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Cleaner Production of Epoxidized Cooking Oil Using A Heterogeneous Catalyst

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Abstract: A cleaner solvent-free process of used cooking oil epoxidation has been developed. The epoxidation reactions were carried out using "in situ"-formed peroxy acid. A variety of ion exchange resins with different cross-linking percentages and particle sizes such as Dowex 50WX2 50-100, Dowex 50WX2 100-200, Dowex 50WX2 200-400, Dowex 50WX4 50-100, Dowex 50WX4 100-200, Dowex 50WX4 200-400, Dowex 50WX8 50-100, Dowex 50WX8 100-200, Dowex 50WX8 200-400 were used in the synthesis as heterogeneous catalysts. No significant effect of the size as well as porosity of the catalysts on the properties of the final products was observed. In order to develop a more economically beneficial process, a much cheaper heterogeneous catalyst—Amberlite IR-120—was used and the properties of the epoxidized oil were compared with the bio-components obtained in the reaction catalyzed by the Dowex resins. The epoxidized waste oils obtained in the experiments were characterized by epoxy values in the range of 0.32–0.35 mol/100 g. To reduce the amount of waste, the reusability of the ion exchange resin in the epoxidation reaction was studied. Ten reactions were carried out using the same catalyst and each synthesis was monitored by determination of epoxy value changes vs. time of the reactions. It was noticed that in the case of the reactions where the catalyst was reused for the third and fourth time the content of oxirane rings was higher by 8 and 6%, respectively, compared to the reaction where the catalyst was used only one time. Such an observation has not been reported so far. The epoxidation process with catalyst recirculation is expected to play an important role in the development of a new approach to the environmentally friendly solvent-free epoxidation process of waste oils.

Keywords: ion exchange resins; waste cooking oil; reuse of catalyst; epoxidation; Circular Economy

1. Introduction

The increasing price of petrochemical raw materials, their limited availability and the growing problem of environmental pollution draw the attention of the chemical industry to sustainable development. One of its assumptions is searching for new renewable raw materials that can be successfully used in the synthesis of chemical compounds. An example of such raw materials is vegetable oils, which in terms of chemical structure consist of triglycerides, i.e., esters of glycerol and three fatty acids, mainly unsaturated [1–3]. Waste vegetable oils are also an interesting raw material [3–6]. Syntheses based on such materials are a more ecological solution owing to the possibility of managing waste generated during the frying process. Such an approach implements the requirements of Circular Economy.

Double bonds in fatty acid chains are reactive sites that allow chemical modifications of vegetable oils to increase their possible applications. One of such modifications is the epoxidation process. During this process unsaturated bonds are oxidized to epoxy groups, which are also called oxirane rings [1]. Among several epoxidation methods, the most important process is the use of carboxylic peracids as an oxidizing agent. Industrially, peracetic acid is the most commonly used material, although the process can also be carried out using performic acid, perfluoroacetic acid, perbenzoic acid, m-chloroperbenzoic acid, and m-nitroperbenzoic acid [7]. Carboxylic peracid is formed by the reaction of a proper organic acid with hydrogen peroxide in the presence of a catalyst, usually in the form of strong mineral acids, acidic ion exchange resins (AIER), or enzymes [8].

The process of epoxidation can be carried out in one or two stages. The one-step method is often called in situ epoxidation. In this process, all components, i.e., vegetable oil, organic acid, hydrogen peroxide and catalyst, are mixed in one reaction vessel. In the two-step method, two reactors are used. In the first one, peracid is obtained and then placed in the second vessel where the main epoxidation of the vegetable oil is carried out [9].

During the epoxidation process of vegetable oils, side reactions may occur, especially when the process is carried out in the presence of strongly acidic catalysts. The type of catalyst has a significant impact on the epoxidation process. On an industrial scale, homogeneous catalysts, mainly strong mineral acids, are most commonly used. The use of such compounds leads to a reduction of the process costs and allows obtaining epoxidized oils with a low content of unsaturated bonds [10]. Examples of mineral acids used in the epoxidation process of vegetable oils, both fresh and waste, are H_2SO_4, HNO_3, H_3PO_4, HCl. It has been found that among these catalysts, H_2SO_4 is the most efficient and effective [7,11,12]. However, the disadvantage of homogeneous catalysts is the relatively low selectivity of converting unsaturated bonds into epoxy groups. This effect is caused by the occurrence of side reactions, especially the oxirane ring-opening reaction, which are catalyzed by strong mineral acids. Moreover, the process in the presence of these catalysts leads to considerable amounts of waste water that is difficult to purify [10].

Improvement of process selectivity, by reducing side reactions, can be achieved using heterogeneous catalysts such as acidic ion exchange resins [13]. The most commonly used resins are Amberlyst 15, Amberlite IR-120, and Dowex 50WX2. These catalysts are copolymers of styrene and divinylbenzene and differ in the form and content of the cross-linking agent. It has been proved that the type of the ion exchange resin that is used has an impact on the epoxidation process of vegetable oils [14]. In addition, increasing the concentration of the heterogeneous catalyst usually results in increasing the conversion of unsaturated bonds into epoxide groups [15–18]. The advantages of using acidic ion exchange resins include also the ease of separating them from the finished product and the possibility of re-use. Even after several uses, the loss of activity of this type of catalyst is observed to be insignificant and the efficiency of the process is slightly reduced [15,19,20].

The oxidation of double bonds in fatty acid chains can also be carried out in the presence of enzymatic catalysts, thanks to which the epoxidation process of vegetable oils is more environmentally friendly. What is more, this method allows reducing the number of side reactions and achieve high efficiency and selectivity of the process [21–23]. However, enzymes are characterized by low stability and their activity decreases with an increasing temperature [23]. In addition, re-use of enzymes for catalytic purposes results in a significant reduction in the efficiency of the epoxidation reaction [21].

Temperature also has an important influence on the process of epoxidation of vegetable oils. According to the literature, as the reaction temperature increases, the time needed to achieve high efficiency decreases [24]. However, too high a temperature intensifies side reactions, mainly the opening of oxirane rings [24].

Other factors that affect the epoxidation reaction include the type of oxidizing agent [7], the molar ratio of reactants [8] and the intensity of mixing [25]. Epoxy compounds derived from vegetable and waste oils have many applications. They can be used directly as plasticizers and stabilizers for plastics [26,27]. Epoxy oils are also a raw material for the preparation of many chemical compounds, such as alcohols, glycols, olefinic and carbonyl compounds, epoxy resins, polyesters, or polyurethanes.

This paper reports on the epoxidation of waste oil from a local restaurant with peroxyacetic acid formed in situ from acetic acid and hydrogen peroxide in the presence of ion exchange resin as a heterogenous catalyst. Emphasis was mainly put on determining the process conditions that are consistent with cleaner production. The following four main aspects were taken into account: easy removal of the catalyst, an inexpensive catalyst ensuring adequate product properties, the lowest possible catalyst concentration ensuring adequate conversion in a relatively short epoxidation reaction time, the possibility of reusing the catalyst. The conversion of waste oil into useful chemicals has attracted significant attention in the fields of green and sustainable chemistry and has prompted the implementation of the Circular Economy rules in the polymer technology.

2. Results and Discussion

The experimentally determined initial iodine number of the used cooking oil was 104 gI_2/100 g meaning 0.41 mol of double bonds per 100 g of the used cooking oil. Acidic Ion Exchange Resin (AIER) is an insoluble gel type catalyst in the form of small yellowish organic polymer beads. AIER offers considerable advantages over conventional chemical methods of epoxidation of vegetable oil by improving the selectivity and reducing undesirable side reactions to a certain level [1,5]. In order to determine the most favorable conditions of used cooking oil epoxidation, the effects of different reaction modifications were studied as described further. Firstly, the effect of the content of a heterogenous catalyst on the epoxidation of waste oil was analyzed. The effect of the catalyst concentration on the in situ epoxidation expressed by the changes of the epoxy value over time is presented in Figure 1.

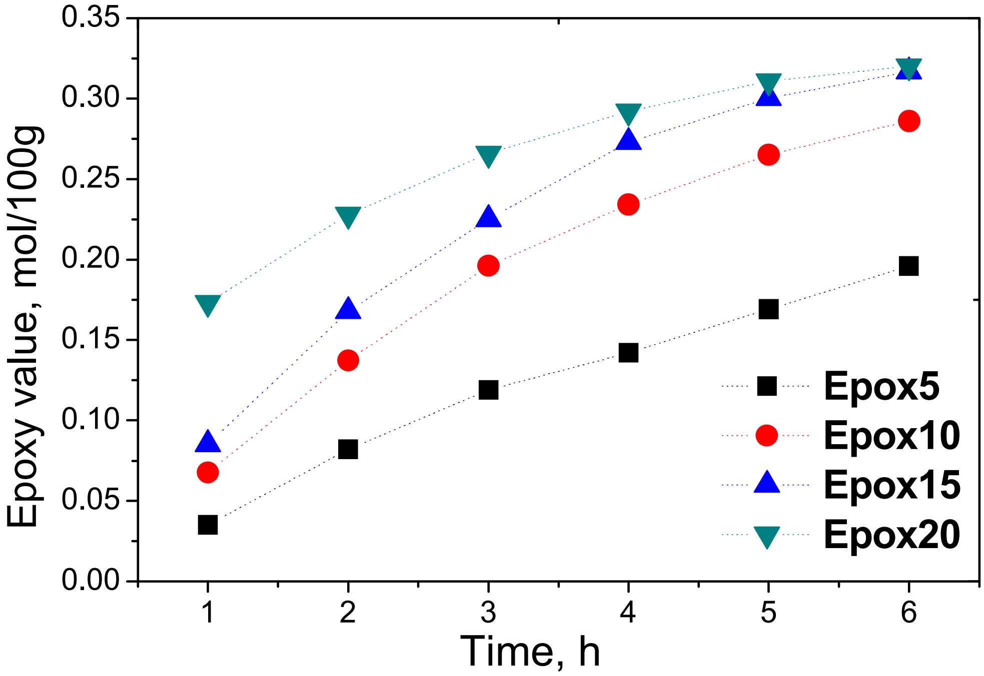

Figure 1. Effect of increasing catalyst concentration on epoxy value of epoxidized used cooking oil.

The oxirane rings content increased monotononically with the reaction time for all reactions. As expected, the efficiency of the reaction is greater when the catalyst concentration is higher. It was observed that after 6 h of the reaction the epoxy values of Epox15 and Epox20 are similar and it is not necessary to increase the catalyst concentration up to 20%. The increase in the intensity of the absorption band during the reaction, characteristic of epoxy groups depending on the catalyst concentration, is presented in Figure 2.

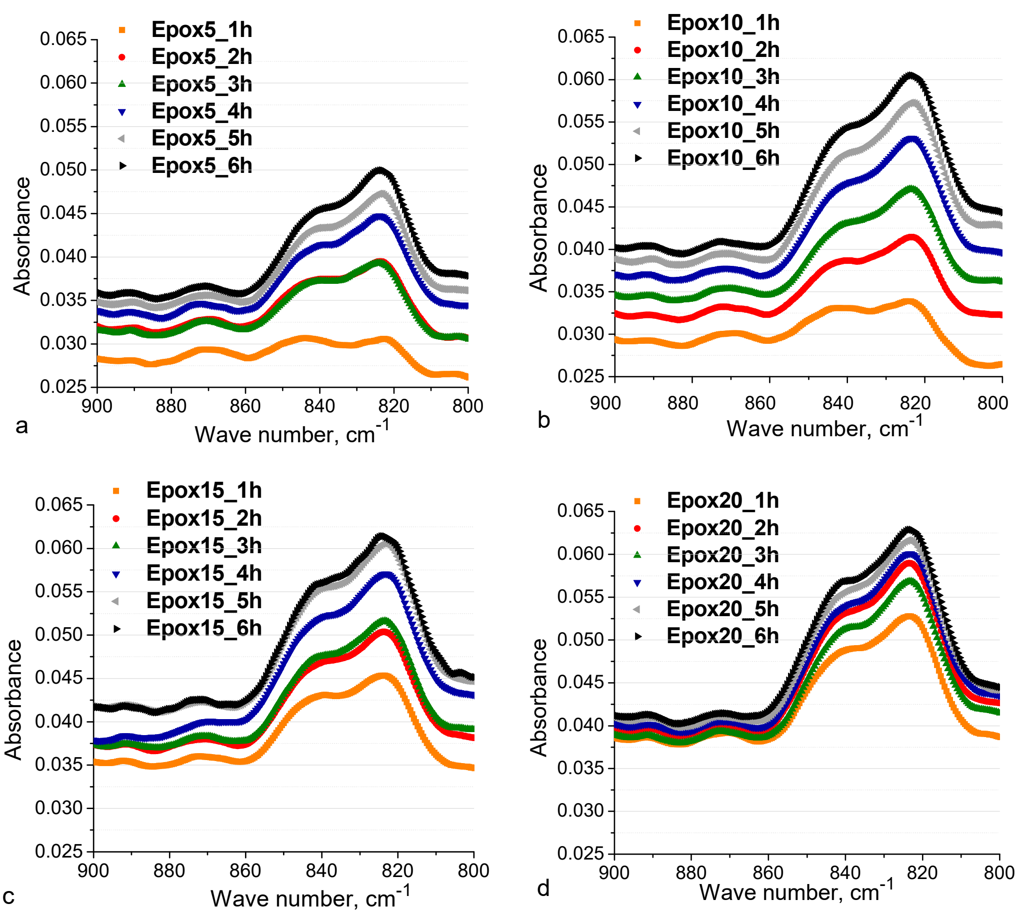

Figure 2. Dependence of absorption band characteristic of epoxy groups on catalyst concentration. (**a**) 5%, (**b**) 10%, (**c**) 15%, and (**d**) 20%.

For Epox5, the peaks in the spectrum exhibit lower intensities compared to the corresponding Epox15 (Figure 2c) and Epox20 (Figure 2d) peaks. The absorbance band intensities correlate with the epoxy number values.

As can be seen in Table 1, the iodine value of the epoxidized used cooking oil confirms a successful epoxidation of the double bonds of the waste oil. Epox20 was characterized by the highest epoxy value and in consequence the lowest iodine value. For all reactions, conversion, efficiency, and selectivity were determined. The epoxy numbers of Epox15 and Epox20 are comparable. Epox15 was characterized by higher selectivity than Epox20, which is associated with a stronger tendency for side reactions to occur when a higher concentration of the catalyst was used.

Table 1. Characteristics of epoxidized UCOs.

Sample	Ev, mol/100 g	Iv, gI$_2$/100 g	Hv, mgKOH/g	C, %	E, %	S, %	Mn, g/mol	Mw, g/mol	D	η, mPa·s
UCO	-	104.0	-	-	-	-	915	921	1.01	68
Epox5	0.241	33.9	3.3	67.4	58.8	87.3	905	912	1.01	145
Epox10	0.313	12.3	1.8	88.2	76.3	86.6	908	915	1.01	218
Epox15	0.334	5.8	2.3	94.4	81.5	86.3	914	921	1.01	226
Epox20	0.339	2.6	2.9	97.5	82.7	84.9	919	926	1.01	266

Ev—content of epoxy groups; Iv—iodine value; Hv—hydroxyl value; E—efficiency; C—conversion; S—selectivity; Mn—number average molecular weight; Mw—weight average molecular weight; D—dispersity; η—viscosity.

As the concentration of the catalyst used in the reaction increases, the viscosity of the epoxidized oils is increased. S. Zoran et al. have shown that an increase in the degree of conversion to oxirane rings correlates with an increase in the viscosity of an epoxidized oil, which is a result of side reactions that can also increase viscosity [13]. There are no major changes in the hydroxyl or acid value that can be correlated with the change in the concentration of the catalyst used in the reaction.

Dinda et al. analyzed the influence of the AIER concentration (10–25 wt.%) on the epoxidation reaction of cottonseed oil. They concluded that when the catalyst loading was increased from 10 to 15 wt.%, the oxirane conversion increased and it was on the same level as after an addition of a greater amount of the catalyst [18]. In the case of Jatropha oil epoxidation, Goud at al. obtained similar results. The maximum conversion to oxirane in an epoxidation reaction conducted with 16% Amberlite IR-120 loading was lower by only 2.7% than that achieved with 20% [28]. It can be concluded that the process of epoxidation of waste oil is the same as in the case of fresh oils and does not require higher catalyst loading due to the presence of oxidation products in used cooking oil.

The efficiency (E), conversion (C), and selectivity (S) of all reactions (Table 1) were found according to the following equations:

$$\mathrm{E} = \frac{\mathrm{Ev}}{\mathrm{Ev_{max}}} \cdot 100\% \tag{1}$$

Ev—the epoxy number of the ester of a vegetable oil after the epoxidation reaction, mol/100 g of epoxidized oil

$\mathrm{Ev_{max}}$—the epoxy number calculated based on the number of unsaturated bonds, mol/100 g of epoxidized oil

$$C = \frac{Iv_0 - Iv}{Iv_0} \cdot 100\% \tag{2}$$

Iv_0—the iodine number of the methyl ester/vegetable oil before epoxidation, $\mathrm{gI_2}$/100 g of oil.

Iv—the iodine number of the methyl ester/vegetable oil after epoxidation, $\mathrm{gI_2}$/100 g of oil.

$$S = \frac{Ev}{Iv_0 - Iv} \cdot 100\% \tag{3}$$

In the reactions carried out, the maximum conversion rate was 97.5%. Espinoza Perez et al. have obtained a conversion rate of 98.5% for the rapeseed oil epoxidation reaction [29]. Espinoza Perez et al. showed a significant effect of conducting the reaction in a solvent (toluene) environment that allows higher conversion rates than the analogous reaction carried out without a solvent [29].

Oil epoxidation may affect its average molar mass. In the environment of epoxidation reactions, partial triglyceride breakdown may occur, resulting in lower molecular weight products such as mono- and diglycerides, free fatty acids, and glycerin. Newly formed epoxide rings may also be opened, and derivatives of higher molecular weight may be formed, which in turn increases the molecular weight. Both trends result in an increase in the dispersion of the resulting reaction product [5].

Based on our research, we concluded that the content of the heterogeneous catalyst did not have a significant effect on the average molar masses of epoxidized waste oils and the compounds obtained were monodisperse. The low dispersion value of the epoxidized oils obtained indicates a small amount of by-products resulting from reactions such as oligomers.

In order to find the effect of particle size and degree of cross-linking AIER on the properties of the epoxidized oil, the experiments were conducted using three different sizes of resin particles as well as resins containing three different amounts of the cross-linking agent. Nine different Dowex resins were used in the study and the results were compared with commonly used Amberlite IR-120. The characteristics of the heterogeneous catalysts are presented in the Table 2 and photographs of the catalysts are shown in Figure 3.

The progress of the reaction was monitored by determining the epoxy number and by a FTIR analysis during the reaction. The epoxy number changes during the reaction and the changes of characteristic bands in the FTIR spectrum are presented in Figures 4 and 5.

Table 2. Characteristics of acidic ion exchange resins (AIER).

AIER		Content of Cross-Linking Agent in Resin, %	Name of Oil Sample	Grain Size, mm	Moisture Content, %	Price [PLN/100 g]
Dowex 50WX2	50–100	2	Epox_2_50-100	0.15–0.30	93.2	713
	100–200	2	Epox_2_100-200	0.07–0.15	87.2	699
	200–400	2	Epox_2_200-400	0.04–0.07	84.9	699
Dowex 50WX4	50–100	4	Epox_4_50-100	0.15–0.30	89.3	600
	100–200	4	Epox_4_100-200	0.07–0.15	89.4	538
	200–400	4	Epox_4_200-400	0.04–0.07	87.9	500
Dowex 50WX4	50–100	8	Epox_8_50-100	0.15–0.30	89.9	523
	100–200	8	Epox_8_100-200	0.07–0.15	89.7	500
	200–400	8	Epox_8_200-400	0.04–0.07	93.5	476
Amberlite IR-120		8	Epox_15	0.62–0.83	85.0	32.1

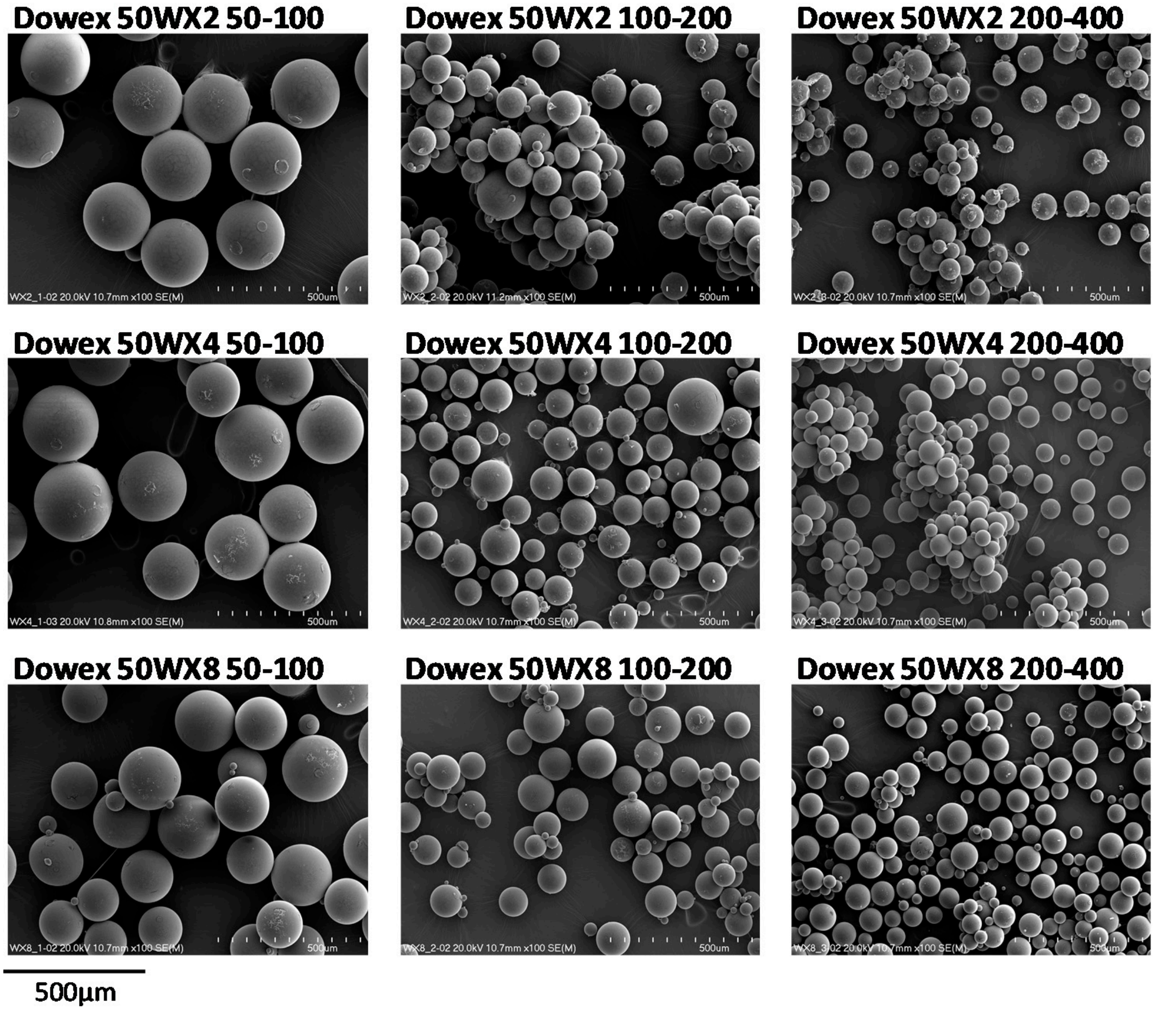

Figure 3. SEM micrographs of Dowex ion exchange resins.

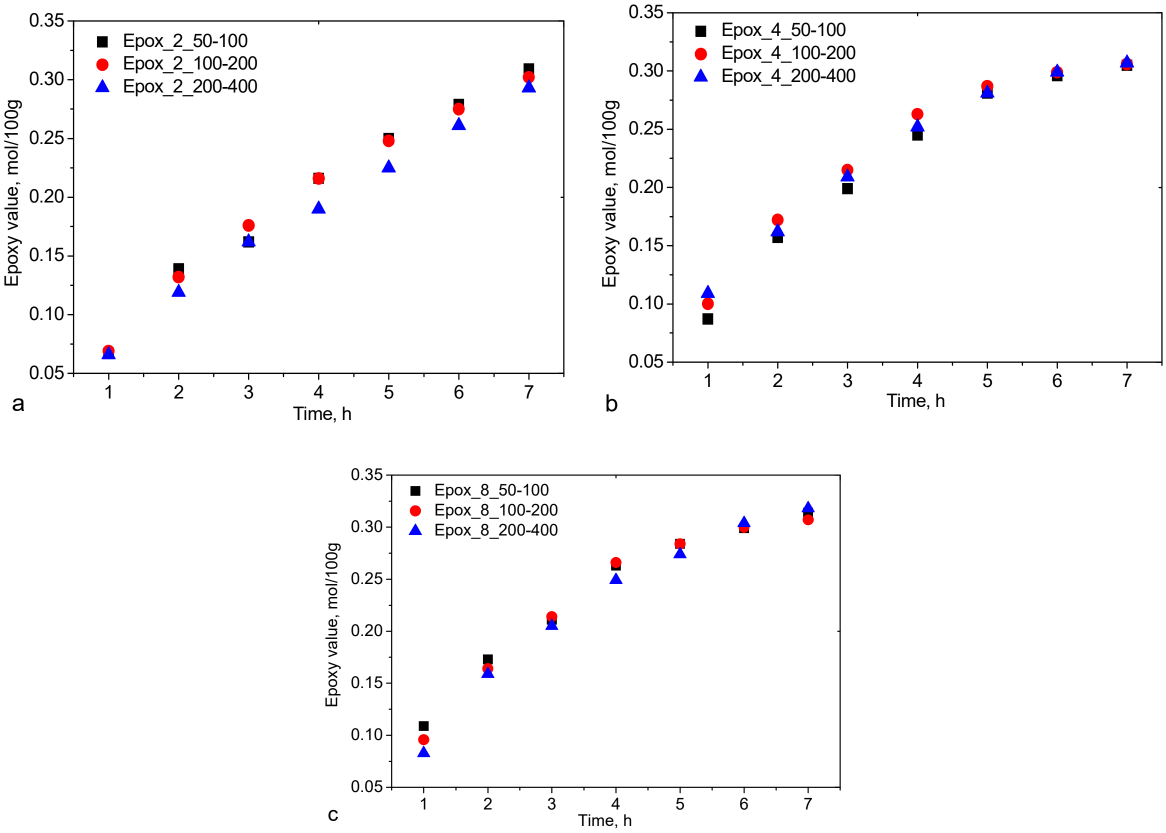

Figure 4. Influence of different grain size of (**a**) Dowex50 × 2, (**b**) Dowex50 × 4, and (**c**) Dowex50 × 8.

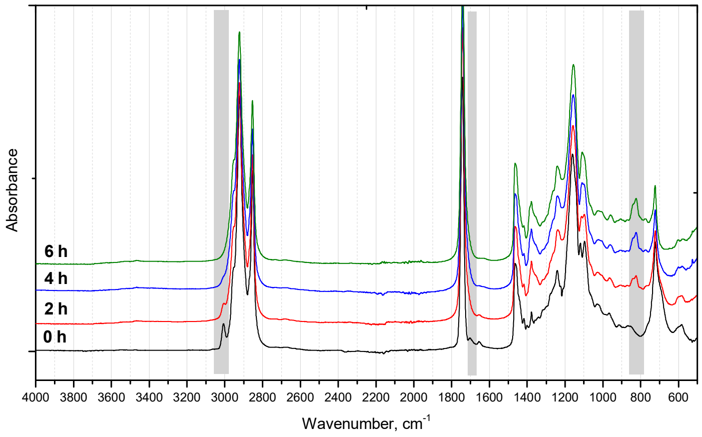

Figure 5. FTIR spectra of samples taken during epoxidation process of Epox_8_200-400.

During all processes, the Ev increased as the reaction progressed, which indicates double bond oxidation in fatty acid chains to form oxirane rings (Figure 4). Slightly lower initial epoxy values were noted for the reaction in the presence of a catalyst containing 2% of the cross-linker. However, no significant difference was observed in the final Evs depending on the type of the catalyst used in the synthesis.

The analysis of FTIR spectra collected during the reaction allowed on-line detection of characteristic groups. In Figure 5, the FTIR spectra of the used cooking oil epoxidation with Dowex50X8 200-400 are shown. In the FTIR spectrum of the waste rapeseed oil, with wave numbers of about 3010 cm^{-1} and about 1650 cm^{-1}, the bands corresponding to the vibrations of the double bonds between carbon atoms are visible. These signals lose their intensity as the epoxidation reaction progresses. Along with the decrease in the intensity of the bands corresponding to the vibrations of unsaturated bonds, the FTIR spectra of the epoxidized oil samples show signals in the range 800–850 cm^{-1}, which are characteristic for epoxy groups.

In all spectra, apart from the signals of epoxy groups, there are also bands at about 2925 and 2850 cm^{-1}, characterized by high intensity. They arise as a result of stretching vibrations of bonds between carbon and hydrogen atoms in the groups $–CH_2–$ and $–CH_3$, occurring in fatty acid chains. Another characteristic band in the spectra of the epoxidized oils is the signal visible at approx. 1740 cm^{-1}, which comes from the stretching vibrations C=O of the ester group.

Ev, Iv, and Hv determinations were carried out for the epoxidized oils obtained (Table 3).

Table 3. Characteristics of epoxidized oil obtained using different AIER.

Sample	Ev, mol/100 g	Iv, gI_2/100 g	Hv, mgKOH/g	C	E	S
Used cooking oil	-	104.0	-	-	-	-
Epox_2_50-100	0.346	9.76	8.89	91	84	93
Epox_2_100-200	0.319	11.11	12.29	89	78	87
Epox_2_200-400	0.324	7.09	12.89	93	79	85
Epox_4_50-100	0.331	9.96	11.29	90	81	89
Epox_4_100-200	0.344	6.36	10.01	94	84	89
Epox_4_200-400	0.337	6.74	12.32	94	82	88
Epox_8_50-100	0.338	8.76	9.85	92	82	90
Epox_8_100-200	0.341	7.54	9.79	93	83	90
Epox_8_200-400	0.353	8.35	8.93	92	86	94

Based on our research it was found that in the case of Dowex resins containing 2% cross-linking agent the highest epoxy value was obtained for the resin with the largest grain size. In the case of resins containing 8% divinylbenzene, the opposite effect was observed. However, the differences in the epoxy numbers are insignificant. Therefore, the results obtained were compared with the epoxy oil (Epox_15) obtained through a reaction with Amberlite resin. This resin has a much lower price compared to Dowex resins. From the point of view of waste oil recycling, it is important to develop a low-cost process. The epoxy number of Epox_15 is slightly lower than the epoxy numbers obtained for the oils synthesized in the presence of Dowex resins containing 8% divinylbenzene, and comparable to resins with 4% cross-linking agent. Dinda et al. conducted epoxidation of cottonseed oil using two very different sizes of resin particles under otherwise similar conditions. The particle sizes were greater than 620 µm and smaller than 120 µm. They concluded that both particle sizes gave nearly the same oxirane conversion [18]. Goud et al. also analyzed the intraparticle diffusional limitations by using two widely differing particle sizes of resin, namely >599 and <64 µm under otherwise the same reaction conditions. They concluded that both particle sizes gave practically the same results [30].

During all epoxidation processes, double bond conversion in the range of 89–94% was achieved. The conversion value for the reaction with Amberlite was 94%. Comparing to the literature data and cases where fresh oils were epoxidized, the values obtained in this study are very favorable. According to literature reports, during oil epoxidation using acetic peroxyacid and in the presence of Amberite IR-120 ion exchange resin, it is possible to achieve about 90% efficiency after 7 h of the process at 65 °C [15]. The oxidation reaction of unsaturated soybean oil bonds, using the same oxidizing agent and catalyst for 10 h and at 60 °C allows achieving about 86.8% double bond conversion and about 86% selectivity [31]. On the other hand, the epoxidation of karanja oil with the use of acetic peracid and Amberlite IR-120 resin leads to approx. 85% yield.

Waste rapeseed oil and its derivatives, in the form of epoxidized oils, were also characterized by a similar molar mass distribution (Figure 6).

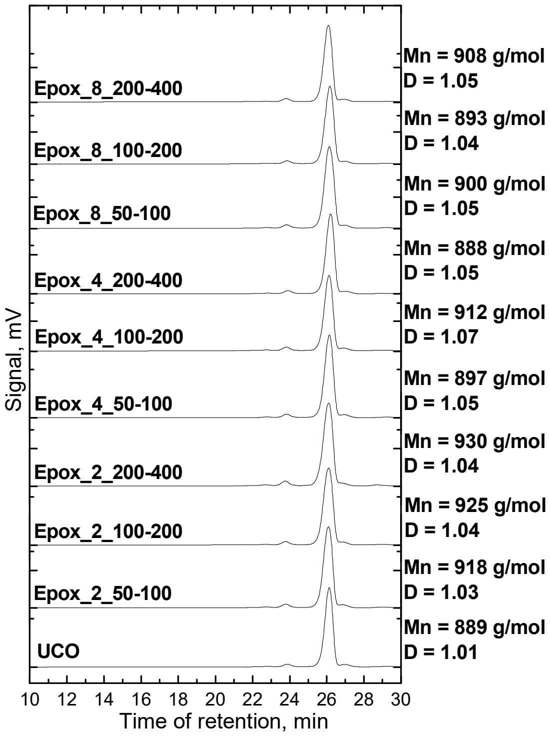

Figure 6. Chromatograms of bio-polyols obtained with Dowex catalysts.

The highest intensity signal present in all chromatograms corresponds to the weight of triglyceride. Its retention time is about 26 min. Peaks characterized by low intensity, with a retention time of about 24 min, indicate the presence of oligomers in the epoxidized oils. The signal is also visible in the chromatogram of waste rapeseed oil, hence the oligomerization products may have arisen as a result of a processes related to the thermal treatment of vegetable oil. The waste oil and epoxidized oils were characterized by similar average molar masses.

The dispersion of the products was slightly higher than the dispersion of the starting oil and ranged from 1.03 to 1.07. A small dispersion of the masses of the synthesized epoxidized oils is their advantage. In the production on an industrial scale, striving to obtain materials with low dispersion is sought as it has a positive effect on their performance and the possibility of further processing.

The advantage of heterogeneous catalysts should be easiness of separating them from products. Our experiments showed that in the case of the processes catalyzed by Dowex ion exchange resins, due to their small size, it was not possible to remove the catalyst from the epoxidized oil thoroughly using methods available on a laboratory scale. This resulted in turbid products. For the Amberlite IR-120 resin, this problem did not occur. The epoxidation process in the presence of Dowex ion exchange resins is not economical resulting from high prices of catalysts. Catalysts with smaller grain diameters and lower cross-linker content are generally more expensive. In contrast, the use of Amberlite resin allows obtaining epoxidized oils that can be used as plasticizers as well as intermediates for subsequent syntheses whereas the costs of waste oil modification are reduced.

The life of AIER is limited due to deactivation after a few cycles and the disposal of used catalyst is a major problem faced by industry [32]. In order to create a more environmentally friendly process, the possibility of repeated use of the same catalyst has been analyzed in the literature. Such an experiment was described for the epoxidation of fresh vegetable oils such as cotton seed oil [18], castor oil [33]. In the case of used cooking oil, there are oxidation products and other impurities confirmed by high peroxide and anisidine values, as well as the presence of polycyclic aromatic hydrocarbons and polychlorinated biphenyls [34]. In order to analyze such impurities and their influence on the efficiency of AIER, in this part of our work the same catalyst was used ten times for the epoxidation reactions. The microphotographs of Amberlite after each reaction are shown in Figure 7.

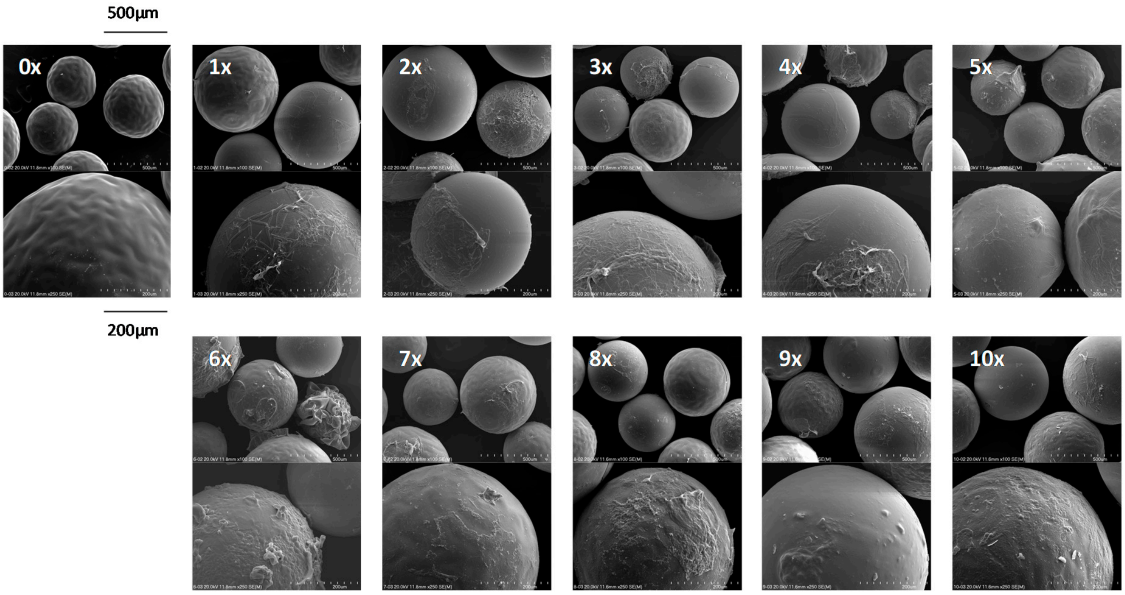

Figure 7. SEM microphotographs of Amberlite IR-120 catalyst before epoxidation reaction (0×) and after each reaction (1×–10×).

Regardless of the reaction, contaminants are present on the resin surface. This effect is associated with the method of resin preparation for synthesis. In order to minimize the costs and make the process simpler, we only separated the catalyst by filtration from the epoxidized oil and washed with water in order to remove acetic acid.

It was observed that after the first recycle the epoxy value of sample 2× was 6% lower (Figure 8). However, interesting results not described in the literature before were obtained in the case of the 3× and 4× reactions where the same catalyst was used for the 3rd and 4th time. The epoxide number of the modified oils was 8 and 6% higher, respectively, compared to the 1× reaction. This effect can be associated with the swelling of the catalyst, which results in easier access to the acid sulfonic groups of the resin.

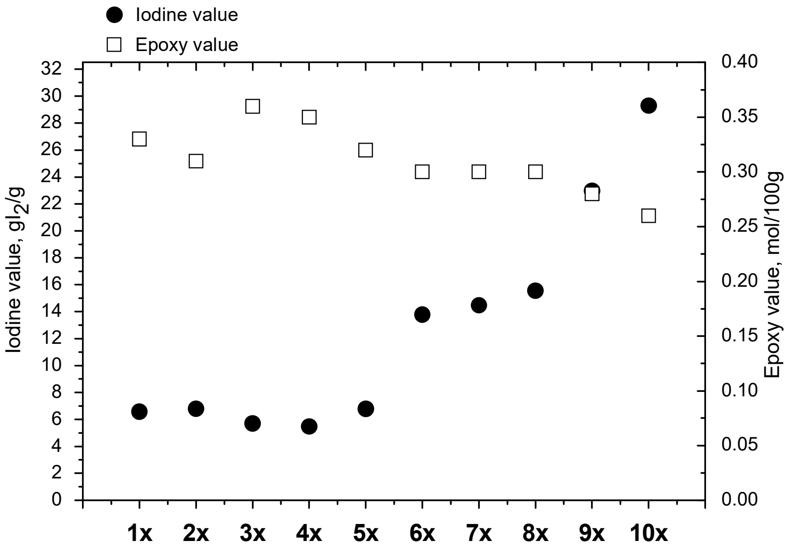

Figure 8. Changes in Ev and Iv depending on the number of times the catalyst was used.

In the literature there are descriptions of solid catalyst recycling. Dinda et al. used the same Amberlite IR-120 in four consecutive experiments and concluded that after the first recycle the catalyst activity decreased gradually with the number of recycles [18]. Mungroo et al. [17] found that AIER can be reusable and exhibited a negligible activity loss. After the catalyst had been used four consecutive times, the relative conversion to oxirane and the iodine conversion were 83 and 85%, as compared to 90 and 88.4%, respectively, obtained with the fresh catalyst. Goud et al. [16] based on their studies on the epoxidation of karanja oil found that it is possible to repeat recirculation of the catalyst Amberlite IR-120 four times. After each synthesis, the catalyst was regenerated. The regeneration relied on the filtration of resin, rinsing with water and diethyl ether, and drying in ambient temperature.

3. Materials and Methods

3.1. Materials

Glacial acetic acid (min. 99.5–99.9 wt.%), hydrogen peroxide (30 wt.%), were purchased from Avantor Performance Materials Poland S.A (Gliwice, Poland). Ion-exchange resins—Amberlite® IR-120 (Sigma-Aldrich, St. Louis, MO, USA), Dowex 50WX2 50-100, Dowex 50WX2 100-200, Dowex 50WX2 200-400, Dowex 50WX4 50-100, Dowex 50WX4 100-200, Dowex 50WX4 200-400, Dowex 50WX8 50-100, Dowex 50WX8 100-200, Dowex 50WX8 200-400 were purchased from Sigma-Aldrich (St. Louis, MO, USA). Used cooking oil was collected from 3 local restaurants (Kraków, Poland). The iodine and acid values of the used cooking oil mixtures were 104 gI_2/g.

3.2. Epoxidation Procedure

In the experiment, 250 g of used cooking oil and 0.5 mol of acetic acid and 2 mol hydrogen peroxide per mole of unsaturated bonds of oil as well ion exchange resin were added to a reactor. The content of Amberlite 120 was 15 wt.% (with respect to oil mass). The reactions were carried out for 6 h at a temperature of 60–65 °C using continuous stirring. Samples were taken out at the 1st, 2nd, 3rd, 4th, 5th and 6th h. After six hours the reaction mixture was separated into two phases, organic and aqueous. The organic phase was washed successively with warm water until it was acid free. The organic phase was distilled under vacuum (10 mbar) for 2 h in order to remove of water [5].

3.3. Methodology of Epoxidized Oil Characterization

The designation of Iv was done using the Hanus method according to the standard PN-87/C-04281, in which the iodine atoms are added to unsaturated bonds. The unsaturation degree of a given fat is then expressed by the amount of the iodine added.

Ev was determined according to the PN-87/C-89085/13 standard. The method involves a quantitative reaction of hydrogen chloride with a reactive epoxy group in dioxane at room temperature and titration of the hydrogen chloride excess using a solution of sodium hydroxide in methanol in the presence of cresol red as an indicator.

Hv of the polyol was determined according to the standard PN-93/C-89052/03, in which the hydroxy groups of a polyol undergo acetylation using acetic anhydride. The excess of the acetic anhydride is decomposed by a water addition (formation of acetic acid) and followed by titration using a solution of potassium hydroxide in the presence of an indicator.

Viscosity (η) was determined using a rotational rheometer HAAKE MARS III (Thermo Scientific, Waltham, MA, USA) at 25 °C. The control rate mode was used in the plate-plate arrangement with the plates having a diameter of 20 mm and rotation speeds of 100 cycles/min.

Number average molecular weight (Mn) and dispersity (Đ) were determined by a gel permeation chromatography (GPC) analysis. GPC measurements were performed using a Knauer chromatograph (Warsaw, Poland). The calibration was performed using polystyrene standards. Tetrahydrofuran (Avantor Performance Materials Poland S.A, Gliwice, Poland) was used as an eluent at a 0.8 mL/min flow rate at room temperature.

FTIR spectroscopy was performed using a FT-IR SPECTRUM 65 spectrometer (Perkin Elmer, Waltham, MA, USA).

4. Conclusions

The results presented in this paper allow verification of the influence of the heterogeneous catalyst concentration, its structure and particle size, as well as repeated use on the waste oil epoxidation process. No significant differences were observed in the final properties of the epoxidized waste cooking oil depending on the particle size and the cross-linking degree of the ion exchange resins used in the synthesis. The results were compared with the reaction in which Amberlite 120 resin was used, characterized by a larger grain size and a lower price. It was found that the Amberlite 120 resin can be successfully used in used cooking oil epoxidation reactions. Aiming at waste reduction in technological processes, an attempt was made to reuse a heterogeneous catalyst. The catalyst Amberlite IR-120 was reused without further treatment and no significant differences in the epoxy value were observed. Application of the same resin eight times in epoxidation allows obtaining products with epoxy values of 0.3 mol/100 g and higher. It was noticed that in the case of the reactions where the catalyst was reused for the third and fourth time the content of oxirane rings was higher by 8 and 6% compared to reaction where the catalyst was used one time only. Such an observation has not been reported so far.

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References

1. Saurabh, T.; Patnaik, M.; Bhagt, S.L.; Renge, V.C. Epoxidation of vegetable oils: A review. *Int. J. Adv. Eng. Technol.* **2011**, *4*, 491.
2. Guner, F.S.; Yagci, Y.; Erciyes, T. Polymers from triglyceride oils. *Prog. Polym. Sci.* **2006**, *31*, 633. [CrossRef]
3. Panadare, D.C.; Rathod, V.K. Applications of Waste Cooking Oil Other Than Biodiesel: A Review. *Iran. J. Chem. Eng.* **2015**, *12*, 55–76.
4. Kurańska, M.; Benes, H.; Polaczek, K.; Trhlikova, O.; Walterova, Z.; Prociak, A. Effect of homogeneous catalysts on ring opening reactions of epoxidized cooking oils. *J. Clean. Prod.* **2019**, *230*, 162. [CrossRef]
5. Kurańska, M.; Benes, H.; Prociak, A.; Trhlíkova, O.; Walterova, Z.; Stochlińska, W. Investigation of epoxidation of used cooking oils with homogeneous and heterogeneous catalysts. *J. Clean. Prod.* **2019**, *236*, 117615. [CrossRef]
6. Turco, R.; Di Serio, M. Sustainable Synthesis of Epoxidized Cynara, C. Seed Oil. *Catalyst* **2020**, *10*, 721. [CrossRef]
7. Dinda, S.; Patwardhan, A.V.; Goud, V.V.; Pradhan, N.C. Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids. *Bioresour. Technol.* **2008**, *99*, 3737. [CrossRef]
8. Milchert, E.; Smagowicz, A. The Influence of Reaction Parameters on the Epoxidation of Rapeseed Oil with Peracetic Acid. *J. Am. Oil Chem. Soc.* **2009**, *86*, 1227. [CrossRef]
9. Milchert, E.; Malarczyk-Matusiak, K.; Musik, M. Technological aspects of vegetable oils epoxidation in the presence of ion exchange resins: A review. *Pol. J. Chem. Technol.* **2016**, *18*, 128. [CrossRef]
10. Patil, H.; Waghmare, J. Catalyst for epoxidation of oils: A review. *Discovery* **2013**, *3*, 10–14.
11. Goud, V.V.; Patwardhan, A.V.; Pradhan, N.C. Studies on the epoxidation of mahua oil (Madhumica indica) by hydrogen peroxide. *Bioresour. Technol.* **2006**, *97*, 1365. [CrossRef] [PubMed]
12. Silviana, S.; Anggoro, D.D.; Kumoro, A.C. Waste Cooking Oil Utilisation as Bio-plasticiser through Epoxidation using Inorganic Acids as Homogeneous Catalysts. *Chem. Eng. Trans.* **2017**, *56*, 1861.
13. Petrović, Z.S.; Zlatanić, A.; Lava, C.C.; Sinadinović-Fišer, S. Epoxidation of soybean oil in toluene with peroxoacetic and peroxoformic acids-Kinetics and side reactions. *Eur. J. Lipid Sci. Technol.* **2002**, *104*, 293–299. [CrossRef]
14. Rios, L.A.; Echeverri, D.A.; Franco, A. Epoxidation of jatropha oil using heterogeneous catalysts suitable for the Prileschajew reaction: Acidic resins and immobilized lipase. *Appl. Catal. A Gen.* **2011**, *394*, 132. [CrossRef]

15. Mungroo, R.; Goud, V.V.; Naik, S.N.; Dalai, A.K.; Reaction, C.; Laboratories, E.; Delhi, N. Utilization of green seed canola oil for in situ epoxidation. *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 768. [CrossRef]
16. Goud, V.V.; Patwardhan, A.V.; Dinda, S.; Pradhan, N.C. Epoxidation of karanja (Pongamia glabra) oil. *Eur. J. Lipid Sci. Technol.* **2007**, *109*, 575. [CrossRef]
17. Mungroo, R.; Pradhan, N.C.; Goud, V.V.; Dalai, A.K. Epoxidation of Canola Oil with Hydrogen Peroxide Catalyzed by Acidic Ion Exchange Resin. *J. Am. Oil Chem. Soc.* **2008**, *85*, 887. [CrossRef]
18. Dinda, S.; Goud, V.V.; Patwardhan, A.V.; Pradhan, N.C. Selective epoxidation of natural triglycerides using acidic. *Asia-Pac. J. Chem. Eng.* **2011**, *6*, 870. [CrossRef]
19. Goud, V.V.; Pradhan, N.C.; Patwardhan, A.V. Epoxidation of Karanja (Pongamia glabra) Oil by H_2O_2. *J. Am. Oil Chem. Soc.* **2006**, *83*, 635. [CrossRef]
20. Narowska, B.E.; Kułażyński, M.; Łukaszewicz, M. Application of Activated Carbon to Obtain Biodiesel from Vegetable Oils. *Catalysts* **2020**, *10*, 1049. [CrossRef]
21. Vlcek, T.; Petrovic, Z.S. Optimization of the Chemoenzymatic Epoxidation of Soybean Oil. *J. Am. Oil Chem. Soc.* **2006**, *83*, 247. [CrossRef]
22. Rusch, M.; Warwel, S. Complete and partial epoxidation of plant oils by lipase-catalyzed perhydrolysis. *Ind. Crop. Prod.* **1999**, *9*, 125. [CrossRef]
23. Sun, S.; Ke, X.; Cui, L.; Yang, G.; Bi, Y.; Song, F.; Xu, X. Enzymatic epoxidation of Sapindus mukorossi seed oil by perstearic acid optimized using response surface methodology. *Ind. Crop. Prod.* **2011**, *33*, 676. [CrossRef]
24. Mindaryani, A.; Rahayu, S.S. Epoxidation of Candlenut Oil. In Proceedings of the 2010 International Conference on Chemistry and Chemical Engineering, Kyoto, Japan, 1–3 August 2010; p. 102.
25. Goud, V.V.; Dinda, S.; Patwardhan, A.V.; Pradhan, N.C. Epoxidation of Jatropha (Jatropha curcas) oil by peroxyacids. *Asia-Pac. J. Chem. Eng.* **2010**, *5*, 346. [CrossRef]
26. Monono, E.M.; Haagenson, D.M.; Wiesenborn, D.P. Characterizing the epoxidation process conditions of canola oil for reactor scale-up. *Ind. Crop. Prod.* **2015**, *67*, 364. [CrossRef]
27. Chieng, B.W.; Ibrahim, N.A.; Then, Y.Y.; Loo, Y.Y. Epoxidized Vegetable Oils Plasticized Poly(lactic acid) Biocomposites: Mechanical, Thermal and Morphology Properties. *Molecules* **2014**, *19*, 16024. [CrossRef]
28. Goud, V.V.; Patwardhan, A.V.; Dinda, S.; Pradhan, N.C. Kinetics of epoxidation of jatropha oil with peroxyacetic and peroxyformic acid catalysed by acidic ion exchange resin. *Chem. Eng. Sci.* **2007**, *62*, 4065. [CrossRef]
29. Perez, J.D.; Haagenson, D.M.; Pryor, S.W.; Ulven, C.A.; Wiesenborn, D.P. Production and characterization of epoxidized canola oil. *ASABE* **2009**, *52*, 1289. [CrossRef]
30. Goud, V.V.; Patwardhan, A.V.; Pradhan, N.C. Kinetics of in situ Epoxidation of Natural Unsaturated Triglycerides Catalyzed by Acidic Ion Exchange Resin. *Ind. Eng. Chem. Res.* **2007**, *46*, 3078. [CrossRef]
31. Sinadinović-Fišer, S.; Janković, M.; Petovic, Z.S. Kinetics of in situ Epoxidation of Soybean Oil in Bulk Catalyzed by Ion Exchange Resin. *J. Am. Oil Chem. Soc.* **2001**, *78*, 725. [CrossRef]
32. Malshe, V.C.; Sujatha, E.S. Regeneration and reuse of cation-exchange resin catalyst used in alkylation of phenol. *React. Funct. Polym.* **1997**, *35*, 159. [CrossRef]
33. Sinadinović-Fišer, S.; Janković, M.; Borota, O. Epoxidation of castor oil with peracetic acid formed in situ in the presence of an ion exchange resin. *Chem. Eng. Process. Process. Intensif.* **2012**, *62*, 106. [CrossRef]
34. Kurańska, M.; Banaś, J.; Polaczek, K.; Banaś, M.; Prociak, A.; Kuc, J.; Uram, K.; Lubera, T.J. Evaluation of application potential of used cooking oils in the synthesis of polyol compounds. *Environ. Chem. Eng.* **2019**, *7*, 103506. [CrossRef]