

Comparative Evaluation of Catalytic Methods for Soybean Oil Epoxidation: Physicochemical Characterization and Process Performance

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Abstract

Epoxidized soybean oil (ESBO) is a valuable bio-based intermediate for plasticizers, adhesives, and biocomposites, yet the influence of catalytic system selection on its physicochemical properties remains insufficiently benchmarked under standardized conditions. This study comparatively evaluated three catalytic epoxidation systems for soybean oil (SBO); (i) 85% formic acid (FA) with 35% hydrogen peroxide (H₂O₂), (ii) FA combined with sulfuric acid (H₂SO₄) and H₂O₂, and (iii) glacial acetic acid (AA) with H₂O₂, under identical reaction conditions (65 °C, 600 rpm, H₂O₂ loading of 2 mol/mol of C=C, 50 min addition time (t_{add}), and 6 h stirring (t_{str}), for a total reaction time (t) of 6.8 h). The resulting epoxidized products (ESBO1, ESBO2, and ESBO3, respectively) were characterized for oxirane oxygen content (OOC), iodine value (IV), acid value (AV), viscosity (η), density (ρ), color, and conversion of unsaturation (XSBO). The AA system (ESBO3) achieved the highest OOC (6.8 wt%), the lowest IV (1.91 ± 0.01 g/100 g) and AV (0.60 ± 0.01 mg KOH/g), the highest η (332 ± 1 cP) and ρ (0.996 ± 0.001 g/mL), and the lightest product color, corresponding to an XSBO of 98.53% within 6.8 h. In contrast, the FA-only system (ESBO1) exhibited the lowest OOC (3.5 wt%) and the highest IV (8.65 ± 0.01 g/100 g) and AV (0.87 ± 0.01 mg KOH/g), while the mixed FA/ H₂O₂ system (ESBO2) showed intermediate performance (OOC 5.8 wt%; IV 3.12 ± 0.01 g/100 g). These results, which are comparable to or exceed literature benchmarks (OOC 6.2–7.45 wt%; XSBO 95.2–98.53% at t of 2.3–10.42 h), indicate that AA system provides a superior balance of epoxidation efficiency, product stability, and t relative to FA systems, and represents the most promising catalytic procedure for the epoxidation of SBO under the tested conditions.

Highlights

- Three in-situ peracid catalytic systems for soybean oil epoxidation were evaluated under identical reaction conditions.
- The glacial acetic acid/H₂O₂ system (ESBO3) achieved the highest oxirane oxygen content (6.8 wt%) and lowest iodine value (1.91 g/100 g), outperforming formic acid systems.
- ESBO3 reached 98.53% epoxidation conversion (X_{SBO}) within 6.8 h, demonstrating competitive time efficiency relative to literature benchmarks.
- Minimum acid value (0.60 mg KOH/g) in ESBO3 confirms suppressed oxirane ring-opening and enhanced product stability.
- Comprehensive physicochemical characterization (for OOC, IV, AV, η , ρ , and color) provides a multi-parameter performance framework for industrial plasticizer and lubricant applications.

1. Introduction

The increasing global emphasis on sustainable and environmentally friendly materials has led to significant research and development efforts toward using renewable resources. Within this context, the growing preference for biobased resources underscores the importance of developing methodologies that optimize the properties of bio-oils and technologies. One of the most widely used bio-oils is soybean

oil (SBO), which primarily consists of triglycerides derived from soybean. It consists predominantly of unsaturated fatty acids (UFAs), including linoleic acid (polyunsaturated) and oleic acid (monounsaturated), as well as a smaller proportion of saturated fatty acids (SFAs). The high number of double bonds in its fatty acid composition makes SBO well-suited for epoxidation. The conversion (X_{SBO}) of these double bonds into epoxide groups enhances the oil's reactivity and thermal stability while enabling a wide range of functional applications. Epoxidation changes the structure of SBO, making it a versatile starting material for creating biobased chemicals. Compared with unmodified SBO, ESBO results in several enhanced properties. These enhancements include increased crosslinking potential due to the presence of epoxide groups, improved mechanical properties such as tensile strength and elasticity, and increased chemical resistance. Understanding the structure-property relationships allows researchers to tailor ESBO for specific applications. These applications include their use as plasticizers in poly (vinyl chloride) (PVC) formulations, where it enhances flexibility and mechanical performance [1–3]; in adhesives and coatings, where it contributes significantly to improved adhesion properties and durability [4–6]; and in biocomposite matrices, where it enhances biodegradability and mechanical performance [5].

The epoxidation process involves adding an oxygen atom to the double bonds of UFAs, leading to the formation of an epoxide (or oxirane) ring (see points A and A* in Fig. 1). Common reagents used in this reaction include peracids, such as peracetic acid and performic acid [7], as well as hydrogen peroxide (H_2O_2) in the presence of acid catalysts. Studies have indicated that mixed acid catalysis using formic and mineral acids such as sulfuric acid (H_2SO_4) can enhance the epoxidation of kapok seed oil [8]. Previous studies have demonstrated that several catalytic systems, including performic acid, peracetic acid, H_2SO_4 -assisted systems, and heterogeneous catalysts, are capable of producing epoxidized soybean oil (ESBO) with acceptable oxirane yields. However, most investigations have focused on optimizing a single catalytic route, making direct comparisons among commonly employed homogeneous catalytic systems under comparable laboratory conditions relatively scarce. Consequently, there remains insufficient experimental evidence to clearly compare the relative advantages, limitations, reaction efficiency, and physicochemical characteristics obtained from these conventional catalytic systems under similar experimental conditions. Various other catalytic systems have been investigated to increase the efficiency of the epoxidation process. Cai et al. [9, 10] significantly demonstrated that the use of titanium silicalite-1 (TS-1) zeolite as a catalyst could increase the yield and selectivity of the epoxidation of linoleic acid. The epoxidation reaction mechanism is often concerted, meaning that the reaction occurs in a single step, with the epoxide ring formed as the double bond is attacked by the electrophilic oxygen. Current studies have assessed critical factors such as the oxirane oxygen content (OOC), iodine value (IV), acid value (AV), viscosity (η), density (ρ), and color, all of which are vital for determining the suitability of oil for specific applications. The catalytic system is one of the key parameters influencing the epoxidation reaction. Optimization of this parameter can enhance the reaction yield and selectivity, thereby expanding the potential applications of ESBO. Ongoing research aims to optimize the epoxidation process through various innovative approaches, including catalyst development and process intensification [11]. As research progresses, new formulations may leverage

the unique properties of ESBO, expanding its applications [3]. Previous studies consistently reported that performic acid systems provide relatively high epoxidation efficiency but may promote oxirane ring-opening reactions under strongly acidic conditions. H_2SO_4 -assisted systems were shown to accelerate reaction kinetics; however, excessive acidity may also increase side reactions. Acetic acid (AA)/ H_2O_2 systems generally produce higher oxirane contents with improved product quality but usually require longer reaction times [12, 13]. Petrović et al. [14] investigated the epoxidation of SBO using in situ generated peroxyacetic and peroxyformic acids and reported that the reaction followed approximately first-order kinetics with respect to the double-bond concentration. They found that the apparent rate constants increased markedly with temperature (T) and that peroxyformic acid exhibited higher reaction rates than peroxyacetic acid at 40 and 60°C, whereas the difference diminished at higher T . Importantly, their results also demonstrated that increasing X_{SBO} can be accompanied by deviations from the expected kinetic behavior, indicating the contribution of secondary reactions at advanced stages of epoxidation. In another study, Boyacá and Beltrán [15] reported a maximum OOC of 6.4% for SBO epoxidized using H_2O_2 , AA, and H_2SO_4 at 80°C, demonstrating the effectiveness of homogeneous acid catalysis for generating ESBO. However, subsequent kinetic investigations showed that sulfuric-acid-catalyzed systems can also promote oxirane-ring-opening reactions, particularly under conditions of increased acidity, T , and interfacial contact, thereby reducing the attainable oxirane content and selectivity. More recently, Meadows et al. [12] directly compared formic- and acetic-acid-based epoxidation of SBO at different H_2O_2 ratios and reaction times. Their results showed that the formic-acid system provided higher OOC and X_{SBO} under the investigated conditions, with the optimum condition reported at 6 h and a H_2O_2 -to-unsaturation molar ratio of 2.0, yielding an OOC of 7.45% and approximately 98% relative X_{SBO} . These studies collectively demonstrate that the catalytic system and reaction conditions substantially influence both X_{SBO} and oxirane formation; however, the reported results were generally obtained under different experimental conditions, making direct comparison among FA/ H_2SO_4 -assisted, and AA-based systems difficult.

Despite these advances, direct comparison of conventional catalytic systems for SBO epoxidation remains challenging because previous studies have employed substantially different reaction temperatures, acid concentrations, H_2O_2 excesses, and mixing conditions. Consequently, differences in reported OOC or X_{SBO} cannot always be attributed exclusively to the catalytic system. In this context, the present study does not seek to introduce a new catalyst or claim optimization of an individual catalytic route. Instead, its objective is to comparatively evaluate three established catalytic systems, formic acid (FA)/ H_2O_2 , FA– H_2SO_4 / H_2O_2 , and AA/ H_2O_2 , under standardized experimental conditions and using a common stoichiometric basis defined by the initial C = C content of SBO. The resulting OOC, IV, AV, η , ρ , and color are evaluated together to identify the differences and trade-offs associated with each catalytic system.

2 Methods

2.1 Materials

The main raw material used in the present study is refined SBO, obtained from Kamjed Co. (Tehran, Iran). The specifications can be found in Table 1.

Table 1
Specifications of primary SBO

Parameter	Result	Unit	Standard
EV	0.5	meq/kg	ASTM D1652-11(2019) [16]
IV	130	g/100 g	ASTM D5554-15(2021) [17]
AC	0.2	mg(KOH)/g	ASTM D1045-19 [18]
η	82	cP @ 25°C	-
ρ	0.914	g/ml @ 20°C	-
Color	Bright yellow	-	-
Moisture	0.06	%wt	-
Solid Particles	None	-	-

FA (85%), H₂SO₄ (98%), and H₂O₂ (35%) were supplied by Neutron Co. (Tehran, Iran), whereas glacial AA and all analytical-grade reagents were purchased from Merck (Darmstadt, Germany). FA was employed in procedures 1 and 2, H₂SO₄ in procedure 2, and glacial AA in procedure 3, while H₂O₂ served as the oxidizing agent in all epoxidation experiments. For OOC determination according to ASTM D1652-11(2019), tetramethylammonium bromide (TMAB) and perchloric acid (HClO₄) were used. IV was determined following ASTM D5554-15(2021) using sodium thiosulfate (Na₂S₂O₃), sodium bicarbonate (NaHCO₃), sodium chloride (NaCl), glacial AA, and starch indicator. AV was measured according to ASTM D1045-19 using potassium hydroxide (KOH) and glacial AA. Distilled water was used for the preparation of solutions and throughout all analytical procedures. All reagents were of analytical grade and were purchased from Merck (Darmstadt, Germany).

2.2 Experimental

This study employed three distinct procedures to produce ESBO. The detailed procedures for each method are described below. All procedures were executed to compare epoxidation of SBO based on background studies. The varying catalysts and conditions allowed for a comparative analysis of the performance of each method in producing ESBO.

Procedure 1 (ESBO1) ESBO1 was synthesized in a 500 mL three-neck glass reactor equipped with a mechanical stirrer, thermometer, and dropping funnel. A total of 195.2 g of refined SBO, containing approximately 1.00 mol of C = C double bonds (calculated from the IV of the oil), was introduced into

the reactor. The reaction mixture was heated in a thermostatically controlled water bath and maintained at $65 \pm 1^\circ\text{C}$ under continuous stirring at 600 rpm. According to a molar ratio of C = C bonds:FA:H₂O₂ = 1.0:0.5:2.0, 27.1 g (0.50 mol) of 85 wt.% FA was added to the reactor. Subsequently, 194.3 g of 35 wt.% H₂O₂ solution (equivalent to 2.00 mol H₂O₂) was added dropwise over 50 min (t_{add}) while maintaining the reaction T below 65°C to control the exothermic reaction. After complete addition of H₂O₂, the reaction mixture was maintained at 65°C for 6 h (t_{str}) under continuous stirring. Upon completion of the reaction, the mixture was transferred to a separatory funnel, and the organic phase was separated. The product was washed successively with 5 wt.% NaHCO₃ solution, 5 wt.% NaCl solution, and finally 1 wt.% NaHCO₃ solution until a neutral pH was achieved. Residual water and volatile compounds were removed under reduced pressure using a rotary evaporator [12].

Procedure 2 (ESB02) The epoxidation reaction was carried out following the same experimental procedure described for ESB01. Briefly, 195.2 g of refined SBO (equivalent to approximately 1.00 mol of C = C double bonds) was introduced into the reactor and heated to $65 \pm 1^\circ\text{C}$ under continuous stirring at 600 rpm. FA (27.1 g, 0.50 mol) was added together with 0.39 g of H₂SO₄ (0.2 wt.% relative to SBO), which served solely as a homogeneous catalyst and therefore was excluded from the stoichiometric molar ratio calculations. Subsequently, 194.3 g of 35 wt.% H₂O₂ solution (2.00 mol H₂O₂ equivalent) was introduced dropwise over 50 min. After complete H₂O₂ addition, the reaction was continued for 6 h at 65°C . The reaction product was purified following the same washing and drying process described for procedure 1 [8, 12, 19, 20].

Procedure 3 (ESB03) The experimental procedure was similar to that described in ESB01, except that glacial AA was used as the oxygen carrier instead of FA. A total of 195.2 g of refined SBO (approximately 1.00 mol of C = C double bonds) was charged into the reactor and heated to $65 \pm 1^\circ\text{C}$ under continuous stirring at 600 rpm. Based on a molar ratio of C = C bonds:AA:H₂O₂ = 1.0:0.5:2.0, 30.0 g (0.50 mol) of glacial AA was added to the reactor. Subsequently, 194.3 g of 35 wt.% H₂O₂ solution (2.00 mol H₂O₂ equivalent) was added dropwise over 50 min. After H₂O₂ addition, the reaction mixture was maintained at 65°C for 6 h under continuous stirring. The resulting product was purified following the same washing and drying process described for ESB01 [11, 21]. The simplified typical molecular structure of SBO and a schematic of all the reactions described above are shown in Fig. 1. For a meaningful comparison among the three systems, all experiments were performed under identical operating conditions, including reaction T , stirring speed (n), H₂O₂ addition protocol, reaction time (t), purification process, and reactant stoichiometry. The stoichiometric ratios were established on the basis of the initial C = C bond content of SBO rather than the total triglyceride content. H₂SO₄ in ESB02 was employed solely as a homogeneous catalyst and, therefore, was excluded from the stoichiometric molar ratio calculations. The detailed reaction conditions and reagent compositions used in each procedure are summarized in Table 2.

Table 2
Comparison of the reaction conditions, reagent quantities, and stoichiometric molar ratios used in the three epoxidation procedures. All molar ratios were calculated based on the initial C = C bond content (unsaturation basis) of SBO.

Parameter	ESB01	ESB02	ESB03
Unsaturation basis	1.00 mol C = C	1.00 mol C = C	1.00 mol C = C
FA	0.50 mol	0.50 mol	-
AA	-	-	0.50 mol
H ₂ SO ₄ [*]	-	0.2 wt.% relative to SBO	-
H ₂ O ₂	2.00 mol	2.00 mol	2.00 mol
<i>T</i>	65°C	65°C	65°C
<i>n</i>	600 rpm	600 rpm	600 rpm
<i>t</i> _{add} ^{**}	50 min	50 min	50 min
<i>t</i> _{str} ^{***}	6 h	6 h	6 h
[*] H ₂ SO ₄ was additionally used in ESB02 only			
^{**} H ₂ O ₂ addition time			
^{***} Stirring time after H ₂ O ₂ addition			

The OOC quantifies the amount of oxirane rings present in ESB0 and is a key indicator of the extent of epoxidation. In the present study, the OOC was determined according to ASTM D1652-11(2019) using the manual titration method. The analysis was carried out by titration with standard HClO₄ in the presence of excess TMAB. Under these conditions, hydrogen bromide (HBr) is generated *in situ*, promoting rapid oxirane ring opening and enabling the quantitative determination of OOC. The OOC is widely used to evaluate the efficiency and selectivity of the epoxidation process [19]. Moreover, it directly influences the curing behavior and cross-linking density of epoxy resins derived from ESB0; higher OOC values generally correspond to greater cross-linking potential, resulting in improved mechanical strength and thermal stability [22]. In coating and adhesive applications, OOC is also an important parameter affecting hardness, adhesion, and durability of the final products [23].

The IV (or iodine adsorption value or iodine number) is a critical parameter that addresses the issues of oxidative stability and resistance to degradation of oil. It is defined as the number of grams of iodine absorbed by 100 grams of oil. Oils with higher IVs tend to be more reactive and susceptible to oxidation, which can impact the shelf-life and performance of the final products [10, 24]. A moderate IV ensures an optimal balance between reactivity and stability, contributing to desirable properties in

applications such as coatings and adhesives [25]. The IV was measured for synthesized samples according to *ASTM D5554-15(2021)*.

The AV of ESBO refers to the amount of free fatty acids (FFAs) present in the oil. This indicates the degree of oxidation the oil has undergone, reflecting its quality and stability. A higher AV may suggest the presence of FFAs and can be indicative of oil degradation. A higher AV typically correlates with lower oil quality and increased rancidity. This parameter is an important indicator of oil stability, especially during storage and exposure to heat and light. The AV was determined via the titration method for all the samples according to *ASTM D1045-19*.

The η increases with increasing chain length (number of carbon atoms) and increasing oil saturation. FFAs are responsible for increasing η . As the oxidation of FFAs continues, additional FFAs are produced, resulting in the opening of double bonds and the formation of long-chain heavy molecules, which leads to an increase in η [10]. A rheometer (ViscoStar, PolyVISC) was used to measure the viscosities of the samples.

The increase in ρ is linked to the degree of epoxidation, indicating that more epoxy groups contribute to denser oil due to enhanced intermolecular interactions. The introduction of oxygen from these epoxy groups results in a more compact molecular structure. All samples were measured at 20°C via a stainless-steel liquid pycnometer. The endpoints of the titrations were controlled by the pH values measured by a pH meter (HI 2211 benchtop model).

The color of ESBO can be indicative of its quality and purity. A dark or inconsistent color may suggest degradation or the presence of impurities, which can affect performance. Monitoring color helps maintain high standards in production processes. In many applications, particularly in coatings and finishes, color plays a significant role in the final product quality. The color can also correlate with the chemical composition of the oil, which may influence its physical properties, such as η and curing behavior. Additionally, there is a direct relationship between color change and the degree of oil oxidation [26]. The color of ESBO is typically measured via the *ASTM D1500-24* [27] standardized method, which employs the Gardner color scale in *ASTM D156-23* [28] utilizing the Saybolt color scale. These methods provide a quantitative assessment of color via an automatic colorimeter (PFXi-195/2, Lovibond, England), allowing for consistent evaluation and comparison across different samples. The measurement ensures that the ESBO meets the necessary specifications for various applications. The images of the obtained samples can be found in Fig. 2.

3 Results and Discussion

This study investigated the epoxidation of refined SBO through three distinct catalytic procedures and evaluated various physical and chemical parameters, including the OOC, IV, AV, η , ρ , and color. The results obtained from the three ESBOs are presented in the following sections. The OOC was used as the primary indicator of epoxidation extent, while IV, AV, η , ρ , and color were evaluated as

complementary indicators of the chemical conversion and physicochemical properties of the resulting ESB0s.

3.1 Oxirane Oxygen Content

The OOC increased from 3.5 wt% for ESB01 to 5.8 and 6.8 wt% for ESB02 and ESB03, respectively. This increase indicates that the type of catalytic/oxygen-carrier system had a pronounced effect on epoxide formation under the investigated conditions. Campanella and Baltanás [29], reported that ring-opening degradation occurs rapidly in acidic aqueous H_2O_2 media. The higher OOC obtained in ESB03 may be associated with the in-situ formation of peracetic acid from AA and H_2O_2 , providing an effective pathway for oxygen transfer to the unsaturated sites of SBO. In comparison, FA is more reactive and can generate performic acid more readily, but the resulting system may also be more susceptible to oxirane ring-opening and other acid-catalyzed side reactions [30]. The OOC values obtained in the present study can be further interpreted in comparison with previously reported SBO epoxidation systems. Meadows et al. [12] reported an OOC of 7.45% using FA at 50°C for 6 h with an H_2O_2 to unsaturation ratio of 2.0, whereas Boyacá and Beltrán [15] reported a maximum OOC of approximately 6.4% for an AA/ H_2O_2 system catalyzed by H_2SO_4 . The maximum OOC obtained in the present study (6.8 wt%) is therefore within the range reported for conventional SBO epoxidation systems. However, direct comparison should be made cautiously because the reaction T , acid/catalyst system, reagent ratios, and processing conditions differ among studies. A more comprehensive comparison of the reaction conditions and OOCs is provided in Table 3.

Table 3
Comparison of epoxidation conditions and OOC of synthesized samples and other studies

Sample	Acid/Catalyst	T (°C)	H ₂ O ₂ ratio	Acid/Catalyst ratio	t_{add}^+ t_{str} (h)	OOC (wt%)
ESBO1*	FA	65	2.00 mol/mol C = C	0.50 mol/mol C = C	6.8	3.5
ESBO2*	FA/H ₂ SO ₄	65	2.00 mol/mol C = C	FA:0.50 mol/mol C = C; H ₂ SO ₄ :0.2 wt% SBO	6.8	5.8
ESBO3*	AA	65	2.00 mol/mol C = C	0.50 mol/mol C = C	6.8	6.8
Sun et al. [31]	FA/H ₂ SO ₄	65	0.70 g/g oil	FA:0.13 g/g oil; H ₂ SO ₄ :0.004 g/g oil	3	6.2
Meadows et al. [12]	FA	50	2.0 mol/mol C = C	0.5 mol/mol C = C	6	7.45
Janković et al. [32]	AA / Amberlite IR-120H	65	1.35 mol/mol C = C	AA:0.50 mol/mol C = C; Amberlite:4.04 wt% SBO	10.42	6.58
Mohamed et al. [33]	AA/H ₂ SO ₄	~ 70	1.50 mol/mol C = C	AA:0.50 mol/mol C = C; H ₂ SO ₄ :NR	4.5	6.72
Boyacá & Beltrán [34]	AA/H ₂ SO ₄	80	25% molar excess	AA:5 wt%; H ₂ SO ₄ :2 wt%	2.3	6.4
* Present study						

As shown in Table 3, previously reported OOC values of approximately 6.2–7.45% were obtained using FA or AA-based systems under reaction times ranging from 2.3 h to 10.42 h. The performance of the present catalytic system should therefore be evaluated not only in terms of the maximum OOC achieved, but also considering the reaction time, operating T , and catalyst/acid requirement. This comparison highlights the potential of the proposed system for improving the efficiency of SBO epoxidation.

3.2 Iodine Value

Following the evaluation of OOC, the IV was analyzed to further assess the extent of double-bond consumption during the epoxidation process. The IVs decreased from 8.65 g/100 g in ESBO1 to 1.91 g/100 g in ESBO3. The observed reduction in the IV is likely associated with the conversion of double bonds into epoxy groups. This change reflects a decrease in the degree of unsaturation in the oil produced at higher levels of epoxidation. These findings suggest that the epoxidation conditions in

ESBO3 have significantly improved, facilitating the transformation of UFAs into more stable epoxide structures. Although a lower IV generally indicates higher conversion of C = C bonds, it should not be interpreted as exclusive evidence of epoxy ring formation because side reactions such as ring-opening, hydroxylation, and polymerization may also consume unsaturated bonds [35]. Therefore, simultaneous determination of both IV and OOC is essential for reliable evaluation of the epoxidation process [36].

3.3 Acid Value

To complement the evaluation of epoxidation efficiency, the AV was determined since it provides useful information regarding possible side reactions and residual acidic species. The AVs observed were 0.87 mg (KOH)/g in ESB01, 0.75 mg (KOH)/g in ESB02, and 0.60 mg (KOH)/g in ESB03. Each successive procedure resulted in lower AVs, indicating a reduction in FFAs due to intermolecular interactions. This is because the epoxidation process consumes unsaturated bonds that would otherwise lead to the formation of FFAs. The results align with the understanding of this epoxidation mechanism and confirm the results of the OOC evaluations. The lower AV obtained for ESB03 indicates a reduced concentration of residual acidic species after purification. However, AV is influenced not only by the efficiency of the epoxidation process but also by catalyst residues and hydrolysis reactions. In addition to reflecting the presence of FFAs, elevated AV values may indicate acid-catalyzed epoxy ring-opening reactions occurring during epoxidation. Therefore, the relatively low AV achieved in ESB03 suggests that side reactions were minimized, resulting in improved stability of the synthesized ESBO.

3.4 Viscosity

The η progressively increased: 288 cP for ESB01, 312 cP for ESB02, and 323 cP for ESB03. The η is influenced by the double-bond configuration, with a *cis* double-bond configuration resulting in a lower η than a *trans*-double-bond configuration. The *cis* prefix indicates that the functional groups are on the same side of some plane, whereas the *trans* prefix conveys that they are on opposing (transverse) sides (see Fig. 3). The position of the double bond has a relatively minor effect on η . This increase in η supports the idea that the increased molecular weight and complex structure as a result of greater cross-linking potential is due to a greater degree of epoxidation in oil-based systems. The η increase is likely associated with the introduction of oxygen-containing functional groups together with stronger intermolecular interactions among epoxidized triglycerides. Therefore, η should not be attributed solely to the degree of epoxidation.

3.5 Density

The ρ values recorded across procedures were relatively consistent, with ESB01 having a ρ of 0.988 g/ml, ESB02 also having a ρ of 0.991 g/ml, and ESB03 showing a slight increase to 0.996 g/ml. The increase in ρ correlates with the degree of epoxidation, suggesting that as more epoxy groups are introduced, the oil becomes denser due to increased intermolecular compaction. This is because adding oxygen in the form of epoxy groups can lead to a more compact molecular structure. This relationship highlights the compacting effect of the epoxide groups introduced into the molecular

configuration of the oil. Although this argument is analytically correct and accords with the previous findings, the insignificant difference in the values obtained in this research does not allow us to conclude in this regard. Because the measured ρ differences were very small, ρ alone cannot be considered a reliable indicator of epoxidation efficiency in the present study.

3.6 Color

The color measurements revealed distinct variations across ESB0s. ESB01 displayed a Gardner color number of 1.5, ESB02 had a Gardner color number of 1, and ESB03 had a Saybolt color number of -11. These observations indicate that higher degrees of epoxidation, as seen in ESB02 and ESB03, resulted in lighter colors, reflective of more stable oxidation products and the consumption of chromophoric structures (color-producing) during the reaction. This finding indicates that the chromophoric structures in SBO are the C = C double bonds in the FFA chains, which are partially converted into epoxy rings through the epoxidation process. However, the specific relationship between the degree of epoxidation and color is complex and can depend on other factors, such as the presence of impurities or reaction conditions. In this research, by controlling even possible interfering factors, a significant correlation between color and the degree of epoxidation was observed. The measured properties and the visual observations recorded during each sample are summarized in Table 4.

Table 4
Physicochemical properties and appearance of SBO samples obtained by the three epoxidation procedures

Sample	IV (g/100 g)	AV (mg (KOH)/g)	η (cP @ 25°C)	ρ (g/ml @ 20°C)	Color	Appearance observations
ESB01	8.65 ± 0.01	0.87 ± 0.01	288 ± 1	0.988 ± 0.001	1.5 ^a	Yellow throughout the process
ESB02	3.12 ± 0.01	0.75 ± 0.01	312 ± 1	0.991 ± 0.001	1 ^a	Yellow throughout the process
ESB03	1.91 ± 0.01	0.60 ± 0.01	323 ± 1	0.996 ± 0.001	-11 ^b	Initially white and opaque; became clear and pale yellow after reaction and relaxation
^a ASTM Color according to ASTM D1500-24						
^b Saybolt Color according to ASTM D156-23						

As shown in Table 4, the progressive increase in epoxidation extent was accompanied by changes in the physicochemical properties of the resulting ESB0 samples. The IV decreased from 8.65 ± 0.01 to 1.91 ± 0.01 g I₂/100 g, while the η increased from 275 ± 1 to 332 ± 1 cP at 25°C as the OOC increased from 3.5 ± 0.1 to 6.8 ± 0.1 wt%. This simultaneous decrease in residual unsaturation and increase in η is consistent with the structural modification of the triglycerides during epoxidation. The ρ also increased slightly from 0.988 ± 0.001 to 0.996 ± 0.001 g/mL at 20°C, which is consistent with the incorporation of

oxygen into the oil structure through the formation of oxirane groups. In contrast, the AV decreased progressively from 0.87 ± 0.01 to 0.60 ± 0.01 mg KOH/g, indicating relatively low levels of residual acidic species in the final products. However, AV is affected by residual carboxylic acids, catalyst residues, and hydrolysis and should therefore not be interpreted as a direct measure of epoxidation extent.

The color observations also revealed a clear difference among the procedures. ESB01 and ESB02 retained a yellow appearance throughout the process, whereas ESB03 initially produced a white and opaque mixture that gradually became clear and pale yellow after the reaction and relaxation period. Because ASTM Color and Saybolt Color are different standardized scales, these numerical values should not be directly compared as a single numerical trend. Nevertheless, the visual transition observed for ESB03 suggests a temporary change in the optical appearance of the reaction mixture during epoxidation, followed by clarification after completion of the reaction and relaxation. Overall, the combined OOC, IV, AV, η , ρ , and color results indicate that ESB03 produced the most extensively modified SBO among the three investigated procedures.

3.7 Procedures comparison

ESB01, which utilized FA and H_2O_2 , resulted in the lowest OOC and IVs. This aligns with some findings from Gustavo et al. [11], that suboptimal conditions led to lower performance in terms of SBO epoxidation. In ESB02, the incorporation of H_2SO_4 as an additional catalyst alongside FA improved the OOC, highlighting the efficacy of a mixed acid catalyst and confirming results from other studies that showcased the benefits of using mixed catalyst systems to enhance epoxidation [37]. The IV of the sample is lower than that of the previous sample, which shows that the addition of H_2SO_4 to the catalyst mixture enhances complete conversion. These results are consistent with those of Vianello et al. [13]. For ESB03, the introduction of glacial AA yielded the highest OOC and the lowest IV. Figure 4 compares the OOC and X_{SBO} for the processes investigated in the present study with those reported in previous studies. To calculate the X_{SBO} via the Eq. 1 [38], the IVs of the oil were utilized.

$$X_{SBO} = \frac{(IV_{Initial} - IV_{Final})}{IV_{Initial}} \times 100 \%$$

Equation 1

where $IV_{Initial}$ and IV_{Final} represent the IV values of the starting SBO and final ESB0 products, respectively.

As shown in Fig. 4a, the OOC values obtained in the present study are compared with the corresponding values reported in the literature, while Fig. 4b compares the X_{SBO} of the investigated processes with those reported previously. This comparison provides a direct assessment of the performance of the processes developed in the present study relative to previously reported epoxidation procedures.

To provide an integrated comparison of the overall process performance, the reaction time, X_{SBO} , and OOC of the procedures investigated in the present study were compared with those reported in previous studies, as shown in Fig. 5. In this bubble plot, the reaction time is presented on the x-axis, the X_{SBO} on the y-axis, and the bubble size represents the corresponding OOC. Thus, the figure simultaneously considers process duration, conversion efficiency, and product quality, enabling a more comprehensive assessment of the technical performance of the different epoxidation processes. Processes located toward the upper-left region of the plot, particularly those associated with larger bubbles, represent a more favorable combination of shorter reaction time, higher X_{SBO} , and higher OOC.

Figure 5 provides an integrated comparison of the epoxidation performance of the processes developed in the present study with previously reported approaches. At a constant reaction time of 6.8 h, variation of acid/catalyst resulted in three distinct process profiles (ESB01–ESB03), demonstrating the ability to tune the relationship between X_{SBO} and OOC formation. Among the investigated samples, ESB01 exhibited an OOC of 3.5 wt% at a X_{SBO} of 93.35%, which is substantially lower than the OOC values reported for the literature processes. For comparison, Sun et al. reported an OOC of 6.2 wt% at 95.2% X_{SBO} . Across the literature data considered in this study, OOC values of 6.2–7.45 wt% were generally obtained at X_{SBO} of 95.2–98.53%, with t ranging from 2.3 to 10.42 h. The transition from ESB01 to ESB03 demonstrates the controllability of the epoxidation process. While Janković et al. required longer t to achieve X_{SBO} above 98%, ESB03 attained comparable X_{SBO} (98.53%) within a shorter t of 6.8 h, demonstrating improved time efficiency and systematic control over reaction conditions.

4. Conclusions

Three catalytic systems for the epoxidation of soybean oil, based on FA (ESB01), FA/H₂SO₄ (ESB02), and AA (ESB03), were comparatively evaluated under identical reaction conditions. Among the investigated systems, ESB03 demonstrated the most favorable overall performance, achieving the highest OOC (6.8 wt%) and X_{SBO} (98.53%), together with the lowest IV (1.91 ± 0.01 g/100 g) and AV (0.60 ± 0.01 mg KOH/g). The performance of the AA-based system can be attributed to the efficient in-situ formation of peracetic acid, which promotes epoxidation while limiting acid-catalyzed oxirane ring-opening reactions. In contrast, the FA-based system exhibited lower epoxidation efficiency and greater evidence of oxirane degradation, whereas the addition of H₂SO₄ improved the performance of ESB02 but did not achieve the effectiveness of ESB03. The progressive increase in η and the reduction in color intensity with increasing OOC further supported the observed differences in product quality, while ρ showed limited sensitivity to the extent of epoxidation. Comparison with previously reported systems also indicated that ESB03 achieved an X_{SBO} within the upper range of literature values while maintaining a relatively short t of 6.8 h. Overall, the glacial AA-catalyzed process provided the most favorable balance between conversion, product quality, and t and therefore represents the most promising of the investigated systems for SBO epoxidation under the studied conditions.

Declarations

Author contribution The sole author Mohsen Ghasvari conceived the study, and material synthesis, conducted the experiments, analyzed the data and interpretation, and wrote the original manuscript.

Ethical approval The manuscript is prepared in compliance with the Publishing Ethics Policy.

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Conflict of Interest The authors have declared no conflict of interest.

Data Availability The data supporting the findings of this study are available within the article. Additional raw experimental data are available from the corresponding author upon reasonable request.

References

1. Gilbert M, Patrick S (2017) Poly(Vinyl Chloride). *Brydson's Plastics Materials*. Elsevier, pp 329–388
2. Hahladakis JN, Velis CA, Weber R et al (2018) An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. *J Hazard Mater* 344:179–199. <https://doi.org/10.1016/j.jhazmat.2017.10.014>
3. Sastri VR (2023) Plastics in medical devices. *Handbook of Thermoplastic Fluoropolymers*. Elsevier, p ii
4. Rayung M, Ghani NA, Hasanudin N (2024) A review on vegetable oil-based non isocyanate polyurethane: towards a greener and sustainable production route. *RSC Adv* 14:9273–9299. <https://doi.org/10.1039/D3RA08684D>
5. Jahangiri F, Mohanty AK, Misra M (2024) Sustainable biodegradable coatings for food packaging: challenges and opportunities. *Green Chem* 26:4934–4974. <https://doi.org/10.1039/D3GC02647G>
6. Sobhan A, Ahirekar V, Hoff M, Muthukumarappan K (2023) Derivation and characterization of epoxidized soybean oil and epoxy resin film produced using a three step-washing neutralization process. *Ind Crops Prod* 198:116675. <https://doi.org/10.1016/j.indcrop.2023.116675>
7. Marriam F, Irshad A, Umer I et al (2023) Vegetable oils as bio-based precursors for epoxies. *Sustain Chem Pharm* 31:100935. <https://doi.org/10.1016/j.scp.2022.100935>
8. Putrawan IDGA, Azharuddin A, Jumrawati J (2023) Preparing epoxidized vegetable oil from waste generated by the kapok fiber industry and assessing its thermal stabilization effect as a co-stabilizer for polyvinyl chloride. *Heliyon* 9:e19624. <https://doi.org/10.1016/j.heliyon.2023.e19624>
9. Cai L, Chen C, Wang W et al (2020) Acid-free epoxidation of soybean oil with hydrogen peroxide to epoxidized soybean oil over titanium silicalite-1 zeolite supported cadmium catalysts. *J Ind Eng Chem* 91:191–200. <https://doi.org/10.1016/j.jiec.2020.07.052>

10. Sarin A (2012) Biodiesel : production and properties. Royal Society Of Chemistry, Cambridge SE – 1 vol. (256 p.) : ill. ; 24 cm
11. Olivieri GV, Meira PA, de Mattos TT et al (2023) Microreactor x millireactor: Experimental performance in the epoxidation of soybean oil. *Chem Eng Process - Process Intensif* 193:109562. <https://doi.org/10.1016/j.cep.2023.109562>
12. Meadows S, Hosur M, Celikbag Y, Jeelani S (2018) Comparative Analysis on the Epoxidation of Soybean Oil using Formic and Acetic Acids.pdf. *Polym Polym Compos* 26:289–298. <https://doi.org/10.1177/096739111802600403>
13. Vianello C, Piccolo D, Lorenzetti A et al (2018) Study of Soybean Oil Epoxidation: Effects of Sulfuric Acid and the Mixing Program. *Ind Eng Chem Res* 57:11517–11525. <https://doi.org/10.1021/acs.iecr.8b01109>
14. Petrović ZS, Zlatanić A, Lava CC, Sinadinović-Fišer S (2002) Epoxidation of soybean oil in toluene with peroxyacetic and peroxyformic acids – kinetics and side reactions. *Eur J Lipid Sci Technol* 104:293–299. [https://doi.org/10.1002/1438-9312\(200205\)104:5%3C293::AID-EJLT293%3E30.CO;2-W](https://doi.org/10.1002/1438-9312(200205)104:5%3C293::AID-EJLT293%3E30.CO;2-W)Digital Object Identifier (DOI)
15. Mendivelso LAB, Beltrán ÁA (2010) Soybean epoxide production with in situ peracetic acid using homogeneous catalysis. *Ing e Investig*. <https://doi.org/10.15446/ing.investig.v30n1.15222>
16. ASTM International (2019) Standard Test Method for Epoxy Content of Epoxy Resins. ASTM International, West Conshohocken, PA, USA
17. ASTM International (2021) Test Method for Determination of the Iodine Value of Fats and Oils. ASTM International, West Conshohocken, PA, USA
18. ASTM International (2019) Test Methods for Sampling and Testing Plasticizers Used in Plastics. ASTM International, West Conshohocken, PA
19. Balde I, Kane C, Dime AKD et al (2022) process intensification. *World J Anal Chem* 7:1–6. <https://doi.org/10.12691/wjac-7-1-1>
20. Santacesaria RTRVVRTE, Serio M, Di (2013) Selective epoxidation of soybean oil with performic acid catalyzed by acidic ionic exchange resins.pdf. *Green Process Synth* 2:427–434. <https://doi.org/10.1515/gps-2013-0045>
21. Meadows S, Young C, Abugri D et al (2016) Studies on the synthesis and characterization of epoxidized soybean oil. *Proc Am Soc Compos – 31st Tech Conf ASC 2016*
22. Tan SG, Chow WS (2011) Curing characteristics and thermal properties of Epoxidized soybean oil based thermosetting resin. *JAOCS. J Am Oil Chem Soc* 88:915–923. <https://doi.org/10.1007/s11746-010-1748-x>
23. Mossety-Leszczak B, Pilch-Pitera B, Karaś J et al (2022) The application of liquid crystalline epoxy resin for forming hybrid powder coatings. *Prog Org Coat* 168. <https://doi.org/10.1016/j.porgcoat.2022.106873>
24. Yesilyurt MK, Cesur C, Aslan V, Yilbasi Z (2020) The production of biodiesel from safflower (*Carthamus tinctorius* L.) oil as a potential feedstock and its usage in compression ignition engine:

- A comprehensive review. *Renew Sustain Energy Rev* 119:109574.
<https://doi.org/10.1016/j.rser.2019.109574>
25. Adewale P, Mba O, Dumont MJ et al (2014) Determination of the iodine value and the free fatty acid content of waste animal fat blends using FT-NIR. *Vib Spectrosc* 72:72–78.
<https://doi.org/10.1016/j.vibspec.2014.02.016>
 26. Li X, Wu G, Zheng L et al (2019) Model prediction of color reversion of soybean oil and its quantitative relationship with oxidation under accelerated conditions. *Lwt* 111:270–277.
<https://doi.org/10.1016/j.lwt.2019.05.051>
 27. ASTM International (2024) Standard Test Method for ASTM Color of Petroleum Products (ASTM Color Scale). ASTM International, West Conshohocken, PA, USA
 28. ASTM International (2023) Standard Test Method for Saybolt Color of Petroleum Products (Saybolt Chromometer Method). ASM International, West Conshohocken, PA, USA
 29. Campanella A, Baltanás MA (2005) Degradation of the oxirane ring of epoxidized vegetable oils in liquid-liquid systems: II. Reactivity with solvated acetic and peracetic acids. *Lat Am Appl Res* 35:211–216
 30. Phan HP, Dang-Bao T, Lam H-H (2023) Epoxidation of Soybean Oil and its Blend with Waste Cooking Oil Using H₂SO₄ as Homogeneous Catalyst. *Chem Eng Trans* 106:355–360.
<https://doi.org/10.3303/CET23106060>
 31. ZHAO SUNX, DU X, LIU W D (2010) Preparation of epoxidized soybean oil by catalysis of small amount of sulfuric acid.pdf. *Chin J Process Eng* 10:714–719
 32. Jankovic M, Sinadinovic-Fiser S, Govedarica O et al (2017) Kinetics of soybean oil epoxidation with peracetic acid formed in situ in the presence of an ion exchange resin Pseudo-homogeneous model. *Chem Ind Chem Eng Q* 23:97–111. <https://doi.org/10.2298/CICEQ150702014J>
 33. Mohamed M, Ezzeldin Ramadan AM, Assem Y (2021) Soybean Oil-based Polyol as a Modified Natural Binder for Polyurethane Turf-adhesive. *Egypt J Chem* 64:1093–1099.
<https://doi.org/10.21608/ejchem.2020.31470.2670>
 34. Beltrán ÁA, Boyaca OB (2010) Two-phase kinetic model for epoxidation of soybean oil.pdf. *Ing e Investig* 30:188–196. <https://doi.org/10.15446/ing.investig.v30n2.15749>
 35. FAST AND RELIADLE METHOD FOR MONITORING EPOXIDATION REACTION IN RECYCLED VEGETABLE OILS (ERVO) (2016) USING FTIR-ATR TECHNIQUE.pdf. *J Chil Chem Soc* 61:2763–2766. <https://doi.org/10.4067/S0717-97072016000100003>
 36. Tavassoli-Kafrani MH, van de Voort FR, Curtis JM (2017) The use of ATR-FTIR spectroscopy to measure changes in the oxirane content and iodine value of vegetable oils during epoxidation.pdf. *Eur J Lipid Sci Technol* 119:1600354. <https://doi.org/10.1002/ejlt.201600354>
 37. Sienkiewicz AM, Czub P (2016) The unique activity of catalyst in the epoxidation of soybean oil and following reaction of epoxidized product with bisphenol A. *Ind Crops Prod* 83:755–773.
<https://doi.org/10.1016/j.indcrop.2015.11.071>

38. Martínez RDC, Trujillo CA, Carriazo JG, Castellanos NJ (2023) Soybean Oil Epoxidation Catalyzed by a Functionalized Metal–Organic Framework with Active Dioxo-Molybdenum (VI) Centers.pdf. Catal Lett 153:1756–1772. <https://doi.org/10.1007/s10562-022-04096-y>

Figures

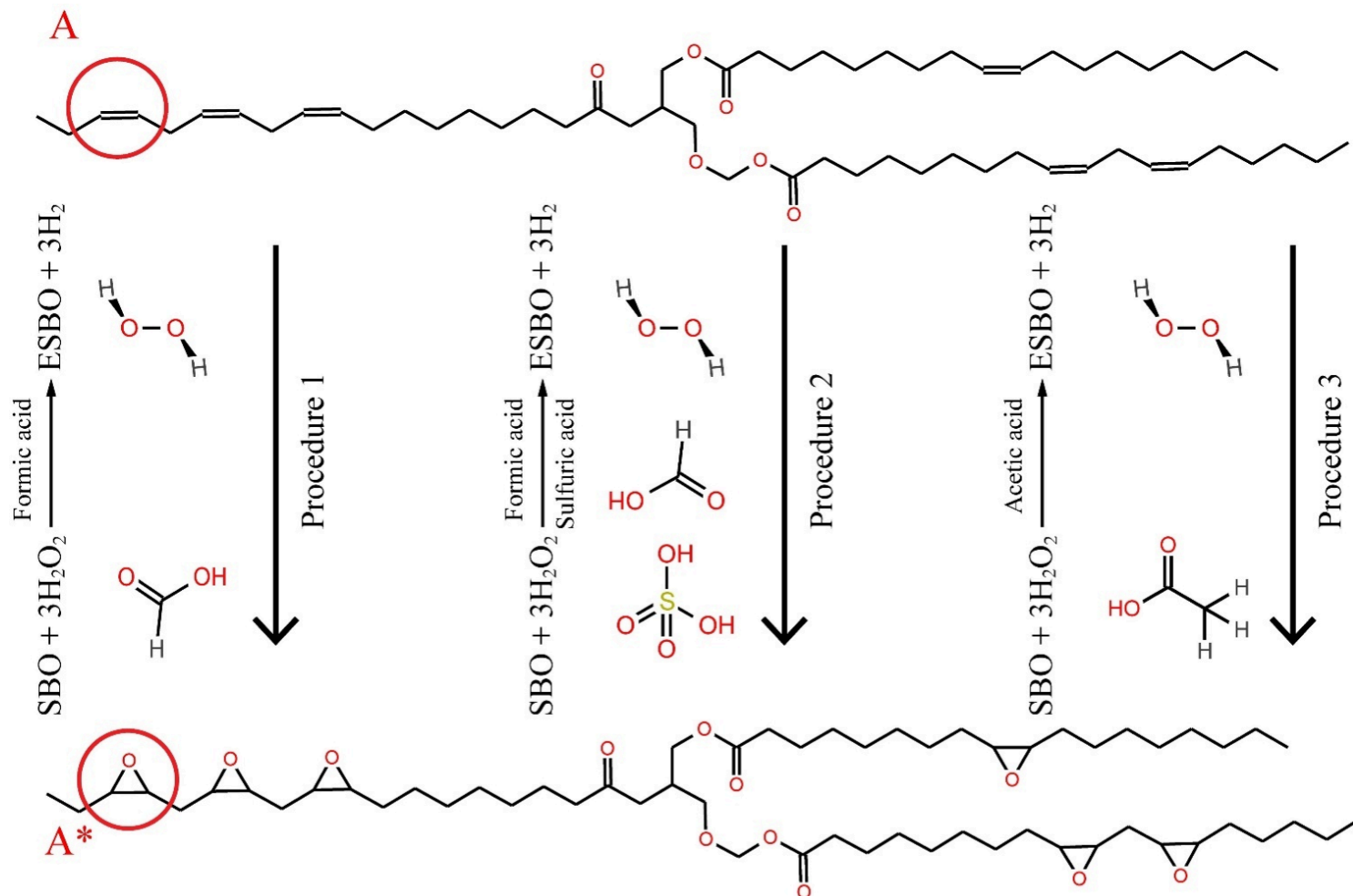


Figure 1

Simplified structure of SBO and epoxidation reactions by various catalysts. Points A and A* illustrated the oxirane ring forming in a site of double bonds.

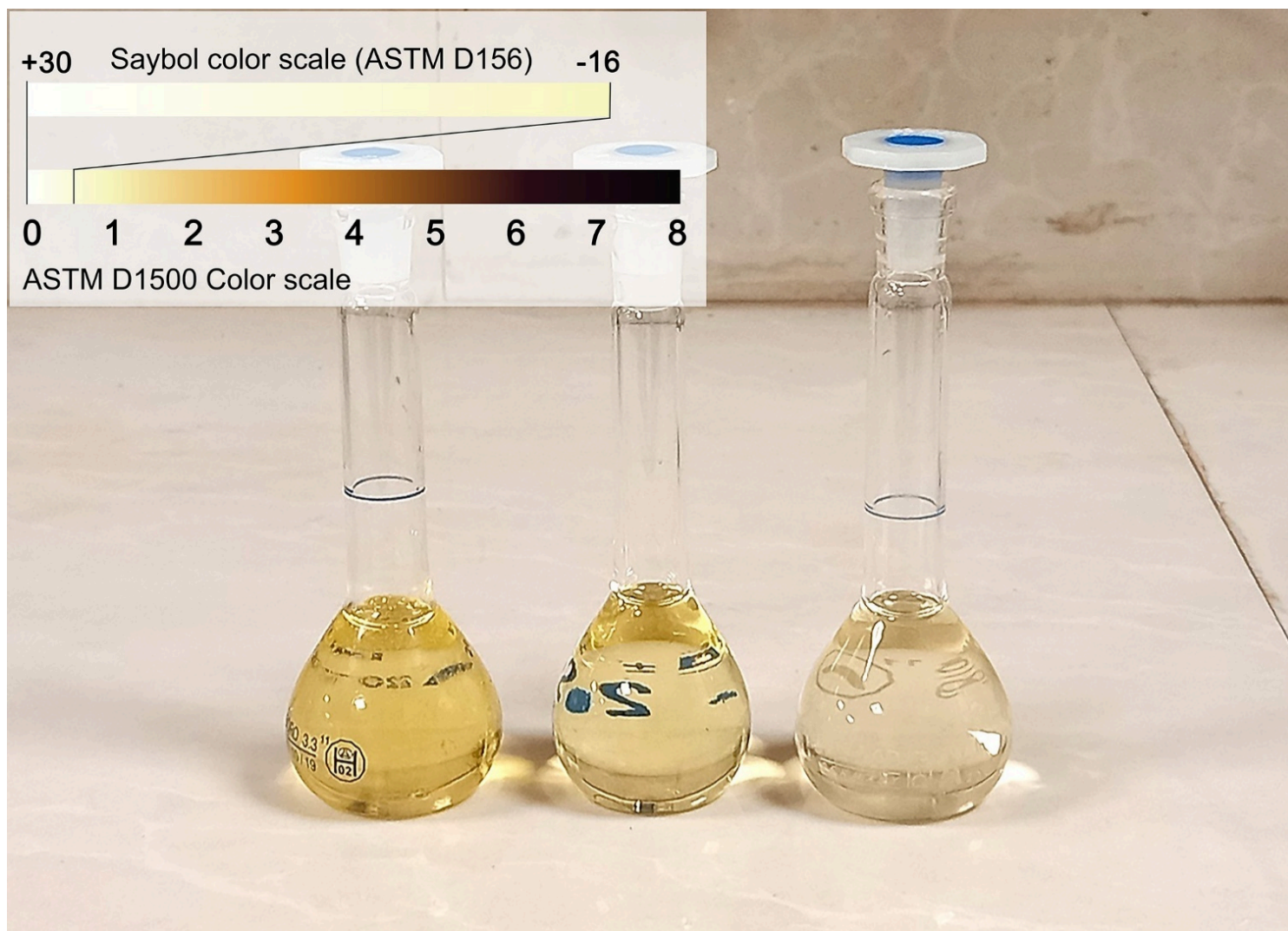


Figure 2

The image of the samples (left) shows ESB01, (middle) ESB02, and (right) ESB03 for visual comparison. The color scale according to ASTM D1500-24 and the saybolt color scale according to ASTM D156-23 can be seen at the top of the image.

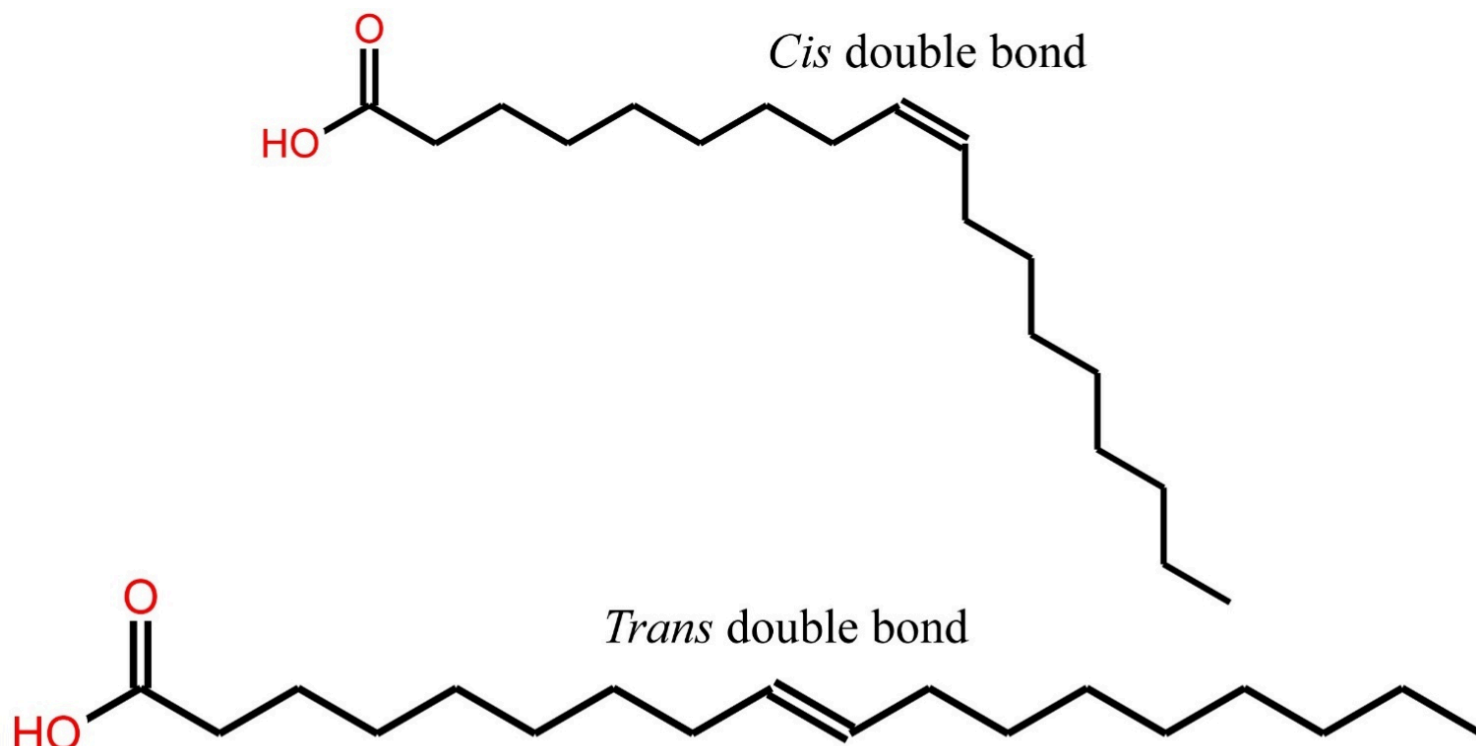


Figure 3

Structure of Cis- and Trans-Fatty Acid (oleic acid)

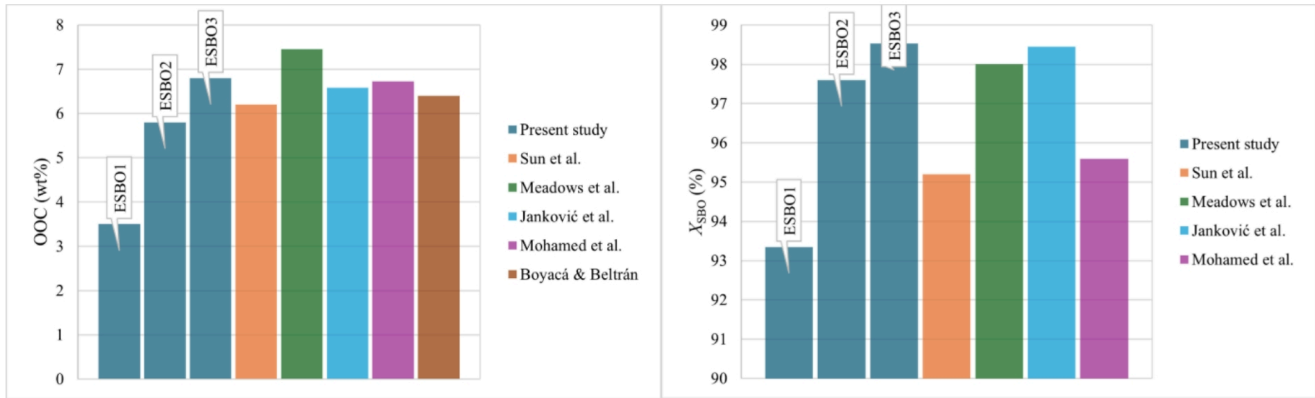


Figure 4

Comparison of the epoxidation performance of the processes investigated in the present study with previously reported processes in terms of (a) OOC and (b) X_{SBO} .

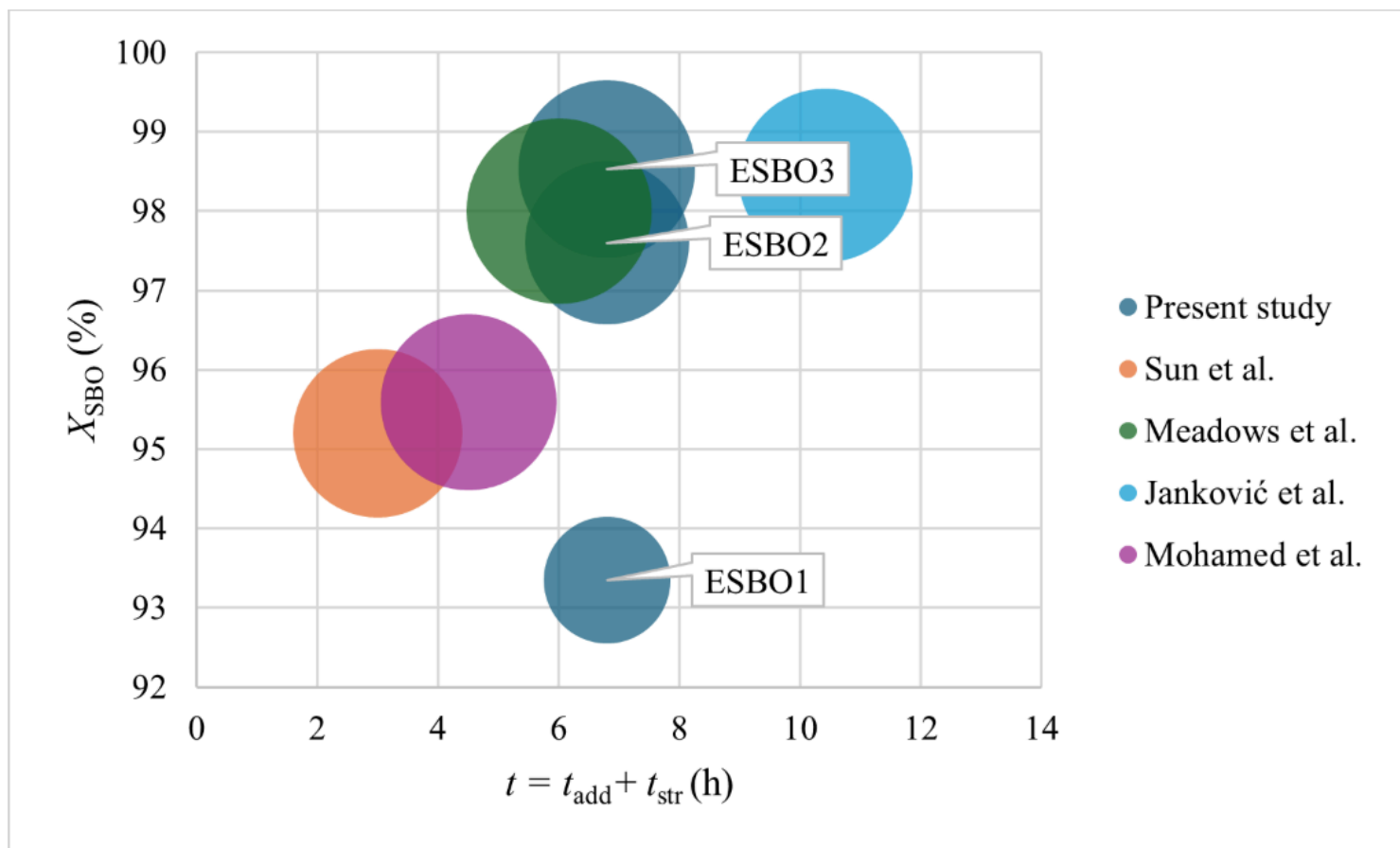


Figure 5

Integrated performance comparison of the epoxidation processes investigated in the present study and previous studies based on reaction time, X_{SBO} , and OOC. The bubble size represents the corresponding OOC, with larger bubbles indicating higher OOC values.

Supplementary Files

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