

Preparation of Polymerized Soybean Oil and Soy-Based Polyols

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ABSTRACT: In the absence of polymerization, soy-based polyols tend to have inadequate hydroxyl equivalent molecular weights for many critical urethane applications. In this article, the polymerization (bodying) of soybean oil is presented as an effective method to increase the molecular weight of soy-based polyols. When bodying is combined with reaction steps for alcohol addition and acid reduction, soy-based polyols suitable for urethane applications can be synthesized. Two different heat-polymerization approaches, catalyzed- and noncatalyzed-bodied soybean

oil (BSBO) were evaluated in continuous and batch processing. The catalyzed-BSBO has lower iodine numbers and high viscosities than the noncatalyzed-BSBO. This approach represents one of the least-costly means to increase the hydroxyl equivalent weights of soy-based polyols. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2127–2135, 2009

Key words: soybean oil; bodied soybean oil; heat polymerization; alcohol reaction; acetol

INTRODUCTION

The use of renewable materials contributes to global sustainability and the diminution of global warming gases. One of the more-inherently useful renewable materials is natural oils. Natural oils can be derived from both plant and animal sources and are available in all parts of the world. They are suitable chemical feedstocks for a variety of commodity and specialty chemicals and plastics.

Polyurethanes (PURs) are usually made from petroleum-based polyols and isocyanates and have widespread applications. Polyols are the key component in the PUR synthesis. Research on bio-based polyols has been increasing for decades with several soy-based alternatives gaining respectable market shares. Soy-based polyols are potentially low-cost materials and reduced impact on the environment. In addition, the introduction of natural oils into the PUR products can provide an opportunity for suppliers and customers to reduce their dependence on crude oil from petroleum.

Fats and oils are comprised primarily of triglyceride molecules. Soybean oil contains fatty acids that vary from 16 to 18 carbons in the length, with 0–3

double bonds per fatty acid. Soybean oil contains 15% saturated fatty acid chains that are mostly palmitic (16 : 0) and stearic (18 : 0) fatty acid; 85% unsaturated fatty acid chains that are oleic (18 : 1), linoleic (18 : 2), and linolenic (18 : 3) fatty acid.¹ This fatty acid distribution leads to an average fatty acid functionality of 1.58 carbon–carbon π -bonds. The average functionality of the soybean oil triglyceride is three times this, or 4.74.

The iodine value is an ASTM method that characterizes unsaturation in triglycerides. Soybeans iodine value is typically between 120 and 143 (0 represents no unsaturation).² Soybean oil is a preferred feed stock for developing new industrial oil products because of its prominence as the largest oilseed crop in the America and its unsaturated content that allows for a variety of chemical modifications.

Heat polymerization of soybean oil is known to create triglyceride oligomers. Subsequent functionalization can then convert these oligomers to polyols. Powers³ reports different reactions that can take place during the heat polymerization like isomerization, ring formation, and diene conjugation. Adams and Powers^{4–6} reported a statistical analysis and derived equations to predict the amount of fatty acid present in accordance with the extent of the reaction. The extend of reaction was calculated from iodine number and molecular weight, postulated that in the disappearance of a double bond two fatty acid chains are bonded together through a six-member ring or intrapolymer.

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Patents on bodying reactions were published early in the 1940–1950's.⁷ The US patent 2,471,577⁸ describes bodying with heat and incorporating oil promoters designed to increase the rate of reaction at epoxy and alkenes groups. The US patent 2,669,573⁹ proposes adding catalysts to promote the bodying reaction. The US patent 2,317,915¹⁰ presents a semicontinuous process for bodying of drying oil, involving the continuous feed stream of the oil into a pool of oil of appropriate size in a bodying kettle and simultaneously withdrawing corresponding amounts of the bodied oil.

Soybean oil is relatively unreactive in typical polymer formulations designed around petroleum-based monomers; soybean oil must be functionalized. The carbon–carbon double bonds in the soybean oil are reactive moieties that can be converted into hydroxyl groups. Several studies have been published on developing soy-based polyols from soybean oil. Different reactions such as epoxidation followed by epoxy-ring opening,^{11–13} ozonolysis,^{14,15} hydroformylation,¹⁶ halogenations,¹⁷ esterification, and transesterifications have been evaluated for PUR applications.^{18,19}

The main objective of this work is based on the polymerization of soybean oil by two different reactor configurations: batch (closed) and continuous (flow) reactor. A solid catalyst has been evaluated in the bodying reaction at mild temperatures. The functionality of bodied soybean oil (BSBO) was improved by alcohol addition reaction and acid neutralization forming primary and secondary alcohols moieties in the final oligomer.

EXPERIMENTAL

Materials

Anthraquinone (AQ, 90%), hydroxyacetone (acetol, technical grade 90 vol % in water) and dicyclopentadiene (DCP, 95%) were purchased from Sigma-Aldrich (St. Louis, MO). Soybean oil RBD (0.1–0.2 wt % of water, iodine number 130) was purchased from a retail supplier. Epoxidized soybean oil (ESBO; Vikoflex 7170) was purchased from Atofina Chemicals (Philadelphia, PA). High-purity grade nitrogen was obtained from Praxair (St. Louis, MO).

Bodying reaction experimental setup

Batch reactor setup

Heat polymerization was carried out in a 2 L stainless steel closed reactor that includes an omega controller, heater, stirrer, and two-port valve (for sampling and volatiles removing). The reactor was purged constantly with nitrogen to remove the volatiles compounds and moisture, and heated to reach

temperature up to 330°C for reaction. Longer reaction times lead to products with lower iodine numbers and higher viscosities. Unless otherwise specified, batch reactions were performed at a reaction time of 60 min.

The heat-catalyzed polymerization procedure was similar to the heat polymerization except for the addition of 2.5 wt % of (9, 10)-AQ catalyst. The reactor temperature were 260, 280, and 300°C. Reaction times were from 3 to 12 h depending on the reaction temperature, the desired viscosity, and the desired iodine number.

Continuous flow-reactor setup

The flow-reactor system consisted of a stirred feed tank wrapped in heating tapes; a peristaltic pump drew the premixed feed from the feed tank, 25 ft of 0.75 OD copper tubing providing a reaction volume of 510 mL, a furnace for housing the reactor, a water/ice bath through which effluent flowed, and an open steel product tank. Typical conditions for the heat-polymerized reaction included a feed flow rate of 0.075–0.35 mL/s and a reaction temperature of 350 and 370°C.

For heat-catalyzed polymerization, 2.5 wt % of the (9, 10)-AQ powder catalyst was added to the reaction mixture in the feed tank. Typical conditions included a feed flow rate of 0.09 mL/s and reaction temperatures of 320 and 350°C.

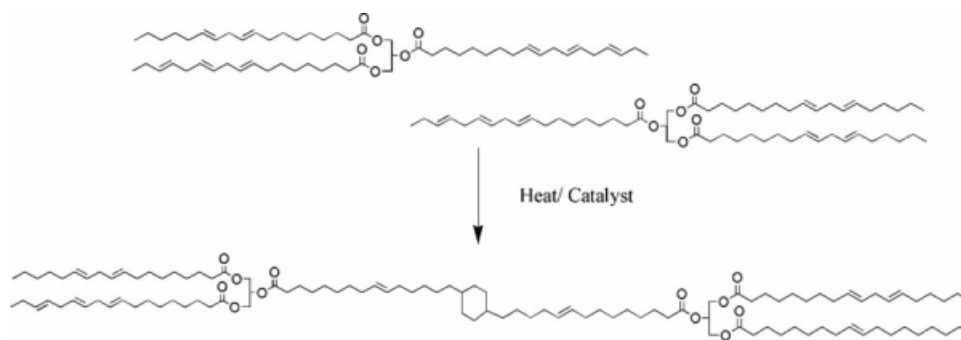
Soy-based polyol reaction experimental setup

Alcohol addition to BSBO

To create the BSBO : acetol-modified, BSBO, DCP, and acetol were placed in a 125 mL closed stainless steel vessel equipped with a thermocouple, stirrer, heating element, and omega controller. Two different alcohol (acetol) and DCP concentrations were evaluated at temperatures of 180, 200, and 220°C. After 20 h of reaction, the samples were left at room temperature to cool, and subsequently washed several times with distilled water.

Acid reduction with ESBO

BSBO : acetol-modified products were combined with epoxy in an epoxy : acid molar ratio of 1 : 0.5. The acidity of the BSBO : acetol-modified was evaluated to identify the amount of epoxy to add. The mixture was reacted in an Erlenmeyer flask equipped with a magnetic stirring bar and under a nitrogen purge at 170°C. Reaction time was typically a few hours until the acid number of reaction mixture was <10 mg KOH/g.



Scheme 1 Possible polymerization reaction of soybean oil.

Analytical methods

The final product was analyzed for acid number, iodine number, hydroxyl number, oxirane content, and dynamic viscosity. The acid number (mg KOH/g sample) indicates a number of carboxylic acid functional group per gram of a dry sample, according to the AOCS official method (AOCS Te 1a-64 1997). The iodine value characterizes the concentration of carbon-carbon double bonds (unsaturation) according to ASTM D1959-97. The hydroxyl number (mg KOH/g sample) is a measure of the hydroxyl groups in the polyester and polyether polyols according to ASTM D 4274-05. The epoxy content percent of a dry sample is analyzed by AOCS method Cd 9-57 (1997), oxirane oxygen content in epoxidized materials. The dynamic viscosity of the samples was measured in centipoises (cP) at 22°C using a Model RS100 Rheometer Haake—Thermo-electron (Newington, NH).

Gel permeation chromatography (GPC), gas chromatography (GC-FID), and infrared spectroscopy (FTIR) analytical analyses

Gas chromatography (GC-FID) analysis of esters derived from soybean oil and BSBO was performed to investigate the compositions of the fatty acid moieties in the oils. Ester triglycerides were esterified with *n*-butanol and H₂SO₄ catalyst. To make butyl esters, a 4.5 mL vial contained 100 mg of sample was filled with HPLC grade *n*-butanol and 1 drop of H₂SO₄ (concentrated) was added. The reaction was

allowed to take place at 70°C for 24 h. The butyl ester products were analyzed by GC, HP 6890 GC (Wilmington, DE). The column was HP MXTWAX 70624, capillary 30.0 × 280 × 0.25 m³ nominal and the detector was flame ionization (FID). The injection port temperature was 250°C. The temperature program was set from 160 to 220°C at 10°C/min and hold at 220°C for 12 min. Carrier gas was H₂ (40 mL/min), make up gas was N₂ (35 mL/min), air flow was 260 mL/min, and the split ratio was 75 : 1.

Gel permeation chromatography (GPC) was used to investigate molecular weight (M_w) distribution chromatograph. Dry sample (50 mg) was dissolved in 5.0 g of tetrahydrofuran (THF, Chromasol[®] from Sigma-Aldrich, St. Louis, MO) and 500 μL of the sample solution was transferred to a 1.0 mL vial. A standard curve, a plot of M_w against retention time, was generated from the GPC retention times of polyethylene glycols ($M_w = 3800, 1600, 1500, \text{ and } 600$), soybean oil, and linoleic acid.

The HPLC, Hewlett-Packard series 1100 with degasser, quaternary pump and autosampler was used. Data acquisition, program control, and analysis were set and done by the HP Chemstation software version 06.01 (Palo, Alto, CA). The detector was a light scattering detection, Altech 500 ELSD (Deerfield, IL). Two Viscogel-columns, I-MBLMW-3078 from Viscotek (Houston, TX) were connected in series. The mobile phase was THF with a flowrate of 0.5 mL/min at a pressure of 16.2 psig. Drift-tube temperature for ELSD was 60°C. Compressed air was the nebulization gas with a flowrate of 3.0 L/min at a pressure of 7.5 psig. Sample injected

TABLE I
Final Properties for Heat Polymerized Soybean Oil with 2 L Batch Reactor

Sample	Temperature (°C)	Time (h)	Iodine no.	Acid no.	Viscosity (cP)
SBO no reaction	–	–	135	1.5	52
BSBO no catalyst	330	1	100	15	68
BSBO catalyzed with AQ	260	6	104	15	253
BSBO catalyzed with AQ	280	6	91	15	1158
BSBO catalyzed with AQ	300	6	70.5	15	2998

volume was set at 25 μL and the needle injector was cleaned by THF after each sample injection. Analyzing time was 40 min per sample.

A FTIR Nicolet (Madison, WI) model Magna 550 with Omnic 5.1 software was used to follow the chemical functional groups in the polyols. The polymerization (bodying) and alcohol addition (acetol) reactions were monitored as the disappearance of carbon-carbon π -bonds peaks at 1680–1600 cm^{-1} , and the appearance of the hydroxyl peaks at 3330–3500 cm^{-1} .

RESULTS AND DISCUSSION

Polymerization of soybean oil

Soybean oil averages 4.74 carbon-carbon π -bonds per molecule, and so, the Diels-Alder reaction can result in dimerization, trimerization, and higher degrees of oligomerization when the reaction is between fatty acid groups of different triglycerides. The prominent fatty acid groups participating in oligomerization is linoleic acid which has two double bonds separated by methylene carbon, and linolenic acid has three double bonds similarly separated.

If the unsaturated acid is a nonconjugate acid, it is possible for heat to shift the structure to conjugated moiety. Conjugated moieties are more reactive. At heat bodying temperatures the double bonds migrate and conjugated dienes are formed. These conjugated dienes may then undergo the Diels-Alder reaction as illustrated in Scheme 1.

Table I summarizes heat-polymerization results for soybean oil in a batch reactor. A reduction in the iodine number characterizes the reduction in carbon-carbon π -bonds. The simultaneous increase in viscosity indicates that oligomerization is occurring.

The catalyst plays an important role in the reaction by allowing the reaction to proceed at lower temperatures. The viscosity of the final product is a function of time and temperature. Depending on the

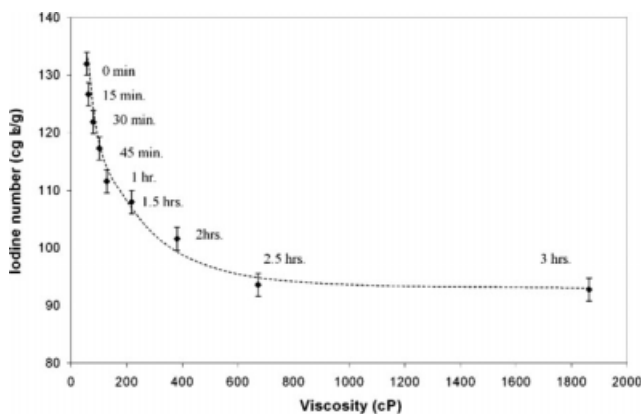


Figure 1 Kinetic study of heat polymerization of soybean oil in a batch reactor at 330°C.

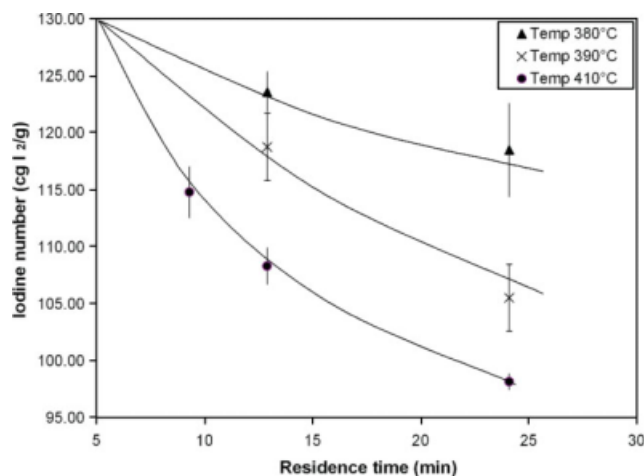


Figure 2 Iodine numbers as a function of residence time and temperature in the flow reactor. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperature, the final product may have a light yellow to dark brown color. Since a nitrogen purge is applied to keep oxygen from the system, the increase in acid number could be due for oil degradation as a result of high temperature applied.

Figure 1 provides the kinetic data for the batch reaction at 330°C. The viscosity increases with time, as the iodine number decreases. The rapid decrease in iodine number at the start of the reaction suggests that different reactions occur initially. During the heat process, linolenic was converted completely forming new fatty acids with similar stereochemistry as linoleic and oleic acid, as described in GC analysis later.

Figures 2 and 3 summarize the impact of residence time on iodine number and acidity for the flow reactor at temperatures of 380, 390, and 410°C. At higher temperatures, the final products become

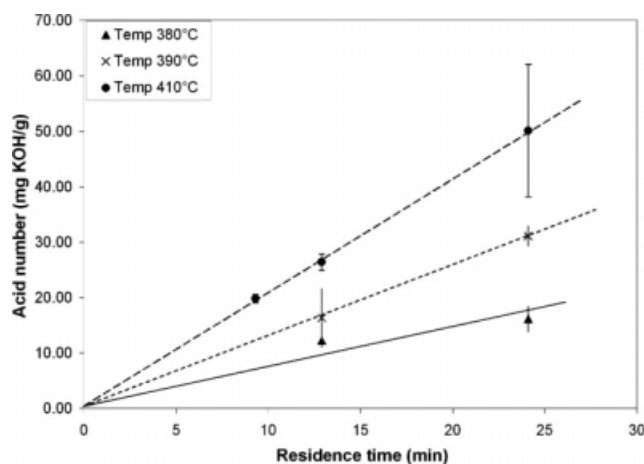


Figure 3 Acid numbers as a function of residence time and temperature in the flow reactor.

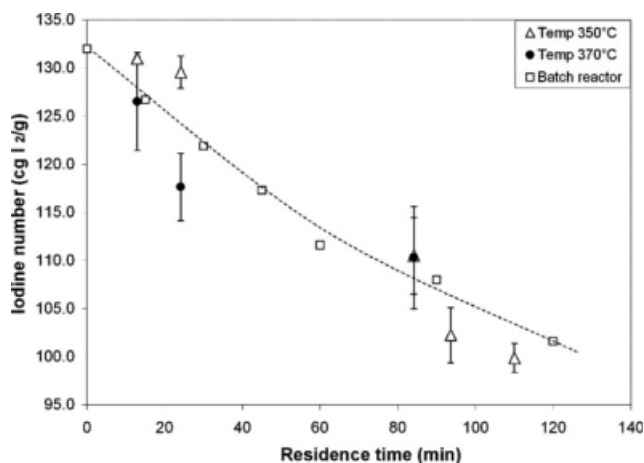


Figure 4 Iodine numbers as a function of residence time and temperature in the flow reactor at lower temperatures.

darker and the acid numbers increase. Considerable reductions in iodine values were possible at short residence times at temperatures of 410 and 390°C.

The reaction profiles at lower temperatures are plotted separately (longer residence times) in Figures 4 and 5. Superimposed are values for the batch reactions. Higher temperatures were used for the flow reactor due to the long times necessary to attain steady state and then to attain product.

The trends from 410 to 350°C follow theory with increasing temperatures leading to higher reaction rates (faster reductions in iodine values). Interestingly, the batch reactor data at 330°C has conversion trends substantially similar to flow reactions at 350°C. This could be due to experimental temperature measurement deviation by assumption reaction temperature was tubing temperature $\pm 10^\circ\text{C}$. However, the flow-reactor performance is close enough to the batch reactor performance to allow batch reactor data to be used to identify the general operating conditions necessary for bodying in a flow reactor.

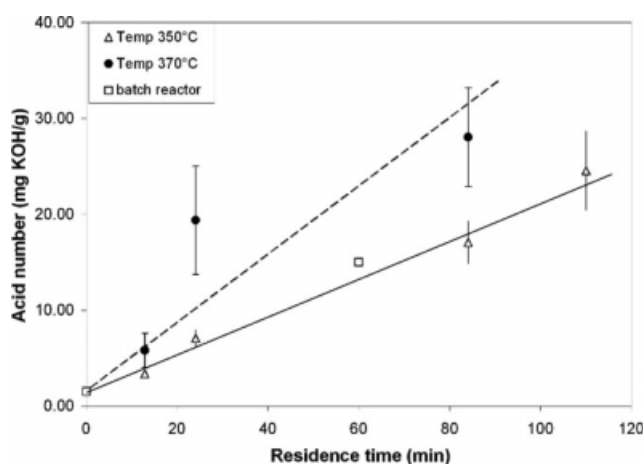


Figure 5 Acid numbers as a function of residence time and temperature in the flow reactor at lower temperatures.

TABLE II
Temperature Influence in the Final Properties of Heat-Catalyzed Polymerization of Soybean Oil

Sample	Temperature ($^\circ\text{C}$)	Residence time (min)	Iodine no.	Acid no.	Viscosity (cP)
F1	320	94	108	6.0	263.2
F2	320	94	104	7.0	263.2
F3	320	94	106	5.2	263.2
F4	350	94	87	13.4	671.0
F5	350	94	86	14.0	671.0

For both batch- and flow-reactor studies, the iodine values of the BSBO asymptotically approach an iodine value near 90 for reactions without catalysts. Erhan and Bagby²⁰ presented several heat-polymerization methods for soybean oil. They used viscosity to estimate reaction rates. Following their approach, the rate constant values were about $0.0019\text{--}0.005\text{ min}^{-1}$ for a batch reactor and $0.006\text{--}0.01\text{ min}^{-1}$ for continuous reactor, based on viscosity measures shown in Tables I and II. The behavior is that of a second-order reaction mechanism (first order in conjugated diene moieties and first order in carbon-carbon π -bonds) where the reaction substantially ends as the conjugated dienes are consumed. The conversion profile for acid generation is different.

Within the experimental error of the data, the acid generation was proportional to the residence time, means that increase linearly as the reaction take place. Higher temperatures created acidity faster; however, the rate of acid generation relative to the rate of iodine number decrease was about the same during the initial phases of reaction. The acid generated in batch reaction was the same as the flow reactor of similar reaction times. Hence, the hypothesis in regard to free acids promoting an auto-catalytic mechanism for acid generation cannot be substantiated. A possible explanation for this behavior is the

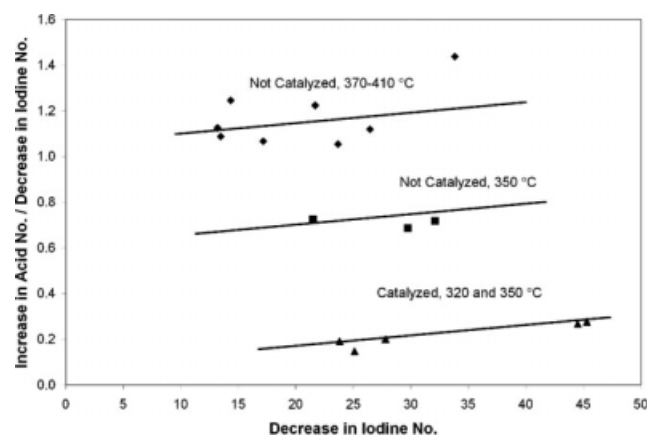
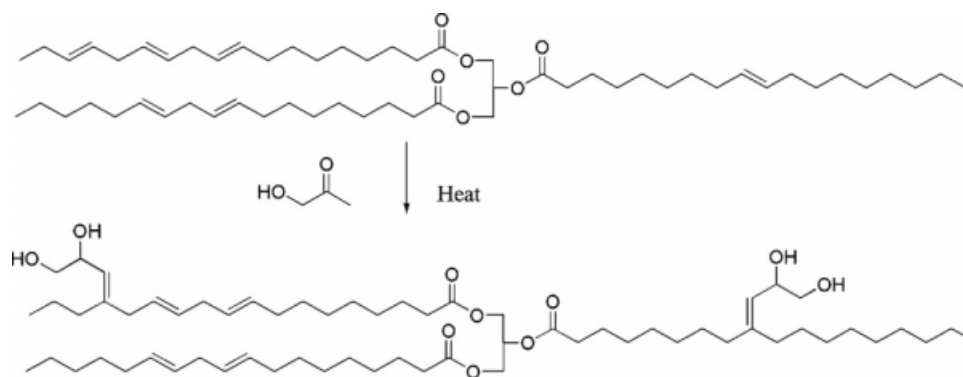


Figure 6 Acidity influence related with iodine value for polymerization reaction catalyzed and noncatalyzed reaction in batch and flow reactor.



Scheme 2 Possible reaction of alcohol addition (soybean oil and acetol reaction).

degradation of ester bonds during the polymerization reaction results by high temperatures.

Table II shows the final properties for the heat-catalyzed BSBO in the flow reactor at two temperatures. Lower iodine numbers of 86–87 were readily attained using the catalyst, whereas longer residence times and higher temperatures did not attain iodine values <95 for the noncatalytic reactions. It is possible that the catalyst allows for more reaction possibilities and greater degrees of polymerization.

Figure 6 compares the ratio of acid generated to iodine value reduction as a function of reaction time for catalyzed and noncatalyzed flow reactors. The graph of these trends readily illustrates that the catalyzed reaction produces less acidity at the same degrees of polymerization. Lower temperature bodying, and especially lower-temperature catalyzed bodying, promote low acidity for a given degree of oligomerization.

Soy-based polyols

Hydroxyacetone (acetol-alcohol) was added to both SBO and BSBO to attach hydroxyl functional groups to soy-based molecule. Scheme 2 illustrates a possi-

ble allyl addition reaction mechanism for attaching an alcohol to the soybean oil (similar approach is established for BSBO).

As proposed in Scheme 2, the unsaturated functionality in SBO and BSBO provide a location for addition reactions to attach hydroxyl to fatty acid chains of the triglycerides. An iodine number reduction accompanies the reaction as two carbon-carbon π -bonds react to form a single carbon-carbon π -bond.

Table III summarizes the reaction studies on addition of acetol to SBO and BSBO. DCP, a cross-linking monomer, was used at similar concentration to help in the addition reaction and increases viscosity in the final polyol. Acetol was added at 15 and 20%, and DCP was added at 14 and 20%.

The results show a reduction in the iodine number which corroborated the alcohol addition to the carbon-carbon π -bond. The product was washed with water to remove unreacted acetol after the reaction. The hydroxyl numbers represent the bound hydroxyl functionality attributed to acetol addition.

The increased concentrations of acetol did not lead to increased hydroxyl numbers. The addition reaction seemed to be limited. A few possible

TABLE III
Properties for Reactants and Products in the Alcohol Addition Reaction

No.	Reactants			Reaction conditions		Product properties				
	Oil	Acetol %	DCP %	Temp. (°C)	Time (h)	Acid no.	Iodine no.	OH no.	% Red. iodine	Viscosity (cP)
A	SBO	20	14	220	20	55	119	75	24	265
B	SBO	20	14	200	20	52	120	53	23	202
C	BSBO	15	14	220	20	48	106	63	26	665
D	BSBO	20	14	200	20	56	109	57	21	416
E	BSBO	20	20	210	20	45	118	58	22	514
F	BSBO	20	14	220	20	55	104	66	25	775
G	BSBO	20	14	200	20	52	111	42	20	554
H	BSBO	20	14	180	20	59	113	55	18	400
I	BSBO	20	14	200	20	54	92	68	29	1474
J	BSBO	20	20	180	20	57	118	56	13	450
K	BSBO	20	20	200	20	52	116	55	15	500
L	BSBO	15	14	200	20	57	89	56	64	591

TABLE IV
Properties of Reactants and Products in the Acid Reduction Reaction

No.	Molar ratio (epoxy : acid-sample)	Acid		Epoxy		Reaction conditions		Product			
		Mass	Mole	Mole	Mass	Temp. (°C)	Time (h)	Acid no.	Epoxy %	OH no.	Viscosity (cP)
AE	1 : 0.5	40	0.04	0.08	18	160	7	10	0.98	126	1078
BE	1 : 0.5	40	0.04	0.07	18	160	7	12	0.85	108	889
CE	1 : 0.5	40	0.03	0.07	16	170	6	7	0.57	98	3075
DE	1 : 0.5	35	0.04	0.07	16	170	6	7	0.44	102	2807
EE	1 : 0.5	80	0.06	0.13	30	170	6	6	0.50	94	1026
FE	1 : 0.5	30	0.03	0.06	14	170	6	5	0.59	101	5570
GE	1 : 0.5	40	0.04	0.08	20	170	6	7	0.66	105	2096
HE	1 : 0.5	100	0.09	0.19	44	180	6	6	0.48	95	3606
IE	1 : 0.5	40	0.04	0.08	19	180	6	10	0.43	92	11212
JE	1 : 0.5	40	0.04	0.07	18	180	6	5	0.59	99	3243
KE	1 : 0.75	35	0.03	0.07	15	180	6	7	0.73	98	3642
LE	1 : 0.5	40	0.04	0.07	18	170	8	20	0.93	95	2270

explanations for this behavior might be the reactivity of fatty acid present in the starting material such as: (1) the amount of carbon-carbon π -bonds and (2) the stereochemistry.

However, the high reaction temperatures used lead to increase the acid number in the final polyol. This has been attributed to the cleavage of ester bonds as consequences of the water dissolves in the acetol. With acid numbers greater than 45, the products of Table III are considerably higher than preferred acid numbers of <2 or even <1. If the ESBO reacts with the products of Table III, it could be possible to reduce the acid number to <15.

Kiatsimkul et al.²¹ demonstrated the reaction mechanism cleavage of ESBO with a fatty acid product, similar mechanism was used for acid reduction of BSBO : acetol-modified products with ESBO. In this reaction, the epoxy groups react with the acid to form a hydroxyl group and ester linkage. An excess of ESBO was necessary, especially when residual acidity is not desirable in the final polyols.

Use of ESBO can lead to cross-linking or ramification compounds, increasing molecular weight of the polyol, and increasing viscosity. Other epoxy compounds like butylene oxide or propylene oxide will neutralize the acid without the cross-linking and no significant increase in viscosity. Table IV provides reaction conditions and final polymer properties for the indicated reactions of ESBO with the products of Table III.

GC-FID, GPC, and FTIR analytical results

The GC-chromatographs of fatty acid butyl esters of soybean oil and BSBO are presented in Figure 7.

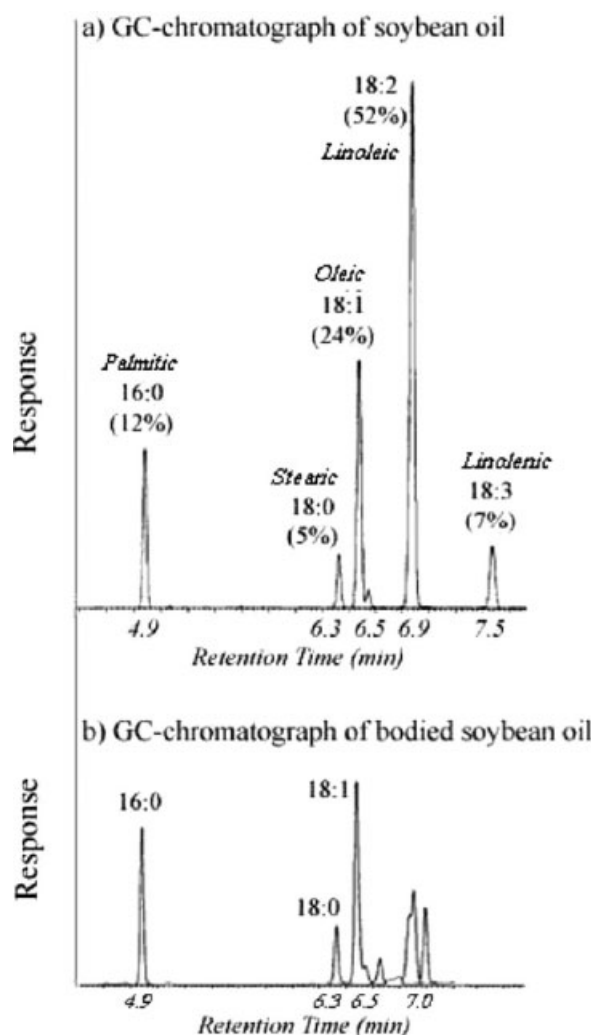
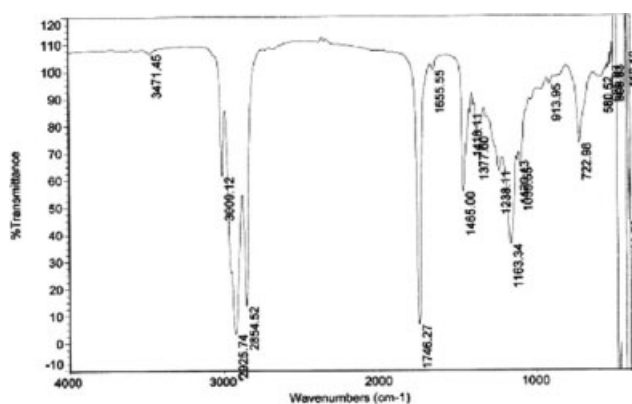


Figure 7 GC-MS chromatographs of acid moieties in soybean oil (a) and bodied soybean oil (b) at 330°C for 1 h.

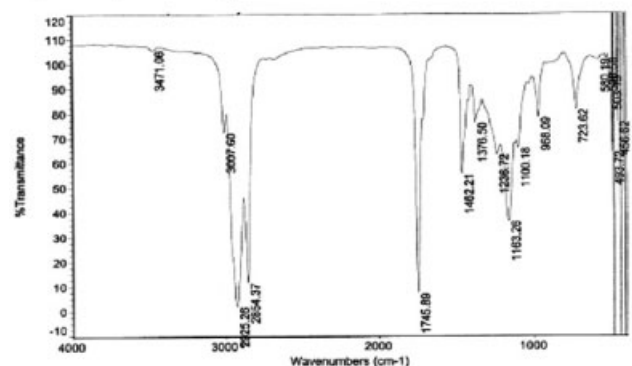
TABLE V
GPC Properties for SBO, BSBO Catalyzed (Flow Reactor 330°C for 94 min), BSBO : Acetol Modified (15 wt % Acetol) and BSBO : Acetol Modified (20 wt % Acetol)

Properties	Samples			
	SBO	BSBO	BSBO : Acetol 15	BSBO : Acetol 20
Acid no.	0.5	13	17.3	5.2
Iodine no.	132	87	69.1	66.5
OH no.	15	23.84	95.37	105.27
Epoxy %	N/A	N/A	0.93	0.79
Viscosity (cP)	56.52	671.05	2270.15	2095.2
GPC analysis				
Monomer %	100	34.68	14.89	11.97
Oligomer %	0	57.23	57.36	67.72
FA/FAME %	0	8.09	27.75	20.31
M_n	292	948	599	776
M_w	280–300	2422	1682	2054

Soybean oil was not fully polymerized after 60 min of heat bodying process. Soybean oil has 85% unsaturated fatty acid chains: 22% oleic (18 : 1), 56% linoleic (18 : 2), and 7% linolenic (18 : 3) fatty acid. The linolenic acids (C18 : 3) were converted completely after 30 min of the heating process, but some of linoleic acid (C18 : 2) and oleic acid (C18 : 1) remained in the BSBO.



a.) FT-IR spectra of soybean oil



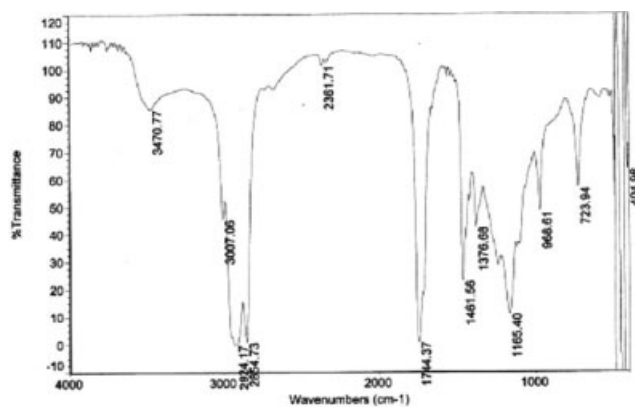
b.) FT-IR spectra of bodied soybean oil

Figure 8 FTIR spectra for soybean oil (a) and bodied soybean oil (b).

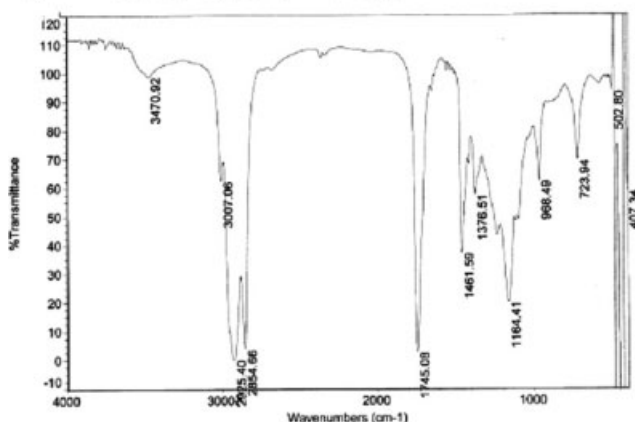
The reactivity of fatty acid depends on the amount and location of the carbon–carbon double bond or double allylic hydrogen present. The three carbon–carbon π -bond of linolenic acid has more activity to polymerize by oxidation or heat than linoleic (18 : 2) and oleic (18 : 1) acids as the conjugate fatty acid has more reactivity than a nonconjugated fatty acids.^{22,23} Erhan et al.²⁴ also found the rapid reaction of linolenic acid moiety in the bodying reaction of soybean oil.

The GC-chromatograph of BSBO revealed new fatty acid peaks next to the oleic acid and linoleic acid peaks. These new peaks could not be fully resolved by extending the heating time and decreasing the heating rate. These new peaks could be conjugates and isomers of linoleic acid and oleic acid.

GPC analyses of the BSBO catalyzed in the flow reactor, soy-based polyol products of BSBO with acetol at 15 and 20 wt % concentrations are shown in Table V. The BSBO-catalyzed GPC analysis confirms oligomers at a concentration of 57%, single-acid esters at 8%, and 35% monomer triglycerides. The oligomers present in BSBO-catalyzed consist of dimers (17.85%), trimers (12.06%), and tetra + (27.31%).



a.) FT-IR spectra of soybean oil with acetol



b.) FT-IR spectra of bodied soybean oil with acetol

Figure 9 FTIR spectra for alcohol addition of soybean oil with acetol (a) and bodied soybean oil with acetol (b).

Comparing GPC analysis of two different BSBO : acetol products, 15 and 20 wt %, the sample prepared with a higher acetol loading had an increase in oligomer and decrease in free fatty acid concentrations. Most of the oligomers present in the acetol products are dimers (12–14%) and trimers (43–55%).

The GPC peaks calibrated at FA/FAME are likely fatty acid esters with acetol. The alcohol in acetol could readily undergo transesterification with the esters of the glycerides to yield single-acid esters.

FTIR spectra of soybean oil, BSBO, and acetol-alcohol addition to soybean oil and BSBO were presented in Figures 8 and 9. In comparison with the soybean oil spectra, the disappearance of carbon-carbon double bond at 1655 cm^{-1} , and the emergence of hydroxyl groups at 3470 cm^{-1} are obvious. These results confirm the mechanism for heat polymerization of soybean oil and the alcohol addition to add functionality in the final polyol.

CONCLUSION

Bodying of soybean oil was used to create a higher molecular weight feed stock for synthesizing polyols. Bodying increased the average molecular weight of SBO from its starting molecular weight of 948 to 1000–2400 for the bodied products.

Bodying in a flow reactor followed conversion trends as a function to temperature and residence time as projected in the batch reactor. Acidity increased steadily during the bodying process. Relative to the noncatalyzed reaction, the use of (9, 10)-AQ as a catalyst led to decreased reaction times for the same increase in viscosity, led to lower iodine values, and to a decrease in acidity for a given decrease in iodine number (or increase in viscosity).

Acetol was able to undergo a reactive addition to both SBO and BSBO to provide alcohol functionality confirmed by FTIR spectra. Polyols prepared using acetol exhibited marked increases in acid number due by the hydrolytic effect in the reaction. The average molecular weight for soy-based polyols made

from the reaction of BSBO and acetol were about 1500–2100 depending on the iodine value of the starting material.

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