



Kinetic Study of Rubber Seed Oil Epoxidation Using Tungstate-based Catalyst

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Abstract: The thermodynamic properties of the epoxidation of rubber seed oil (RSO) and modified rubber seed oil (eRSO) using tungstate-based catalyst were determined by performing the epoxidation for one hour at three different temperatures. The rate constants of these epoxidations ranged from $0.57 \cdot 10^{-2}$ to $1.01 \cdot 10^{-2} \text{ l.mol}^{-1} \cdot \text{s}^{-1}$ with RSO and $0.97 \cdot 10^{-2}$ to $1.76 \cdot 10^{-2} \text{ l.mol}^{-1} \cdot \text{s}^{-1}$ with eRSO, and the activated energies of reaction were 6.2 and 6.6 kcal.mol^{-1} , respectively. The enthalpy ΔH was positive, which indicated that the epoxidation process was an endothermic reaction, but as the free-energy ΔF was also positive, there was a specific temperature at which the epoxidation process was the most effective. The experiment results show that 60°C was the most suitable temperature for epoxidation of both RSO and eRSO with the conversion of 91.37% (RSO) and 94.87% (eRSO), the yield of 75.06% (RSO) and 89.56% (eRSO), and the selectivity was 0.82 (RSO) and 0.94 (eRSO).

Keywords: Epoxidized rubber seed oil, kinetic, tungstate-based catalyst.

1. Introduction

Epoxidized vegetable oils are very interesting because they are not only environmentally friendly but also be produced from natural renewable sources. Application areas of the epoxidized vegetable oil is also very diverse. They can be used as a lubricant, sealing substances, surfactant, plasticiser for polymers, resin for materials of polymer composite or coatings, adhesives. They also

are used as raw material for the synthesis of organic compounds [1].

At present, there are many new epoxidation methods in place of low efficiency traditional method such as ion exchange resins, metal catalysts, enzyme methods ... [2]. In which, the metal catalyst is a method based on the mechanism of complex formation between metals and oxidants, that minimizes side reaction, shortens reaction time and increases epoxidation efficiency.

In Vietnam, metal catalysts have also been used by scientists a long time ago. In 2001, Phan Van Ninh used ammonium molybdenum catalyst to modify rubber seed oil to epoxidized

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oil [3]. Recently, Nguyen Thi Thuy and et al. have success in using tungstate-based catalysts to modify sunflower oil [4], soybean oil [5,6] into epoxidized oil with very high efficiency and shortening reaction time down to one hour. The kinetics of epoxidation reaction using tungstate-based catalyst is also investigated with soybean oil [7], sunflower oil [8].

This work focuses on the kinetic study of epoxidation reaction of rubber seed oil using tungstate-based catalyst by determining the rate constant, the activation energy, the enthalpy, the entropy, and the free energy of the reaction.

2. Experiment

2.1. Materials

Wijs solution was purchased from a Merck, Gemany. Hydrogen bromide solution (33 wt.%) was obtained from a Sigma-Aldrich, USA. Sulfuric acid (98 wt.%) and glacial acetic acid were obtained from Xilong Chemical, China. Rubber seeds collected in Long Khanh, Dong Nai were dried and pressed in EC company in 364/1 Cong Hoa, Tan Binh to get rubber seed oil.

2.2. Methods

2.2.1. Epoxidation procedure

The epoxidation reaction is performed in a 500 ml four neck flask equipped with a stirrer, thermometer and reflux cooler., The oils, oxidant, and catalyst with $\text{DB}/\text{H}_2\text{O}_2/\text{Na}_2\text{WO}_4/\text{H}_3\text{PO}_4$ molar ratio of 1/2/0.15/0.3 were added to this flask (DB-double bond). After charging, the reaction continued by mixing at a certain temperature for a definite time. After that, the mixture was cooled down and neutralized by water. The final product was dried out by heating about 60°C in a vacuum oven until constant weight.

2.2.2. Analytical techniques

The density and viscosity are determined by using pycnometer 25ml (China) and Brookfield Model RVT (Germany) respectively. Iodine

value, acid value and hydroxyl content are determined according to standard ASTM D5768, D974 and D1957 respectively.

3. Results

3.1. Modification of rubber seed oil and characteristics

Rubber seed oil (RSO) was modified with methanol to reduce acid value according to a published procedure [9]. The characteristics of rubber seed oil (RSO) and modified rubber seed oil (eRSO) are shown in table1.

Table 1. Characteristics of RSO and eRSO

Characteristics	RSO	eRSO
Iodine value, cgI_2/g	146.9	146.9
Acid value, mgKOH/g	39.03	1.12
Hydroxyl content, mgKOH/g	58.22	11.41
Density 20°C, g/ml	0.951	0.924
Viscosity 23°C, cP	250	80

The iodine value of RSO and eRSO were the same but the acid value of eRSO is much smaller than that of RSO.

3.2. Evaluating the result of epoxidation reaction

In this experiment the RSO and eRSO were used as starting materials to perform epoxidation reaction for the kinetic study.

It was easy to calculate the theoretic oxygen-oxirane content of RSO and eRSO (8.475%) when the iodine value of them was 146.9 cgI_2/g . The yield of the epoxidation reaction (Y) was calculated by ratio between the oxygen-oxirane content of epoxidized oils and theoretic oxygen-oxirane content.

$$\text{Yield (\%)} = \frac{O_x}{8.475} \quad (1)$$

O_x : Oxygen-oxirane content of epoxidized oil

The conversion of the epoxidation reaction (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

A series of epoxidation reactions were carried out at 50°C, 60°C and 70°C temperature, stirring was fixed at 2000 rpm. The products of epoxidation reaction of RSO and eRSO were ERSO and EeRSO, respectively. Progress of reaction was monitored by measurement of the oxygen-oxirane content and the iodine value of products of these reactions.

Fig.1 showed that the plots of oxygen-oxirane content versus reaction time for reactions of RSO (fig.1a) and eRSO (fig.1b) were almost identical.

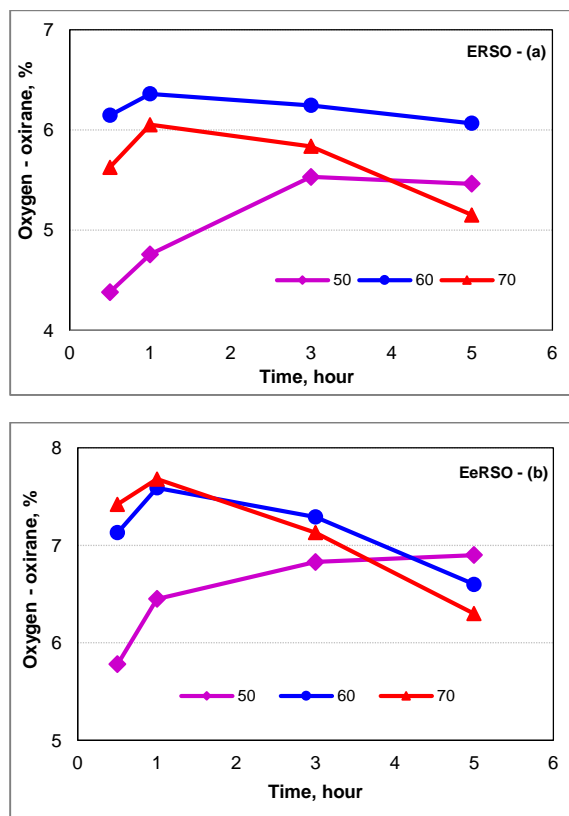


Fig.1. The effect of temperature and time on oxygen oxirane content: (a)-ERSO, (b)-EeRSO.

At 50°C, the oxygen-oxirane content of epoxidized oils was small (4.38% with ERSO (fig.1a) and 5.78% with EeRSO (fig.1b) for 0.5 hour) and increased slowly versus reaction time (5.53% with ERSO (fig.1a) and 6.9% with EeRSO (fig.1b) for 5 hours)). It showed that the rate of epoxidized reactions at 50°C were slow.

At higher reaction temperature, 60°C, the oxygen-oxirane content of epoxidized oils raised strongly from 4.76 to 6.36% at 1 hour with ERSO (fig.1a) and 6.45 to 7.59% at 1 hour with EeRSO (fig.1b). That means that, epoxidized reaction with RSO and eRSO occurred remarkably at 60°C. However, the plots were upward curved up to about an hour, downward curvature were observed afterwards. This region was believed to mark the beginning of oxirane ring opening reaction that could lead to a decrease in the oxygen-oxirane content.

However, there was the difference between epoxidized reaction of RSO and eRSO at 70°C. Although the oxygen-oxirane content of ERSO for an hour reaction at 70°C was much bigger than that at 50°C, but smaller than that at 60°C (fig.1a). That means, the effect of epoxidation reaction of RSO at 70°C was higher than that at 50°C, but smaller than that at 60°C. Whereas, the oxygen-oxirane content of EeRSO for 0.5 hour at 70°C was rather higher than that at 60°C, but they were nearly the same for 1 hour (fig.1b). So, it indicated that the effect of epoxidation reactions of eRSO at both temperatures was almost the same. Moreover, after one hour of reaction, the oxygen-oxirane content of both ERSO and EeRSO reduced due to the oxirane ring opening reaction occurred.

With all temperature and reaction time, the oxygen-oxirane content of the EeRSO was always higher than that of the ERSO (fig.1). That means, that the epoxidation reaction of eRSO took place with more intense. Definitely, the higher acid value of RSO was the reason of this. For example, after 1 hour of reaction at 50°C, 60°C, 70°C, the oxygen-oxirane content of EeRSO was 6.45, 7.59, 7.68, respectively and they were bigger than that of ERSO (4.76%, 6.36%, 6.05%, respectively).

To continue the investigation, the epoxidized oils were titrated with solution of sodium thiosulfate to have iodine value. Using formula (2) to calculate the conversion and (1) to calculate the yield of epoxidation reaction of RSO and eRSO. Selectivity of catalyst was a ratio between yield and conversion. It showed how many double bonds broken was able to convert into epoxy groups, so the maximum of selectivity is 1. The higher selectivity, the less side reaction. The results were presented in fig.2 and fig.3

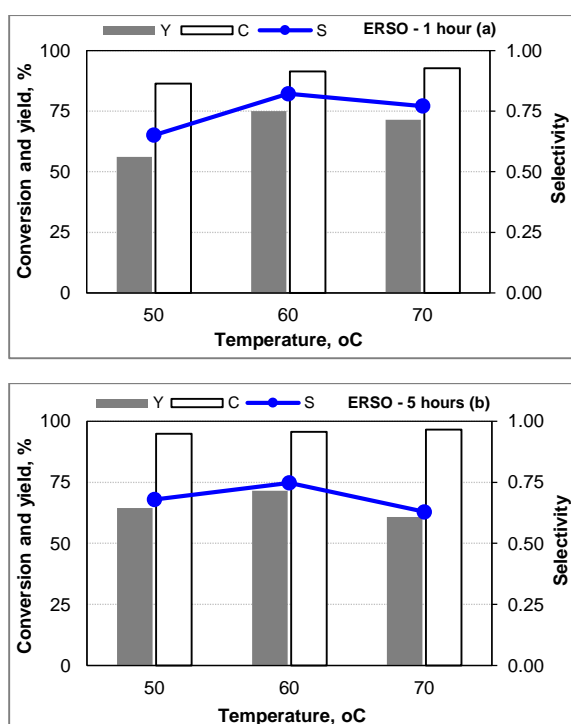


Fig.2. The effect of temperature and time on yield, conversion of reaction of RSO and selectivity of catalyst

As can be seen from fig 2a, as the reaction temperature increased from 50 to 70°C, the conversion raised slightly from 86.32 to 92.65%. The yield of epoxidation at 50°C was small (56.15%) and reached 71.59% at 60°C and then reduced slightly at 70°C. Thus, the selectivity of catalyst reached the maximum value (0.82) when the reaction was carried out at 60°C.

Looking at fig. 2b, it can be seen that, upon prolongation of the reaction, the conversion of three reactions continued to increase while the yield decreased, thus the selectivity of catalyst reduced (0.75 with reaction carried out at 60°C), except for the reaction carried out at 50°C. As it is known that the decrease of catalytic selectivity is due to more side reactions occurred.

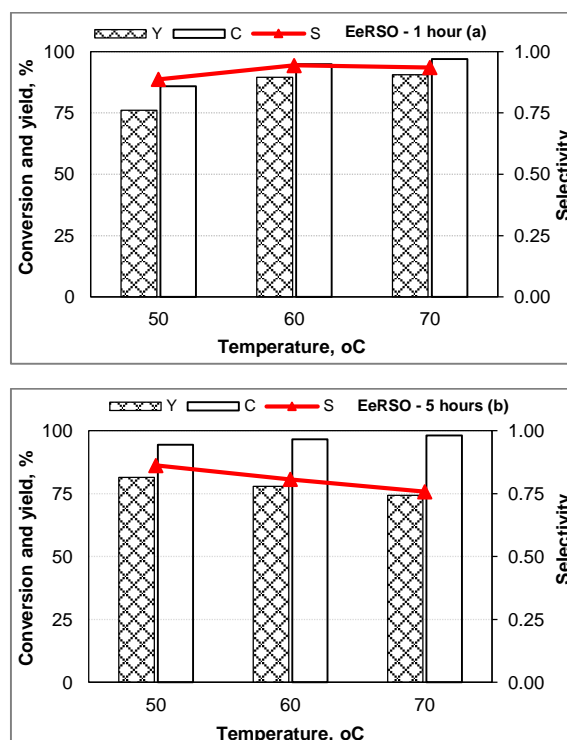


Fig.3. The effect of temperature and time on yield, conversion of reaction of eRSO and selectivity of catalyst

For the EeRSO, both the yield and conversion of reactions were carried out at 60 and 70°C for 1 hour (fig 3a) were very high and the selectivity of catalyst in these two reactions was also very big (0.94). So, most of the broken double bonds are converted into epoxy groups and there were a few side reactions at these reaction temperatures. In contrast, both the yield and conversion of reaction at 50°C for 1 hour (fig 3a) were lower and the selectivity of catalyst in this case was also smaller.

For the case when the reaction time was extended to 5 hours (fig.3b), the conversion of both reactions at 60°C and 70°C increased slightly while the yield of them lessened and the selectivity of catalyst in these cases reduced significantly. This means that, the longer the reaction time was, the more side reaction occurred. Unlike the reactions at 60°C and 70°C, both the yield and conversion of reaction at 50°C grew up, so the selectivity of catalyst in this case only slightly decreased, from 0.89 down to 0.86. The conclusion from this is that the extension of the reaction time at 50°C almost did not increase the side reaction.

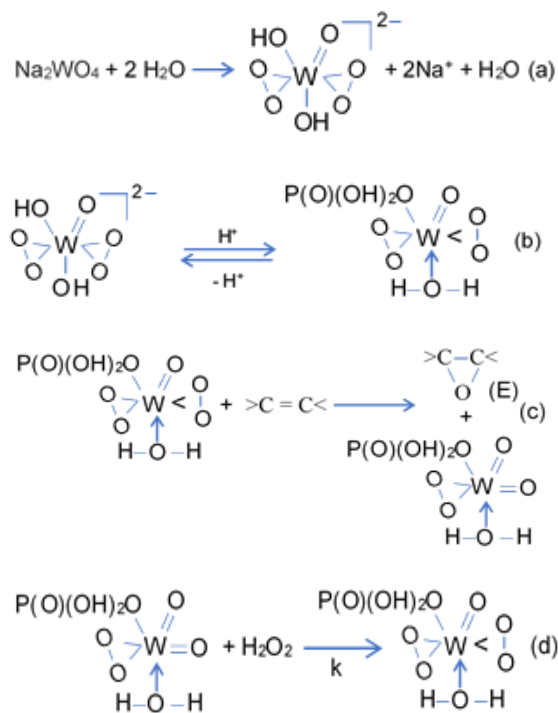
As can be noticed from fig.2a and fig.3a, both the yield and conversion of epoxidation reaction of eRSO at all three reactions temperature were higher than that of RSO and the selectivity of catalyst in epoxidation reaction of eRSO was much higher compared to that of RSO. For example, the yield, conversion and selectivity of epoxidation reaction of eRSO at 60°C were 89.56%, 94.87%, 0.94 respectively while they were 75.06%, 91.37%, 0.82 with the epoxidation reaction of RSO. Thus, this is clear that the lower acid value of eRSO not only increased the possibility of double bond breakage, but also reduced the side reaction and raised the formation of epoxy groups.

The similarity can be seen for the case of 5-hour reaction time where the yield, conversion and selectivity of catalyst in epoxidation reaction of eRSO were also higher than that of RSO (fig.2b and fig.3b).

3.3. Kinetic study of epoxidation reaction of rubber seed oil

The process of epoxidation of vegetable oil in general and of rubber seed oil in particular with tungstate-based catalyst followed the scheme [10-13].

Where, (a) and (b) were the complex catalyst formative reactions and they occurred very quickly. (c) was the epoxy ring formative reaction and (d) was the return reaction of peroxy complex. The theoretical rate of epoxidation was calculated by the formula of (3) and (4).



$$\frac{d[\text{E}]}{dt} = k \cdot ([\text{H}_2\text{O}_2]_0 - 2[\text{Na}_2\text{WO}_4]_0 - [\text{E}]) \cdot [\text{Na}_2\text{WO}_4]_0 \quad (3)$$

$$\ln([\text{H}_2\text{O}_2]_0 - 2[\text{Na}_2\text{WO}_4]_0 - [\text{E}]) = -k \cdot [\text{Na}_2\text{WO}_4]_0 \cdot t + \ln([\text{H}_2\text{O}_2]_0 - 2[\text{Na}_2\text{WO}_4]_0) \quad (4)$$

Where, $[\text{H}_2\text{O}_2]_0$ and $[\text{Na}_2\text{WO}_4]_0$ were the initial molar concentration of $[\text{H}_2\text{O}_2]_0$ and $[\text{Na}_2\text{WO}_4]_0$, respectively; $[\text{E}]$ was the molar concentration of epoxy group; k was the rate constant; t was the reaction time. The plot of $\ln([\text{H}_2\text{O}_2]_0 - 2[\text{Na}_2\text{WO}_4]_0 - [\text{E}])$ versus t gave a straight line, whose gradient could be used to determine speed constant.

The fig.4 showed the experimental relationship between $\ln([\text{H}_2\text{O}_2]_0 - 2[\text{Na}_2\text{WO}_4]_0 - [\text{E}])$ and t . It was the curve due to the contribution of the epoxy ring-opening reaction [11-14]. However, in the initial period of the reaction, it was linear. So, by identifying the tangent at the beginning of the curve, it was possible to determine the gradient ($-k [\text{Na}_2\text{WO}_4]_0$) and the rate constant k could be determined. The results were presented in table 2.

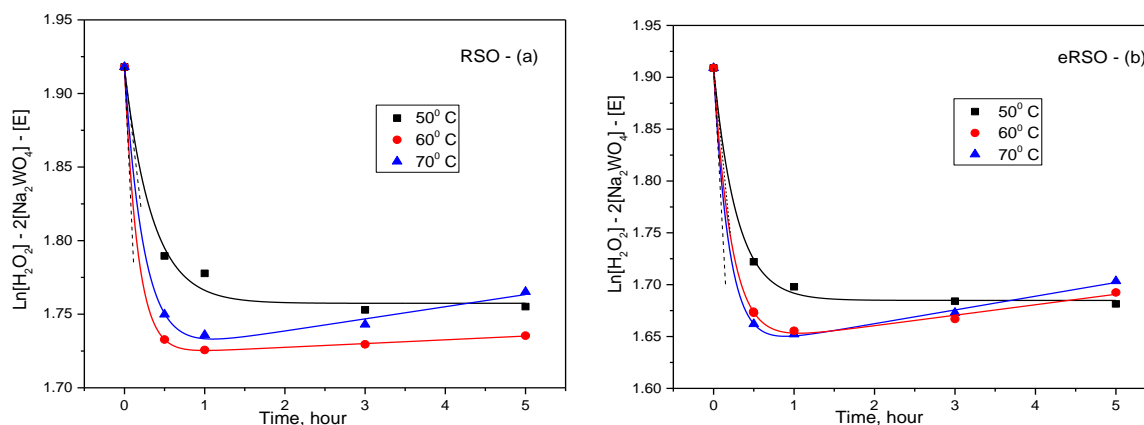
Fig. 4. The effect of time on $\ln([H_2O_2]_0 - 2[Na_2WO_4]_0 - [E])$

Table 2. The thermodynamic properties of epoxidation reaction

Oil	Reaction Temp. °C	Rate constant k, $L \cdot mol^{-1} \cdot s^{-1}$	ΔH , $J \cdot mol^{-1}$	ΔS , $J \cdot mol^{-1}$	ΔF , $J \cdot mol^{-1}$
RSO	50	0.57×10^{-2}	23242	-216.6	93232
	60	1.01×10^{-2}	23159	-214.5	94622
	70	1.00×10^{-2}	23075	-217.1	97585
eRSO	50	0.97×10^{-2}	25060	-206.6	91819
	60	1.49×10^{-2}	24977	-205.8	93542
	70	1.76×10^{-2}	24894	-207.1	95963

As can be seen from table 2, the rate constant depended on both the reaction temperature and the nature of the oil used. Like in the case of sunflower ($1.34 \div 3.32 \times 10^{-2} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) [8] and soybean oil ($0.45 \div 1.16 \times 10^{-2} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) [7], the rate constant of epoxidation reaction of RSO and eRSO using tungstate-based catalyst was about $10^{-2} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and 1000 times higher than that of epoxidation reaction using traditional catalyst such as rubber seed oil ($1.46 \times 10^{-5} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) [15], cotton oil ($0.23 \times 10^{-5} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) [16], mahua oil ($0.68 \times 10^{-5} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) [17] and palm olein methyl ester ($0.86 \times 10^{-5} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) [18].

The Arrhenius equation (3) showed the linear relationship between $\ln k$ and $1/T$ according to

the equation (4), where $(-\frac{E_a}{R})$ was the variational coefficient, k was the rate constant, E_a was the activation energy, T was the absolute temperature in kelvins, R was the universal gas constant ($8,314 \text{ J/K} \cdot \text{mol}$), A was the pre-exponential.

$$k = A \cdot e^{\frac{-E_a}{RT}} \quad (5)$$

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \ln A \quad (6)$$

The equation (6) showed the $\ln(k)$ was the reciprocal of T . The relationship between $\ln k$ and $1/T$ with three pairs of experiment data of the epoxidation reaction of RSO and eRSO was showed in fig.5.

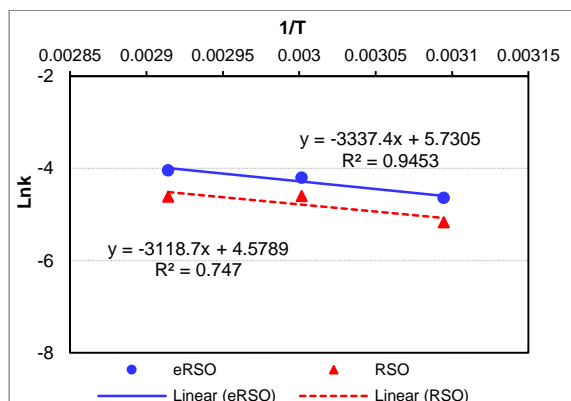


Fig. 5. The relation between $\ln k$ and $1/T$

As it shows in fig. 5, the plot of $\ln k$ versus T^{-1} gave the straight line whose gradient and intercept can be used to determine E_a and A . Here, the activation energy of epoxidation reaction of RSO and eRSO E_a were $25928.9 \text{ J}\cdot\text{mol}^{-1}$ ($6.2 \text{ kcal}\cdot\text{mol}^{-1}$) and $27747.1 \text{ J}\cdot\text{mol}^{-1}$ ($6.6 \text{ kcal}\cdot\text{mol}^{-1}$), respectively. They were almost the same but smaller than that of epoxidation reaction of soybean oil ($10.6 \text{ kcal}\cdot\text{mol}^{-1}$) using the same tungstate-based catalyst [7] and much smaller than that of epoxidation reaction using traditional catalyst of, for example, cotton oil ($11.7 \text{ kcal}\cdot\text{mol}^{-1}$) [16], mahua oil ($14.5 \text{ kcal}\cdot\text{mol}^{-1}$) [17] and palm olein methyl ester ($15.1 \text{ kcal}\cdot\text{mol}^{-1}$) [18].

The enthalpy (ΔH), free energy (ΔF) and entropy (ΔS) were calculated by using formulas (7), (8), (9) [7, 8] and the results were shown in table 2.

$$\Delta H = E_a - RT \quad (7)$$

$$\Delta F = \Delta H - T\Delta S \quad (8)$$

$$k = \frac{RT}{Nh} e^{\frac{\Delta S}{R}} e^{\frac{-\Delta H}{RT}} \quad (9)$$

N : Avogadro constant, h : Planck constant

It is found that, because of the positive enthalpy ΔH , the epoxidation reaction was endothermic reaction and the yield of reaction grew up with increasing temperature from 50 to 70°C.

On the other hand, the reverse reaction such as epoxy ring-opening reaction could also take place because of the positive free energy ΔF .

The higher temperature reaction was, the more positive free energy and the easier epoxy ring-opening reaction occurred. The free energy of epoxidation reaction of RSO was bigger than that of eRSO meaning the epoxy ring-opening reaction in case of RSO also took place more. This result was consistent with the lower yield and selectivity in section 3.2.

4. Conclusion

It was determined the thermodynamic properties of the epoxidation reactions. The rate constant of them was about $10^{-2} \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and the activation energy E_a was 6.2 (RSO) and 6.6 (eRSO) $\text{kcal}\cdot\text{mol}^{-1}$.

The positive enthalpy ΔH demonstrated the epoxidation reaction was endothermic one but the free energy ΔF was also positive, so there was a specific temperature at which the epoxidation reaction had the greatest efficiency. The experimental results showed the 60°C was the most suitable temperature for both two epoxidation reactions with the conversion, yield and selectivity were 91.37%, 75.06%, 0.82 with RSO and 94.87%, 89.56%, 0.94 with eRSO, respectively.

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Nghiên cứu động học phản ứng epoxy hóa dầu hạt cao su sử dụng xúc tác trên cơ sở muối vonfram

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Tóm tắt: Bằng việc thực hiện phản ứng trong 1 giờ tại ba nhiệt độ khác nhau đã xác định được các tính chất nhiệt động của phản ứng epoxy hóa dầu hạt cao su và dầu hạt cao su biến tính khi sử

dụng xúc tác trên cơ sở muối vonfram. Hằng số tốc độ của phản ứng epoxy hóa thay đổi từ $0,57 \cdot 10^{-2}$ tới $1,01 \cdot 10^{-2} \text{ l.mol}^{-1} \cdot \text{s}^{-1}$ với RSO và $0,97 \cdot 10^{-2}$ tới $1,76 \cdot 10^{-2} \text{ l.mol}^{-1} \cdot \text{s}^{-1}$ với eRSO. Năng lượng hoạt hóa đạt $6,2 \text{ kcal.mol}^{-1}$ (RSO) và $6,6 \text{ kcal.mol}^{-1}$ (eRSO). Giá trị entanpy hoạt hóa ΔH đều dương cho thấy quá trình epoxy hóa là phản ứng thu nhiệt nhưng năng lượng hoạt hóa tự do ΔF cũng đều dương nên tồn tại một nhiệt độ mà tại đó quá trình epoxy hóa đạt hiệu quả cao nhất. Các kết quả thực nghiệm đã chỉ ra 60°C là nhiệt độ phù hợp nhất cho quá trình epoxy hóa cả RSO và eRSO với mức độ chuyển hóa nối đôi đạt 91,37% (RSO) và 94,87% (eRSO), hiệu suất epoxy hóa đạt 75,06% (RSO) và 89,56% (eRSO) và xúc tác có độ chọn lọc đạt 0,82 (RSO) và 0,94 (eRSO).

Keywords: Dầu hạt cao su epoxy hóa, động học phản ứng, xúc tác vonfram.