Diesel Fuel from Thermal Decomposition of Soybean Oil[1]

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Soybean oil was thermally decomposed and distilled in air or in nitrogen sparge with standard ASTM distillation apparatus. GC-MS analysis showed that approximately 75% of the products were made up of alkanes, alkenes, aromatics and carboxylic acids with carbon numbers ranging from 4 to more than 20. Fuel properties of the pyrolyzed materials were characterized and compared with those of the parent oil. The pyrolyzates had lower viscosities and higher cetane numbers than the parent vegetable oil. Thermally decomposed soybean oil shows promise as alternative fuel for the direct-injection diesel engine.

Soybean oil has good potential as alternative diesel fuel, but its use in the direct-injection engine is limited by high viscosity, low volatility and the polyunsaturated character of the triglycerides (1). These properties may be changed by pyrolysis. Engler (2) in 1888 first studied vegetable oil pyrolysis when he attempted the synthesis of petroleum from vegetable oils in order to confirm the theory of the origin of petroleum from organic matter. Since World War I, many investigators have studied the pyrolysis of vegetable oils to obtain products suitable for fuel (3-22). Grossley (23) has described the temperature effect on the type of products obtained from heated triglycerides. Many studies use catalysts, largely metallic salts, to obtain paraffins and olefins similar to those present in petroleum sources. Unfortunately, lack of suitable instrumentation and analytical methods did not permit adequate characterization of the thermal decomposition products of the pyrolyzed oils. This manuscript will present data obtained by gas chromatography-mass spectrometry (GC-MS) from thermally decomposed soybean oil in the presence of air and nitrogen. Because an oil with a greater degree of saturation was expected to provide a different mix of pyrolysis products, high-oleic safflower oil was evaluated in part for comparison. Catalytic systems are not included and many be the subject of future studies. A major objective of this manuscript is to characterize the predominant thermal decomposition products of soybean and high oleic safflower oils and to evaluate their potential usage as alternative diesel fuels.

EXPERIMENTAL

The ASTM standard method for distillation of petroleum products D86-82 was used to thermally decompose the vegetable oils. ASTM standard distillation equipment AE 133-78 was used with minor modifications.

Soybean oil was a refined grade obtained from the C&T Refinery, Charlotte, South Carolina. A sample of high oleic safflower oil obtained from Argo Ingredients Inc., Des Plaines, Illinois, was included for comparison. Compositional analyses of the oils are given in Table 1. Acid values were 0.2 and 0.3, respectively, and P contents were 32.1 and 0.4, respectively, for soybean and high oleic safflower oil.

Pyrolysis and distillation were performed in air or with a nitrogen sparge. After distillation was started the nitrogen flow was diminished to a rate sufficient to prevent air flow back to the flask. Rate of sparge affects the efficiency of the condenser.

Chromatographic analyses of the distillate samples were performed on a Beckman GC Gas Chromatograph with a hydrogen flame ionization detector and a 16′ long, 1/8″ o.d. OV-17 column. Mass spectrometry was used to identify the volatile components obtained from soybean high-oleic safflower distillate samples injected on a Packard model 873 Gas Chromatograph which was connected to a Nuclide 12-90-G mass spectrometer.

In addition to chromatographic and mass spectrometric analyses of the distillate, samples of the filtered distillates of soybean oil were sent to Phoenix Chemical Laboratory, Inc., Chicago, Illinois, and Southwest Research Institute, San Antonio, Texas, to obtain cetane numbers and other fuel properties. The soybean distillate samples were filtered with No. 2 and No. 4 Whatman filters to remove visible waxy semisolids and other large particulates that settled upon standing overnight at ambient temperatures.

RESULTS AND DISCUSSION

Figure 1 illustrates the distillation curves in air for soybean and high oleic safflower oils compared to that of No. 2 diesel fuel. The distillation curves for the vegetable oils do not represent just distillation, but a combination of distillation and cracking (destructive distillation). Seventy-seven percent of the soybean oil and 79% of the high oleic safflower oil were collected as volatiles from the distillations. The actual temperature of the oil in the feeder flask was ca. 100 C higher than the vapor temperature throughout the distillation. Anal-

TABLE 1

Pertinent Compositional Data of Oils

	Weight percent	
Component	Soybean	High oleic safflower
Myristic	0	0.3
Palmitic	11.7	5.5
Stearic	3.2	1.8
Arachidic	0	0.2
Oleic	23.3	79.4
Linoleic	55.5	12.8
Linolenic	6.3	0

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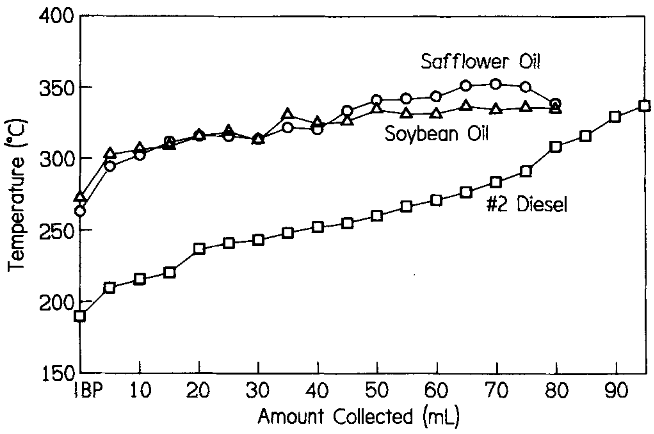

FIG. 1. ASTM distillation curves.

yses of the waxy phases were not carried out, but the residues amounted to slightly more than 5% of the weight of the original oil. Another 10% loss included nondistillables and noncondensed volatiles.

The 10-ml fractions from the soybean and high oleic safflower distillations were stored undisturbed at ambient temperatures of 21 C. After 48 hr, the initial and final fractions remained clear, with slight yellow and dark brown colors, respectively. The fractions obtained between the extremes contained varying amounts of a white semisolid waxy substance of greater density than the liquid. This waxy semisolid substance was not analyzed independently of the liquid phase, but a relationship existed between the amount of free acids in each fraction and the amount of semisolid material present.

TABLE 2

Acid Values of Soybean Oil Distillate Fractions (Nitrogen Sparge)

Fraction (ml)	Acid value
0-10	132.9
10-20	176.2
20-30	182.9
30-40	166.3
40-50	118.0
50-60	62.1
60-70	29.1

Acid numbers of the fractions for a soybean oil distillate are given in Table 2.

Fuel properties. The fuel properties of the distilled (nitrogen sparge) soybean oil appear in Table 3. ASTM test E191 for carbon-hydrogen ratio showed 79.00% carbon and 11.88% hydrogen, indicating considerable amounts of oxygenated compounds in the distillate. This accounts, in part, for the lower heating value than that of No. 2 diesel fuel but not for the higher value than soybean oil. The heating value of the distilled soybean oil was ca. 89% of that of No. 2 diesel fuel, indicating an expected increase in the brake-specific fuel consumption if used in a diesel engine. Table 3 shows that the cetane number of distilled soybean oil is greater than the minimum specified for No. 2 diesel fuel. Also, a two-thirds reduction in the viscosity from that of soybean oil was obtained by distillation. As diesel fuel substitutes, distilled vegetable oils possess acceptable amounts of sulfur, water and sediment and give acceptable copper corrosion values but have unacceptable ash, carbon residue amounts and pour point temperatures.

TABLE 3

Comparison of Fuel Properties

ASTM test no.	Specification	Distilled soybean oil (nitrogen sparge)	No. 2 diesel fuel	Soybean oil	High oleic safflower oil
D613	Cetane rating	43[a]	40 minimum	37.9[a]	49.1
	Higher heating value, BTU/lb	17,333	19,572	17,035	17,030
D129	Sulfur, %	<0.005	<0.5	0.01	0.02
D130	Copper corrosion 3 hr at 50 C standard strip	1a	<3	1a	1a
D524	Carbon residue at 10% residium	0.45%	<0.35%	0.27%	0.24
D1796	Water and sediment % by volume	0.05	<0.05	trace	trace
D482	Ash, % by weight	0.015	<0.01	<0.01	<0.01
D97	Pour point	+7 C	-7 C maximum	+12 C	-21 C
D445	Viscosity, mm^2/sec at 38 C	10.21	1.9-4.1	32.6	38.2
DE191	Carbon, %	79.00	86.61	-	-
	Hydrogen, %	11.88	13.20	-	-

[a] ASTM test D613 with ignition delays observed visually.

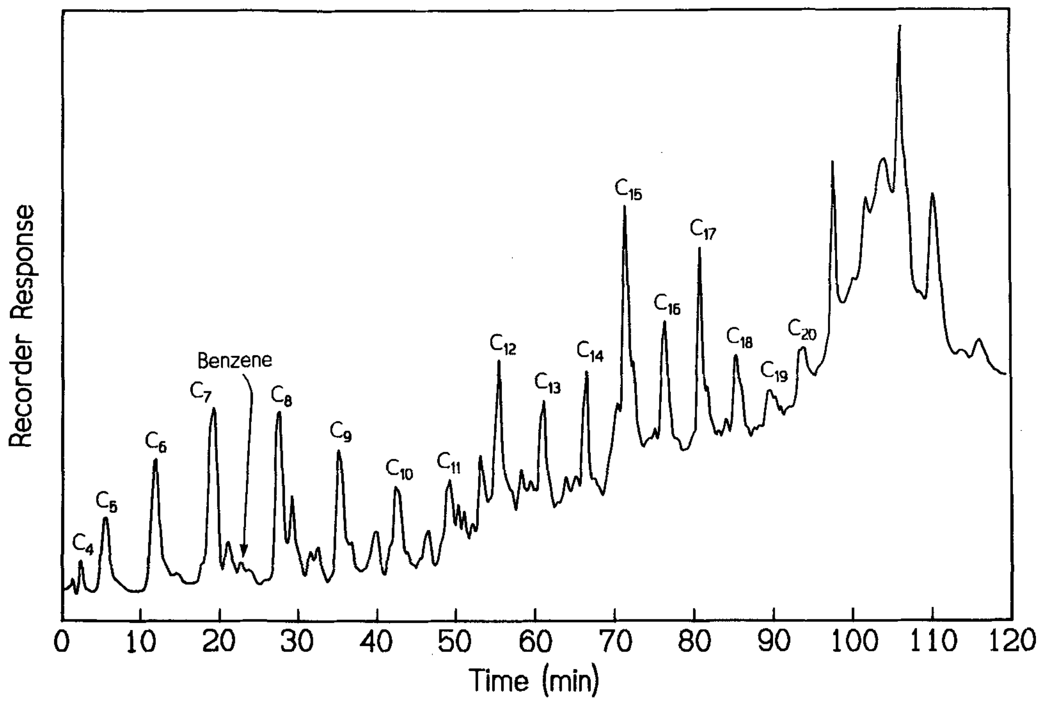

FIG. 2. Gas chromatogram of pyrolyzed soybean oil under air showing products ranging from four to over 20 carbon atoms.

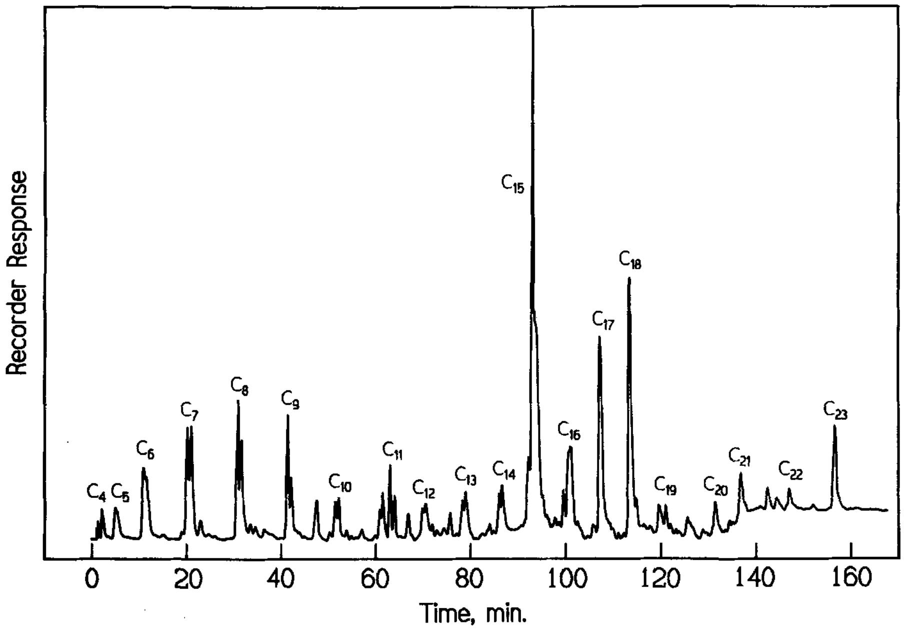

FIG. 3. Gas chromatogram of pyrolyzed high oleic safflower oil under air showing products ranging from four to over 20 carbon atoms.

Gas chromatography-mass spectrometry. Volatiles of soybean and safflower oils pyrolyzed under nitrogen and air were analyzed by GC. For example, see gas chromatograms of soybean and high oleic safflower oil pyrolyzed under air, Figures 2 and 3, respectively. Products from both oils are qualitatively similar but vary slightly in compositional analysis. Eluting volatiles of each treatment were analyzed in a mass spectrometer for compound identification. Among the classes of compounds formed were alkanes, alkenes, alkadienes, aromatics and carboxylic acids. These classes and amounts are listed in Table 4. Only small differences in composition are noted for different treatments, but large differences were noted between oil types. The total identified hydrocarbons obtained from the distillations of soybean and high oleic safflower oils were 73 to 77%

TABLE 4

Compositional Data of Pyrolyzed Oils

	Percent by weight			
	High oleic safflower		Soy	
	N_2 sparge	Air	N_2 sparge	Air
Alkanes	37.5	40.9	31.3	29.9
Alkenes	22.2	22.0	28.3	24.9
Alkadienes	8.1	13.0	9.4	10.9
Aromatics	2.3	2.2	2.3	1.9
Unresolved unsaturates	9.7	10.1	5.5	5.1
Carboxylic acids	11.5	16.1	12.2	9.6
Unidentified	8.7	12.7	10.9	12.6

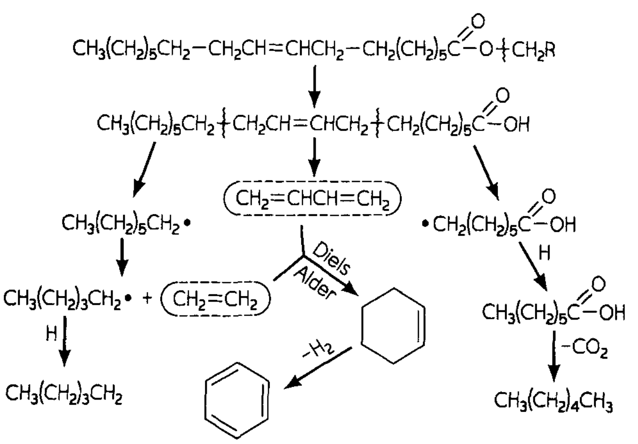

FIG. 5. Decomposition mechanisms.

and 80 to 88%, respectively. Alkanes made up 31.3% and 37.5% by weight of the soybean and high oleic safflower distillates, respectively under nitrogen sparge. Comparable results (29.9 and 40.9%) were obtained in the presence of air. The small differences probably are not significant.

The alkene contents of the soybean and high oleic safflower distillates (in air) were 24.9 and 22.0%, respectively. The values differ only slightly from the corresponding values of 28.3 and 22.2% obtained with nitrogen sparge. The alkadiene contents found with nitrogen sparge were 9.4 and 8.1%, and were lower than the values of 10.9 and 13.0% for those obtained with air. Additional unsaturated compounds were present but unresolved. The aromatic hydrocarbon contents in the distillates (in air) were small, consisting of only 1.9 and 2.2% by weight of the soybean and high oleic safflower distillates, respectively. These values agree well with the 2.3% obtained with nitrogen sparge. Greater amounts of aromatics appeared as the distillation progressed.

Carboxylic acids account for 9.6 to 12.2% and for 11.5 to 16.1% of the soybean and high oleic safflower distillates, respectively. Figure 4 is a gas chromatogram of the methyl esters prepared from the carboxylic acids formed during pyrolysis of soybean oil under air. This is a temperature-programmed run on a 10 m × 0.32 mm fused filica SE-30 column. Identifiable is a series of esters ranging from C_5 to over C_{18}. Figure 5 outlines a schematic that accounts for the formation of alkanes, alkenes, alkadienes, aromatics and carboxylic acids from the pyrolysis of triglycerides. Figure 6 is a total ion curve of volatiles collected in the dry ice trap of the soybean oil-in-air distillate and establishes the presence of these compounds in the pyrolyzate.

Mechanisms for the thermal decomposition of triglycerides are likely to be complex because of the many structures and multiplicity of possible reactions of mixed triglycerides. Generally, thermal decomposition of these structures proceeds through either a free-radical or

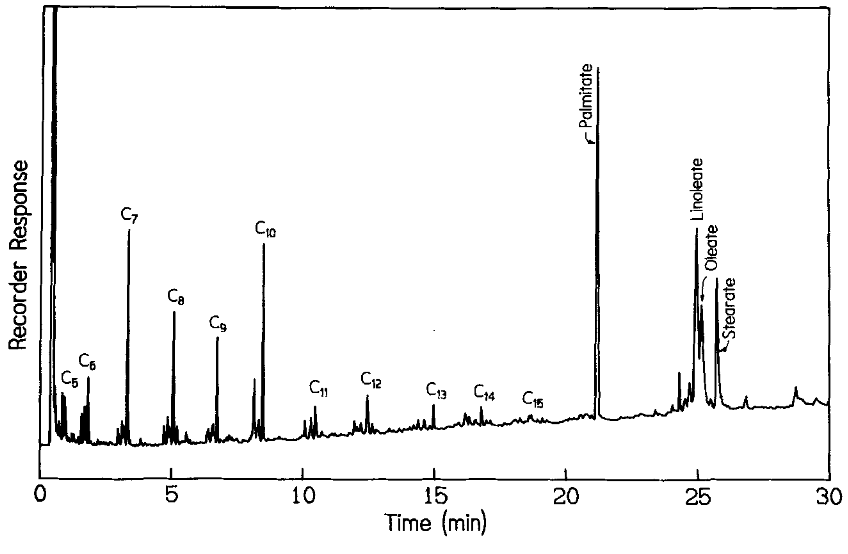

FIG. 4. Gas chromatogram of the methyl esters of the carboxylic acids obtained from the pyrolysis of soybean oil under air.

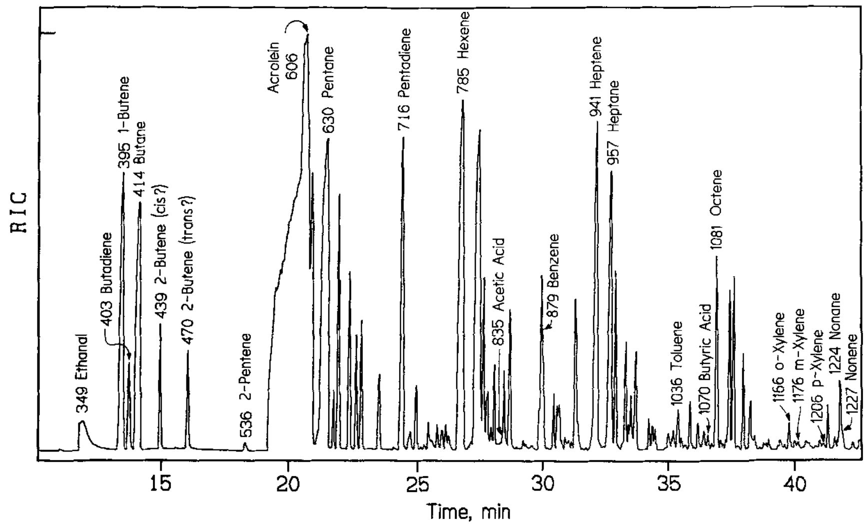

FIG. 6. Total ion curve of volatiles from dry ice trap of soybean oil in air distillate.

carbonium ion mechanism (22, 24). Alencar (22) has proposed a scheme for the probable thermal decomposition pathway of saturated moieties of triglycerides during pyrolysis. Basically this follows the Rice free radical theory modified by Kossiakoff and referred to as the RK theory (25). Formation of homologous series of alkanes and alkenes is accountable from the generation of the RCOO radical from the triglyceride cleavage and subsequent loss of carbon dioxide. The R radical, upon disproportionation and ethylene elimination, gives the odd-numbered carbon alkanes and alkenes. Chang and Wan (20) originally proposed this mechanism, which later was confirmed by Greensfelder et al. (26). The presence of unsaturation enhances cleavage at a position α,β to the unsaturation. Such cleavage is a predominant reaction which was supported by the relative abundance of C_7 (11.0%) in the 0-10 ml fraction from high-oleic safflower oil. Thermal positional isomerization and subsequent cleavage could account for the higher amounts of C_5 to C_{10} alkanes obtained from safflower compared with soybean oil. The formation of aromatics is supported by a Diels-Alder addition of ethylene to a conjugated diene formed in the pyrolysis reaction. Michaels et al. (27) suggested such a mechanism, which involves proton extraction followed by ring closure. Hydrogen elimination occurs at high temperatures, and the thermal reaction of olefins and diolefins with the formation of aromatics has been reported by Sakai et al. (28).

Carboxylic acids formed during the pyrolysis of vegetable oils probably result from cleavage of the glyceride moiety, as suggested by Nawar (29). In this mechanism, acrolein is released, and it was detected by GLC in pyrolysis experiments in which a dry ice trap was used to collect volatiles.

A pint-size sample of pyrolyzed soybean oil was run in a direct-injection diesel engine which did perform satisfactorily (unpublished data). As an emergency fuel, thermally decomposed vegetable oil liquid fractions would approach diesel fuel and would be an improvement over undistilled vegetable oils in the direct-injection diesel engine.

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