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# Investigation of Conjugated Soybean Oil as Drying Oils and CLA Sources

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**Abstract** Better sources of drying oils for coatings and conjugated linoleic acid (CLA) for potential health benefits are of continuing interest. Iodine under photochemical conditions in hexanesB at reflux temperatures was investigated as a catalyst for conjugating soybean oil (SBO) for use as drying oils and as a potential source of CLA. Variations in catalyst loading, SBO, light source, free radical catalyst, solvent and temperature strongly affected the efficiency of the process. Changes in fatty acid isomer distributions in conjugated SBO (CSBO) influenced drying properties of CSBO. Conjugated dienes formed were predominantly *trans*-9,*trans*-11, which contrasts distributions found with catalysts such as strong base and metal compounds. Drying times of some of the CSBOs were superior to that of raw linseed oil. Iodine was partially recovered.

**Keywords** Fats and oils · Nutraceuticals or functional foods · Food and feed science · Nutrition and health · Processing technology · Polymers or coatings · Biobased products · Drying oils

## Abbreviations

| | |
|---|---|
| SBO | Soybean oil |
| CSBO | Conjugated soybean oil |
| CLA | Conjugated linoleic acid |
| VOCs | Volatile organic compounds |
| GC–MS | Gas chromatography–mass spectrometry |
| NMR | Nuclear magnetic resonance spectroscopy |
| ESI | Electronic supplementary information |
| AIBN | Azobisisobutyronitrile |
| AICN | 4,4′-Azobis(4-cyanovaleric acid) |
| LO | Linseed oil |
| RBD | Refined bleached deodorized |

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## Introduction

Tung and dehydrated castor oils are conjugated and both have been used as drying oils in alkyd resins [1]. Widely adopted strict volatile organic compounds (VOCs) rules ban the use of low-solids solvent-borne alkyd resins, despite their advantages of easy use and better economy [2]. Although alkyds with higher solids and waterborne alkyds are now available, their drying, storage, hydrolytic susceptibilities and cost are not as favorable as alkyds with higher VOCs [3]. The presence of C–C double bonds in plant oils also plays an important role in the chemistry of vegetable oils, as for example in the formation of biopolymers [4–7].

Over the past 70 years, a variety of methods have been reported for conjugating vegetable oils [8] including heterogeneous catalytic approaches [9, 10]. Many of these methods have drawbacks such as poor product yield, catalyst instability, unwanted side reactions, the necessity for elevated temperatures (>100 °C), high catalyst cost, the

requirement of pressure, and poor catalyst recovery. Conjugated soybean oil (CSBO) is a valuable source of conjugated linoleic acid (CLA) [11], (which is also found in beef and dairy products) and has a variety of salutary biological activities [12] such as the reduction of fatty liver, serum cholesterol and carcinogenesis in animal studies [13, 14].

Using $I_2$ as a catalyst, methyl linoleate can be conjugated, up to 80 %, with a high-pressure Hg lamp [15]. Using a similar approach, SBO was recently converted to ∼25 % total CLA [16] and a pilot-scale apparatus capable of yielding 20 % CLA (w/w) in 12 h using $I_2$ as a catalyst has also been described [17].

Because better sources of drying oils for coatings and CLA for potential health benefits are of continuing interest, we investigated an intermediate-scale photochemical conjugation of soybean oil catalyzed by $I_2$ in a hydrocarbon solvent using four different specially designed glass reactors. The method we report here avoids the use of toxic metals and elevated temperatures, and leads to virtually quantitative yields of CSBO, some samples of which possessed drying times comparable with or superior to raw linseed oil. Moreover, the iodine catalyst was found to be partially recoverable.

## Experimental Section

### Materials

Refined bleached, deodorized SBO samples were gifts from Cargill and Renewable Energy Group. Salad grade corn oil and Lo-Sat SBO were Hy-Vee brand products purchased at a local Hy-Vee grocery store. Iodine was purchased from Fisher and used as received. Potato starch [18] samples were kindly supplied by Prof. John Robyt of Iowa State University. HexanesB, heptane (both HPLC grade), 0.5 M sodium methoxide in methanol (ACS reagent grade), dibenzoyl peroxide, dilauroyl peroxide, azobisi-sobutyronitrile (AIBN), 4,4′-azobis(4-cyanovaleric acid) (AICN), and tBuOCl were purchased from Sigma-Aldrich and used as received. Pure raw LO was purchased from Sunnyside. The chain transfer catalyst bis-$BF_2$-bridged-bis-dimethylglyoximate cobalt(II) was synthesized via a literature preparation [19].

GC–MS standards, methyl palmitate (>99 %) methyl stearate (>99 %), methyl oleate (>99 %), methyl elaidate (>99 %), methyl 9-cis,11-trans conjugated linoleate (>90 %), methyl 10-trans,12-cis conjugated linoleate (>90 %), methyl conjugated linoleate (mixed isomers, >99 %), and GLC 15 Reference Standard (mixture of C16 and C18 fatty methyl esters) were from Nu Check Prep and used as received.

## Methods of Analysis

### $^1$H-NMR Data Collection

Spectra of oil samples were recorded at ambient temperature on a DRX (400 MHz) or VXR (400 MHz) spectrometer using standard procedures. The percentage conversion of unconjugated C=C bonds to conjugated bonds was calculated from $^1$H-NMR spectra obtained on oil samples in $CDCl_3$ solvent. Spectra were acquired for the starting SBO and were integrated using the glycerol backbone peaks at 4.15 and 4.30 ppm as standards since this moiety is unaffected by conjugation. The percentage change in the area of the peak at 2.7 ppm for the $CH_2$ moiety between two unconjugated C=C bonds in SBO, was calculated by taking the difference between the integrals of the 2.7 ppm proton peaks for SBO and CSBO, dividing by the integral of the 2.7 ppm peak of SBO and multiplying by 100.

### Oil Sample Collection

Samples were collected from the reactors via a port by passing the solution through activated charcoal (or stirring with activated charcoal followed by filtration) to remove $I_2$. The nearly colorless eluate, or filtrate was subjected to reduced pressure to remove the solvent. The residual oil was kept under dry $N_2$ or Ar to inhibit polymerization of conjugated species.

### Oil Isomer Analysis

An ∼200-mg sample was transferred to a 25-mL flask and two 2.5-mL aliquots of NaOMe solution (0.5 M in methanol) were added, followed by mixing. After 1 h at room temperature for derivatization, 1 mL of 10% acetic acid in water and two 5-mL aliquots of heptane were used for extraction. Then ∼1.5 mL of the heptane extract was transferred to a GC sample vial.

### Gas Chromatography–Mass Spectrometry (GC–MS)

A Hewlett Packard 5890 GC series II plus system equipped with a 6890 series injector and a 5970 MSD detector in EI mode was employed. An SPB 35 (30 m × 320 μm) column was used with a He flow rate of ∼0.9 mL min$^{-1}$. The detector and injector temperatures were 280 and 250 °C, respectively. The temperature program began at 150 °C and then ramped to 290 °C at 5 °C min$^{-1}$. HP-MS Chemstation software was used for data collection/processing. Compound identities were confirmed by the mass spectral analysis and by comparison to standards.

### ASTM 5895 BK Drying Tests

A BK drier consisting of a slide-holding plate, uniformly and thinly coated (51 microns) with oil-containing drying additives was used. Solidified fractions were melted for coating application. A simultaneous control was run with raw LO. BK drying test results were kindly provided by Dr. John Massingill of the Texas State University, San Marcos, and by Dr. Michael Van De Mark of the Missouri University of Science and Technology.

### Oil Treatment

#### Lamps and Reactors Employed

The 500-W projector bulb has a near-maximum output at 520 nm (the wavelength associated with the energy of the I–I bond) whereas both low (35 W) and high-pressure (150 W) Na lamps have a major output at the sodium D line at 589 nm [see Fig. 7 (ESI) for UV–Vis spectra]. The D line of the high-pressure Na lamp is "pressure broadened" to higher as well as lower wavelengths, including the 520 nm region. The greater conjugation efficiency of the high-pressure Na lamp (see below) may not merely be due to augmented intensity at 520 nm (which is expected to be weak at the short wavelength "wing" of the broadened Na D line). Thus, other wavelengths within the Na D band could enhance conjugation. A 30-cm 35-W (Model SOX

Pro) low-pressure Na bulb and its ballast were purchased from a local vendor. An 18-cm 150-W high-pressure Na vapor lamp (Lumalux® Osram Sylvania Products Inc.) was also purchased locally, but its ballast was constructed at ISU. See ESI for advantages of the high-pressure lamp over the projector lamp. Four reactors [Figs. 1 (ESI)–6 (ESI)] were constructed with solution volumes of 26, 16, 0.7 and 3 L for reactors 1, 2, 3 and 4, respectively. It should be noted that all experiments with reactors 1–3 were carried out with 500-W lamps, while experiments with reactor 4 employed either a low-pressure or a high-pressure Na lamp.

#### Iodine-Catalyzed SBO Photoconjugation

As detailed below, the reactors were charged with oil and solvent while purging with argon. (Corn oil and other oils were also used in a few instances—see below.). The argon flow was decreased to a few bubbles per second, and the lamp was turned on to achieve the desired temperature, after which the lamp was turned off and a solution of $I_2$ in solvent was added (see below) while purging. The lamp was then turned on again and a flow of ca. 1 bubble every 2 seconds was maintained in the reactor. See Table 1 for representative runs for the conjugation of SBO in reactors 1, 2 and 4. Plots of % conjugation versus time in hours [Fig. 8 (ESI)–22 (ESI)] generally consisted of curves whose slopes decreased with time as conjugation reached 100 %, unless pointed out otherwise.

**Table 1** Representative runs for the conjugation of SBO under various conditions in reactors 1, 2 and 4 (see Electronic Supplementary Information for reactor details)

| Entry | Reactor | SBO (g) | HexanesB (mL) | Total $I_2$ added (g) | No. $I_2$ portions added | Total time (h) | Conjugation (%) | Temp range (°C) | Fig. # in ESI |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 3,686 | 16,470 | 15.55 | 3 | 314 | 99 | 70–80 | 8 |
| 2 | 2 | 980 | 7,890 | 1.465 | 1 | 13 | 97 | 70–80 | 9 |
| 3 | (2)[a] | 2,450 | 19,950 | 3.6637 | 1 | 108 | 99 | 70–80 | 10 |
| 4 | 4 (lp) | 220.5 | 1,760 | 0.762 | 2 | 49 | 99 | 70–80 | 11 |
| 5 | 4 (lp) | 220.5 | 1,760 | 0.762 | 1 | 42 | 100 | 70–80 | 12 |
| 6 | 4 (lp) | 220.5 | 1,760 | 0.762 | 3 | 22 | 99 | 70–80 | 13 |
| 7 | 4 (lp) | 220.5 | 1,760 | 0.762 | 6 | 28 | 100 | 70–80 | 14 |
| 8 | 4 (hp) | 220.5 | 1,760 | 0.762 | 1 | 6 | 100 | 80–90 | 15 |
| 9 | 4 (hp) | 220.5 | 1,760 | 0.762 | 1 | 6 | 100 | 70–80 | 16 |
| 10 | 4 (hp) | 220.5 | 1,760 | 0.381 | 1 | 8 | 100 | 70–80 | 17 |
| 11 | 4 (hp) | 441.0 | 1,540 | 0.762 | 1 | 73 | 91 | 70–80 | 18 |
| 12 | 4 (hp) | 441.0 | 1,540 | 0.762 | 1 | 118 | 87 | 95–105 | 19 |
| 13 | 4 (hp) | 441.0 | 1,540 | 0.762 | 1 | 121 | 97 | 65–75 | 20 |
| 14 | 4 (hp) | 220.5 | 1,760 | 0.762 | 1 | 10 | 100 | 50 | 21 |
| 15 | 4 (hp) | 441.0 | 1,540 | 0.762 | 1 | 221 | 100 | 50 | 22 |

Charcoal (3 % w/w relative to SBO) was used to remove $I_2$ in all cases except one (see entry 3)

*lp* low-pressure Na lamp, *hp* high-pressure Na lamp

[a] Reactor that was the precursor to reactor 2 (see description of reactor 2 under reactors employed in ESI)

*Removal of I₂ from Reaction Mixtures with Starch Followed by Charcoal*

These solutions were completely siphoned from reactors 1–4 into amber bottles followed by addition of solvent washings from the reactor. To 50 mL of CSBO/hexanesB solution, 6.998 g of potato starch was added to remove residual iodine and then the solution was magnetically stirred at room temperature for 24 h. The solution was filtered under reduced pressure (Whatman filter paper #1) rebottled in fresh amber bottles and treated with 6.615 g of charcoal to remove additional iodine that was manifested by the dark color of the solution. The mixture was stirred for 24 h at room temperature, filtered with #1 Whatman filter paper to give a light yellow solution, and then excess solvent was distilled under Ar. After removing residual solvent under reduced pressure, the residual CSBO was transferred to a flask and stored under Ar.

*Removal of I₂ from Reaction Mixtures Using Charcoal or Starch*

Iodine was removed from photolyzed solutions by adding a 27:1 weight ratio of Calgon activated charcoal:I₂. After stirring for 12 h, the I₂-laden charcoal was removed by filtration through a bed of diatomaceous earth (to remove fine particulates) using Whatman #1 filter paper. Iodine was also removed from reaction mixtures with a 17:1 weight ratio of potato starch:I₂. These experiments were conducted using 50 mL of a solution of 163 ppm I₂ in hexanesB to mimic I₂ concentrations in conjugation reactions. The potato starch (5 g) was wetted with distilled water (50 g) before addition to the photolyzed solution. After stirring for 12 h, the starch-iodine complex was

filtered from the reaction mixture with Whatman #1 filter paper.

*Fractionation of CSBO*

Formation of the solid and liquid CSBO phases was achieved in a refrigeration box insulated with Styrofoam® insulation board. Inside the box was a bench-top centrifuge and a copper cooling coil for coolant circulation by a refrigeration bath. Samples (50 mL) of 99–100 % CSBO were frozen at 0 °C in 50 mL centrifuge tubes mounted in the centrifuge. Warm-up of the samples to ca. 17 °C over ca. 6 h in the closed box was then facilitated by halting coolant circulation. This protocol gave solid and liquid portions in approximately equal amounts. Changing the temperature interval to ca. 0–8 °C, afforded a 20:80 liquid-to-solid ratio (Table 2). The phases were separated by centrifugation at 1,000 rpm (20*g*-force) for 6 h followed by decantation.

CSBO Samples Produced

In Table 1 are summarized representative experimental data.

## Results and Discussion

Experiments with a 500-W Projector Lamp in Reactor 1

*Solids Formed in CSBO Samples over Time at Room Temperature*

Experiments were conducted under Ar to hinder polymerization of SBO associated with autoxidation. Analysis of

**Table 2** Isomer analyses (in percentages) of 99–100 % CSBO samples obtained from reactor 1 as described in "Experimental Section" and in entry 1 of Table 1

| Entry | Sample (L/S) | C16:0 | C18:0 | C18:1 | C18:2 | CLA 9C11T | CLA 10T12C | CLA trans–trans |
|-------|--------------|-------|-------|-------|-------|-----------|------------|-----------------|
| 1 | S + L(50L/50S)[a] | 14.3 ± 0.4 | 6.7 ± 0.6 | 29.6 ± 0.2 | 2.1 ± 0.1 | 6.0 ± 0.2 | 3.6 ± 0.1 | 37.7 ± 0.5 |
| 2 | S + L(50L/50S)[b] | 15.7 ± 0.4 | 6.6 ± 0.3 | 30.8 ± 1.9 | 1.1 ± 1.5 | 5.2 ± 1.1 | 2.6 ± 0.9 | 38.0 ± 1.0 |
| 3 | L(50L/50S)[c] | 13.1 ± 1.0 | 6.7 ± 1.0 | 30.2 ± 1.1 | 2.9 ± 0.8 | 8.1 ± 0.5 | 4.7 ± 0.7 | 34.4 ± 0.8 |
| 4 | S(50L/50S)[d] | 15.3 ± 0.4 | 8.0 ± 0.9 | 26.9 ± 0.5 | 2.6 ± 0.4 | 6.9 ± 0.03 | 4.0 ± 0.2 | 36.4 ± 0.4 |
| 5 | L(20L/80S)[e] | 12.0 ± 0.2 | 6.2 ± 0.1 | 33.0 ± 0.7 | 2.9 ± 0.1 | 8.2 ± 0.4 | 4.9 ± 0.2 | 32.9 ± 0.1 |
| 6 | S(20L/80S)[f] | 14.8 ± 0.6 | 8.3 ± 0.4 | 27.6 ± 0.8 | 2.4 ± 0.3 | 6.9 ± 0.2 | 3.8 ± 0.4 | 36.3 ± 0.1 |

L, liquid; S, solid

[a] Darkened, unseparated oil not bleached with Fuller's earth

[b] Sample in entry 1 after bleaching with Fuller's earth

[c] Unsolidified 50 % of the oil left after repeated cycles of cooling to 0 °C/warming to ca. 17 °C the sample in entry 1 in a refrigerator/centrifuge

[d] Solidified 50 % of the oil left after repeated cycles of cooling to 0 °C/warming to ca. 17 °C the sample in entry 1 in a refrigerator/centrifuge

[e] Unsolidified 20 % of the oil left after centrifuging while warming from 0 to 8 °C the sample in entry 1

[f] Solidified 80 % of the oil left after centrifuging while warming from 0 to 8 °C the sample in entry 1

solution $^1$H-NMR spectra taken of solid portions of a CSBO sample that had been aged for weeks in CDCl$_3$ revealed no discernible change in the ratio of olefinic to aliphatic protons, showing that polymerization had not occurred. Even solids that formed in a sample left open to the atmosphere for 24 h showed no change in this ratio. CSBO production over lengthy photoconjugation times at solvent reflux temperatures in the presence of I$_2$ resulted in no detectable change in the aforementioned $^1$H-NMR ratio. This indicated that the CSBO was solidifying/crystallizing rather than polymerizing. Separation of the solid and liquid CSBO phases was achieved as described in the "Fractionation of CSBO" section.

Saturated fatty acids have higher melting points than unsaturated analogues, *trans*-fatty acids melt at higher temperatures than *cis* analogues, conjugated fatty acids melt at higher temperatures than unconjugated analogues, and single fatty acid changes in triglycerides alter their melting properties [20]. Also, conjugated fatty acids are better drying oils than unconjugated analogues [21]. Because fatty acid compositional changes very likely lead to melting point differences and variations in drying properties, isomer analyses of CSBOs were carried out. The solid portions generally possessed higher concentrations of *trans,trans* conjugated C=C bonds (Table 2, entries 3–6) and also higher concentrations of saturated fatty acids (entries 3–6) compared with the liquid fractions. Thus, solidification would be favored in the fraction possessing higher concentrations of saturated and *trans,trans*-fatty acids. On the other hand, the lower-melting liquid fraction could be expected to have a lower *trans,trans* content and also a lower concentration of saturated C16:0 and C18:0 fatty acids (as in entries 3 and 5). Moreover, higher *cis,-trans* and higher *trans,cis*-CLA (entries 3 and 5) as well as higher C18:1 (oleic) and C18:2 (linoleic) percentages in the liquid fraction could be due to the domination of *cis* linkages, which do not order well in a crystal lattice and therefore depress the melting point.

*Drying Properties*

The CSBO BK drying test results are summarized in Table 3. Interestingly, at least in the case of entries 1–3, both the liquid and the solid fraction formed at low temperature were better drying oils than the original unseparated sample in entry 1. We expected that the solidified fractions would have slower dry times due to their higher concentration of saturated fatty acid triglycerides. However, their higher percentage of *trans,trans*-CLA may have overcompensated for a high concentration of saturated fatty acid triglycerides.

The failure of the BK dryer to respond to the dry-through time for either the raw LO standard or the CSBO samples for most of the runs in Table 3 precludes making comparisons among the CSBO samples. It is interesting, however, that depending on the fractionation conditions (see Table 3 footnotes for entries 2, 3, 11 and 12) that dry-through times superior to those for raw LO can be achieved, and that dry-times equal to or better than raw LO can be achieved for other stages of the drying process recorded in all the entries except 8 and 9. Thus, the BK data show that fractionation can produce oils with excellent drying times.

To support the observation that unfractionated CSBO had poorer dry-through properties than the separated fractions, we coated each of three glass slides with one of the CSBO samples from entries 1–3 in Table 3. A coating of the solid fraction solidified on the glass slide in ca. 24 h at room temperature and a little over 5 days was required for dry-through. A coating made from the liquid fraction remained liquid for over 48 h and also required about 5 days for dry-through. The coating made from the unfractionated CSBO contained small particles of solidified oil dispersed throughout the coating after approximately 24 h at room temperature, and required ca. 12 days for dry-through. This suggests that two phenomena could be responsible for the better drying performance of the solid and liquid fractions compared with the unfractionated CSBO.

For one of these phenomena, we hypothesize that: (1) the improved drying properties of the solid fraction was favored not only by the higher percentage of higher-melting *trans,trans* conjugated linoleic acid than was present in the liquid, but also by the opportunity for parallel alignment of the linear saturated fatty acid molecules with the quasi-linear unsaturated *trans,trans* conjugated linoleic acid. This in turn would favor stronger attractive van der Waals forces between these chains and hence favor close contact of their reactive regions. For the second phenomenon, we hypothesize that: (2) liquid fractions contain higher concentrations of *cis*-fatty acids, which are less reactive than their *trans* counterparts in the drying process. This would inhibit alignment of reactive centers on the chains. Because the localized solid areas on the slide bearing the unfractionated oil appeared well before dry-though occurred, the unseparated oil apparently dried heterogeneously. Why heterogeneity slows drying is unclear.

The two aforementioned phenomena favoring drying in the separated fractions would impede drying in the unseparated oil owing to the difficulty of molecular organization imposed by dilution caused by the combination of the two phenomena. An SEM image in Fig. 1 of the completely dried portions appear somewhat ordered relative to the less-ordered unsolidified portions in the "valleys". This image reveals the heterogeneity of the coating made from unfractionated CSBO.

**Table 3** Twenty-four hour BK dry times using oxalate driers on oils obtained from reactor 1

| Entry | Sample | Set-to-touch[a] | Tack free[a] | Dry hard[a] | Dry through[a] | Cargill oil[b] |
|---|---|---|---|---|---|---|
| 1 | S + L(50L/50S)[c] | 34 % faster | 4 % faster | _[d] | _[e] | Sample 1 |
| 2 | L(50SL/50S)[f] | 25% faster | _[e] | _[d] | 37 % faster | Sample 1 |
| 3 | S(50L/50S)[g] | _[d] | _[d] | Just as fast | 29 % faster | Sample 1 |
| 4 | L(90L/10S)[h] | 15 % faster | 4 % faster | _[d] | _[e] | Sample 1 |
| 5 | S(90L/10S)[i] | 53 % faster | 13 % slower | _[d] | _[e] | Sample 1 |
| 6 | L(50SL/50S)121[j] | Just as fast | 27 % slower | 29 % slower | _[d] | Sample 1 |
| 7 | S(50SL/50S)121[k] | Just as fast | 36 % slower | 29 % slower | _[d] | Sample 1 |
| 8 | S + L(20L/80S)[l] | 8 % slower | 1 % faster | 20 % slower | _[d] | Sample 2 |
| 9 | L(20L/80S)[m] | 8 % slower | 14 % slower | 33 % slower | _[d] | Sample 2 |
| 10 | S(20L/80S)[n] | 8 % faster | Just as fast | 27 % slower | _[e] | Sample 2 |
| 11 | L(50L/50S)[o] | 44 % slower | 50 % slower | 55 % slower | 4 % faster | Sample 2 |
| 12 | S(50L/50S)[p] | 44 % slower | 50 % slower | 55 % slower | 9 % faster | Sample 2 |

Drying results reported in this table (all entries) were obtained from Prof. John L. Massingill of Texas State University-San Marcos, USA

[a] These percentages are relative to raw linseed oil (raw LO)

[b] The two Cargill samples represent different five gallon shipments of RBD SBOs which were assumed to be of sufficiently similar fatty acid composition that differences would not result in significant drying property differences

[c] Un-separated conjugated oil not bleached with Fuller's earth

[d] The BK drier did not respond to this stage for raw LO

[e] The BK drier did not respond to this stage for the conjugated oil sample

[f] Unsolidified 50 % of the oil left after repeated cycles of cooling to 0 °C/warming to ca. 17 °C S + L(50L/50S) in entry 1 in a centrifuge tube

[g] Solidified 50% of the oil after repeated cycles of cooling to 0 °C/warming to ca. 17 °C S + L(50L/50S) in entry 1 in a centrifuge tube

[h] Unsolidified 90 % obtained from S + L(50L/50S) in entry 1 by centrifuging while cooling from RT to −4 °C over 6 h

[i] Solidified 10 % obtained from S + L(50L/50S) in entry 1 by centrifuging while cooling from RT to −4 °C over 6 h

[j] Unsolidified 50 % obtained from S + L(50L/50S) in entry 1 by centrifuging while warming from 0 to 8 °C over 6 h

[k] Solidified 50 % obtained from S + L(50L/50S) in entry 1 by centrifuging while warming from 0 to 8 °C over 6 h

[l] Un-separated conjugated oil

[m] Unsolidified 20 % of the oil left after centrifuging while warming the sample in entry 8 from 0 to 8 °C over 6 h

[n] Solidified 80 % of the oil left after centrifuging while warming the sample in entry 8 from 0 to 8 °C over 6 h

[o] Unsolidified 50 % of the oil left after centrifuging while warming the sample in entry 8 from 1 to 17 °C over 6 h

[p] Solidified 50 % of the oil left after centrifuging the sample in entry 8 while warming from 1 to 17 °C over 6 h
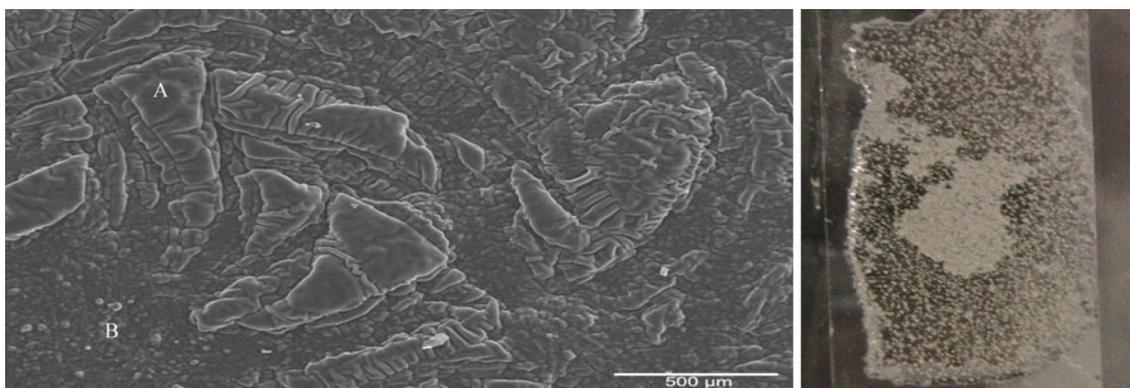


**Fig. 1** SEM image (*left*) **a** Region of CSBO coating in which oil solidified before drying. **b** Region of dried CSBO coating in which the oil remained liquid until dry-through. Photograph (*right*) of coating used to obtain the SEM image during drying, showing formation of small solidified particles

## Use of Granulated Charcoal for $I_2$ Removal

Using excess $I_2$/hexanesB solution and measurement of the $I_2$ concentration before and after charcoal removal, it was determined that a 27:1 weight ratio of charcoal to $I_2$ was required to efficiently remove $I_2$ by stirring the reaction mixture overnight. During stirring, granules of charcoal collided with each other and with the magnetic stir bar, causing fine powder formation, requiring a bed of Celite to facilitate filtration. This problem is avoidable in an industrial setting by passing the reaction mixture through a packed charcoal column. Additionally, attempts to remove $I_2$ from the charcoal (e.g., toluene extraction or sublimation) were only marginally successful. The best method was Soxhlet extraction with hexanesB. The removal of less than 50 % of the bound $I_2$ by this method was also found by Bahatia et al. [22] who observed reversible and irreversible charcoal absorption of $I_2$; the latter due to pore blockage. As expected, charcoal re-use after soxhlet extraction was less effective than fresh charcoal. Polymer-bound $Ph_3P$ was also effective for $I_2$ removal from hexanesB, but attempts at $I_2$ regeneration from the polymer were unsuccessful. After 23 cycles of using the same charcoal sample with a 10 % CSBO solution, the $I_2$ content of the charcoal remained low (ca. 0–11%) indicating that considerable additional loading of the charcoal remained possible.

## Use of Starch for $I_2$ Removal

In iodometry, starch functions as an indicator for $I_2$ by forming a blue starch-iodine complex. Using a slurry of 10 % Lintner's potato starch (Fischer soluble starch) or ordinary potato starch in water, complete removal of $I_2$ was achieved. Debate exists on the role of water in iodometry since the structure of the starch–iodine complex is presently not clear. The complex consists of linear poly-iodine species trapped inside the helix formed by the $\alpha$-1,4-linked glucose units [23]. Some believe that water's role is to permit hydrolytic disproportionation of part of the $I_2$ to form iodide ions required to form poly-iodide components for the complex [23, 24]. Others believe that water is necessary to facilitate a conformation of starch capable of accepting $I_2$ molecules for complex formation [25]. In the case of wetted starch, apparently insufficient water is present to drive $I_2$ from the complex formed upon $I_2$ extraction from the hexanesB. Liberation of $I_2$ from the starch-$I_2$ complex driven by replacement of $I_2$ with water [26] is consistent with these results. Given the advantage that "wetted" starch filters more easily than dry starch, and that using Lintner's starch adds the additional step of acid treatment to achieve "lintnerization", using wetted potato starch to remove $I_2$, followed by water addition to

regenerate $I_2$ appears optimum. Also promising for iodine recycling is that $I_2$ adsorbed by a 10 % starch aqueous slurry was successfully extracted into hexanesB, and that $I_2$ co-distils with water to form water-insoluble crystals.

## Effect of Reducing $I_2$ Concentration on Conjugation

Typically we used 3.02 g of $I_2$ for quantitative conjugation of 2.01 L of Cargill RBD SBO in 12 h in reactor 1. Not surprisingly, using only half the $I_2$ mass allowed 94 % conjugation in 20 h at the same temperature (70–80 °C). As seen in Table 1, entry 1 [wherein Fig. 8 (ESI) features a "double humped" curve owing to two additions of $I_2$, $t = 314$ h]. Here we doubled the SBO volume in reactor 1 from 2.01 to 4.02 L and reduced the hexanesB volume by 2.01 L. After 96 h, only a 62 % conversion was recorded. Addition of two more aliquots of $I_2$ (3.03 g in 1.5 L hexanesB at 96 h, and also at 188 h at 88 % conversion) indicates that when conjugation is incomplete, it can continue by injecting additional $I_2$. Although conversion was 99 %, a longer time was required than would be anticipated.

## Experiments Involving a 500-W Projector Lamp in Reactor 2

With reactor 2, we initially used the conditions in Table 1, entry 2 [Fig. 9 (ESI) $t = 13$ h]. Conversion was 39 % in 2 h and 97 % in 13 h. Since further progress was negligible, the reaction was quenched in order to prepare two CSBO samples for drying time measurements. Sample one was obtained from an 850-mL aliquot of reaction solution placed in an amber bottle and stirred with 6.0 g of charcoal for 24 h. After filtration, excess hexanesB was removed under reduced pressure for 6 h leaving a yellow CSBO sample which was treated with 1.2 wt% of TroyMax 2002 dryer for 24 h under Ar. The second sample was prepared the same way using 257 g of starch wetted with 128.5 g of water for $I_2$ removal. The dry-times for these two samples in Table 4 (entries 16 and 17, respectively) indicate that both samples were sluggish in the set-to-touch stage whereas in the dry-through stage, both compared favorably with raw LO (entry 1).

An experiment was conducted (Table 1, entry 3) in a precursor reactor to reactor 2. This reactor lacked the glass liner (and its cradle), employing the PVC tank itself as the reactor. The lid was sealed to the PVC rim with a silicone liquid gasket. The run was carried out at 70–80 °C using SBO (2,450 g), $I_2$ (3.6637 g), hexanesB (19.95 L) and a 500-W projector bulb. In 3 h conjugation was 76 % and in 20 h it was 91 % [Fig. 10 (ESI) $t = 108$ h] but 99 % required 88 h.

**Table 4** BK dry times of conjugated SBO using TroyMax-2002 drying agent on oils from reactors 2, 4 and a precursor reactor to 2

| Entry | Entry in Table 1 | Reactor | Set-to touch time (min)[b] | Tack free[a] time (min)[b] | Dry hard[a] time (min)[b] | Dry through[a] time (min)[b] |
|---|---|---|---|---|---|---|
| 1[c] | | NA | 283 | 422 | 876 | 975 |
| 2 | 4 | 4 (lp) | 599 | 675 | 703 | 1,038 |
| 3 | 8 | 4 (hp) | 481 | 524 | 637 | >24 h |
| 4 | 9 | 4 (hp) | 326 | 359 | 592 | 715 |
| 5 | 13 | 4 (hp) | 427 | 503 | 741 | 1,086 |
| 6 | 3 (sample 3.2c) | (2)[d] | 578 | 637 | 920 | 1,128 |
| 7 | 3 (sample 3.2d) | (2)[d] | 500 | 559 | 828 | 883 |
| 8 | 3 (sample 3.2e) | (2)[d] | 514 | 569 | 682 | 873 |
| 9 | 14 | 4 (hp) | 411 | 460 | 772 | 986 |
| 10 | 15 | 4 (hp) | 184 | 236 | 604 | 739 |
| 11 | 5 | 4 (lp) | 361 | 481 | 741 | 949 |
| 12 | 6 | 4 (lp) | 656 | 769 | 812 | 1,031 |
| 13 | 11 | 4 (hp) | 437 | 481 | >24 h | >24 h |
| 14 | 12 | 4 (hp) | 345 | 385 | >24 h | >24 h |
| 15 | 10 | 4 (hp) | 465 | 531 | 779 | >24 h |
| 16 | 2 (sample 3.2a) | 2 | 472 | 505 | 571 | 833 |
| 17 | 2 (sample 3.2b) | 2 | 493 | 517 | 670 | 909 |

lp, low-pressure Na lamp; hp, high-pressure Na lamp

[a] 1.2 wt% of TroyMax-2002 drying agent was used in all samples listed here. All results reported are 24 h BK drying times obtained by Dr. Michael van De Mark of Missouri University of Science and Technology, Missouri S&T Coatings Institute in Rolla, MO, USA

[b] Dry-time (min) average of two runs

[c] Raw LO was used in place of conjugated soybean oil

[d] Reactor that was the precursor to reactor 2 (see description of reactor 2 under reactors employed in ESI)

To obtain the drying properties of the CSBO produced in this experiment, 2,550 mL of reaction solution was placed in an amber bottle and stirred with 6.0 g of charcoal for 1 h. After filtration, the filtrate was divided into three equal portions of 850 mL, each of which were stored in amber bottles under argon in the dark at room temperature. HexanesB evaporation under reduced pressure from one of these portions provided CSBO sample 3.2c which was stored in the dark at room temperature under argon. Six hours later, the second 850 mL portion was stirred at room temperature for 1 h with 2.00 g of charcoal. Evaporation of the hexanesB gave CSBO sample 3.2d which was stored in the dark at room temperature under Ar. One week later, the third 850 mL portion of filtrate was stirred with 2.0 g of charcoal for 1 h at room temperature. After filtration and evaporation of the hexanesB under reduced pressure, sample 3.2e was obtained which was stored in the dark under Ar. The first two samples were then simultaneously sent for residual iodine analysis, and the third was shipped for the same purpose 9 days later. All three samples were light yellow and all revealed the presence of 0.1 % iodine, thus indicating that aging the CSBO did not affect the color or residual iodine content whether it received a second charcoal treatment or not. This suggests that charcoal does not adsorb detectably more iodine upon aging. However,

the drying times of these three samples recorded in Table 4 reveal that sample 3.2c (not treated a second time with charcoal) is a poorer drying oil than raw LO in all four drying stages. By contrast, sample 3.2d treated with charcoal a second time the same day as 3.2c, and sample 3.2e which received a second charcoal treatment a week later, are better drying oils than raw LO in the dry-hard and Dry-Through stages, with 3.2e being significantly better than 3.2d. This suggests that aging the CSBO after the initial charcoal treatment drys faster after the second charcoal treatment. It would appear that the second charcoal treatment removes a drying inhibitor that forms on aging or that perhaps aging is accompanied by autoxidation (drying) via a free radical that forms or is present (e.g., iodine).

Experiments with a 500-W Projector Lamp in Reactor 3

Conjugation data for two types of SBOs and salad grade corn oil appear in Tables 5 and 6, respectively. Table 5 (entries 4 and 5) shows that upon approximately tripling the oil-to-solvent weight ratio, the conjugation time required at 25 °C somewhat more than triples. This suggests that the oil/solvent ratio can be considerably increased at relatively low temperatures. Comparison of entry 1 in Table 5 and entry 1 in Table 6 shows that both

**Table 5** SBO in *n*-pentane or hexanesB using reactor 3

| Entry | Oil (% by wt) | Solvent | T (°C) | Time (min) | % conjugation |
|-------|---------------|---------|--------|------------|---------------|
| 1 | LoSat (14) | *n*-pentane | 32 | 120 | ≥99 |
| 2[a] | LoSat (14) | *n*-pentane | 32 | 60 | ≥99 |
| 3[b] | LoSat (14) | *n*-pentane | 32 | 300 | 78 |
| 4 | LoSat (20) | *n*-pentane | 25 | 300 | ≥99 |
| 5 | LoSat (54) | *n*-pentane | 25 | 960 | ≥99 |
| 6 | LoSat (14) | HexanesB | 15 | 300 | 64.5 |
| 7 | LoSat (14) | HexanesB | 32 | 60 | ≥99 |
| 8 | LoSat (14[c]) | HexanesB | 72 | 10 | ≥99 |
| 9 | Alkali washed (14) | HexanesB | 32 | 90 | 97.9 |
| 10 | Alkali washed (14) | HexanesB | 52 | 20 | 98.5 |
| 11 | Alkali washed (14) | HexanesB | 62 | 10 | 97.8 |
| 12 | LoSat (14) | *n*-heptane | 52 | 120 | 93.0 |

[a] Catalyst amount (0.15 % by wt) doubled

[b] Catalyst amount (0.15 % by wt) cut in half

[c] Duplicate experiments with Hy-Vee (a grocery store) salad grade canola, safflower and sunflower oil performed comparably

Hy-Vee Lo Sat SBO and Hy-Vee corn oil conjugate at ca. the same rate in *n*-pentane. A comparison of the data in entries 6 and 7 in Table 5 and entry 2 of Table 6 indicates (though not with great certainty) that at 52 °C, SBO would have been >99 % conjugated in ca. 30 min, as was the corn oil in entry 2 of Table 6. This compares with 120 min for SBO to reach only 93 % conjugation in heptane (entry 12 of Table 5). Similarly, ≥99 % conjugation of Lo Sat SBO at 32 °C in hexanesB (entry 7, Table 5) proceeds ca. twice as fast in *n*-pentane (entry 1). HexanesB are ca. 30 % cheaper than HPLC-grade hexane but can facilitate ca. 100 % SBO conjugation equally as fast.

Entries 2 and 3 in Table 6 show that hexanesB performed at least as well as HPLC certified hexane. Cyclohexane (entry 6, Table 6) also performed as well as HPLC certified hexane. Entries 5–7 in Table 6 show the ca. linear decrease in conjugation time with increasing temperature, and entries 8–10 show that, as expected, 100 % conjugation is achieved faster as the temperature rises. Comparing entries 2 and 9 in Table 6 indicates that alkali washed corn oil also conjugates faster with temperature, and that alkali washed corn oil conjugates faster than salad grade corn oil. Both corn oils are alkali washed, but the salad grade oil is further refined as discussed above. Why further refinement lengthens conjugation time is unclear.

Use of Low- and High-Pressure Na Vapor Lamps in Reactor 4

Na vapor lamps are quite efficient for converting electrical energy into light. Compared with incandescent lamps (e.g., tungsten and halogen lamps which are only ca. 2–5 % efficient) Na vapor lamps are 22 % (low pressure) to 27 % (high pressure) efficient. Thus Na vapor lamps emit ca. 5–10 times more light per watt than tungsten or halogen lamps, and much less heat. Low-pressure Na vapor lamps maximize intensity at 600 nm. The Na D line is the main source of light from the high-pressure Na lamp. This line is pressure broadened by its relatively high Na vapor pressure.

*Conjugation of SBO Using a Low-Pressure Na Vapor Lamp in Reactor 4*

Aliquots for $^1$H-NMR analysis were drawn into pre-evacuated septum-sealed flasks via a stainless steel cannula. Excess hexanesB was removed under reduced pressure. With 0.6 mol% of $I_2$, 57 % conversion to CSBO was achieved in 25 h [Table 1, entry 4; Fig. 11 (ESI) $t = 50$ h]. An additional 0.6 mol% of $I_2$ led to 99 % conjugation in 49 h at 70–80 °C. (With a 500-W projector bulb in reactor 1, 99 % SBO conjugation occurred in 12 h at 70 °C; see above). After transferring the solution to an amber bottle under Ar, 6.998 g of potato starch and 3.5 g of water were

**Table 6** Corn oil in *n*-pentane, hexanesB, hexane, heptanesC or cyclohexane in reactor 3

| Entry | Oil | Solvent | Temp (°C) | Time (min) | % Conjugation |
|-------|-----|---------|-----------|------------|---------------|
| 1 | Salad grade | *n*-pentane | 32 | 120 | ≥99 |
| 2 | Salad grade | HexanesB | 52 | 30 | ≥99 |
| 3 | Salad grade | Hexane (HPLC certified) | 52 | 30 | ≥99 |
| 4 | Salad grade | HeptanesC | 52 | 60 | ≥99 |
| 5 | Salad grade | Cyclohexane | 32 | 90 | ≥99 |
| 6 | Salad grade | Cyclohexane | 52 | 60 | ≥99 |
| 7 | Salad grade | Cyclohexane | 72 | 30 | ≥99 |
| 8 | Alkali washed | HexanesB | 32 | 60 | ≥99 |
| 9 | Alkali washed | HexanesB | 52 | 20 | ≥99 |
| 10 | Alkali washed | HexanesB | 62 | 5 | 99 |

added, followed by stirring for 24 h at room temperature. To this mixture was added 6.615 g charcoal followed by stirring for 24 h at room temperature. The solution was filtered and excess hexanesB was removed under reduced pressure.

The reaction of the preceding paragraph was repeated except that the $I_2$ was added in one portion. The data in Table 1, entry 5 [Fig. 12 (ESI) $t = 42$ h] show that conjugation was 100 % complete in 42 h, although 99 and 96 % conjugation was achieved in 27 h in 18 h, respectively. Because of the sublimable nature of $I_2$ and a possibility of rapid deposition of $I_2$ on reactor surfaces and in condensers not submersed in solution, we repeated the experiment by adding the $I_2$ in three portions to determine if that protocol was superior to a single addition. The iodine was added in three portions of 1 mmol each dissolved in 100 mL hexanesB [Table 1, entry 6; Fig. 13 (ESI) $t = 23$ h] at the 25, 54 and 82 % conjugation marks after 2, 4 and 6 h, respectively, with 94 % conjugation reached at 10 h. Because the reaction time seemed to be reduced from 27 to 23 h (see earlier in this paragraph) with excellent conversion, we repeated the experiment using six doses of $I_2$ (0.500 mmol each) dissolved in 50 mL of hexanesB. The data appear in Table 1, entry 7 [Fig. 14 (ESI) $t = 28$ h]. The first portion gave 9 % conjugation in 2 h, the second portion 21 % in 4 h, the third 34 % in 6 h, the fourth 42 % in 8 h, the fifth 60 % in 10 h, and the sixth 80 % in 12 h. Further reaction for 23 and 28 h gave 97 and 100 % conjugation, respectively. From these results, 1.2 mol% of catalyst is optimum for complete conversion in a reasonable time span using a low-pressure Na lamp.

If we consider the points in time at which 99 % conjugation was achieved for the above four experiments, it would appear that adding the $I_2$ in portions is beneficial. Thus, adding the $I_2$ in one or two portions provides 99 % conjugation in 42 and 49 h, respectively, whereas adding the catalyst in three or six portions reduces the time to 99 % conjugation to 23 and 29 h, respectively. Because of the relatively small slope of the lines in Figs. 11–14 (ESI) in the 99 % conjugation region, there could be substantial error associated with the corresponding time estimates to (perhaps up to ±3 h). However, the at-least 20-h gap between the two pairs of aforementioned times appears to be real. Possibly there is a faster consumption of $I_2$ in a side reaction compared with the catalytic rate when $I_2$ concentrations are high.

*Conjugation of Soybean Oil Using a High Pressure Na Lamp in Reactor 4*

Using a 150-W high-pressure lamp, $I_2$ (1.2 mol%, 6.00 mmol) was added in one portion in 100 mL of hexanesB. The temperature range accidentally reached 80–90 °C rather than the usual 70–80 °C used for the low-pressure lamp runs. The data [Table 1, entry 8; Fig. 15 (ESI) $t = 6$ h] show that conjugation reached 99 % in 2 h, which persisted until the 4 h mark, and then it reached 100 % at 6 h. This experiment was repeated in the 70–80 °C range [Table 1, entry 9; Fig. 16 (ESI) $t = 6$ h]. Conjugation reached 78, 92, 95 and 98 % after 0.5, 1, 1.5 and 2 h, respectively, which closely matches the result in the previous experiment. The 70–80 °C range experiment was repeated except with half the $I_2$ amount (0.6 mol%). The $I_2$ was added in one portion in 100 mL hexanesB [Table 1, entry 10; Fig. 17 (ESI) $t = 8$ h]. After 2, 4, 6 and 8 h, conjugations were 96, 98, 99, and 100 %, respectively. Thus, reducing the $I_2$ content by half does not result in a significant decrease in the conjugation using a high-pressure sodium lamp.

By further dropping the $I_2$ level to 0.3 mol%, conversions were 38, 55, 63, 63 and 64 % in 0.5, 2, 22, 34, and 47 h, respectively, indicating that the $I_2$ level with a high-pressure Na lamp should be at least 0.6 mol% for 100 % conversion in a reasonable time. The dry times were poor for the 0.3 mol% run, except at the Dry-Hard stage where it was slightly better than raw LO (Table 4, entry 15).

*Effect of SBO/Solvent Ratio on Conjugation*

We then doubled the SBO/solvent ratio by decreasing the volume of hexanesB. Iodine (0.6 mol% in 100 mL hexanesB) was added in one portion at 70–80 °C [see Table 1, entry 11; Fig. 18 (ESI) $t = 73$ h]. After 1 h, 44 % conjugation occurred, and after 73 h it was 91 %. As with the 500-W projector lamp with higher SBO/solvent ratios (see earlier discussion) the rate of conversion was sluggish.

*Effect of Temperature on Conjugation*

The poor conversion rate [Fig. 18 (ESI)] described in the preceding section prompted us to repeat that run at 95–105 °C [Table 1, entry 12; Fig. 19 (ESI) $t = 118$ h]. In 1, 21 and 118 h, conversions were 44, 74 and 87 %, respectively. Side reactions or $I_2$ sublimation at higher temperature may have decreased conversions in this experiment.

The preceding experiment was repeated at 65–75 °C with no external heating, using only heat generated by the lamp. Iodine (0.6 mol%) was added in one portion in 100 mL hexanesB [see Table 1, entry 13; Fig. 20 (ESI) $t = 121$ h]. Conversion was 56, 88, 93 and 97 % in 3, 12, 73 and 121 h, respectively. Because of the retarded rate of conjugation at this lower temperature, this experiment was halted.

At a constant reactor temperature of 50 °C, $I_2$ (1.2 mol%) was added in one portion in 100 mL of

hexanesB [Table 1, entry 14; Fig. 21 (ESI) $t = 10$ h]. Conversions were 10, 86 and 100 % after 3, 4 and 10 h, respectively. The oil had a faster Dry-Hard stage than raw LO (Table 4, entry 9). This experiment was repeated with the SBO solvent ratio doubled [Table 1, entry 15; Fig. 22 (ESI) $t = 221$ h]. After 2 and 221 h, 14 and 100 % conjugation was reached, respectively. Despite the slowness of conjugation, an excellent drying oil was produced (Table 4, entry 10) exhibiting significantly faster dry times than raw LO at all four stages, suggesting that the high level of *trans,trans*-CLA relative to the *cis* isomers is the cause.

Drying Oil Properties of CSBO Using TroyMax-2002

These data are given in Table 4. All of the CSBOs in this table performed more poorly than raw LO at the Set-to-Touch stage except for the CSBO in entry 10. All the oils performed better than raw LO in the Dry-Hard stage except those in entries 6, 13 and 14. The CSBO in entry 10 is the only one that performed better than raw LO in all four drying stages. The superiority of this CSBO was rationalized in the preceding paragraph.

Fatty Acid Profiles of CSBO

The fatty acid profiles of CSBO (Table 7) were obtained using a standard method (see "Experimental Section"). The use of this base-catalyzed protocol is superior to acid-catalyzed transesterification because the fatty esters produced are not isomerized. Each component of the fatty acids was identified by retention time and MS analysis. A linear response factor was determined for each of the commercially available products, and the one unavailable product (the *trans,trans*) was estimated. As expected, the response factors were all similar.

The total of the C18:2 and the three CLA fractions was ~48–65 % consistent with the expected fatty ester profile in SBO. The amounts of C18:0, C18:1, and C16:0 in the SBO were also in the expected ranges, confirming that saturated and mono-unsaturated fatty chains were not altered. As expected, C18:3 was not detected, indicating complete conjugation, and probable co-elution with the *trans,trans*-CLA isomer.

Most of the results show 0 or low levels of non-conjugated C18:2. This agrees with the NMR results which also show conjugation near 100 %. The two samples with the largest amounts of unreacted C18:2 (entries 2 and 3 in Table 7) also showed the least conjugation by NMR (entries 11 and 12 in Table 1). The distribution of conjugated isomers was interesting. The *trans,trans* isomer level was consistently high in all cases, whereas the 10-*trans*,12-*cis* isomer varied from a low value of ~10 entries 1, 7–11 in Table 7) to a value of ~20 (entries 2–6 in Table 7). The values for the 9-*cis*,11-*trans* isomer were consistently around 5, with two notable exceptions where it was not observed at all (entries 10 and 11 in Table 7).

**Table 7** The fatty acid profiles (in percentages) of CSBOs made from reactor 4 according to the figure numbers in ESI listed in the second column

| Entry | Fig. # in ESI | C16:0 | C18:0 | C18:1 | C18:2[a] | CLA 9C11T | CLA 10T12C | CLA *trans–trans* |
|---|---|---|---|---|---|---|---|---|
| 1 | 17 (hp) | 14.3 (±0.3) | 6.5 (±0.2) | 29.0 (±0.0) | 0.00 | 5.6 (±0.01) | 10.4 (±0.1) | 34.3 (±0.3) |
| 2 | 18 (hp) | 14.7 (±0.7) | 6.3 (±0.1) | 28.4 (±0.8) | 6.6 (±0.1) | 4.5 (±0.1) | 19.3 (±0.1) | 30.8 (±1.3) |
| 3 | 19 (hp) | 13.3 (±0.9) | 6.4 (±0.2) | 27.3 (±0.6) | 9.5 (±0.2) | 4.1 (±0.1) | 19.6 (±0.1) | 32.1 (±0.4) |
| 4 | 20 (hp) | 12.7 (±0.2) | 6.5 (±0.4) | 29.0 (±1.4) | 3.0 (±0.02) | 4.7 (±0.1) | 21.8 (±0.2) | 35.4 (±1.0) |
| 5 | 22 (hp) | 13.7 (±1.7) | 6.3 (±0.0) | 28.4 (±0.04) | 2.8 (±0.04) | 3.8 (±0.1) | 23.0 (±0.2) | 38.0 (±1.4) |
| 6 | 21(hp) | 14.4 (±1.5) | 6.7 (±0.04) | 29.1 (±0.1) | 0.00 | 5.3 (±0.1) | 21.8 (±0.2) | 35.3 (±1.4) |
| 7 | 11 (lp) | 16.9 (±1.2) | 6.7 (±0.2) | 28.9 (±0.6) | 0.00 | 4.9 (±0.7) | 8.7 (±1.0) | 33.8 (±1.3) |
| 8 | 15 (hp) | 13.9 (±0.2) | 5.9 (±0.3) | 29.8 (±2.8) | 0.7 (±1.0) | 5.2 (±0.8) | 8.4 (±0.3) | 35.9 (±3.4) |
| 9 | 16 (hp) | 15.7 (±2.8) | 6.2 (±0.2) | 30.8 (±2.3) | 0.00 | 5.7 (±0.1) | 9.2 (±0.8) | 32.3 (±1.4) |
| 10 | 12 (lp)[b] | 14.6 (±0.5) | 7.0 (±0.1) | 28.5 (±1.2) | 0.8 (±1.0)[c] | 0.00 | 9.0 (±0.4) | 40.1 (±0.5) |
| 11 | 13 (lp)[b] | 14.0 (±0.6) | 6.0 (±0.3) | 29.8 (±0.6) | 0.8 (±1.0)[c] | 0.00 | 9.5 (±0.1) | 39.7 (±0.4) |

Samples were prepared and evaluated twice

lp, low-pressure Na lamp; hp, high-pressure Na lamp

[a] There were multiple isomers of the small amounts of C18:2, which were all included in this number. However, the natural *cis,cis* isomer was predominant

[b] The percentages of these products led to an overall mass balance that was slightly lower than for samples in entries 1–9. An unresolved late-eluting broad peak with an area ~10 % of the total, was also observed

## Viscosity Results

CSBO viscosities varied widely [Table 1 (ESI)] with the lowest appearing in entries 5 and 16 with values near that of normal CSBO (~28 mPa s at 40 °C). The viscosities of the other samples were significantly higher, especially those in entries 13 and 14. There were no obvious trends in, or differences between the solid and liquid fractions of the CSBO samples. The sample with the best drying time [entry 26 in Table 1 (ESI), entry 10 in Table 4, entry 15 in Table 1] possessed one of the higher viscosities, but there is no apparent direct correlation of dry time with viscosity.

## Efficacy of Other Free Radical Sources for SBO Conjugation

Several well-known free radical polymerization initiators were thermally activated in SBO/refluxing hexanesB solutions. However, 10 mol% dibenzoylperoxide, dilauroyl peroxide, azobisisobutyronitrile (AIBN), 4,4′-azobis(4-cyanovaleric acid) (AICN), t-BuOCl and the chain transfer catalyst bis-$BF_2$-bridged-bis-dimethylglyoximate cobalt(II) all gave <5 % conjugation even after 24 h.

## Cost of CSBO Production Considerations

We calculated the cost of utilizing the present method to produce CSBO on a ¢(US)/kg basis (Table 8) using the following assumptions: 5.98 ¢/kWh (current average retail price for industrial electric power in the west north central, east south central, west south central and the mountain states [27]). We also calculated it using the current rate of 4.07 ¢/kWh in state of Washington. Also used in the calculations were the average of the price range of feedstock SBO for 2010 (51.5–55.5 ¢/lb) [28], the approximate bulk price $35/kg (3.5 ¢/g) estimated for iodine for 2009 [29], $553/ton (0.07 ¢/g) for charcoal [30], and $1,160–1,180/1,000 kg (76.61 ¢/L) for hexanesB [31, 32]. Costs not included were: hexanesB stripping, heating the reaction mixture to 50 or 70 °C (the optimum temperature range), alkali washing the SBO (if necessary), spent charcoal removal as waste, and CSBO loss on charcoal (which is probably small). Some potential cost savings estimates not included are: $I_2$ and charcoal recovery by sublimation or superheated steam distillation, $I_2$ and starch recovery from wetted starch via water treatment, heat recovery from the hot hexanesB reaction solution before charcoal filtration or wetted starch treatment, utilization of lamp heat, use of spent charcoal or wetted starch as fuel, commercial viability of <100 % CSBO (involving less photolysis time), and "double use" of the hexanesB by running the SBO/hexanesB extract directly from the soybean crushing/extraction process into a continuous flow reactor. The charcoal cost is reduced by the observation that at least 23 batches of reaction solution can be passed through the charcoal employed, without $I_2$ saturation of the charcoal (see, Experiments with a 500-W projector lamp in reactor 1 in "Use of Granulated Charcoal for $I_2$ Removal").

In column A of Table 8 it is assumed that the hexanesB, $I_2$ and charcoal are not recycled, while in column B it is assumed that at least 95 % of the hexanesB can be recovered (which is very easily achieved in industry). For both columns A and B the 5.98 ¢/kWh price is utilized and in column C the 4.07 ¢/kWh is assumed along with 95 % recovery of the hexanesB. The 95 % recovery rate is intentionally overly conservative since there is an energy cost associated with hexane recovery. It may be noted that industrial recovery of hexanes typically reaches 99 %. Costs for usage of drying oils obtained by refrigeration/fractionation are probably too high for consideration. In

**Table 8** Summary of SBO conjugation data for cost estimates of 1 kg of SBO in cents (¢)

| Entry | Reactor no. | Fig. 1 Entry | HexanesB (L, ¢) | SBO (kg) | Charcoal (g, ¢) | Time (h) | $I_2$ (g, ¢) | Bulb (W) | Bulb type | kWh (¢)[a] | A (¢)[b] | B (¢)[c] | C (¢)[d] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 16.47, 342 | 3.686 | 111, 2.10 | 314 | 15.55, 14.77 | 500 | Proj. | 25.4, 17.3 | 613 | 277 | 207 |
| 2 | 2 | 2 | 7.89, 615 | 0.980 | 29.4, 2.10 | 13 | 1.465, 5.23 | 500 | Proj. | 39.7, 27.0 | 662 | 77.8 | 52.9 |
| 3 | 4 | 5 | 1.76, 610 | 0.221 | 6.615, 2.10 | 42 | 0.762, 12.1 | 35 | Lo-P Na | 39.8, 27.1 | 664 | 84.8 | 71.7 |
| 4 | 4 | 6 | 1.76, 610 | 0.221 | 6.615, 2.11 | 22 | 0.762, 12.1 | 35 | Lo-P Na | 20.6, 14.0 | 645 | 65.3 | 58.7 |
| 5 | 4 | 9 | 1.76, 610 | 0.221 | 6.615, 2.11 | 6 | 0.762, 12.06 | 150 | Hi-P Na | 24.3, 16.5 | 649 | 69.5 | 61.7 |
| 6 | 4 | 10 | 1.76, 610 | 0.221 | 6.615, 2.11 | 8 | 0.381, 6.0 | 150 | Hi-P Na | 32.5, 22.1 | 651 | 71.1 | 60.7 |
| 7 | 4 | 14 | 1.76, 610 | 0.221 | 6.615, 2.11 | 10 | 0.762, 12.1 | 150 | Hi-P Na | 40.6, 27.6 | 665 | 85.3 | 72.3 |
| 8 | 4 | 15 | 1.54, 268 | 0.441 | 13.23, 2.10 | 221 | 0.762, 6.05 | 150 | Hi-P Na | 45.0, 30.6 | 726 | 471 | 327 |

[a] Power cost at 5.98 and at 4.07 ¢/kWh, respectively (see text)

[b] Cost estimate assuming 5.98 ¢/kWh and no recycling of hexanesB, charcoal, or $I_2$

[c] Cost estimate assuming 5.98 ¢/kWh, 95 % recovery of hexanesB and no recycling of hexanesB, charcoal, or $I_2$

[d] Cost estimate assuming 4.07 ¢/kWh, 95 % recovery of hexanesB and no recycling of hexanesB, charcoal, or $I_2$

Table 1, the reaction conditions given in entry 5 or 10 would be optimum choices for industrial production. Judging by the percentage conjugation recorded in these entries, an $I_2$ concentration between 0.6 and 1.2 mol% could allow quantitative conjugation to be attained with less than 1.2 mol% catalyst concentration.

The market price for raw linseed oil and soybean oil in 2010 was 66–70 ¢/lb (68 ¢/lb average) and 51.5–55.5 ¢/lb (53.5 ¢/lb average), respectively. Assuming from Table 8 that the cost of conjugating SBO could be as low as 60 ¢/kg (i.e., 27 ¢/lb) CSBO would cost ca $0.81/lb, rendering it uneconomical as a drying oil in today's market. However, our process would be advantageous in converting plant oils which are high in oleic acid contents, to high-concentration value-added sources of CLA isomers with various distributions (depending on process parameters) for maximizing their health benefits [33] if their medical efficacy should become more firmly established [34].

## Summary and Conclusions

In this research we achieved 100 % conjugation of up to pound quantities of SBO using $I_2$ (an eco-friendly non-metallic catalyst) in hot hexanesB (an easily recoverable solvent) under photochemical conditions. Fatty acid dienes in our CSBOs were predominantly *trans*-9,*trans*-11 rather than the mostly *cis* analogues produced with other catalysts. Recovery of the $I_2$ catalyst from reaction mixtures appears feasible either with wetted starch or with charcoal (both of which are also recyclable). Some of our CSBOs have drying properties superior to commercial raw LO.

Our CSBOs are stable to autoxidation on storage, as well as to polymerization during long conjugation times at elevated temperatures in the presence of photolyzed $I_2$. Upon cooling, CSBOs can be fractionated into solid and liquid fractions of different ratios. The solidified portions tend to have higher concentrations of *trans,trans* conjugated C=C bonds and of saturated fatty acids compared with the liquid portions. There are no obvious trends in or differences between viscosities in the solid and liquid fractions of the CSBO samples. As expected, higher temperatures accelerate conjugation. However, doubling the oil/solvent ratios of SBO/iodine results in sluggish conjugation, and adding the iodine in portions can be beneficial for reasons that are not clear.

Using a high-pressure Na lamp, the CSBO oil produced at 50 °C has faster drying times than CSBO produced at higher temperatures. Although this lower temperature also results in higher concentrations of *cis* isomers, the Dry-Hard stage is reached faster than for raw LO. Repeating this experiment with double the ratios of SBO/solvent and $I_2$/solvent lengthens the time for 100 % conjugation by a factor of 20, and lowers the concentration of *cis* isomers. However, the oil from this experiment gave much faster dry times than raw LO in all four drying stages.

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