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EPOXIDATION OF THE RAPESEED OIL WITH PERACETIC AND PERFORMIC ACID

EPOKSYDOWANIE OLEJU RZEPAKOWEGO KWASEM NADOCTOWYM I NADMRÓWKOWYM

Abstract

The results of epoxidation of the rapeseed oil (RO) with peracetic and performic acids which were prepared *in situ* in the reaction of 30 wt.% hydrogen peroxide and appropriate carboxylic acid have been presented. The influence of temperature (30–75°C), the molar ratio of H₂O₂/RO (1.5:1–4.0:1), the molar ratio of carboxylic acid/RO (0.2:1–0.65:1), stirring speed (100–900 rpm) and the reaction time (2.5–7 h) were studied. The degree of oil epoxidation was determined by means of the epoxy number.

Keywords: epoxidation with peracids obtained in situ, peracetic acid, performic acid

Streszczenie

Przedstawiono wyniki badań epoksydowania oleju rzepakowego za pomocą kwasów nadocetowego i nadmrówkowego, otrzymywanych *in situ* w reakcji 30% nadtlenu wodoru i odpowiedniego kwasu karboksylowego. Ustalono wpływ: temperatury (30–75°C), stosunku molowego H₂O₂/OR (1,5:1–4,0:1), stosunku molowego kwasu karboksylowego/OR (0,2:1–0,65:1), intensywności mieszania (100–900 rpm) i czasu reakcji (2,5–7 h). Stopień epoksydowania oleju określono wartością liczby epoksydowej.

Słowa kluczowe: epoksydowanie nadkwasami in situ, kwas nadocetowy, kwas nadmrówkowy

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Symbols

RO	– rapeseed oil
CA	– carboxylic acid
AA	– acetic acid
FA	– formic acid
IN	– iodine number
EN	– epoxy number
C _{IN}	– conversion of the rapeseed oil to epoxide calculated from the iodine number
C _{EN}	– conversion of the rapeseed oil to epoxide calculated from the epoxy number
S _{EN/IN}	– selectivity of the transformation to epoxidized rapeseed oil calculated from the epoxy number and iodine numbers

1. Introduction

Epoxidized vegetable oils have received growing interest in recent years. Nowadays, one of the most important epoxidized vegetable oil is soyabean oil and its worldwide production amounted to about 200,000 Mg in 1990 [1, 2].

Vegetable oils are used to introduce the epoxy groups, because of the presence of unsaturated bonds in such fatty acids as oleic, linolic and linolenic [1, 2].

The major applications of epoxidized vegetable oils are plasticizers and stabilizers of plastics, especially polyvinyl chloride, because they are compatible with this material. They are used in mixtures with polymers in the production of alkyd paints instead of traditional solvents which are emitted to the atmosphere [3, 4]. With regard to the improvement in the elasticity of material, these materials are important in the production of packing polymer materials, as for example wrapping foils [5]. Due to the high reactivity of the oxirane ring in epoxidized oils, they are used as renewable raw materials for manufacturing such intermediate products as: alcohols, glycols, alkoxyalcohols, hydroxyesters, N-hydro-xyalkylamides, mercaptoalkohols, hydroxynitriles, alkanolamines, carbonyl compounds [1, 2, 6].

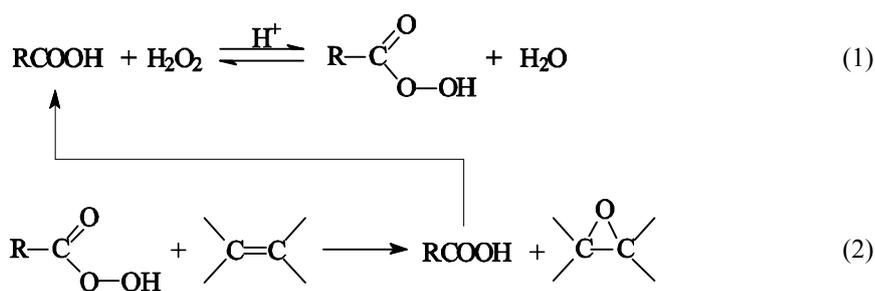


Fig. 1. The main reactions of epoxidation of the rapeseed oil with peracids formed in situ

Rys. 1. Reakcje główne epoksydowania nadkwasami *in situ*

A widely used method of the epoxidation of vegetable oils relies on the application of peracids (previously prepared or generated in situ). During the epoxidation with peracids

generated in situ, simultaneously proceeds a reversible reaction of generated peracid from hydrogen peroxide and acid, and the epoxidation of an unsaturated compound (Fig. 1) [7, 8]. An acid formed in reaction 2 reacts again with the hydrogen peroxide to form a peracid.

The rate limiting stage of the process is the generation of peracid. The course of the reaction of peracids preparation is accelerated by strong mineral acids, most often by sulphuric acid [6, 9]. The selection of process parameters so that the epoxidation will proceed faster than the generation of peracid is an important issue. Otherwise, the generated peracid may decompose under the reaction conditions and the yield of the epoxidation recalculated on the consumed hydrogen peroxide will be quite low [7, 8].

The reaction environment contains water, mineral (catalyst) and organic acid which may cause the decomposition of the epoxy groups as a result of the hydrolysis and acylation (Fig. 2).

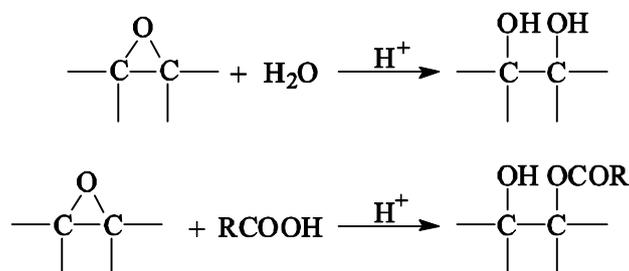


Fig. 2. Side reactions of the epoxidation process

Rys. 2. Reakcje uboczne procesu epoksydowania

Various methods are used to limit the course of these reactions. For this purpose the sulphuric acid should be cautiously neutralized, or cation exchangers, e.g. sulphonated styrene – divinylbenzene copolymer – should be used.

2. Experimental

Rapeseed oil manufactured in the plants of the Fat Industry in Warsaw was used in the studies. The molar mass of oil calculated on the basis of percentage content of the carboxylic acids was 281.2 g/mol. The following raw materials were used in the syntheses: glacial acetic acid (99.5 wt.%, POCh Gliwice), formic acid (85 wt.%, POCh Gliwice), hydrogen peroxide (30 wt.% aqueous solution, POCh Gliwice) and sulphuric acid (Chempur).

The epoxidation of rapeseed oil was carried out with the use of peracetic and performic acid, generated directly in the environment of the reaction as a result of the reaction of 30 wt.% solution of hydrogen peroxide and acetic or formic acid respectively. The following parameters were varied during the epoxidation of RO: the temperature, the molar ratio of reagents, stirring speed and the reaction time. Rapeseed oil, carboxylic acid and concentrated sulphuric acid as a catalyst were placed in a flask. The 30 wt.% hydrogen peroxide was added to this solution with the speed (10–40 min) enabling to maintain the constant reaction temperature. After separation of the phases of the reaction mixture, the

resulting organic layer was neutralized with 20 wt.% sodium hydroxide and washed with distilled water. The remainder of the water was removed with anhydrous magnesium sulphate(VI). The aqueous layer resulting from the separation of the reaction products was subject to column distillation in order to recover the carboxylic acid.

The conversion of the rapeseed oil and the selectivity of the transformation to epoxidized oil was calculated on the basis of the determined values of iodine and the epoxy number. The iodine and epoxy numbers were calculated in accordance with obligatory standards [10, 11]. The conversion and the selectivity of the transformation were calculated according to the following equations

$$C_{IN} = \frac{IN_{be} - IN_{ae}}{IN_{be}} \cdot 100\% \quad (3)$$

where:

C_{IN} – conversion of the rapeseed oil to epoxide calculated from the iodine number,

IN_{be} – iodine number of the rapeseed oil before epoxidation,

IN_{be} – 79.72 g/100 g RO = 0.314 mol/100 g RO,

IN_{ae} – iodine number of the rapeseed oil after epoxidation

$$C_{EN} = \frac{EN_{ae}}{EN_{max}} \cdot 100\% \quad (4)$$

where:

C_{EN} – conversion of the rapeseed oil to epoxide calculated from the epoxy number,

EN_{ae} – epoxy number of the rapeseed oil after epoxidation,

EN_{max} – epoxy number of the rapeseed oil calculated from the number of unsaturated bonds of used RO, $EN_{max} = 0.314$ mol/100 g RO

$$S_{EN/IN} = \frac{EN_{ae}}{IN_{be} - IN_{ae}} \cdot 100\% \quad (5)$$

where:

$S_{EN/IN}$ – selectivity of the transformation to epoxidized rapeseed oil calculated from the epoxy number and iodine number.

3. Results and discussion

The influence of temperature on a value of the epoxy number of an obtained product was studied in the range of 30–75°C. Based on the literature data and preliminary investigations, the following initial conditions were assumed: sulphuric acid – catalyst – 2 wt.% in relation to the epoxidizing mixture, stirring speed – 500 rpm, the reaction time – 4 h, the molar ratio of reagents RO/H₂O₂/CA = 1:1.5:0.5. An analysis of the influence of temperature on the changes in the epoxy number (Fig. 3) demonstrates that the temperature of 60°C was the most advantageous during the epoxidation of rapeseed oil. The temperature

of 60°C was chosen with regard to a high EN in a comparison with syntheses carried out in other temperatures. An increase in the temperature from the room temperature to 60°C causes an increase in the epoxy number. However, the value of the epoxy number decreases above 60°C. The obtained epoxy groups undergo the hydrolysis with the formation of glycols and in acetylation resulting in the formation of acetates and diacetates of rapeseed oil.

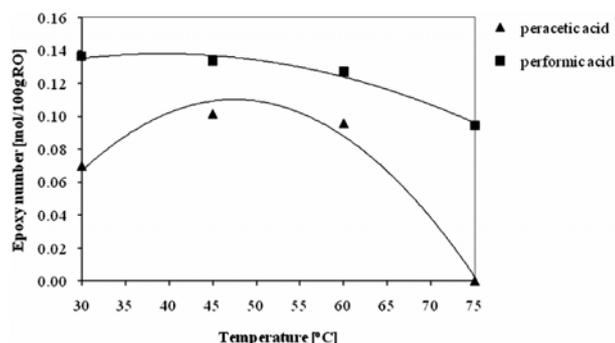


Fig. 3. The influence of temperature on the RO epoxidation

Rys. 3. Wpływ temperatury na epoksydowanie RO

In order to determine the influence of the molar ratio of H_2O_2/RO on the course of the epoxidation process, the syntheses were carried out in the range: 1.5:1–4.0:1. A temperature of 60°C and the molar ratio of carboxylic acid to rapeseed oil were established in these studies. The remaining parameters were the same as during the studies of the influence of temperature. On the basis of changes of the epoxy number (Fig. 4) it was found that the molar ratio $H_2O_2/RO = 3:1$ was the most advantageous when the acetic acid was used, wherein in the case of using formic acid the most advantageous ratio was $H_2O_2/RO = 3.5:1$. Under these conditions the highest epoxy numbers were achieved.

The influence of the molar ratio of CA/RO was studied in the range 0.2:1–0.65:1. A temperature of 60°C and the molar ratio $H_2O_2/RO = 3:1$ for the acetic acid and $H_2O_2/RO = 3.5:1$ for the formic acid were established in these studies. The remaining parameters were the same as in the previously performed experiments. On the basis of the obtained results (Fig. 5), it was found that the molar ratios of $AA/RO = 0.35:1$ and $FA/RO = 0.5:1$ are the most advantageous during the preparation of epoxidized oil.

In order to study the influence of stirring, the syntheses were carried out at various stirring speeds in the range of 100–900 rpm. In these studies the following parameters were established: a temperature of 60°C, a reaction time of 4 h, and the molar ratio of reagents $RO/H_2O_2/AA = 1:3:0.35$ and $RO/H_2O_2/FA = 1:3.5:0.5$. Similarly to the previous experiments, the amount of sulphuric acid amounted to 2 wt.% in relation to the epoxidizing mixture. On the basis of the changes of the epoxy number (Fig. 6) it was found that the highest conversion of rapeseed oil to the epoxy compounds was achieved at the stirring speed of 500 rpm. A decrease of the epoxy number after exceeding 500 rpm demonstrates that too intensive stirring (dispersion of oil – water emulsion) causes the intensification of the successive reactions of hydration and esterification of the oxirane groups of epoxidized rapeseed oil.

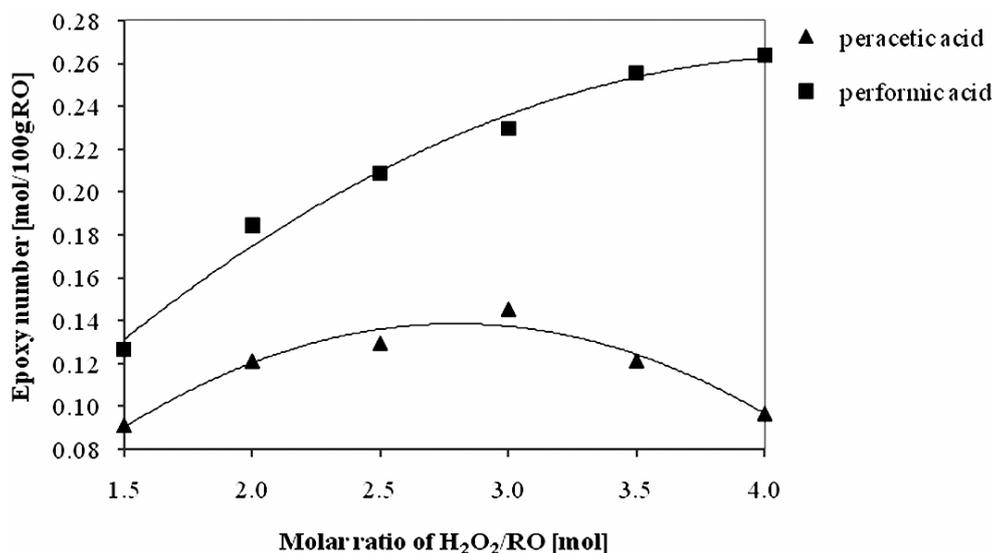
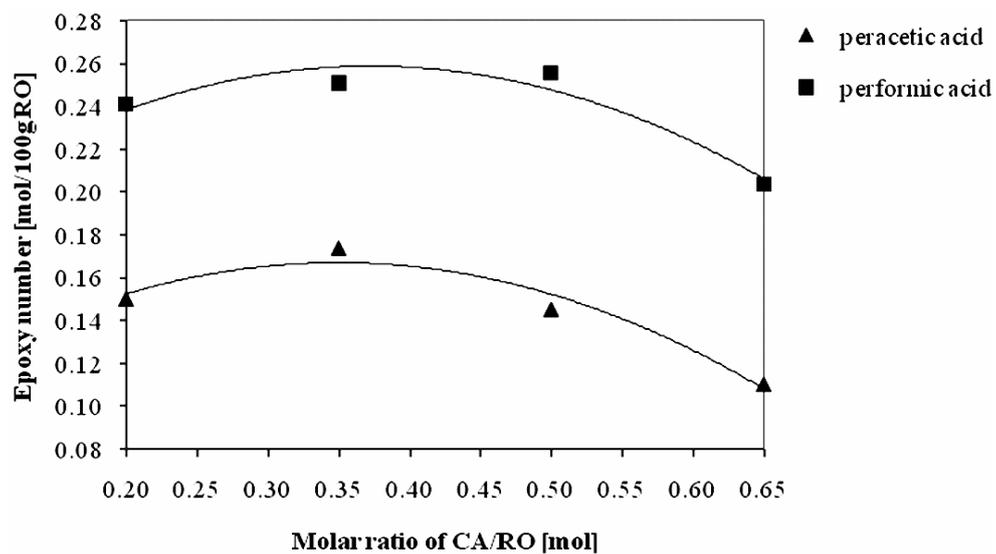
Fig. 4. The influence of the H₂O₂/RO molar ratio on the RO epoxidationRys. 4. Wpływ stosunku molowego H₂O₂/RO na epoksydowanie RO

Fig. 5. The influence of the CA/RO molar ratio on the RO epoxidation

Rys. 5. Wpływ stosunku molowego CA/RO na epoksydowanie RO

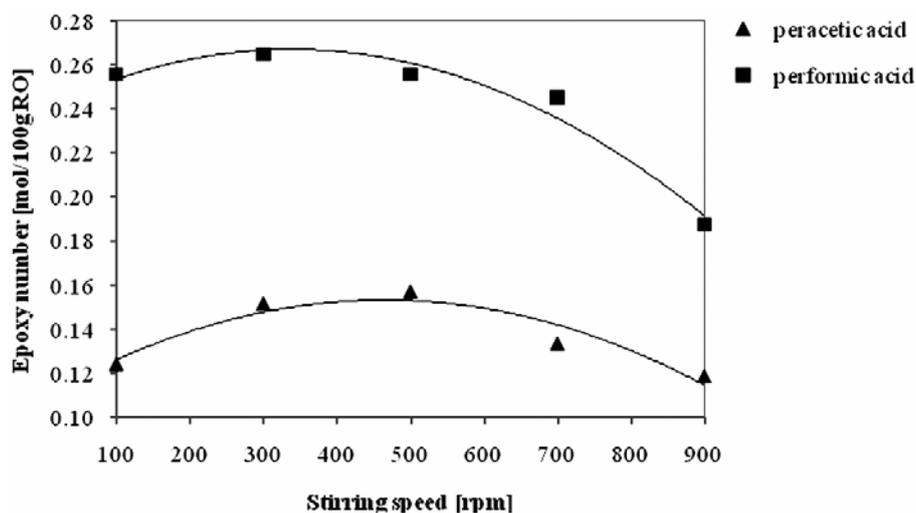


Fig. 6. The influence of stirring speed on the RO epoxidation

Rys. 6. Wpływ szybkości mieszania na epoksydowanie RO

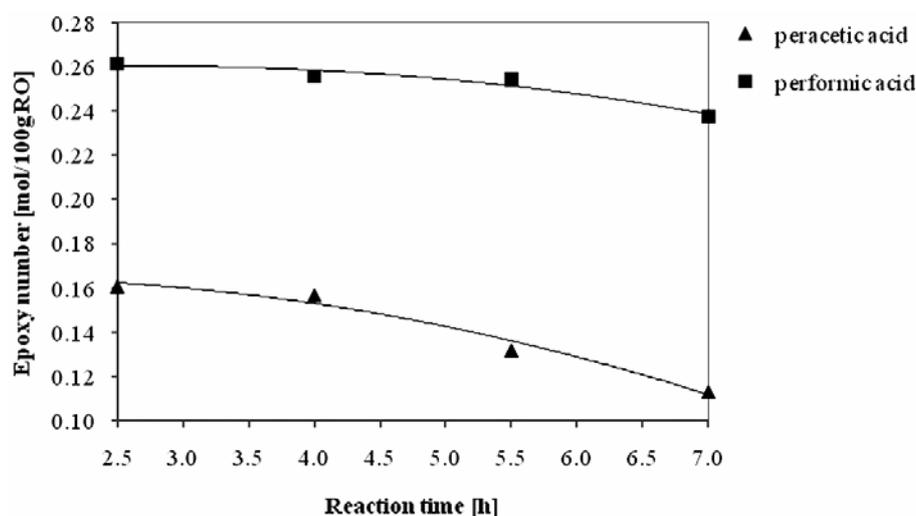


Fig. 7. The influence of a reaction time on the RO epoxidation

Rys. 7. Wpływ czasu reakcji na epoksydowanie RO

The influence of the reaction time on the course of epoxidation was studied in the range 2.5–7 h. The following parameters were established in the studies: a temperature of 60°C, the molar ratio of RO/H₂O₂/AA = 1:3:0.35 and RO/H₂O₂/FA = 1:3.5:0.5 and the stirring speed of 500 rpm. Sulphuric acid was used as a catalyst in the amount of 2 wt.% in relation

to the epoxidizing mixture. By carrying out the process under a/m conditions and changing the reaction time (Fig. 7) it can be seen, that the highest values of the epoxy number – $EN = 0.16 \text{ mol}/100 \text{ g RO}$ for acetic acid and $EN = 0.26 \text{ mol}/100 \text{ g RO}$ for formic acid were achieved after 2.5–4 h. Hence, the reaction time of 4 h is the most advantageous for the preparation of epoxidized rapeseed oil irrespective of the kind of carboxylic acid.

4. Conclusions

The best results of epoxidation were obtained under the following conditions: a temperature of 60°C , stirring speed – 500 rpm, the reaction time – 4 h. The molar ratio of the reagents in the presence of peracetic acid was $RO/H_2O_2/AA = 1:3:0.35$, and that for performic acid: $RO/H_2O_2/FA = 1:3.5:0.5$. The best technological parameters are similar for both acids, but the conversion and the selectivity are higher for the process carried out in the presence of performic acid (Fig. 8).

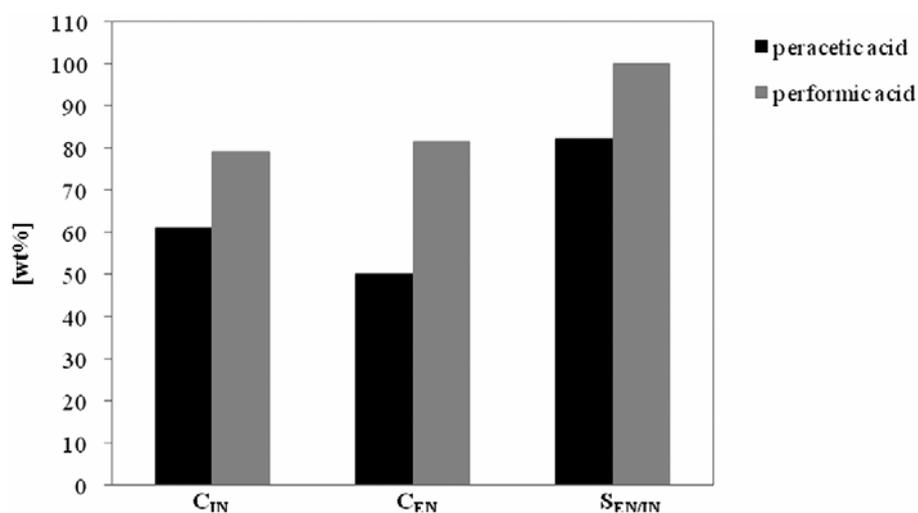


Fig. 8. A comparison of the conversion and the selectivity of the epoxidation process of RO with the use of peracetic and performic acids

Rys. 8. Porównanie konwersji i selektywności procesu epoksydowania RO za pomocą kwasu nadoctowego i nadmwrótkowego

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