OBTAINING OF EPOXIDIZED SUNFLOWER OILS AND THEIR RESEARCH

[1]Turaev Kh.Kh.,[2]Kulbasheva Kh.Kh.,[3]Alikulov.R.V, [4]Charieva G.D.

[1]Doctor of Chemical Sciences, Professor

[2] Doctor of philosophy of technical sciences, Termiz State University

[3]Doctor of Chemical Sciences, Professor

Organic department *teacher* Termiz State University

Abstract. *This article is aimed at revealing the epoxidation process of different vegetable oils. It is noted that epoxidation was carried out with various physical and chemical parameters and various homogenous or heterogenous catalysts. Methods such as a mixture of dihydroxy and epoxy derivatives, molecular reaction affects the dynamics of various proportions, interaction, and the dynamics of molecules reaction, and conducting the dynamics of anti-molecules and substances, are illuminated by the molecular structure of epoxy oils, including molecular structures of epoxy oils, depending on the conditions of synthesis. It has been analyzed whether epoxidized oils can be used to improve the physicochemical properties of various polymers. Also, the interaction of epoxidized sunflower oil and its derivatives with tetrabutyl titanate has been studied. It has been shown that a mixture of dihydroxy and epoxy derivatives is formed in different proportions, depending on the synthesis conditions.*

Keywords*- Vegetables oils, epoxidation, heterogeneous catalysts, homogeneous catalysts, epoxidized vegetable oils, Prileschajew method, acetic acids, hydrogen peroxide,* Soybean oil, Sunflower oil.

ПОЛУЧЕНИЕ ЭПОКСИДИРОВАННЫХ ПОДСОЛНЕЧНЫХ МАСЕЛ И ИХ ИССЛЕДОВАНИЕ

Тураев Х.Х., Кулбашева Х.Х., Аликулов Р.В, Чариева Г.Д.
Доктор химических наук, профессор
Доктор философии технических наук, Термезский государственный университет
Доктор химических наук, профессор
Преподаватель кафедры органики Термезского государственного университета

Аннотация: Целью данной статьи является раскрытие процесса эпоксидирования различных растительных масел. Отмечается, что эпоксидирование проводилось при различных физико-химических параметрах и различных гомогенных или гетерогенных катализаторах. Такие методы, как смесь дигидрокси- и эпоксидных производных, молекулярная реакция влияет на динамику различных пропорций, взаимодействие и динамику реакции молекул, а также проведение динамики антимолекул и веществ, освещаются молекулярной структурой эпоксидных масел, в том числе молекулярные структуры эпоксидных масел в зависимости от условий синтеза. Проанализировано, можно ли использовать эпоксидированные масла для улучшения физико-химических свойств различных полимеров. Также изучено взаимодействие эпоксидированного подсолнечного масла и его производных с тетрабутилтитанатом. Показано, что смесь дигидрокси- и эпоксидных производных образуется в разных соотношениях в зависимости от условий синтеза.

Ключевые слова: Растительные масла, эпоксидирование, гетерогенные катализаторы, гомогенные катализаторы, эпоксидированные растительные масла, метод Прилещаева, уксусные кислоты, перекись водорода, соевое масло, подсолнечное масло.

Introduction

Vegetables oils are a sustainable and renewable raw material resource extracted from plants and wood. These vegetables oils are used like starting material and they offers numerous advantages such as low toxicity and inherent biodegradability. In the last years, the epoxidation of vegetables oil received a great interest from industry. Thanks to the epoxidation reaction the unsaturations present in vegetables oils can be chemically modified to a value added product. The most important sources of these oils are palm, soybean, rapeseed and sunflower. In this chapter, vegetable oils are presented and in particular Soybean oil, Sunflower oil, Rapeseed oil will be analyzed. After introducing oils studied in this work, the focus will be shifted towards the epoxidation reaction , and above all on the biphasic reaction with a conventional method[1].

Epoxidation methods

Epoxidation is a reaction widely used to form oxirane rings from ethylenic unsaturations (C=C) [2]. The cyclical structure of oxirane rings has a bond angle of 60 °C, making them highly strained and highly reactive. Typically, the method to promote epoxidation of double bonds uses hydrogen peroxide and acetic acid as oxygen carriers in acid media (by mineral acid). Materials like vegetable oils, biodiesel and some rubber compounds belong in this class.

Classic methods employed for the oxidation of vegetable oils use homogeneous catalytic processes that generate a lot of waste, corrode equipment and require large amounts of reagents. Heterogeneous catalysts have the advantage of easy separation and recycling of the catalyst. For this reason, ion exchange resin has been studied to promote epoxidation of vegetal oils .

Biobased metal cutting fluid (MCF) is an important material that has wide use in industry as a substitute for cutting fluids based on fossil-derived hydrocarbons. MCFs can be made from vegetable oils, but some oils have low stability, mainly at high temperature. To solve this problem, epoxidation reactions are applied to convert unsaturations to oxirane rings followed by opening of the rings with water, to form the vicinal diol [2]. In some cases it is only necessary to convert a double bond with bis-allylic hydrogen (poly--unsaturated), which is more susceptible to the oxidation process, maintaining intact the double bond with allylic hydrogen only. This procedure should improve the oxidation stability but tends to maintain viscosity and the liquid state.

Several authors have investigated heterogeneous catalysts based on the sulfonation of incomplete pyrolyzed biomass, such as sucrose, glucose and biochar [3]. Some seeds have been suggested in recent years to produce biochar, but to the best of our knowledge, no studies have been carried out of biochar produced by low-temperature pyrolysis combined with sulfonation.

Catalysts based on biomass have advantages such as low cost and surface chemical properties that can be tailored appropriately. An additional advantage of this work was the use of cake from *Jatropha curcas*. This cake, left over after oil extraction for biodiesel production, has high toxicity and cannot be used as animal feed.

Among the desirable characteristics of the catalyst support are stability, inertness, reusability, high surface area, porosity and appropriate chemical structure . The process usually produces sulfonated carbon with low surface area and low acid site content .

Conventionally, the production of epoxidized vegetable oils is carried out by the Prileschajew method It is a liquid–liquid reaction system, where there are several consecutive and parallel exothermic reactions [4]. The first step is the formation of percarboxylic acid in the aqueous phase from the reaction between hydrogen peroxide and the corresponding carboxylic acid. Then, the percarboxylic acid diffuses in the organic phase to epoxidize the unsaturated groups of the vegetable oils. Due to the presence of several exothermic reactions, the risk of thermal runaway exists. As mentioned in the study of Dakkoune et al.

Hence, direct epoxidation of vegetable oils by oxygen and hydrogen peroxide is seen as the best option concerning thermal safety, waste treatment and selectivity. Scotti et al have shown that epoxidation of oleic acid by a cumene–O_2 system on CuO/Al_2O_3 presents good results of conversion and selectivity. Nevertheless, there is still the problem of organic waste, i.e., cumene.

Sepulveda et al, tested different alumina catalysts for the epoxidation of methyl oleate and soybean oil methyl ester by hydrogen peroxide in different organic solvents. epoxidation of methyl ricinoleate. As previously mentioned, the direct epoxidation of vegetable oils by hydrogen peroxide might be thermally safer than by the Prileschajew method. [5]. To the best of our knowledge, we did not find any study proposing such comparison. In the Prileschajew method, hydrogen peroxide might be more stable because of the acidity of the reaction mixture [6]. Such a comparison is not easy because the chemical systems are different. Figure 1 shows a typical reaction scheme for the Prileschajew epoxidation.

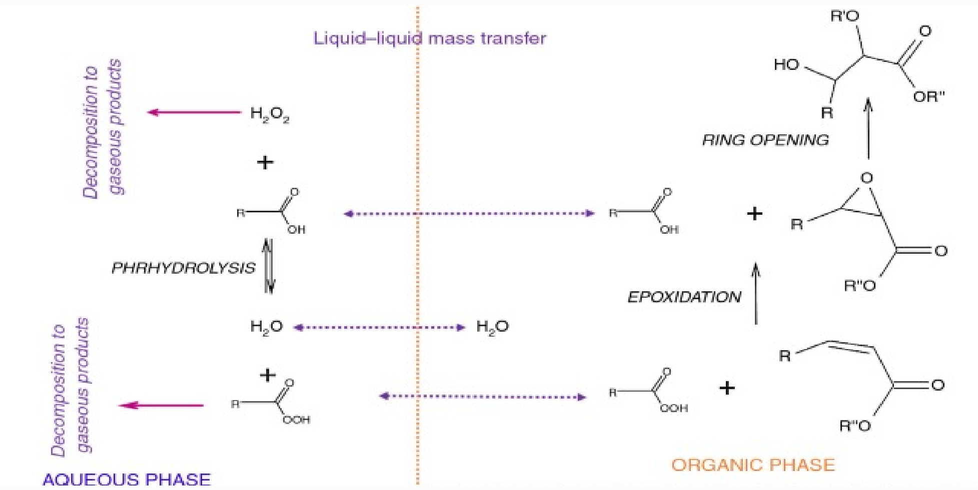


Figure 1. Reaction scheme for the Prileschajew epoxidation.

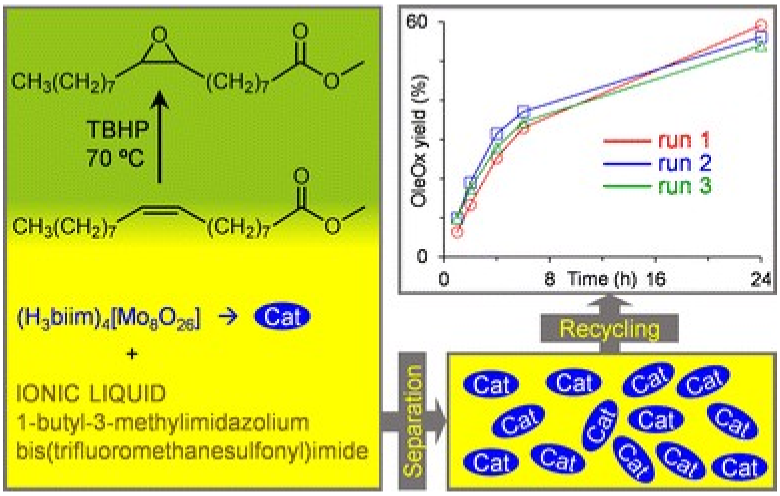
In this article describe methyltrioxorhenium (MTO)-CH_2Cl_2/H_2O_2 biphasic system for epoxidizing soybean oil. The reactions were optimized (reactant ratio, time, and temperature), which resulted in a better performance (higher conversion and selectivity) than those described in the literature. The rhenium-epoxidized soybean oil remained stable in the absence of stabilizers for up to 30 d when stored at mild conditions[7].

Compared to pure corn oil, the differential scanning calorimetry of both corn oil-based polyols displayed the absence of any detectable melting peaks. However, the epoxidized derivative had a higher thermal stability than the ozonated sample, as shown by thermogravimetric analysis.

. Hydroxyl groups are further classified based on their presence in polyols. Primary hydroxyl groups present in polyols hold the mechanical and thermal performance of final polyurethanes better. In this context, the recent advancements in increasing the primary hydroxyl groups in bio-based polyols through different chemical transformation has been focused on here.

This study investigated the production of epoxidized soybean oil by conventional and ultrasound-assisted methods. Epoxidized soybean oil was synthesized by reacting soybean oil, hydrogen peroxide, and carboxylic acid (formic or acetic acid). Sulfuric acid was used as a peroxidation catalyst. The effects of sonication, the carboxylic acid (formic and acetic acid), peroxidation catalyst (H_2SO_4), and temperature (50, 60, and 80 °C) were evaluated on the yield .and productivity of epoxidized soybean oil. In both conventional and ultrasound-assisted methods, soybean oil yields into epoxidized soybean oil surpassed 90% only when formic acid and sulfuric acid were applied. The conventional method occurred faster than the sonochemical method for yields of up to 90%. The ultrasound-assisted method was the best technological option to attain a product of high purity (98%). The sonochemical method could be considered a promising technology if the ultrasound equipment’s limitations can be overcome[8].The octamolybdate salt

$(H_3biim)_4[\beta\text{-}Mo_8O_{26}]$ (**1**) has been prepared in good yield by hydrolysis of the complex $[MoO_2Cl_2(H_2biim)]$ (H_2biim = 2,2′-biimidazole). Compound **1** showed a good performance as a (pre)catalyst for the epoxidation of olefins using either *tert*-butylhydroperoxide (TBHP) or hydrogen peroxide as oxidant.



With the ionic liquid (IL)1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide) as co-solvent and TBHP as oxidant, the catalyst system could be reused several times without loss of activity for the epoxidation of the bio-olefin methyl oleate (Ole). Compound **1** is the first polyoxomolybdate used for the Ole/TBHP reaction in IL medium[9].

The epoxidation reaction was successfully carried out; with the GC-MS analysis indicating the formation of epoxidized esters derived from linoleic and oleic acids. The addition of the epoxidized esters to the EEF films caused an increase in film thickness, opacity, solubility in water, tensile strength and elongation, while the solubility in acid presented the same value as compared to the blank sample. In the EEFPHA samples, addition of filmogenic solution of epoxidized esters from corn and macauba presented a value exceeding the standard in the thickness, opacity, water solubility, water vapor permeability and tensile strength analyses. [10].

Conclusion.

The results of scientific works published in foreign and domestic publications on the development perspectives and fields of application of scientific research in the field of obtaining epoxidized vegetable oils are analyzed in detail. Vegetable oils in industry have been widely used as lubricant, as monomer for polymer production.

Based on the analysis of the data obtained as a result of studying the literature, it should be noted that it is necessary to scientifically base the technology of obtaining epoxidized vegetable oils with the range of catalysts, such as Octamolybdate Salt, methyl oleate over various amorphous Ti–SiO_2, HPW/TiO_2–SnO_2–ZrO_2, methyltrioxorhenium-CH_2Cl_2/H_2O_2 catalytic biphasic system and tetrabutyl titanate. In addition, it was explained that the epoxidation of vegetable oils, in addition to catalysts, is also an important factor, such as the temperature of the stream. Therefore, it was found that the technology for obtaining new epoxidized vegetable oils with tetrabutyl titanate catalyst was not studi

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