Reactivity in Epoxidation: Comparison Between Soybean Oil and High Oleic Soybean Oil

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Highlights

- Performance comparison between the epoxidation of soybean oil and high oleic soybean oil;
- Insights about the reactivity of different fatty acid derivatives in the epoxidation;
- Improvement of a kinetic model for the reaction system.

1. Introduction

The epoxidized soybean oil (ESO) is a compound that has been studied for applications as a plasticizer component for polyvinyl chloride (PVC), in replacement to phthalates. The ESO is typically produced in a liquid-liquid system, with soybean oil (SO), hydrogen peroxide, and a carboxylic acid as the main reactants. The SO consists of mixtures of triglycerides derived from different fatty acids (different carbon chain lengths and number of double bonds), in which the linoleic acid (18 carbon atoms, and 2 double bonds) is preponderant [1].

As the name suggests, the high oleic soybean oil (HOSO) represents a soybean oil version richer in oleic acid derivatives (18 carbon atoms, and 1 double bond). Preliminary tests involving the epoxidation of HOSO led to an epoxidized product (epoxidized high oleic soybean oil – EHOSO) with a color different than ESO, which can be applied for products sensitive to color [2].

The epoxidation reaction itself occurs in the double bonds of the SO/HOSO, generating the oxirane groups that characterize the ESO/EHOSO. The double bond content is typically described by the iodine index, which represents the iodine amount (in g) that can react with 100 g of oil, and this value emphasizes the difference between the oils: 131 g I_2/100 g for SO, and 91 g I_2/100 g for HOSO. The oxirane index quantifies the weight percentage of oxygen atoms from oxirane groups in the epoxidized oil [2].

Since the SO and the HOSO present different iodine indexes, and, considering that the HOSO is mostly composed of carbon chains with only one double bond, it is of great interest to deeply explore the reactivity of the chains that compose these oils in the epoxidation reaction. This is particularly useful for improving kinetic models of the reaction system, with posterior applications to develop or optimize industrial reactors.

2. Methods

Soybean oil (acquired in a supermarket), high oleic soybean oil (Airable Research Labs), formic acid (85 wt%, industrial grade), and hydrogen peroxide (70 wt%, industrial grade) were acquired without further purification. 250 g of SO or HOSO, 15 g of formic acid, and 85 g of hydrogen peroxide were weighted for the reaction. No additional catalysts were employed.

The epoxidation reaction was conducted during 3 h in a glass reactor with mechanical stirring, supported by a thermostatic bath at 60 ºC (isoperibollical approach), and with single addition of the reactants. The purified samples (periodically collected) were analyzed in terms of iodine and oxirane indexes, according to the methods described by the American Oil Chemists' Society [3].

3. Results and discussion

The epoxidation of vegetable oils is highly exothermic, with an efficient thermal exchange essential for avoiding thermal runaway problems [4]. Considering that, the isoperibollical approach provides valuable information about the thermal effects in the reaction system. Figure 1 pairs the main values considered for comparison between the epoxidation of SO and HOSO.

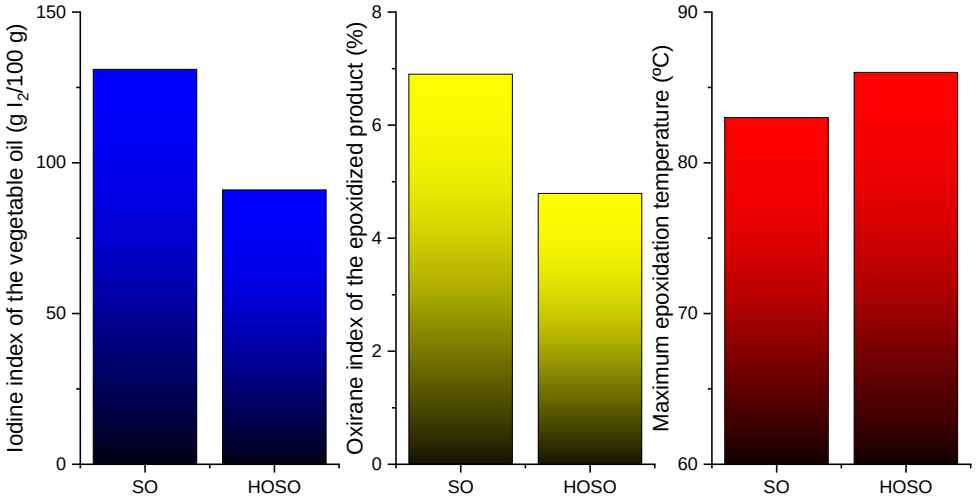

Figure 1. Iodine index of the vegetable oil (SO/HOSO), oxirane index of the epoxidized product (ESO/EHOSO), and maximum temperatures achieved in the epoxidation process.

As expected, since SO presents a higher iodine index than HOSO (i.e., a higher double bond content), the correspondent epoxidized products followed the same tendency in terms of oxirane groups generated: ESO achieved a higher oxirane index than EHOSO. Both experiments resulted in a temperature overshoot due to the exothermicity of the reaction, followed by a decrease in temperature due to the thermal effects of the bath. However, even with a lower amount of double bonds available for epoxidation, HOSO achieved a higher value for the maximum temperature in the epoxidation reaction. Considering that HOSO is richer in one double bond chains, while SO contains a much higher amount of two and three double bond chains, the experimental results suggested that the first double bond tends to be more reactive than the second and third double bonds, possibly due to steric hindrance effects [2].

The results were also used to improve a kinetic model for the epoxidation system, separating the kinetics of the epoxidation reaction itself into three contributions, each one associated with the number of double bonds present in the chain. The estimated kinetic constants corroborated the experimental observations, leading to a higher kinetic constant for chains containing one double bond than for chains with two and three double bonds [2,4].

4. Conclusions

The present study aimed to better understand the reactivity of different double bonds in the epoxidation of vegetable oils, comparing conventional soybean oil and high oleic soybean oil. The experimental and modeling results suggested differences in the reactivity of the double bonds.

References

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Keywords

Epoxidation; Reactivity; Soybean oil; High oleic soybean oil.