

Carbonated SBO 4.2: 09-28-05

Green Chemistry

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Supporting Information

The Improved Synthesis of Carbonated Soybean Oil using Supercritical Carbon Dioxide at a Reduced Reaction Time.

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Section S-1

The NMR data for carbonated soybean oil.

NMR spectroscopy was performed on a Bruker Avance 500 NMR operating at
5 500 MHz for ^1H and 125 MHz for ^{13}C . Bruker Icon NMR software was used running on
an HP x1100 Pentium 4 workstation. Peaks were referenced to sodium 3-
trimethylsilylpropionate-2,2,3,3- d_4 (TSP) at 0.0000 ppm. Simulations of ^{13}C NMR
spectra were performed by ACD/CNMR predictor version ACD/Labs 6.00, running on a
Gateway Pentium 4 CPU with a 2.53 GHz processor

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The carbonated soybean oil solution was dried in a Kugel-Rohr® and characterized by
 ^1H NMR, and ^{13}C NMR. ^1H NMR: δ 5.3 ppm multiplet, ppm glycerol backbone single
proton; δ 4.49–4.90 ppm, multiple signals, cyclic carbonate ring protons; δ 4.11-4.29
ppm, multiplet, glycerol backbone, 4 proton signal; δ 2.32 ppm, triplet, protons on carbon
15 α to backbone, 2 proton signal; δ 0.86 ppm triplet, end of fatty chain, 3 proton signal;
other signals from δ 1.2-2.2 ppm, many signals. ^{13}C NMR: δ 173 and δ 172, glycerol
backbone carbonyl carbons; δ 153 and δ 154, cyclic carbonate carbons from both oleic
and linoleic moieties; δ 79-82 ppm, cyclic ring carbons; δ 69 and δ 62, glycerol backbone
signals; δ 20-35 multiple signals.

The reaction products of different reaction times were studied by ^1H NMR and ^{13}C NMR. Both the ^1H and ^{13}C NMR show the conversion to the expected product. The carbonated product has new peaks in the ^1H NMR at δ 4.49–4.9 ppm corresponding to the protons on the carbons in the cyclic carbonate rings. Additionally the disappearance of the protons in the δ 2.89–3.13 ppm region can be followed and used to help quantitate the reaction progress at each reaction time (Table 1). The size of these peaks was compared to the signal at δ 0.86 ppm, a triplet corresponding to the end of the fatty chains which did not change position with reaction progress. It can be seen that the reaction is ~94% complete in only 20 hours, less than 1/3 of the reaction time required to achieve the same extent of completion in the literature synthesis.¹ Another ^1H NMR signal of note is the shift of the peak at δ 1.49 ppm slightly downfield to δ 1.61 ppm but it was not resolved sufficiently to attempt quantitation. In the ^{13}C NMR, the appearance of the carbonyl signals of the cyclic moieties at δ 153 and 154 ppm are clearly visible. Additionally, the corresponding signals in of the epoxy carbons of the starting material at δ 58–62 ppm are not present.

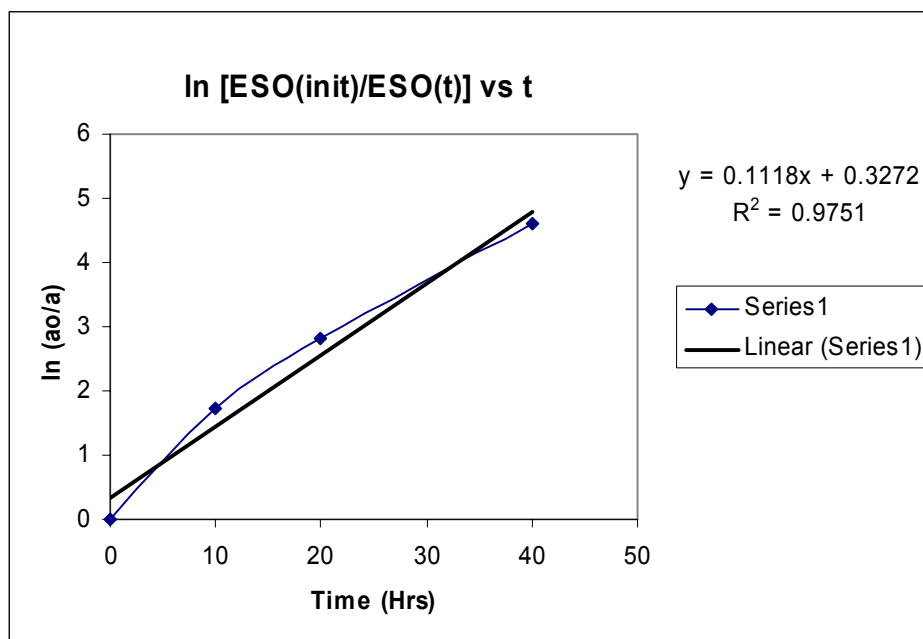
Section S-2

A Plot to obtain the apparent 1st order kinetic rate constant

Using the ¹H NMR spectroscopy data, A plot of the $\ln ([\text{ESO}]_{\text{initial}}/[\text{ESO}]_t)$ vs time was
5 performed for our system and from the literature synthesis.¹

A 1st order kinetic rate constant of 0.1118 hr⁻¹ was calculated in our system,
giving a $t_{1/2}$ of 6.2 hrs. From literature data, a rate of ~0.0402 hr⁻¹ and $t_{1/2}$ of 17.2 hrs can
be calculated in a similar manner. In other words, we have increased the observed
reaction rate by a factor of three.

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References

- 15 1 B. Tamami, S. Sohn, G. L. Wilkes, and B. Tamami, *J. Appl. Polym. Sci.*, 2004,
92, 883.