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Kinetics of petroleum resin epoxidation by peracetic acid

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Abstract

The *in situ* oxidation of the petroleum resin under soft condition was investigated. The oxidation was carried out by using hydrogen peroxide and acetic acid as the oxidants, and sulphuric acid as a catalyst for *in situ* formation of the peracetic acid. The infrared spectroscopy analysis shows the changes in the molecular structure: the amount of the epoxy, hydroxyl and carbonyl groups increases and the number of unsaturated bonds decreases. The new method for the determination of the reaction rate constant was presented. For the determination of the reaction rate constants the relative intensity of absorption band in the area of epoxy and carboxyl groups vibration was used. Obtained data are in a very good correlation with the reaction rate constants obtained with the epoxy and acid number valuation. That allows to conclude the validity of using presented algorithm. Kinetic calculation indicates the occurrence of the oxidation reaction by the first order. According to average reaction rate constant the process has a high selectivity for epoxy groups.

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Keywords: *in situ* epoxidation, petroleum resin, kinetics, modification.

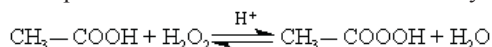
1. Introduction

The olefin production is still growing and changing constantly. Production of ethylene through pyrolysis produces about 20 % of by-products, which can be used for different applications. The polymerization of different fractions of pyrolysis by-products is a widely investigated process. Obtaining products are known as petroleum resins (PRs), which are widely used for paints as a substitute of natural oil¹. Coverings based on PRs are applicable in paint and

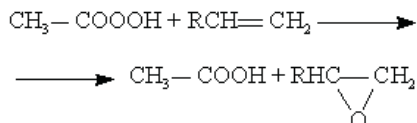
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varnish industry. However, the adhesion of coatings based on PRs is generally poor and, therefore, requires additional substrate preparation for proper paint adhesion. The most popular way to modify PRs is their oxidation with using different oxidants²⁻⁴. Use of peracetic acid (PAA) as an oxidant of unsaturated bonds allows to obtain PRs with high amount of epoxy groups⁵. *In situ* epoxidation passes under soft conditions⁶⁻⁸ with almost complete conversion of unsaturated carbon⁹. *In situ* epoxidation of unsaturated bonds of PRs with peracetic acid is a heterogeneous catalytic process in which peracetic acid formation is an acid-catalyzed reaction:



whereas the main reaction involving the epoxy group formation is an uncatalyzed reaction¹⁰:



The objective of this work is to investigate the kinetic reproducibility of the *in situ* petroleum resin epoxidation with use of hydrogen peroxide and acetic acid.

2. Experimental part

Oxidation of PRs by peracetic acid, which was synthesized *in situ* during a reaction of PRs with H₂O₂ and acetic acid. Oxidation of 50% PR solution in toluene was carried out using system H₂O₂:CH₃COOH. The weight ratio PR:H₂O₂ was 1:0.5 and the molar ratio H₂O₂:CH₃COOH was 1:0.5. Sulfuric acid was chosen as the catalyst for peracetic acid formation. Adding an oxidizing system was performed at 55 °C, the mixture was kept under constant stirring at 75 °C for 2 hours. Neutralization of the acid was carried out by repeated washing of the reaction mixture with water to pH = 7. Separated from the organic layer the aqueous layer was dried in air at 20 – 25 °C.

The structure of initial and oxidized samples of PRs was analyzed by infrared and Fourier transformed infrared spectroscopy (Infralume FT 801) in the 600 – 4000 cm⁻¹ range. The acid and epoxy numbers were tested by standard titrimetric analysis.

3. Results and discussions

The molecular structures of the initial and oxidized PRs are shown in Fig. 1.

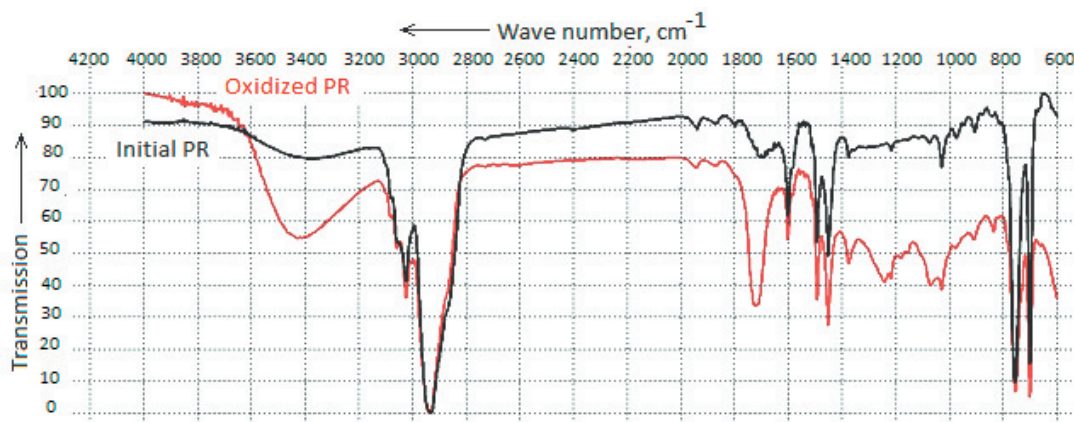


Fig.1. IR-spectra of initial and oxidized PR (285 min)

The initial PR spectra is characterized by a strong (broad) peak at 1601 cm^{-1} indicating the C=C of olefin bonds vibration and the numerous weak peaks (vibrations) in the 1700 to 2000 cm^{-1} area (“comb”) are due to the ν ring C—C vibrations (so-called styrene blocks). The medium peaks in 1375 cm^{-1} area are characterized by the deformation vibrations of $-\text{CH}_2$, which also indicate the aliphatic fragments presented in resin structure. The spectra of the oxidized resins show a large decrease in the C=C vibration and appearance of peaks at 3440 cm^{-1} and 1720 cm^{-1} due to hydroxyl and carboxyl vibrations. The appearance of new peaks at 1240 and 1070 cm^{-1} indicates the epoxy groups vibrations and asymmetric stretching vibrations of ether groups, respectively.

Using the valuation of relative intensity of absorption band in the area of 1240 and 1720 cm^{-1} it is possible to determine epoxidation and carboxylation reaction rate constants. Relative intensity of absorption band in the area of 1240 and 1720 cm^{-1} , epoxy and acid numbers are shown in the table 1.

Table 1. . Relative intensity of absorption band in the area of 1240 and 1720 cm^{-1} , epoxy and acid numbers of initial and oxidized PR

Time, min	Relative intensity of absorption band in IR-spectra		Epoxy Number, %	Acid number, g KOH/1 g PR	Time, min	Relative intensity of absorption band in IR-spectra		Epoxy Number, %	Acid number, g KOH/1 g PR
	I_{1240}^{1240}	I_{1720}^{1720}				I_{1240}^{1240}	I_{1720}^{1720}		
0	0.00	0.21	0.47	0	105	0.14	1.35	11.29	6.51
10	0.00	0.34	2.8	2.59	135	0.23	1.46	12.56	7.22
20	0.00	0.50	3.74	3.86	165	0.27	1.53	13.23	7.77
30	0.01	0.63	4.19	4.83	195	0.29	1.61	13.59	8.02
35	0.01	0.73	4.69	5.39	255	0.31	1.72	13.63	9.87
45	0.03	0.96	5.91	5.56	285	0.31	1.91	13.98	9.87

The in situ oxidation of petroleum resins has the first order⁷ therefore the reaction equation is the following:

$$\frac{dx}{dt} = k(1 - x)$$

where x – functional conversion;
 k – reaction rate constant.

The reaction rate constant in this case is defined as the angle of inclination of the line to the axis absciss. The line equation is the following:

$$y = \ln \frac{1}{1-x}$$

Functional conversion is defined using the equation:

$$x = \frac{n_0 - n}{n_0},$$

Where $n_0 = n_{\max} - n_{\min}$ is the initial valuation of the parameter, $n = n_{\max} - n_t$ is the parameter valuation in the current moment.

Earlier it was established that technically, the entire process can be divided into two main stages:

- adding an oxidant into the solution of modified resin;
- direct PR oxidation for a specified period of time⁵.

According to this fact the process becomes stable only after adding all the oxidant. Consequently the reaction rate constants can be calculated only for the second period- carboxylation and epoxidation of the PR (from the 105th minute).

Fig 2 shows the plots to determine the epoxidation and carboxylation reactions rate constants with the use of relative intensity of absorption band in the area of 1240 and 1720 cm^{-1} .

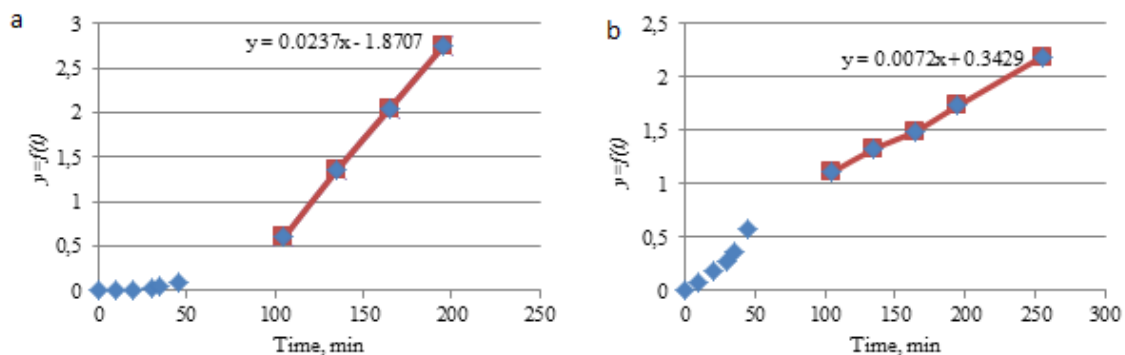


Fig. 2 Plots to determine the epoxidation(a) and carboxylation(b) reactions rate constants with the use of relative intensity of absorption band in the area of 1240 and 1720 cm^{-1}

According to the data the epoxidation reaction rate constant is 0.0237 min^{-1} or $3.95 \cdot 10^{-4} \text{ s}^{-1}$ and the carboxylation reaction rate constant is 0.0072 min^{-1} or $1.2 \cdot 10^{-4} \text{ s}^{-1}$. There is a clear linear dependence $y = f(t)$ after the 105th minute, that indicates the occurrence of the oxidation reaction by the first order.

Reaction rate constants were also determined by using the epoxy and acid numbers valuations (Fig. 3).

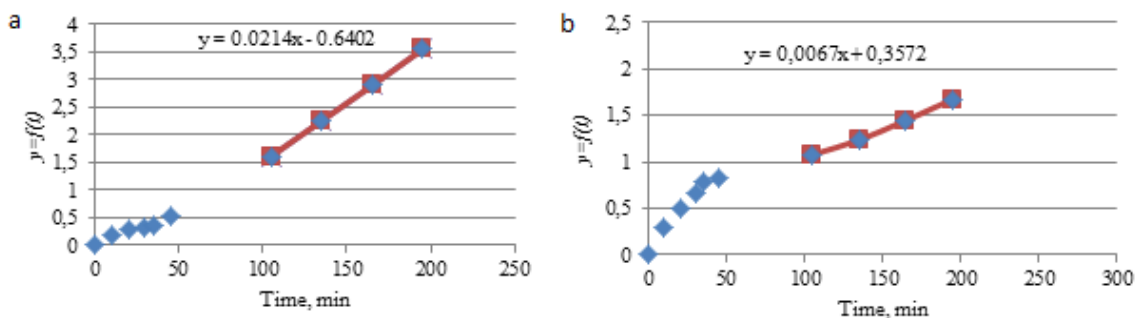


Fig. 3 Plots to determine the epoxidation(a) and carboxylation(b) reactions rate constants with the using of epoxy and acid numbers valuations

According to the data the epoxidation reaction rate constant is 0.0214 min^{-1} or $3.57 \cdot 10^{-4} \text{ s}^{-1}$ and the carboxylation reaction rate constant is 0.0067 min^{-1} or $1.1 \cdot 10^{-4} \text{ s}^{-1}$. This fact allows us to conclude the validity of using presented algorithm to determine the reaction rate constants. Average constants values are: for epoxidation $3.76 \cdot 10^{-4} \text{ s}^{-1}$ and for carboxylation $1.15 \cdot 10^{-4} \text{ s}^{-1}$, this is in 3.26 times slower.

4. Conclusion

Summing up, the in situ oxidation of the PRs leads to the appearance of epoxy and carboxyl groups. According to average reaction rate constant the process has a high selectivity for epoxy groups.

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