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FEATURES OF EPOXIDATION OF VEGETABLE OILS IN THE PRESENCE OF FORMIC ACID AND HYDROGEN PEROXIDE

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Abstract: *The epoxidation reaction of various vegetable oils (soybean, sunflower, corn, cottonseed, palm, etc.) was carried out using super formic acid as an oxidizing agent, which was formed in situ by the interaction of formic acid with hydrogen peroxide. As a result of palm oil epoxidation, the formic acid/hydrogen peroxide system, at a molar ratio of 1.0: 5.0: 2.0 (VO : HCOOH: H_2O_2), stirring speed 350 turns/min, temperature 60°C and reaction time 180-240 min. was used as an optimal condition for the epoxidation reaction of other vegetable oils. It found that the introduction of the entire amount of hydrogen peroxide for 30 minutes leads to a sharp decrease in the efficiency of epoxidation due to decomposition of hydrogen peroxide due to an uncontrolled increase in the temperature of the reaction medium) where toluene was used as a solvent (yield of epoxidized products is 64-71%). And, with a portioned supply of hydrogen peroxide 50 + 30 + 30g every 10-30 minutes, without the use of a solvent, the yield of epoxidized oils reaches 67-78%.*

Keywords*: vegetable oils, formic acid, hydrogen peroxide, sulfuric acid, epoxidation, epoxidized vegetable oils*

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Introduction

Vegetable oils are derived from biomass, especially by processing plant matter, fruit seeds, or wood. The annual production of such oils is 168.4 million tons; the bulk (80%) of which is used in the food industry, and the rest in the production of soaps, household detergents, lubricants and biofuels [1,2]. The most important industrial vegetable oils are palm, soybean, rapeseed, cottonseed and sunflower oils.

In connection with the advent of new technologies of “green chemistry” aimed at replacing petroleum products with renewable biological resources, both the demand for vegetable oils and their production have been steadily growing over the years [3,4].

It is known that in the vegetable oil molecule there are saturated bonds, as well as mono- and polyunsaturated double bonds (Table 1). Table 2 shows some physic-chemical properties and values of the iodine number of some vegetable oils [4].

Table 1. Fatty acid composition of vegetable oils, percentage of saturated (SFA), mono- and polyunsaturated (MUFA + PUFA) fatty acids and their functionality

Fatty acid, %	Oil				
	Sunflower	soybean	palm	corn	cottonseed
Palmitinic (C16:0)	6.0	11.0	41.0	10.8	21.6
Stearic (C18:0)	4.0	4.0	5.0	2.0	2.7
Oleic (C18:1)	42.0	23.5	45.0	26.4	19.6
Linolic(C18:2)	47.0	53.5	9.0	59.6	55.4
Linoleic (C18:3)	1.0	8.0	0.3	1.2	0.8
Saturated (SFA)	10.0	15.0	46.0	12.8	24.3

Mono+Polyunsaturated (MUFA+PUFA)	90.0	85.0	54.0	87.2	75.7
Functionality	4.6	4.5	1.8	4.4	4.3

Table 2. Physical-chemical properties and values of the iodine number of the starting vegetable oils.

Oils	Kinematic viscosity, cSt (at 37,8°C)	Density, (20°C/4°C)	Refractive index. (n_D^{20})	Tmelt, °C	Iodine value., g I_2/100 g of oil
Sunflower	33.31	0.916/0.923	1.473-1.477	from -18 to -16	125-140
Soybean	35.40	0.917/0.924	1.473-1.477	from -23 to -20	123-139
Palm	47.80	0.890/0.893	1.453-1.456	from 33 to 40	50-55
Corn	28.70	0.924/0.927	1.471-1.473	from -10 to -15	118-128
Cottonseed	37.9	0.917/0.930	1.468-1.472	from 0 to -2	99-113

An oxygen atom can be introduced into these unsaturated bonds by various oxidation methods commonly referred to as epoxidation reactions. As a result of the epoxidation of vegetable oils and / or their fatty acids, environmentally friendly and cost-effective epoxidized oils are synthesized.

Today, one of the most important epoxidized vegetable oils is the epoxidized soybean oil (ESO) with its worldwide production making about 2,000,000 tons/year (European market ~ 9,000 tons /year), and production growth is approximately 7% per year.

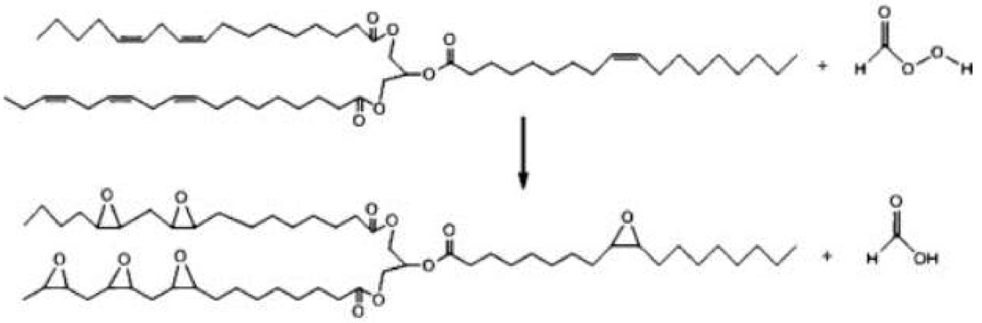
The effectiveness of epoxidized oils is directly related to the amount of the epoxy group in the oil molecule which is expressed by the Oxirane number (ON). Epoxidized oils are natural, non-toxic, non-aggressive and biodegradable products, and therefore can be good substitutes for phthalates and other plasticizers derived from oil, but banned by the EU in many countries, due to their high toxicity [2-4].

Due to the high reactivity of the oxirane ring, epoxides are also used as an intermediate for the synthesis of various chemicals, such as alcohols, glycols, alkanolamines, carbonyl and olefin compounds, as well as polymers such as polyesters, polyurethanes (PUs) and epoxies. Soybean-based modified polyols can be used as a replacement for conventional polyols in the production of elastic polyurethane foams, elastomers and coatings [3,4].

In industry, epoxidized vegetable oils are produced through the use of percarboxylic acids peracids formed in situ (for safety reasons) through acid-catalyzed peroxidation of the corresponding organic (carboxylic) acids with hydrogen peroxide. The formation of percarboxylic acid occurs from the corresponding carboxylic acid and hydrogen peroxide in the aqueous phase in accordance with the following reaction:

$$H_2O_2 + RCOOH \rightleftarrows RCOOOH + H_2O \quad (1)$$

Soluble mineral acids, most often sulfuric or phosphoric acid, are used as a catalyst for this reaction. In industry, it is possible to use various percarboxylic acids, such as performic, peracetic, perbenzoic, m-chloroperbenzoic, trifluoroacetic, 3,5-dinitroperbenzoic, etc., the choice of which depends on many factors, one of which is the Brønsted strength of the corresponding starting acid. Among them, formic and peracetic acids are more preferable because of their easy availability, low cost, high epoxidation efficiency and stability at ordinary temperature. Performic acid received *in situ* migrates into the aqueous phase, immiscible with the oil phase, according to reaction (2):



(2)

Performic acid reacts spontaneously with double bonds of vegetable oil to form epoxy groups, returns to the aqueous phase again and the reaction cycle resumes. It is known that when using formic acid, the rate of epoxide formation is higher than in the case of acetic acid, in the presence of which only 10% conversion of unsaturated bonds is achieved, but with less formation of undesirable by-products. The explanation for this is that due to the very high activity of formic acid, hydrogen peroxide decomposes faster.

The aim of this work is to select such epoxidation conditions that would ensure high yields using the simplest methods, environmentally acceptable, and cheap reagents.

Experimental part

We selected hydrogen peroxide and formic acid as the base-epoxidizing system. Hydrogen peroxide is cheap, non-toxic, and environmentally friendly (decomposes into water and oxygen, and after epoxidation, water is the only by-product). Aqueous solutions of hydrogen peroxide up to 50% concentration are quite stable and easy to handle. The corrosion activity of hydrogen peroxide is low. Formic acid is also cheap and easily neutralized after the reaction.

Vegetable oils, such as soybean, sunflower, corn, cottonseed, palm, as available, renewable bioresources containing a large amount of unsaturated fatty acids were epoxidized (Table 1,2).

Reagents — vegetable oils, hydrogen peroxide (50% solution), formic acid, sulfuric or phosphoric acid catalysts, “pure for analysis (pfa)” sodium bicarbonate, “pfa” potassium carbonate, ethyl acetate — were used without additional purification.

The epoxidation process was carried out in a round bottom flask equipped with a thermometer and a mechanical stirrer, since the process under study was greatly influenced by the efficiency of mixing the heterogeneous reaction mixture. Vegetable oil, formic acid, a certain amount of catalyst sulfuric acid - all were poured into the flask, and gradually, with constant stirring, a 50% solution of H_2O_2 was added. In some experiments, hydrogen peroxide was added in portions. The reaction mixture was heated to 60°C and constantly stirred for a certain period of time.

At certain intervals from the start of the reaction, a sample of the reaction mixture is taken to determine the content of hydrogen peroxide. Upon reaching a hydrogen peroxide content of less than 0.4% (wt.), the process stopped along with turning off heating and stirring.

After completion of the process, ethyl acetate was added to the reaction mixture, and the sample was washed with 5% sodium bicarbonate solution (to neutralize the remaining acid), distilled water and sodium chloride to separate the organic layer from the mixture.

The resulting heterogeneous mixture was separated on a separatory funnel. The organic layer, which is a solution of unreacted and epoxidized oil in ethyl acetate, was evaporated on a rotary evaporator.

To determine the oxirane ring, EVOs were studied using Fourier transform IR spectroscopy (FTIR) and nuclear magnetic resonance (^{13}C-NMR and ^{1}H-NMR) methods. The value of the content of oxirane oxygen (Oxyran number) was determined by the direct method using a solution of hydrobromic acid in ice acetic acid [5,6]. The conversion percentage was calculated based on the theoretical value of the Oxyran number of epoxidized oils [7,8]. The value of the Iodine number was determined in accordance with the Wijs method [9]. Characterization of the properties of the EVO is performed using methods for the study of kinematic and dynamic viscosities according to ASTM D 445-79.

The yield of epoxidized oil was judged from the analysis of ^{1}H-NMR spectra. The decrease in the molar fraction of double bonds in the product was estimated in comparison with the initial sample (Fig. 1 and Table 3).

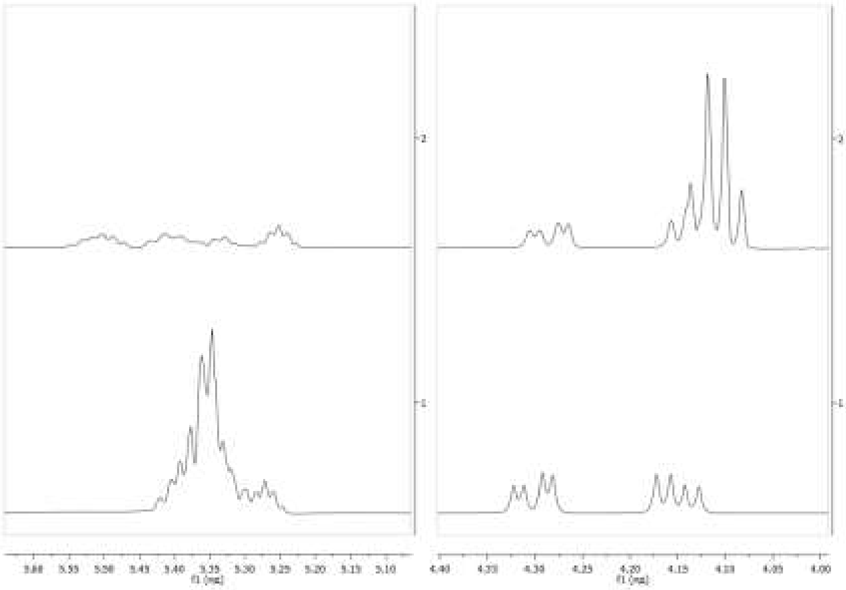


Fig. 1. ^{1}H-NMR spectra of the starting (a) and epoxidized (b) vegetable (palm) oils.

Table 3. Comparative data ^{13}C-NMR and ^{1}H-NMR of the initial (PO) and epoxidized (EPO) palm oil

Product	Chemical shifts, ppm	Chemical shifts, ppm (theoretical)	Bond
^{13}C-NMP			
PO	130.3761; 130.1697; 129.8638; 129.8409	100-150	C=C
EPO	57.3681; 57.3070; 54.4778	40-80	C-O
^{1}H-NMP			
PO	5.3763; 5.3625; 5.3543; 5.3479; 5.3406; 5.3314; 5.2801; 5.2691; 5.2545; 2.0772; 2.0608; 2.0205; 2.0058;	4.5-6.6 1.6-2.6	C=C-H (vinyl hydrogen) C=C-C-H (allyl hydrogen)
EPO	2.9030; 1.4907; 1.4513	2.5-3.5 1.4-1.7	Epoxides R_3CH

Results of optimizing the epoxidation conditions of various vegetable oils with the formic acid/hydrogen peroxide system are given in Table 4.

Research results and discussion

In laboratory studies, we took as a basis the molar ratios of reagents and catalyst components that provide better results: [PO]: [HCOOH]: [H_2O_2] = 1: (1.5-5.0) : (0.5-2.0). Results of the study are given in Table 4.

Table 4. Conditions for epoxidation of various vegetable oils. Taken: oil - 300 g, H_2SO_4 catalyst - 1.2 g, T = 60°C, solvent - 300 ml.

NN.	Vegetable oil	H_2O_2 (50%),г	Formic acid, g	Solvent	Duration, min	Conversion, %	Yield, %
1.	Palm	50+30+30	30	Absence	180	90.5	72.0
2.	Sunflower	50+30+30	30	Absence	180	88.0	67.0
3.	Sunflower	150	50	Толуол	240	86.0	64.0
4.	Corn	50+30+30	30	Absence	180	92.0	67.0
5.	Cottonseed	50+30+30	30	Отсутствие	180	91.0	69.0
6.	Cottonseed	150	50	Absence	240	88.0	70.0
7.	Soybean	150	50	Toluene	240	94.0	71.0
8*.	Soybean	42	11	Absence	180	94.0	72.0
9.	Acid of cottonseed oil	50+30+30	60	Absence	180	90.0	75.0
10.	Oleic acid	50+30+30	60	Absence	180	95.0	78.0

Note: *) Soybean oil - 100 g, H_2SO_4 catalyst - 0.8 g.

From the point of view of economic efficiency, the optimal epoxidation of palm (PO) oil using *in situ* performic acid can be carried out in a molar ratio of 1.0: 5.0: 2.0 (PO: HCOOH: H_2O_2) at a stirring speed of 350 turns/min. and a temperature of 60° C for 180 minutes, without the use of a solvent and with a portioned supply of hydrogen peroxide (50 + 30 + 30) for 30 minutes. At 90.5% conversion, the yield of epoxidized product was 72.0% with a selectivity of 65.0%, which corresponds to the Oxirane number of 3.00% (theoretical value of 3.74%). The density of the EPO was 0.886 g/ml, with a kinematic viscosity of 358.1 cSt and a dynamic viscosity of 317.3 cP.

The formic acid / hydrogen peroxide system at a molar ratio of 1.0: 5.0: 2.0 (PO: HCOOH: H_2O_2), a stirring speed of 350 rpm, a temperature of 60°C, and a reaction time of 180-240 min were used as optimal condition in the epoxidation reaction of other vegetable oils. Results are shown in Table. 4.

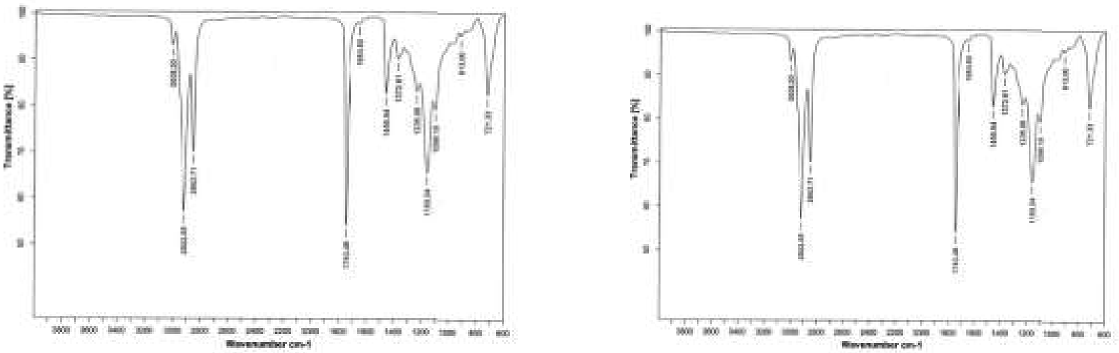
The method of adding hydrogen peroxide has a significant effect, since after 3 hours it is practically consumed/decomposed. If after 10-30 minutes hydrogen peroxide was added in portions (experiments 1, 2, 4), this led to a significant increase in the yield of the product (Table 4).

As can be seen from the Table 4, in experiments 1, 2, 4, 5,9,10 in which the hydrogen peroxide was introduced in portions: 50 + 30 + 30 g every 10-30 minutes, without the use of a solvent, the yield of epoxidized oils reaches 67-78%. With the introduction of the entire amount of hydrogen peroxide in 30 minutes (experiments 3, 6, 7, 8) (faster introduction of hydrogen peroxide leads to a sharp decrease in the efficiency of epoxidation due to decomposition of hydrogen peroxide caused by an uncontrolled increase in the temperature of the reaction medium) in which the solvent used toluene, the yield of epoxidized products is 64-71%.

In Figures 2-8 show the IR spectra of the corresponding starting (a) and epoxidized (b) vegetable oils.

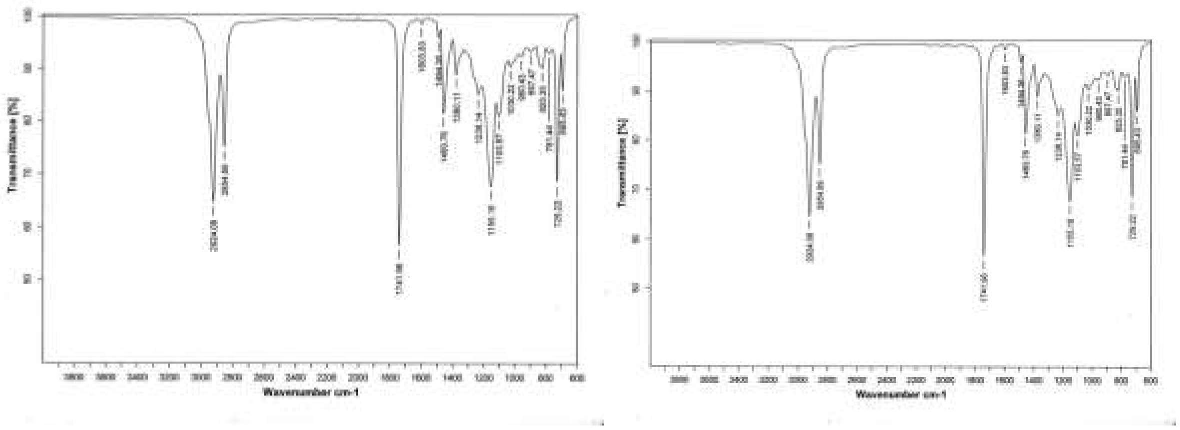
Results of the study show that the yield of the epoxidized product depends both on the type of the starting vegetable oil and the reaction conditions, and on the method of introducing hydrogen peroxide.

Thus, the study showed that the most effective of environmentally friendly and affordable methods of epoxidation is the formic acid system and hydrogen peroxide, while any additives to this system do not increase its effectiveness.



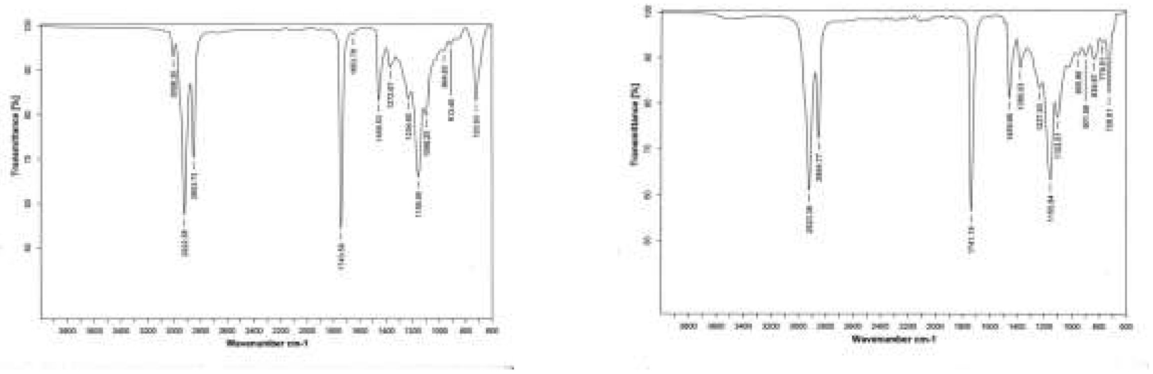
a) b)

Fig. 2. IR spectra of the initial (a) and epoxidized (b) palm oil



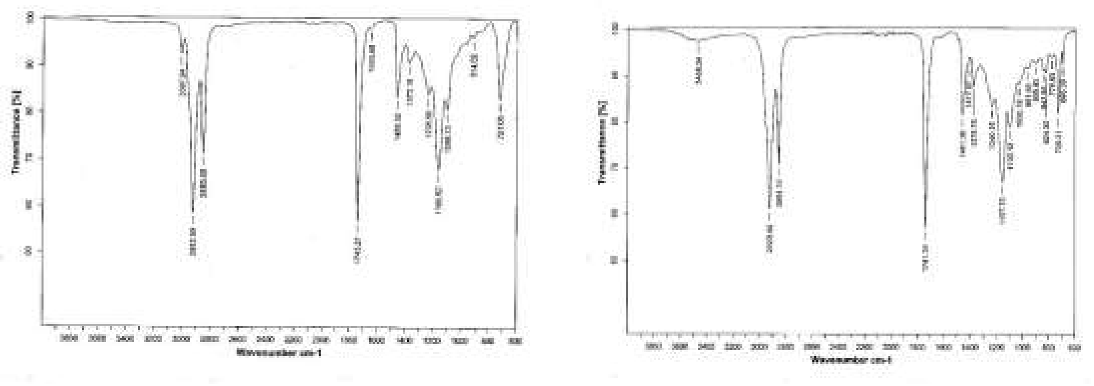
a) b)

Fig. 3. IR spectra of the initial (a) and epoxidized (b) sunflower oil



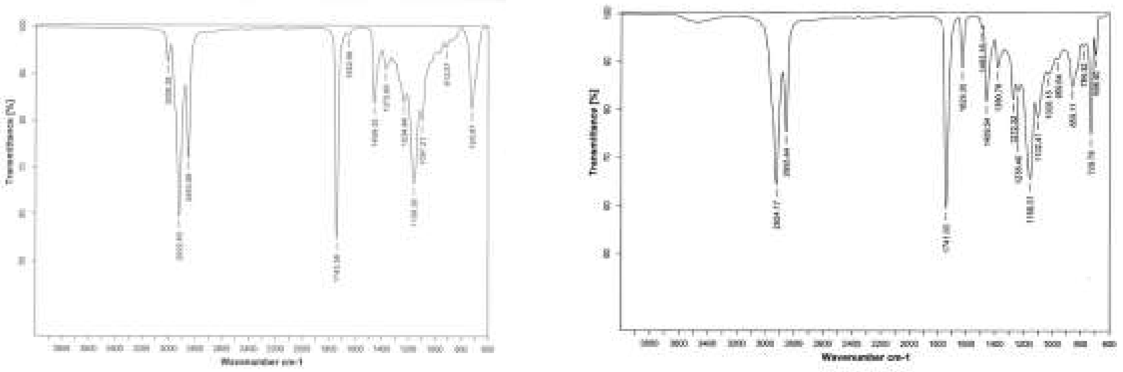
a) b)

Fig. 4. IR spectra of the initial (a) and epoxidized (b) cottonseed oil



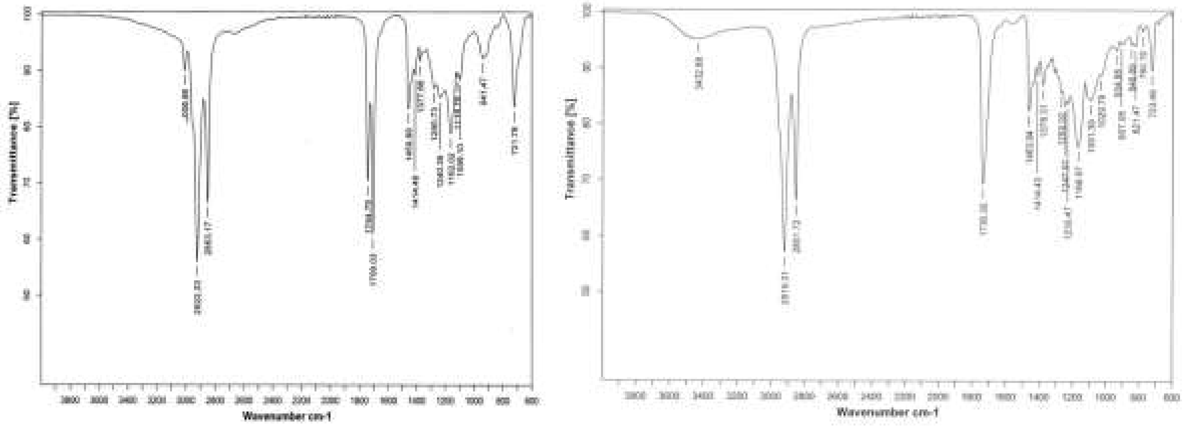
a) **b)**

Fig. 5. IR spectra of the initial (a) and epoxidized (b) corn oil



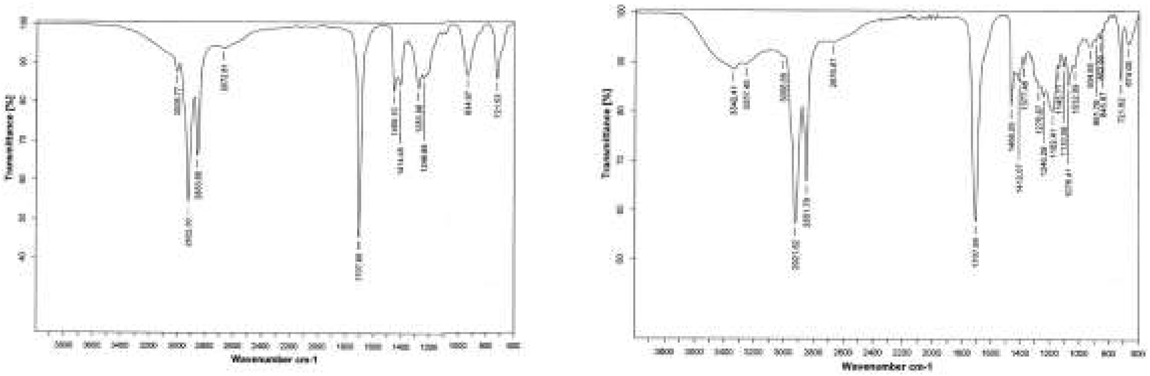
a) b)

Fig. 6. IR spectra of the initial (a) and epoxidized (b) soybean oil



a) b)

Fig. 7. IR spectra of the initial (a) and epoxidized (b) acid of cottonseed oil



a) b)

Fig. 8. IR spectra of the initial (a) and epoxidized (b) oleic acid

Conclusions

1. The epoxidation reaction of various vegetable oils (soybean, sunflower, corn, cottonseed, palm, etc.) was carried out using super formic acid as an oxidizing agent, which was formed in situ by the interaction of formic acid with hydrogen peroxide.

2. As a result of the epoxidation of palm oil, the formic acid / hydrogen peroxide system, with a molar ratio of 1.0: 5.0: 2.0 (PO: HCOOH: H_2O_2), stirring speed 350 turns/min, temperature 60° C and the time of reactions of 180-240 min were used by us as optimal condition in the epoxidation reaction of other vegetable oils.

3. The introduction of the entire amount of hydrogen peroxide in 30 minutes leads to a sharp decrease in the efficiency of epoxidation due to the decomposition of hydrogen peroxide caused by an uncontrolled increase in the temperature of the reaction medium), in which toluene was used as a solvent (the yield of epoxidized products is 64-71%).

4. With a portioned supply of hydrogen peroxide 50 + 30 + 30g every 10-30 minutes, without the use of a solvent, the yield of epoxidized oils reaches 67-78%.

5. The resulting epoxidized palm and soybean oils have an Oxirane number of 3.00% and 4.96, and a kinematic viscosity of 358.1 cSt and 196.0 cSt, respectively.

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BİTKİ YAĞLARININ QARIŞQA TURŞUSU VƏ HİDROGEN PEROKSİD İŞTİRAKI İLƏ EPOKSİDLƏŞMƏSİNİN XÜSUSİYYƏTLƏRİ

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"Yaşıl kimya" yeni texnologiyalarının yaranması ilə hər il bitki yağlarının və onların törəmələrinin xammal kimi istifadəsinə tələbat artır. Bitki yağlarında bir- və daha çox ikiqat rabitələrin olması onların müxtəlif üsullarla modifikasiyasına geniş perspektivlər açır. Bu sahədə epoksidləşmə xüsusi yer tutur. Müxtəlif bitki yağlarının qarışqa turşusu və hidrogen peroksid iştirakı ilə epoksidləşmə reaksiyası aparılmışdır. Palma yağı, qarışqa turşusu, hidrogen peroksid 1:5:2 mol nisbətində götürülməklə, qarışdırma sürəti 350 dövr/dəqiqə, temperatur 60^{o}C, reaksiya müddəti 180-240 dəqiqə olmaqla epoksidləşmənin optimal rejimi seçilmişdir. Müəyyən edilmişdir ki, hidrogen peroksidin hamısının 30 dəqiqə müddətində verilməsi epoksidləşmənin səmərəliliyinin kəskin azalmasına səbəb olur. Buna səbəb reaksiya mühitinin temperaturunun nəzarət edilə bilməyən dərəcədə qalxması hesabına hidrogen peroksidin parçalanmasıdır (həlledici kimi toluol istifadə edilmişdir). Epoksidləşmiş yağın çıxımı 64-71% olur. Hər 10-30 dəqiqiədən bir hidrogen peroksid 50+30+30 paylarla verildikdə və həlledici istifadə edilmədikdə epoksidləşmiş yağın çıxımı 67-78% olur.

***Açar sözlər**: bitki yağları, qarışqa turşusu, hidrogen peroksid, sulfat turşusu, epoksidləşmə, epoksidləşdirilmiş bitki yağı*

ОСОБЕННОСТИ ЭПОКСИДИРОВАНИЯ РАСТИТЕЛЬНЫХ МАСЕЛ В ПРИСУТСТВИИ МУРАВЬИНОЙ КИСЛОТЫ И ПЕРЕКИСИ ВОДОРОДА

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Проведена реакция эпоксидирования различных растительных масел (РМ - соевое, подсолнечное, кукурузное, хлопковое, пальмовое и т.д.) с применением в качестве окислителя надмуравьиной кислоты, образовавшейся in situ взаимодействием муравьиной кислоты с перекисью водорода. Определены оптимальные условия реакции: молярное соотношение (РМ:НСООН:Н2О2)=1.0:5.0:2.0, температура 60°С, время реакции 180-240 мин, скорость перемешивания 350 об/мин. Показано, что введение всего количества перекиси водорода за 30 минут приводит к снижению эффективности эпоксидирования из-за разложения перекиси водорода вследствие неконтролируемого повышения температуры реакционной среды (в качестве растворителя использовали толуол) - выход эпоксидированных продуктов составляет 64-71%. А при порционной подаче перекиси водорода 50+30+30г через каждые 10-30 мин., без применения растворителя, выход эпоксидированных масел достигает 67-78%.

***Ключевые слова**: растительные масла, муравьиная кислота, перекись водорода, серная кислота, эпоксидирование, эпоксидированные растительные масла*