A DSC Study of Z_2–Z_3 Viscosity Blown Soybean Oil

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ABSTRACT: The thermal oxidation of four commercially available neat blown soybean oil samples and a heat-bodied soybean oil sample, obtained from various manufacturers, having Gardner bubble viscosities between Z_2 and Z_3 was investigated using nonisothermal DSC under a constant oxygen flow and a heating rate (β) ranging from 3 to 20°C/min. The extrapolated onset temperatures (T_{e1} and T_{e2}) and maximum temperature of heat flow (T_{p2}) at different β were determined from the DSC curves and used in conjunction with the Ozawa–Flynn–Wall method to estimate the kinetic parameters of oil thermal oxidation. At a β of 10°C/min, the calculated activation energies (E_a) for the blown soybean oil samples investigated ranged between 57.7 and 74.3 kJ/mol for T_{e1}, 37.6 and 55.3 kJ/mol for T_{e2}, and 54.7 and 63.0 kJ/mol for T_{p2}. For comparison, a Z_2–Z_3 heat-bodied soybean oil sample had activation energies of 72.5, 39.8, and 61.9 for T_{e1}, T_{e2}, and T_{p2}, respectively. By ^{1}H NMR, the amount of allylic and bis-allylic hydrogens present in the blown soybean oil samples relative to an unmodified soybean oil sample was determined to range from 40.3 to 48.2% and 14.9 to 22.4%, respectively.

Paper no. J10223 in *JAOCS 79*, 1151–1155 (November 2002).

KEY WORDS: Activation energy, blown soybean oil, differential scanning calorimetry, heat-bodied soybean oil, nuclear magnetic resonance, oxidation, thermal oxidation kinetics.

Blowing air or oxygen through vegetable oils, soybean oil in particular, while heating under controlled conditions, produces materials generally known as blown oils, and this is one of the oldest methods used to modify and promote both conjugation and polymerization of vegetable oils (1,2). Blown soybean oil is routinely used industrially to prepare linoleum, caulking, glazing compounds, lacquers, printing inks, and coatings.

The blowing process is based on well-known autoxidative reactions, whereby the allylic and bis-allylic hydrogen atoms of the fatty compounds in soybean oil are abstracted by a radical initiator at room or elevated temperatures (90–150°C) to generate lipid radicals that enter into chain reactions. The ensuing lipid radicals react with oxygen in a series of complex reactions to generate hydroperoxides as the primary products formed during the initial stages of oxidation (3). Under continued heating, the hydroperoxides undergo numerous highly complex degradative reactions to give oligomeric materials cross-linked by carbon–carbon, ether, and peroxy linkages (4–6). As a result of cross-linking, the blown soybean oil exhibits higher densities, higher viscosities, and lower iodine values compared with the soybean oil from which it was prepared. When the aforementioned properties during the autoxidative blowing reaction are monitored, the properties of the blown oil can be tailored to meet the desired end application.

Because oxidation processes are commonly exothermic, as an initial approach we were interested in examining the thermal oxidation of blown soybean oil using DSC. Ozawa (7) and Flynn and Wall (8) (OFW Method) have independently shown a linear relationship to exist between the heating rate and observed peak temperatures. For oxidation, when a large excess of oxygen is employed, oxygen consumption can be neglected and the reaction rate is independent of oxygen concentration (9). If we assume the reaction to be first order as long as the oxidation initiation rate is constant, the extrapolated onset of oxidation (T_e) and the maximum heat flow (T_p) obtained in the DSC curves represent points of constant conversion (9–11). These presumptions allow researchers to estimate kinetic parameters using the OFW method and data collected from nonisothermal DSC experiments performed over a series of heating rates (10–13). The ease with which nonisothermal DSC methods can be run, in conjunction with the OFW method, has made this combination a valuable tool to follow the oxidation course of many materials and estimate their associated thermal oxidation kinetics (14).

Although nonisothermal DSC methods have been used previously to examine the oxidation kinetics of edible oils (9–13), to our knowledge, no thermoanalytical studies concerning blown soybean oils have been reported. We report here the estimated thermal oxidation kinetic parameters determined for blown soybean oil using nonisothermal DSC experiments between 25 and 300°C run at a series of linear programmed heating rates ranging 3 to 20°C/min.

EXPERIMENTAL PROCEDURES

Materials. Samples of Z_2–Z_3 viscosity blown soybean oils were obtained from Werner Smith (Cleveland, OH), Cargill Inc. (Chicago, IL), and David Frost (Minneapolis, MN). Samples of Z_2–Z_3 heat-bodied soybean oil (HBSBO) were also obtained from David Frost. All oils were used as received. The viscosities of all samples reported were estimated using a Gardner Bubble Viscometer, Class G, 10.65 mm i.d., following ASTM method D1545-63. All acid, iodine, and PV reported for the oil samples were evaluated by Woodson-Tenent Laboratories, Inc. (Memphis, TN).

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Sample preparation. A Cahn microbalance (Beverly, MA) was calibrated and used for weighing all DSC samples. Weighed samples (5.00 ± 0.02 mg, mean ± SD) of blown or heat-bodied oil were immediately analyzed by DSC.

DSC. All DSC analyses were conducted on a TA Instruments (New Castle, DE) model 2910 DSC fitted with a normal pressure cell calibrated with a high-purity indium standard. A TA model 3100 PC-based controller was employed for data acquisition and analysis. A TA Gas Switching Accessory was used to meter high-purity oxygen (99.99%) at 98 cm^3/min and continuously replenish the DSC cell with oxygen. For each scan, a 5.00 ± 0.02-mg sample was placed in an open aluminum pan and referenced against an identical empty aluminum pan. The cell contents were equilibrated at 25°C, then heated from 25 to 300°C with a linear heating rate (β) of 3–20°C/min. Heat flow (W/g) vs. temperature (°C) curves from each scan were analyzed using TA Universal Analysis 2000, version 3.1E (TA Instruments) to determine extrapolated onset temperatures (T_{e1} and T_{e2}) and temperature of maximum heat flow (T_{p2}). The data presented are averages of triplicate scans (duplicate in the experiments utilizing heat-bodied oil) conducted using fresh samples. The apparent activation energies of oxidation (E_a) were calculated using the OFW method (7,8).

NMR. All ^{1}H NMR spectra were recorded in $CDCl_3$ as solvent using a Bruker ARX 400 spectrometer (Billerica, MA) with a 5-mm dual proton/carbon probe operating at 400 MHz. The percentages of bis-allylic (2.9–2.7 ppm, $-HC{=}CH-CH_2-CH{=}CH-$) and allylic (2.1–1.9 ppm, $-HC{=}CH-CH_2-$) hydrogens present in the blown soybean oil samples with respect to those found in soybean oil before thermal oxidation were determined as follows. The areas for hydrogen signals in blown oil that presumably do not undergo reaction during the blowing process, namely, hydrogens α to the ester moiety (2.35–2.25 ppm), saturated lipid alkyl hydrogens (1.15–1.70 ppm), and the terminal methyl hydrogens (0.9–0.7 ppm), were used as internal standards in both the blown and normal soybean oil. The ratios determined for the bis-allylic or allylic hydrogen areas and the areas for each internal standard in the blown oil samples were averaged and divided by the respective ratios found in the soybean oil sample to give the relative percentage of allylic and bis-allylic hydrogens remaining in the blown oil samples (Table 1).

RESULTS AND DISCUSSION

Table 1 summarizes the properties of the blown soybean oil samples. The different blown oil samples appear to be quite uniform with regard to the characteristics examined. The iodine values indicate that a substantial percentage of the double bond character in the blown soybean oils has been consumed during the initial blowing process (the iodine value of soybean oil is typically 120–140); ^{1}H NMR experiments to determine the percentages of bis-allylic and allylic hydrogens present in the blown soybean oil samples relative to soybean oil also confirm this. The approximate percentages of allylic and bis-allylic hydrogens remaining within the blown soybean oil samples after the blowing process with respect to soybean oil ranged from 40.3 to 48.2% and 14.9 to 22.4%, respectively (see paragraph on NMR in the Experimental Procedures section for details). Finally, the acid values for the blown oil samples ranged from 4.9 to 9.4%, and the PV for the blown samples varied from 13 to 102 meq/kg.

Figure 1 shows a representative DSC curve obtained for the blown soybean oil samples run under a constant dry O_2 flow. The DSC curve exhibits three main areas of interest: (i) the temperature of extrapolated onset of exothermic reaction (T_{e1}), determined by the intersection of the baseline with a line tangential to the initial part of the oxidation exotherm; (ii) the rising slope from approximately 140 to 225°C; and (iii) the maximum exothermic heat flow (T_{p2}).

The DSC curves are sensitive to the heating rate, and as can be seen from Table 2, as β increases, the temperatures corresponding to $T_{e1,}$ T_{e2}, and T_{p2} shifted to higher temperatures. Table 2 summarizes the extrapolated onset temperatures (T_{e1}) and T_{p2} DSC results determined for the blown oil samples. Table 2 also shows the extrapolated onset temperature (T_{e2}) determined for heat flow maximum T_{p2} using a sigmoidal baseline. For comparison, T_{e1}, T_{e2}, and T_{p2} ascertained for the David Frost Z_2–Z_3 HBSBO sample using DSC under identical conditions is also shown.

The extrapolated onset temperature (T_{e1}), viewed as the induction period of oxidation where the exothermic changes are minor (15), was above 100°C in all samples investigated. The gradually increasing slope observed in the DSC curves between 140 and 225°C (Fig. 1) followed by the prominent maximum heat flow, T_{p2}, suggests that at least two principal exothermic

TABLE 1
Properties of the Blown Soybean Oil (BSBO) Samples Utilized in the DSC Thermoanalytical Studies

BSBO samples[a]	Iodine value[b]	FFA[b]	PV (meq/kg)	Allylic hydrogens[c] (%)	Bis-allylic hydrogens[c] (%)
1[d]	76.5	8.8	58	41.7 ± 2.4	16.8 ± 1.0
2[d]	74.4	9.4	102	40.3 ± 3.0	15.0 ± 1.1
3	78.2	4.9	81	41.9 ± 2.3	14.9 ± 0.8
4	78.0	7.5	13	48.2 ± 3.5	22.4 ± 1.6

[a] Blown soybean oil samples 1–4 are from the following manufacturers: BSBO 1 = Cargill-1; BSBO 2 = Cargill-2; BSBO 3 = David Frost; BSBO 4 = Werner Smith.
[b] Iodine, FFA, and PV were evaluated by Woodson-Tenent Laboratories, Inc. (Memphis, TN).
[c] Percentage with respect to soybean oil. See NMR paragraph in the Experimental Procedures section for details.
[d] Blown soybean oil samples 1 and 2 represent different batches from Cargill.

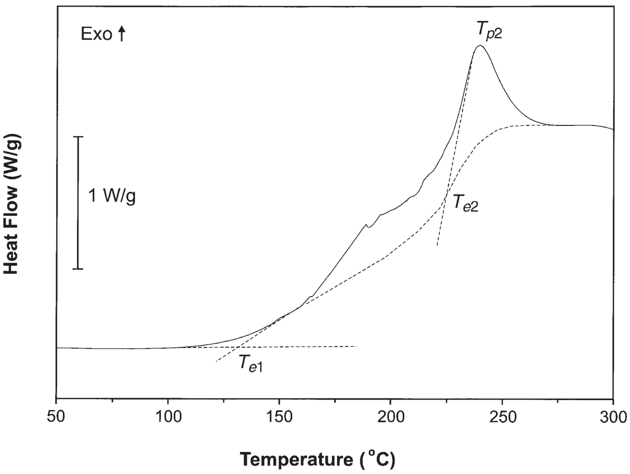

FIG. 1. DSC curve for blown soybean oil (sample 2, Cargill-2) showing the temperatures of extrapolated onset of oxidation (T_{e1} and T_{e2}) and maximum heat flow (T_{p2}). Heating rate 5 = 10°C/min.

processes are occurring. Ideally, each peak can be analyzed and the kinetic parameters associated with each process determined. As can be seen in the DSC curve (Fig. 1), the region between 140 and 225°C for the samples investigated was partially masked by T_{p2}, making it difficult to accurately analyze this region. The gradually increasing slope observed in the DSC curve of the blown soybean oil is similar to that previously observed for HBSBO (16) and, as suggested for the HBSBO, may be due to the reactions of the complex oligomeric structures of the oil.

Based on similar DSC oxidation studies utilizing fats and vegetable oils by Litwinienko and coworkers (10,11,13,15), the onset (T_{e1}) observed in the blown soybean oil samples is likely due to initial oxidation events (i.e., initiation and formation of primary oxidation products). The region between 140 and 225°C in the DSC curve (Fig. 1) may also be attributable to initial oxidation events for the various molecular species contained within the blown oil, whereas T_{p2} may be associated with secondary oxidation processes (i.e., hydroperoxide degradation, cross-linking, and polymerization).

The values recorded for the extrapolated onset temperatures (T_{e1} and T_{e2}) and maximal heat flow (T_{p2}) for the series of fixed linear heating rates (Table 2) were used to determine the kinetic parameters by means of the OFW method utilizing Equation 1:

$$\log \beta = aT^{-1} + b \qquad [1]$$

TABLE 2
Mean Values of Extrapolated Onset Temperatures (T_{e1} and T_{e2}) and Maximum Heat Flow Temperature (T_{p2}) for Thermal Oxidation of the Blown (BSBO) and Heat-Bodied (HBSBO) Soybean Oil Samples at Different Heating Rates (β)

Samples[a]	β (°C/min)	T_{e1} (°C)	T_{e2} (°C)	T_{p2} (°C)
BSBO 1	3	118.2	178.3	198.4
	5	129.6	194.3	213.9
	7	134.8	206.2	226.3
	10	141.0	218.1	237.9
	15	148.8	230.8	253.7
	20	151.1	241.4	265.6
BSBO 2	3	107.5	182.0	200.8
	5	120.9	201.0	218.7
	7	121.0	212.0	229.5
	10	130.4	225.0	244.5
	15	142.1	236.2	258.7
	20	149.4	248.7	272.3
BSBO 3	3	105.8	140.2	189.1
	5	121.3	164.9	203.1
	7	128.5	184.2	217.1
	10	129.5	197.7	225.1
	15	140.7	210.9	238.1
	20	142.2	216.0	245.1
BSBO 4	3	114.4	155.8	187.9
	5	119.5	169.3	202.8
	7	130.3	182.1	209.2
	10	135.6	195.6	220.4
	15	143.1	211.4	234.7
	20	143.8	220.8	246.5
HBSBO	3	114.5	144.8	186.0
	5	115.7	173.9	199.4
	7	118.1	178.2	213.3
	10	130.0	195.0	220.0
	15	132.9	209.7	237.3
	20	143.8	—	240.2

[a] See Table 1 for sources of samples BSBO 1–4.

TABLE 3
Calculated Kinetic Parameters, Activation Energy (E_a), Preexponential Factor (Z), Rate Constant (k) at 90°C, and Parameters of Equation 1 Including Standard Deviations (σ_a) and Square Regression Coefficients (R^2) for Blown (BSBO) and Heat-Bodied (HBSBO) Soybean Oil Samples

Sample[a]	E_a (kJ/mol)	Z (min^{-1})	k (min^{-1})	a (slope)	σ_a	R^2
BSBO 1						
T_{e1}	74.3 ± 4.3	1.2×10^9	2.4×10^{-2}	−4.08	0.24	0.9868
T_{e2}	55.3 ± 1.0	2.1×10^5	2.3×10^{-3}	−3.04	0.06	0.9987
T_{p2}	56.7 ± 0.5	1.6×10^5	1.1×10^{-3}	−3.11	0.03	0.9996
BSBO 2						
T_{e1}	57.7 ± 4.7	1.3×10^7	6.2×10^{-2}	−3.17	0.26	0.9741
T_{e2}	54.4 ± 1.8	1.3×10^5	2.0×10^{-3}	−2.99	0.10	0.9954
T_{p2}	54.7 ± 0.8	8.1×10^4	1.1×10^{-3}	−3.00	0.04	0.9991
BSBO 3						
T_{e1}	63.3 ± 7.8	7.7×10^7	5.9×10^{-2}	−3.48	0.43	0.9426
T_{e2}	37.6 ± 3.7	3.0×10^3	1.2×10^{-2}	−2.06	0.20	0.9631
T_{p2}	63.0 ± 2.7	1.2×10^6	1.1×10^{-3}	−3.46	0.15	0.9928
BSBO 4						
T_{e1}	72.7 ± 6.9	1.0×10^9	3.6×10^{-2}	−3.99	0.38	0.9650
T_{e2}	47.5 ± 1.1	5.1×10^4	7.6×10^{-3}	−2.61	0.06	0.9978
T_{p2}	62.1 ± 2.3	1.2×10^6	1.3×10^{-3}	−3.41	0.13	0.9946
HBSBO						
T_{e1}	72.5 ± 12.4	1.3×10^9	4.9×10^{-2}	−3.99	0.68	0.8947
T_{e2}	39.8 ± 4.2	6.0×10^3	1.2×10^{-2}	−2.18	0.23	0.9673
T_{p2}	61.9 ± 3.6	1.1×10^6	1.4×10^{-3}	−3.40	0.20	0.9865

[a] See Table 1 for sources of samples BSBO 1–4, and Table 2 for other abbreviations.

where T is temperature in K, β is the heating rate, and a and b are coefficients. Arrhenius plots [log β vs. inverse temperature ($1/T$)] for T_{e1}, T_{e2}, and T_{p2} data shown in Table 2 gave linear correlations (R^2, Table 3). The slopes (coefficient a, Table 3) derived from these plots using the least squares method were substituted into Equation 2 to compute the apparent activation energy of oxidation (E_a, Table 3) wherein R is the gas constant (8.314 J/K mol).

$$E_a = -2.19R\frac{d\log\beta}{dT^{-1}} \qquad [2]$$

The Arrhenius preexponential factor (Z, Table 3) was subsequently calculated for T_{e1}, T_{e2}, and T_{p2} by substituting E_a, determined from Equation 2, into Equation 3:

$$Z = \frac{\beta E_a\, e^{E/RT}}{RT^2} \qquad [3]$$

where β is the heating rate, R is the gas constant, and T is the temperature in K. Finally, the basic Arrhenius equation ($k = Ze^{-E_a/RT}$) was used to determine the rate constants (k, Table 3) for the oxidation processes. Errors in activation energy were calculated using the SD in Equation 1.

Table 3 shows that the T_{e1} activation energies of blown soybean oil samples were 74.3, 57.7, 63.3, and 72.7 for samples 1–4, respectively. Litwinienko and coworkers (11) have estimated the overall activation energy ($E_{\text{overall}} = E_{\text{propagation}} + 1/2\ E_{\text{initiation}} - 1/2\ E_{\text{termination}}$) for oleate, linoleate, and linolenate esters to be between approximately 93 and 100, 69 and 76, and 61 and 69 kJ/mol, respectively. Despite the structural differences between the blown soybean oils and those studied by Litwinienko, the activation energies are similar and the residual bis-allylic and allylic hydrogens present in the blown oils may play a role in imparting activation energies within these ranges.

Blown soybean oil and HBSBO share many similar characteristics, although, HBSBO is prepared by heating soybean oil to high temperatures (>330°C) under an inert nitrogen atmosphere. Because oxygen is excluded in the heat-bodying process, soybean oil polymerizes mainly *via* isomerization and Diels–Alder reactions instead of the autoxidative processes observed for blown soybean oils (16). Comparison of the DSC curves and activation energies, specifically T_{e1}, for the blown soybean oils and HBSBO shows them to be similar, suggesting that similar initial oxidative processes may be occurring during the drying of each oil.

ACKNOWLEDGMENTS

The authors thank Robert O. Dunn for helpful comments and David Weisleder for collection of the NMR data.

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[Received January 18, 2002; accepted July 25, 2002]