cetane	50.1	52.7	30.9	45	D613
Acid index	116.2	133.0	207.5	–	D465-9
Sulfur (wt.%)	0.008	0.010	0.013	0.20	D1552 D2622 D4294
Distillation (°C)					
Initial point	90.6	63.5	97.5	Take note	D86
50%	265.9	245.2	254.3	245.0–310.0	
85%	307.5	254.3	273.2	370.0 (max)	
Final point	344.9	274.2	297.0	Take note	

Cetane number (ASTM D613 Cetane index of 43). The differences between the literature values for acid number and Cetane number obtained and those reported in the present work can be explained as far as the light pyrolysis products were separated from the analyzed fraction during the distillation. This light fraction obviously reduce the Cetane number and, as shown in the literature [5], presents a high acid number than the heavy ones.

3.4. Pyrolysis product catalytic deoxygenating

It is known that wood pyrolysis products can be catalytically deoxygenated using different zeolites, such as HZSM-5 and HY [14]. Indeed, in this work the authors claim that pyrolytic oils could be effectively deoxygenated when passed through a bed of HZSM-5, given an enriched hydrocarbon feed.

In order to upgrade the vegetable oil pyrolysis product, a first attempt in its catalytic deoxygenating behavior was carried out using pyrolyzed soybean oil. The vapor feed leaving the reactor was forced to pass through a 2 cm H-ZMS5 zeolite plug at 400 °C before its condensation (for more details see Section 2 and Fig. 1). The resulting two-phase liquid system was separated by decantation and the organic phase was separated by distillation as was done for reactions without the deoxygenating procedure (see Section 3.1). The heavy fraction was analyzed by gas chromatography and compared with non deoxygenated analogue. Fig. 6 shows the two chromatograms and the chromatographic regions that present larger differences are highlighted by arrows. These results show that the peaks corresponding to carboxylic acids diminished or vanish completely, and new peaks emerge, corresponding to hydrocarbon products. This result clearly indicates that it is possible to deoxygenate the vegetable oil pyrolysis product in order to obtain an enriched hydrocarbon diesel like fuel.

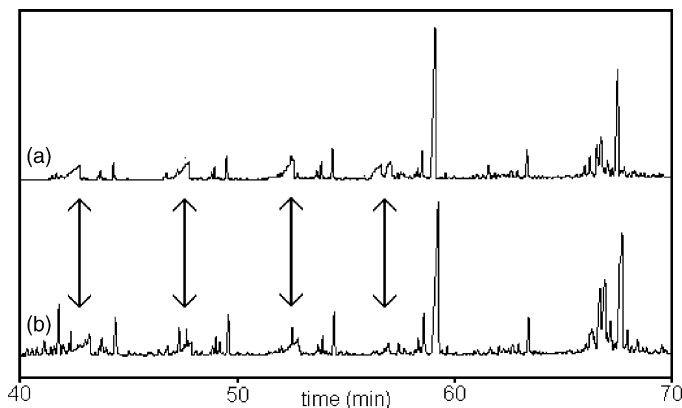


Fig. 6. Catalytic deoxygenation of soybean oil pyrolysis product: (a) gas chromatogram of condensed pyrolysis product without further treatment; (b) gas chromatogram of condensed pyrolysis product with further catalytic deoxygenation using HZMS-5.

4. Conclusions

The results presented in this work have shown that the pyrolysis of soybean, palm tree, and castor oils generate fuels mixtures that can be isolated by an adequate choice of distillation temperatures. The fractions from soybean and palm tree pyrolysis isolated at distillation temperatures above 200 °C present physical–chemical properties comparable to those specified for the petroleum based fuel in Brazil. The GC and FTIR analysis of the pyrolysis products has shown the presence of carboxylic acids in these fuels but their acidity is acceptable within the Brazilian specification norms. Furthermore, no aromatic compound was detected in the fuels. The preliminary tests with HZSM-5 zeolites at 400 °C have shown partial deoxygenation of pyrolyzed soybean oil is possible. Moreover, further studies on this deoxygenating reaction, such as zeolite deactivation and optimal temperature reaction are needed and are currently under investigation in our research group.

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