



# The Selectivity of Tungstate-based Catalyst in Epoxidation of Modified and Non-modified Rubber Seed Oil

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**Abstract:** The study investigated the selectivity of tungstate-based catalyst in the epoxidation of rubber seed oil and modified rubber seed oil by two methods: The titration method was performed according to the ASTM standard and the H-NMR method was based on the peaks of the three different standard groups. The catalyst selectivity of the epoxidation reaction of modified rubber seed oil was much higher than that of non-modified rubber seed oil for both methods. The average catalyst selectivity obtained by using H-NMR method in the modified rubber seed oil epoxidation reaction was equal to that of the titrimetric method, while the selectivity of the rubber seed oil epoxidation reaction was 11% lower than that of the titrimetric method. For both types of oil, the difference between the catalytic selectivity obtained by using the titration method and by using protons in group  $\alpha$ -CH<sub>2</sub>-(C=O)-O- as the standard peak, was the smallest and when the proton in group -CH<sub>3</sub> was used as the standard peak, the difference in selectivity was the biggest.

**Keywords:** Selectivity, tungstate-based catalyst, H-NMR.

## 1. Introduction

Vegetable oils are environmentally friendly, biodegradable, relatively low cost, and readily available. The possible use of this resource as a substitute for petrochemical derivatives has attracted the attention of many researchers. Because of the rich in the unsaturated

linkages of their composition's structure, they may be used to introduce functional groups such as epoxides [1].

Epoxidation occurs when a cyclic ether is formed at sites of ethylenic unsaturation (C=C) located along the fatty acid chains by the addition of an oxygen atom [2]. There are many epoxidation methods such as: epoxidation by conventional method, by using acid ion exchange resin (AIER), enzymes, and metal catalyst... [3].

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In conventional method, the presence of strong mineral inorganic acid as acid catalyst leads to many side reactions such as epoxy ring opening to appear diols, hydroxyl esters... [3, 4]. While AIER method has prominent advantages over conventional one by improving the selectivity and undesirable side reactions can be reduced to a certain level [3, 5]. To avoid side reactions and make the process more environmentally friendly, enzyme catalyst is preferred but the main limitation of this is the low stability of the lipase under reaction conditions [3, 6]. Recent studies have attempted to improve the efficiency of epoxidation under milder conditions that minimize the formation of byproducts [7]. Various metals such as titanium, molybdenum, tungsten is used as metal catalyst [3, 8, 9].

In Vietnam, epoxidation reaction of vegetable oil using molybdenum-based catalyst was also investigated by Phan Van Ninh [10]. The scientists in Polymer center of Hanoi University of Science and Technology have carried out a series of the epoxidation reactions by using tungstate-based catalyst [11-15]. The activity of this catalyst has been evaluated with soybean oil [11-13] and sunflower oil [14,15] and the results showed that high catalytic selectivity due to minimizing side reaction is a prominent feature of this catalyst. In this work, the selectivity of this catalyst in epoxidation reaction of modified and non-modified rubber seed oil was studied by using two different methods: H-NMR and titration. To our knowledge, studying the selectivity of the epoxidation catalyst by using H-NMR method has not been previously reported for the vegetable oil.

## 2. Experiment

### 2.1. Materials

Wijs solution was purchased from Merck, Germany. Hydrogen bromide solution (33 wt.%) was obtained from Sigma-Aldrich, USA. Sulfuric acid (98 wt.%) and glacial acetic acid were obtained from Xilong Chemical, China.

Rubber seeds were collected in Long Khanh, Dong Nai, after 3 months to dry were pressed in EC company in 364/1 Cong Hoa, Tan Binh. The esterified-rubber seed oil (RSOE) with the acid value of 1.12 mgKOH/g was obtained from rubber seed oil with the acid value of 39.03 mgKOH/g (RSO) [16] in Polymer Center of Hanoi University of Science and Technology.

Table 1. The composition of fatty acids [16] and average molecule weight of fatty acids, triglyceride, rubber seed oil, and diglyceride

	Name	Value
% acid	Stearic (18:0)	8.96
	Stearic (18:0)	8.96
	Oleic (18:1)	43.73
	Linoleic (18:2)	38.03
	Arachidic (20:0)	0.25
Average molecular weight of	Fatty acids, $M_{Fa}$	279.17
	Triglyceride, $M_{Tri}$	875.51
	Rubber seed oil, $M_{RSO}$	759.48
	Diglyceride, $M_{di}$	614.34

### 2.2. Methods

#### 2.2.1. Epoxidation procedure

The reaction is performed in a 500 ml four neck flask equipped with a stirrer, thermometer and reflux cooler., The RSO or RSOE, oxidant of  $H_2O_2$  and tungstate-based catalyst were added to this flask. After charging, the reaction continued by mixing at 60°C for hour. After that, the mixture was cooled down, neutralized by water, and purified. The final product was dried out by heating about 60°C in a vacuum oven until constant weight.

#### 2.2.2. Analytical techniques

The iodine value and the oxygen-oxirane content were determined according to standard ASTM D1652 and D5768, respectively. The nuclear magnetic resonance spectroscopic

analysis was performed on the Bruker Advance 500 (USA) with solution of  $\text{CDCl}_3$ .

### 3. Results

ERSO and ERSOE were the products of epoxidation reaction of RSO and RSOE, respectively. These products were titrated with solution of hydrogen bromide and solution of sodium thiosulfate to have the oxygen-oxirane content and the iodine value.

It was easy to calculate the theoretic oxygen-oxirane content ( $O_{th}$ ) of RSO and RSOE (8.475%) when the iodine value of them was 146.9  $\text{cgI}_2/\text{g}$ . The yield of the epoxidation (Y) was calculated by ratio between the oxygen-oxirane content of epoxidized oils ( $O_x$ ) and theoretic oxygen-oxirane content.

$$\text{Yield (\%)} = \frac{O_x}{O_{th}} \quad (1)$$

The conversion of the epoxidation (C) was calculated by the following formula:

$$\text{Conversion (\%)} = \frac{CI_{\max} - CI}{CI_{\max}} \times 100 \quad (2)$$

CI: iodine value of epoxidized oil

$CI_{\max}$ : iodine value of oil

Selectivity of catalyst was a ratio between yield and conversion.

$$S = \frac{Y}{C} \quad (3)$$

The selectivity of catalyst in two epoxidation reactions of RSO and RSOE were showed in table 2.

Table 2. The selectivity of tungstate-based catalyst

	Proton in group	Selectivity	
		ERSO	ERSOE
Standard	$-\text{CH}_3$	0.70 <sup>-14.6%</sup>	0.99 <sup>+5.3%</sup>
	$\alpha\text{-CH}_2\text{-(C=O)-O-}$	0.78 <sup>-4.9%</sup>	0.93 <sup>-1.1%</sup>
	$\beta\text{-CH}_2\text{-CH}_2\text{-(C=O)-O-}$	0.71 <sup>-13.4%</sup>	0.91 <sup>-3.2%</sup>
	Average selectivity by NMR method	0.73 <sup>-11%</sup>	0.94
	Titration method	0.82	0.94

On the other hand, these products were also analyzed in other method by using proton nuclear magnetic resonance spectroscopy. The spectra and their assignment were presented in fig.1 and table 3.

The peak h at 0.8-1.0 ppm related to proton of the terminal  $-\text{CH}_3$  group, peak g at 1.2-1.4 ppm corresponded with proton of  $-\text{CH}_2-$  group, peak j at 1.6 ppm characterized proton of  $\beta\text{-CH}_2\text{-(C=O)O-}$  group and peak d at 2.3 ppm stood for proton of  $\alpha\text{-CH}_2\text{-(C=O)O-}$  group. All of them were present at the H-NMR-spectrum of oils (RSO, RSOE) and epoxidized oils (ERSO, ERSOE) and most of them did not change in the modified process RSO to ERSO and RSOE to ERSOE, but peak g at 1.2-1.4 ppm was an exception because the proton of  $-\text{CH=}$  group in oils would be changed into proton of  $-\text{CH}_2-$  group in the epoxidized oils and it would contribute to peak g. The peak h, j and d were used as standard peaks to determine the yield and conversion of the epoxidation reaction [17, 18] and the selectivity of tungstate-based catalyst was calculated.

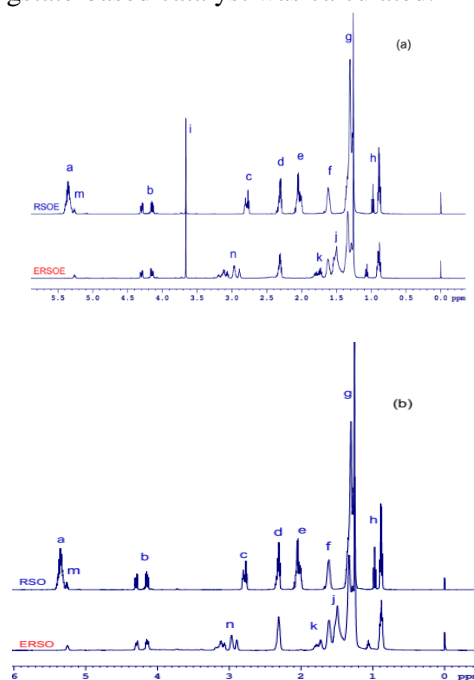


Figure 1.  $^1\text{H-NMR}$  spectra of RSOE and ERSOE (a), RSO and ERSO (b).

Table 3. Assignment of the H-NMR spectra of oil and epoxidized oils

Proton	ppm		Area			
			RSO	ERSO	RSOE	ERSOE
-CH <sub>3</sub>	0.8-1	h	12.096	13.383	11.146	7.652
-(CH <sub>2</sub> ) <sub>n</sub> -	1.2-1.4	g	67.644	62.379	61.736	37.116
-CH <sub>2</sub> -epoxy-CH <sub>2</sub> -epoxy-CH <sub>2</sub> -	1.4-1.5	j	-	20.283	-	14.982
β-CH <sub>2</sub> CH <sub>2</sub> -(C=O)O-	1.6	f	8.731	9.980	8.154	5.928
-epoxy-CH <sub>2</sub> -epoxy-	1.7	k	-	4.500	-	3.620
-CH <sub>2</sub> -CH=CH-	2.0	e	13.204	-	12.012	-
α-CH <sub>2</sub> -(C=O)O-	2.3	d	7.977	8.341	7.469	5.316
-CH=CH-CH <sub>2</sub> -CH=CH-	2.7-2.8	c	5.754	-	5.281	-
-epoxy-	2.9-3.2	n	-	9.629	-	7.447
HO-CH <sub>2</sub> -CH-O-C(O)-   CH <sub>2</sub> -O-C(O)-	3.7	i	-	-	3.078	2.083
-CH <sub>2</sub> -CH-CH <sub>2</sub> -	4.1-4.3	b	3.936	4.73	3.564	2.290
-CH <sub>2</sub> -CH-CH <sub>2</sub> -	5.2-5.3	m*	1	1	1	0.379
-CH=CH-	5.3-5.4	a*	11.789	-	10.729	-

\* The glycerol methine protons and the protons of double bonds maybe had a coincidence

The formula (4) and (6), U and E<sub>p</sub> were the number of double bonds and the epoxy group in one triglyceride. The p in formula (2) was the number of protons per triglyceride molecule that caused the resulting peaks. So, it was 9 or 6 (table 4). A<sub>proton</sub> was the area per proton per molecule and A<sub>2.9-3.2</sub> was the area of peak n. A<sub>5.3-5.4</sub> were the sum of area of peak a and m [18].

$$U = \frac{1}{2} \left( \frac{A_{5.3-5.4ppm}}{A_{proton}} - 1 \right) \quad (4)$$

$$A_{proton} = \frac{A_{chuân}}{p} \quad (5)$$

$$E_p = \frac{A_{2.9-3.2ppm}}{2.A_{proton}} \quad (6)$$

It was easy to calculate average molecular weight of fatty acids (279.171 g/mol) and of triglycerides (875.514 g/mol) in RSO from the fatty acid compositions of RSO in table 1. The molecular ratio of free fatty acids and

triglycerides in RSO (0.4310/0.5690) was calculated from two average molecular weights above and acid value of RSO.

In the modification of RSO, the free fatty acids were converted into free fatty esters. Moreover, some of triglyceride molecules also were converted into diglyceride ones and some new free fatty esters were formed [17, 19]. It is easy to recognize by the peak at 3.7 ppm for the methylene proton in glycerol backbone adjacent to hydroxyl group (fig 1a).

The area ratio between peak b and peak m in RSO was 3.936 and in RSOE was 3.564 (table 3), so it could be calculated the molecular ratio between the triglyceride and diglyceride in RSOE of 0.8079/0.1921. The number of diglyceride molecules were equal to the number of the new formed free fatty esters ones, so the molecular ratio of total free fatty esters/triglyceride/diglyceride in RSOE was 0.4871/0.4144/0.0985.

In the RSO and RSOE cases, there were a lot of free fatty acids in RSO or free fatty esters in RSOE, so the p was the number of protons per standard group per the molecular mixer. Where, the molecular mixer of RSO consisted 0.4310 free fatty acid molecule and 0.5690

triglyceride molecule and the molecular mixer of RSOE included 0.4871 free fatty ester molecule, 0.4144 triglyceride molecule and 0.0985 diglyceride molecule. The number of protons p per standard groups was showed in table 4.

Table 4. The number of protons per standard group of a molecule

Group	Proton (p)				
	FFa or FFe	Tri	Di	RSO or ERSO	RSOE or ERSOE
CH <sub>3</sub>	3	9	6	6.4137	5.7817
α-CH <sub>2</sub> -(CO)O-	2	6	4	4.2758	3.8545
β-CH <sub>2</sub> CH <sub>2</sub> -(CO)O-	2	6	4	4.2758	3.8545

FFa: The free fatty acid, FFe: The free fatty ester

The number of double bonds in the oils (RSO or RSOE) ( $U_o$ ) and in the epoxidized oils (ERSO or ERSOE) ( $U$ ) and the number of epoxy groups per molecular mixer were calculated by using formulas (1), (2), (3) and the area of peaks in table 3 as well as the numbers of proton (p) in table 4. The yield and conversion of the epoxidation reaction and selectivity of catalyst were calculated by using formulas (7), (8) and (9). The results were indicated in table 2.

$$Y (\%) = 100 \times \frac{E_p}{U_o} \quad (7)$$

$$CI (\%) = 100 \times \frac{U_o - U}{U_o} \quad (8)$$

$$S = \frac{Y}{CI} \quad (9)$$

As can be seen from table 2, the selectivity of catalyst in epoxidation reaction of RSOE (0.94) was much higher than that of RSO (0.82). It might be due to the lower acid value of the RSOE. With the same tungstate-based catalyst, and the acid value of oil was lower, the selectivity in the RSOE epoxidation reaction

was higher than that in sunflower oil (0.87 or 0.91) [15] and almost the same in soybean oil (0.94) [13], sunflower oil (0.93) and lower than that in soybean oil (0.96) [12].

The catalytic selectivity obtained by using titration method was different to H-NMR method. Moreover, the selectivity of catalyst obtained by using the different standard peaks was not similar.

The errors between the catalytic selectivity obtained by using titration method and by using protons in group α-CH<sub>2</sub>-(C=O)-O- as the standard peak were the smallest. They were 4.9% with RSO and 1.1% with RSOE. The errors were the biggest (14.6% with RSO and 5.3% with RSOE) when the protons in group -CH<sub>3</sub> was used as the standard peak.

The average selectivity of catalyst obtained by NMR method of RSO and RSOE epoxidation reaction was 0.73 and 0.94, respectively. The errors of the catalytic selectivity obtained by using titration and H-NMR method in epoxidation reaction of RSO were 11% while the catalyst selectivity in epoxidation reaction of RSOE was the same with the two methods.

#### 4. Conclusion

The selectivity of tungstate-based catalyst in the epoxidation reaction of rubber seed oil and modified rubber seed oil was studied in two ways. There were many side reactions occurred in the epoxidation because of high acid value of rubber seed oil, so the selectivity of tungstate-based catalyst in this reaction was much smaller than that in the reaction of modified rubber seed oil. The selectivity of tungstate-based catalyst of the epoxidation reaction of modified rubber seed oil was almost equal to that of other low acid value oils such as soybean oil, sunflower oil.

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## Nghiên cứu độ chọn lọc của xúc tác trên cơ sở muối vonfram trong phản ứng epoxy hóa dầu hạt cao su và dầu hạt cao su biến tính

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**Tóm tắt:** Độ chọn lọc xúc tác trên cơ sở muối vonfram trong phản ứng epoxy hóa dầu hạt cao su và dầu hạt cao su biến tính đã được nghiên cứu theo hai phương pháp. Phương pháp chuẩn độ được thực hiện theo tiêu chuẩn ASTM và phương pháp H-NMR dựa trên pic hấp thụ của ba nhóm chuẩn khác nhau. Độ chọn lọc xúc tác trong phản ứng epoxy hóa dầu hạt cao su biến tính cao hơn nhiều so với trong phản ứng epoxy hóa dầu hạt cao su không biến tính. Độ chọn lọc xúc tác trung bình tính theo phương pháp H-NMR với phản ứng epoxy hóa dầu hạt cao su biến tính thì ngang bằng còn với phản ứng epoxy hóa dầu hạt cao su thì thấp hơn 11% so với tính theo phương pháp chuẩn độ. Với cả hai loại dầu, độ chọn lọc xúc tác tính theo H-NMR khi sử dụng pic hấp thụ của nhóm chuẩn  $\alpha\text{-CH}_2\text{-(C=O)O-}$  có độ sai lệch nhỏ nhất còn của nhóm chuẩn  $\text{-CH}_3$  có độ sai lệch lớn nhất so với tính theo phương pháp chuẩn độ.

*Từ khóa:* Độ chọn lọc xúc tác, phổ cộng hưởng từ hạt nhân, xúc tác trên cơ sở muối vonfram.