Volatile By-products During Heat Polymerization of Soybean Oil

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ABSTRACT: Volatile by-products during heat polymerization of soybean oil at 330°C were analyzed using GC–MS and NMR. Color and viscosity changes were monitored for the heat- polymerized soybean oil and the by-products. About 90% (w/w) of the by-products were decanoic, palmitic, linoleic, oleic, and stearic acids and *cis*-9-tricosene. The by-products also contained small amounts of 3-eicosene, 9,17-octadecadienal, and cyclotetracosene. The weight percentage of decanoic acid increased with reaction time, whereas those of other components showed no trends.

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KEY WORDS: Heat-bodied soybean oil, heat polymerization, soybean oil.

Renewable nontoxic materials for preparation of printing ink vehicles and ink formulations have attracted increasing interest since the mid-1970s because of petroleum shortages and the growing concern for environmental issues. In the early 1980s, the American Newspaper Publishers Association (Reston, VA) introduced blends of gilsonite and tall oil FA as a nonpetroleum-based vehicle for news inks (1). Acceptance of these inks by the industry, however, has been limited by the cost and the difficulty of equipment cleanup caused by gilsonite. Because of their well-known characteristics of being nonvolatile and biodegradable, vegetable oils have been an obvious choice for further investigation. Later, the American Newspaper Publishers Association prepared a vegetable oil-based ink vehicle suitable for lithographic news ink (2).

The vegetable oil-based ink vehicles typically are prepared by two methods. In the first method, vegetable oils are heat-polymerized at a constant temperature in a nitrogen atmosphere to a desired viscosity. In the second method, the heat-polymerization reaction is permitted to proceed to a gel point, and then the gel is mixed with vegetable oils to obtain a desired viscosity.

Since it represents nearly 80% of seed oils produced annually in the United States (3), soybean oil has been emphasized in our studies. We have studied development, characterization, formulation, and biodegradability of new soybean oil-based lithographic and letterpress ink vehicles (4–7). Continuing our research on soybean oil-based ink vehicles, we now report the identification of major volatile by-products from heat polymerization of soybean oil for workers' safety and environmental considerations. To our knowledge, no study has been published on identification of these by-products. NMR and GC–MS have been used to identify the major by-products, and the results were confirmed by comparison with genuine standards.

MATERIALS AND METHODS

Materials. Alkali-refined soybean oil was purchased from Archer Daniels Midland Co. (Decatur, IL). The specifications for this oil, as furnished by the supplier, were: FFA content 0.09%, iodine value 127.7, and saponification value 190.2. Sylon BTZ, which contains trimethylchlorosilane, *N,O*-bis (trimethylsilyl)acetamide (BSA), and *n*-trimethylsilylimidazole was purchased from Supelco Inc. (Bellefonte, PA). Reference standards including decanoic acid, palmitic acid, linoleic acid, oleic acid, stearic acid, and *cis*-9-tricosene (99% purity) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification.

Polymerization of soybean oil. Alkali-refined soybean oil (1000 mL) was placed in a 2000-mL four-necked reactor equipped with a distillation apparatus (three-way distillation adapter, thermometer, and a 50-cm Graham condenser and 200-mL round-bottomed flask). The oil was heated under nitrogen at 330 ± 2°C, and the collection time was counted when the reaction temperature reached 330°C. A slightly reduced pressure was applied to pull over the volatile by-products into the collection flask at a specific reaction time.

Viscosity and color determination. The viscosities of soybean oil and the by-products were determined with a Gardner-Holdt Bubble Viscometer (8). The color of each sample was evaluated on the Gardner Color Scale (9).

GC–MS. GC–MS analysis was conducted on a Hewlett-Packard (Palo Alto, CA) 5890/5970 bench-top GC–MS system, operated with electron ionization (EI) and equipped with a nonpolar column, a J&W Scientific (Folsom, CA) HP-5MS column (30 m × 0.25 mm i.d.). The samples were dissolved in Sylon BTZ or acetone (about 5–10 mg/mL) and filtered through a Teflon Syringe filter, and then injected into the instrument with an autosampler (Hewlett-Packard 7673 GC/SFC injector). Helium was used as carrier gas at fixed conditions: injection temperature of 250°C, GC–MS transfer line

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*To whom correspondence should be addressed at National Center for Agricultural Utilization Research, USDA/ARS, 1815 N. University St., Peoria, IL 61604. E-mail: erhansz@ncaur.usda.gov temperature of 280°C, solvent delay of 8 min, and temperature program of 100°C/2 min. Volatile compounds were tentatively identified by matching mass spectral data of sample components with those of known compounds in a database (MS ChemStation Data Analysis software, G1033A NIST PBM Library).

NMR spectroscopy. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ solution with a Bruker (Rheinstetten, Germany) ARX 400 spectrometer. Chemical shifts are in ppm relative to tetramethylsilane (TMS) for proton NMR, and relative to solvent signal at 77.0 ppm for carbon NMR.

RESULTS AND DISCUSSION

To verify the FA contents, soybean oil used in this study underwent transesterification with methanol in the presence of a catalytic amount (1% w/w) of sodium hydroxide at 60°C for 2 h to give methyl soyate (10). A GC–MS spectrum of the product shows that the composition of the FA in the soybean oil was typical of alkali-refined soybean oil (relative percentage, w/w, in parentheses): 16:0 (11%), 18:0 (5%), 18:1 (23%), 18:2 (53%), and 18:3 (7%) (11).

Heat-polymerization of soybean oil was conducted at a typical reaction temperature (330 ± 2°C) for heat-bodied soybean oil production in industry with stirring under nitrogen. Although detailed studies for the reactions involved in the heat polymerization have not been reported yet, major reactions include double-bond migration and other isomerizations, transesterification, ring formation, and polymerization (12). The double-bond migration to give more reactive conjugated dienes improves drying properties of the oil, and the resulting conjugated dienes also participate in cross-linking reactions through ring formation to increase the viscosity. The viscosity and color of the heat-polymerized soybean oil were measured after 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 h of polymerization using standard methods, ASTM D 1545-63 and ASTM D 1544-63, respectively (8,9). As shown in Table 1, a generally desired viscosity range for use as drying oil in ink, Z_2–Z_3, was obtained in 2 h and the product turned into a gel-like polymer in 3 h. The volatile materials were also collected after 0.5, 1.0, 2.0, 2.5, and 3.0 h; the viscosities and colors of the by-products are summarized in Table 2.

For a preliminary analysis of the by-products produced by heat polymerization, the ^{1}H and ^{13}C NMR spectra were obtained. Figures 1 and 2 show the ^{1}H and ^{13}C NMR spectra of the by-product collected at 0.5 h polymerization. Other spectra obtained at different reaction times up to 3 h are very similar, indicating that the components of the by-products do not change much with time. Peaks between 4.0 and 4.5 ppm in

TABLE 1
Viscosity and Color of Heat-Polymerized Soybean Oil[a]

Reaction time (h)	Viscosity	Color
0.5	G–H	<1
1.0	R–S	2–3
1.5	V–W	2–3
2.0	Z_2–Z_3	3–4
2.5	Z_5–Z_6	4–5
3.0	Gel	Not determined

[a]Gardner–Holdt viscosity. Gardner Color Scale.

TABLE 2
Viscosity and Color of By-Product[a]

Reaction time (h)	Viscosity	Color
0.5	<A	2–3
1.0	<A	<1
1.5	<A	<1
2.0	<A	<1
2.5	<A	<1
3.0	<A	<1

[a]Gardner–Holdt viscosity. Gardner Color Scale.

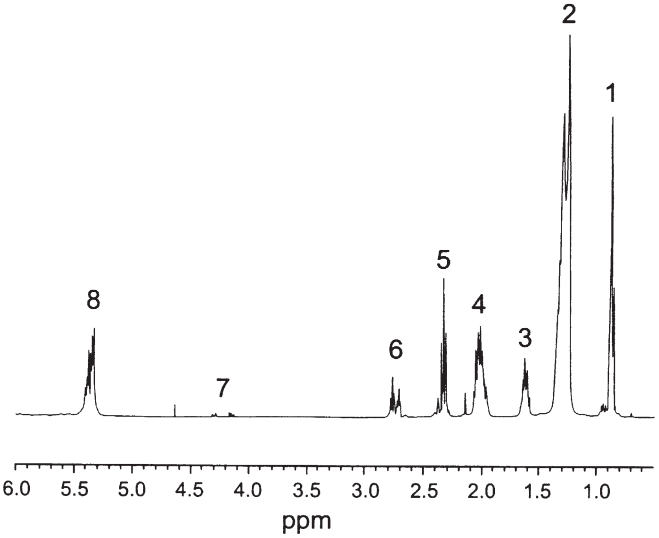

FIG. 1. ^{1}H NMR spectrum of by-products collected at 0.5-h heat-polymerized soybean oil. 1: $–CH_3$; 2 and 3: $(CH_2)_n$ in saturated carbon chain; 4: $=C–CH_2$; 5: $–CH_2–COO–$; 6: $=C–CH_2–C=$; 7: hydrogens in TG backbone; 8: $–CH=CH–$.

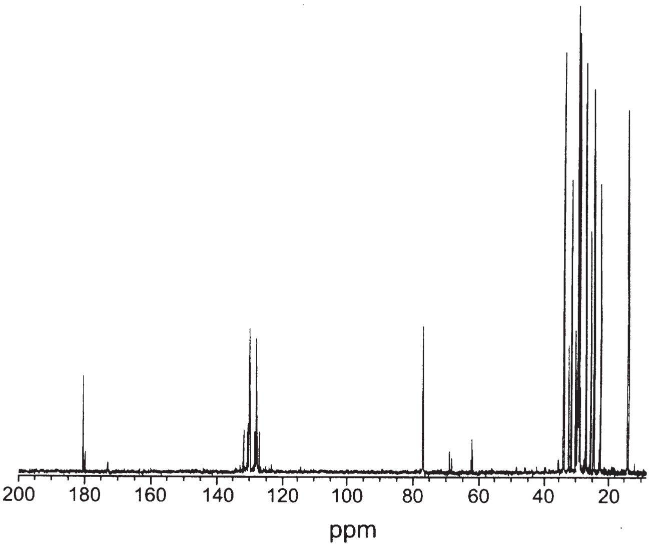

FIG. 2. ^{13}C NMR spectrum of by-products collected at 0.5-h heat-polymerized soybean oil.

TABLE 3
Retention Time and Weight Percentage of By-products Collected at 0.5 h Heat Polymerization

Compounds	Retention time (min)	Wt%
Decanoic acid	10.34	4.22
Palmitic acid	16.98	21.21
Linoleic acid	18.66	27.10
Oleic acid	18.67	24.25
Stearic acid	18.81	8.70
Cis-9-tricosene	18.90	2.91

^{1}H NMR spectra and between 62 and 68 ppm in ^{13}C NMR spectra correspond to the hydrogens and carbons of the glyceride backbone. These indicate that the amounts of glycerides in the by-products are very small. From the hydrogen peaks at 5.3–5.4 ppm in ^{1}H NMR spectra and carbon peaks at 127–133 ppm in ^{13}C NMR spectra, it can be concluded that considerable amounts of double bonds are incorporated in the by-products. No indications of aromatic compounds, cyclic compounds, and conjugated dienes were found in the spectra.

A sample of the by-products was subjected to GC–MS analysis to identify major components in the by-products. Components of the volatile by-products were first identified by matching mass spectral data in a database, and later the retention times of compounds were confirmed by comparison with authentic samples. Six major components, decanoic acid, palmitic acid, linoleic acid, oleic acid, stearic acid, and *cis*-9-tricosene were identified, which account for about 90% (w/w) of the by-products. The concentration of an identified compound (wt%) contributing to the total volatile by-products was determined by comparison of the peak area of the identified compound with the peak area of the known amount of the authentic compound. Table 3 shows the summarized GC–MS data obtained from the by-products collected at the reaction time of 0.5 h. Even though the major by-products are FA obtained by hydrolysis of soybean oil, linolenic acid, constituting about 7% of the FA in the starting material (soybean oil), was not detected in the by-products. The result implies that the more reactive linolenic acid is consumed at an early stage of the polymerization reaction to produce polymeric materials. Similarly, comparison of the content (24.16–28.31%) of the linoleic acid in the by-product with the original content in soybean oil (53%) indicated that linoleic acid was consumed faster than other FA such as palmitic, stearic, and oleic acids. FA with no olefin groups, such as palmitic and stearic acids, are present at a higher weight percentage in the by-product (16.98 and 18.81%, respectively) than in the starting soybean oil (11 and 5%, respectively).

The gas chromatograms of the samples at longer reaction times are very similar to those of the sample at 0.5 h of reaction except for slight changes in composition of the components. Table 4 shows the composition changes of the volatile by-products with time. During the heat-bodying process of soybean oil, the content of decanoic acid increased with reaction time, whereas those of other components changed randomly. It may be noted at this point that with greater abuse, linoleic acid is converted to decanoic acid, which shows an increase in percentage. The randomness in the values presented in Table 4 could be due to sampling error. Small amounts of 3-eicosene, cyclotetracosene, and 9,17-octadecadienal were also identified by matching with mass spectra of known compounds in the database, with higher than 91% match qualities.

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TABLE 4
Component Changes of By-Products from Soybean Oil Heat Polymerization with Time

	Component						Total
Reaction time (h)	Decanoic acid	Palmitic acid	Linoleic acid	Oleic acid	Stearic acid	*cis*-9-tricosene	(%, w/w)
0.5	4.22	21.21	27.10	24.25	8.70	2.91	88.39
1.0	6.76	23.60	25.94	24.65	7.65	3.93	92.53
1.5	7.22	17.14	23.22	22.23	7.83	4.07	81.71
2.0	7.62	17.25	21.93	19.44	7.30	4.11	77.65
2.5	8.03	26.85	28.31	21.49	8.64	3.55	96.87
3.0	8.35	24.80	24.16	20.53	8.93	3.25	90.02

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