The importance of R-(+)-limonene as the raw material for organic syntheses and for organic industry

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Limonene oxidation processes are one of the key methods for its management. Limonene extracted from the orange peels is a valuable raw material for the obtaining of valuable derivatives, for example: perillyl alcohol, which inhibits the growth the cancer of colon and breast.

Introduction

Limonene is a monoterpene compound which has many applications in the chemical industry. It is the main component of essential oils obtained from waste citrus peels (biomass). It can be obtained by the natural and synthetic methods, for example with help of pyrolytic processes. Natural methods (simply distillation or steam distillation citrus peels) allow to recycle the waste citrus peels derived from the food industry and obtain almost pure limonene with a small amount of toxic waste. Pyrolytic methods require high temperatures and generate significant quantities of waste water, moreover this methods are very harmful to the environment. Limonene undergoes very easily oxidation processes. It allow to obtain very valuable oxygenated derivatives of limonene, for example perillyl alcohol. Limonene oxidation process can be carried out using different oxidizing agents such as hydrogen peroxide (30 wt% or 60 wt% water solutions) or t-butyl hydroperoxide (TBHP, 5-6 M solution in decane). Also the utilization the selected microorganisms can cause the formation of oxygenated derivatives of limonene but in these processes the multicomponent mixtures of oxygenated derivatives of this compound are obtained. The methods which used hydrogen peroxide or TBHP as oxidizing agents allow to obtain high yields of the appropriate oxygenated derivatives of limonene at a high conversion of limonene. Now, at the Institute of Organic Chemical Technology, West Pomeranian University of Technology in Szczecin are performed studies on the modern, "green" technology which allows to obtain oxygenated derivatives of limonene by oxidation of limonene with 60 wt% hydrogen peroxide, in various solvents and in the presence of mesoporous titanium silicate materials, such as: Ti-MCM-41 and Ti-SBA-15. In this method, the only by-product connected with the transformation of hydrogen peroxide is water, and other organic by-products can be easily developed. Limonene oxidation processes are carried out at mild conditions (temperatures up to 120°C and atmospheric pressure).

The properties of limonene and the methods of its obtaining

Limonene (4-isopropenyl-1-methylcyclohexene) is a colourless or pale yellow liquid with a molar mass of 136.23 g/mol and with a characteristic citrus smell (R-(+)-limonene) or pine smell (S-(-)-limonene). Limonene occurs in nature in the form of two isomers – thanks to the presence of chiral center on the fourth atom of carbon in the cyclic ring (Fig. 1). Moreover, in nature it occurs often in the form of a racemic mixture. From these two isomers of limonene wider applications and appearance exhibits R-(+)-limonene.

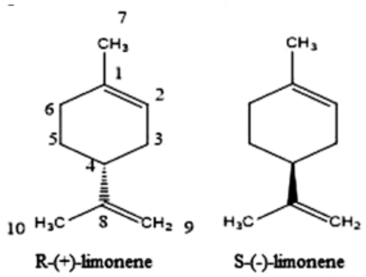

Fig. 1. The isomers of limonene

R-(+)-limonene occurs in the peels of citrus fruits, such as: sweet orange, tangerine, lemon and lime, and it is characterized by the following properties: the boiling temperature 176°C (at 760 mmHg), the melting temperature -80°C, the density of 0.94 g/dm^3 and a good solubility in methanol and ethanol as well as in acetone and benzene [1].

R-(+)-limonene is a major component of essential oils found in the citrus fruits peels. On the laboratory scale R-(+)-limonene is manufactured by the separation of the organic layer from the squeezed juice which was obtained from the whole fruit oranges (it is characterized by the purity of 96–97%) or by the vapor distillation from the waste citrus peels (in this method its purity reaches 95%). Its annual production of limonene achieves 50–75 kg. The greatest importance for the production of limonene on an industrial scale has a production and consumption citrus juices by people. The flourishing of the citrus juices production started in 40th years of the 20th century, and the still growing demand for the juices resulted in the development of methods of this juices obtaining and, at the same time, the great importance have become issues connected with the minimization of waste during this production. The quality of the juice obtained from the citrus depends mainly on the type of the fruit and its structure [2]. Types of fruit can be classified as follows:

- fruits of orang type: sweet orange, bitter orange and tangerine,
- fruit yellow type: lemon, lime, limetta and grapefruit.

Oranges are the basic raw material in the production of juices, including citrus oil containing 95% of limonene. Below is presented a list of the major types of oranges fruit which are planted in the countries which supplier citrus fruits:

- Brazil: Hamlin and Pera,
- USA: Navel, Valencia, Jaffa and Pineapple,
- Italy: Biondo Comune, Ovale,
- Spain/Morocco: Navel, Valencia, Jaffa.

Because citrus fruits are growing the whole year and their ripening time can last for about five months, the collected fruits have different properties. The time in which fruits are gathered is important taking into account the content of fruit acids, sugar and pigment. The different content of the ingredients and the ripening time affect significantly the

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final product. Figure 2 shows a cross section of the orange fruit and the glands, which collect the essential orange oil – the main component of this oil is R(+)-limonene.

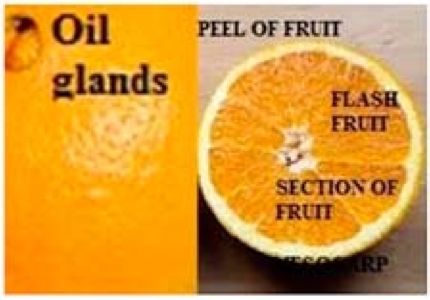

Fig. 2. The cross section of the orange fruit and the oil glands

The orange peel, also known as pericarp, is composed of two layers: the external layer of the peel and albedo [2]. The external layer of the peel is a pigmented, relatively thin layer which contains oil glands. The color of the fruit is connected with the presence in the peel β-carotene (orange pigment). For the special smell of the orange fruits is responsible the aroma oil which is collected oils in the oil glands. The external layer of the orange fruit is protected against loss of water and also against microorganisms by a natural wax. Albedo is the inside part of the peel. It is a white, dense layer that contains high amount of pectin's. The fruit flesh is radiate divided into segments containing a large amount of juice, which is hold by glue like substances.

In the literature there are presented many methods of limonene production on the laboratory and on the industrial scale with the utilization the waste from the food industry. The GEA Westfalia company proposes the production of the orange oil according to the schema which is shown on Figure 3.

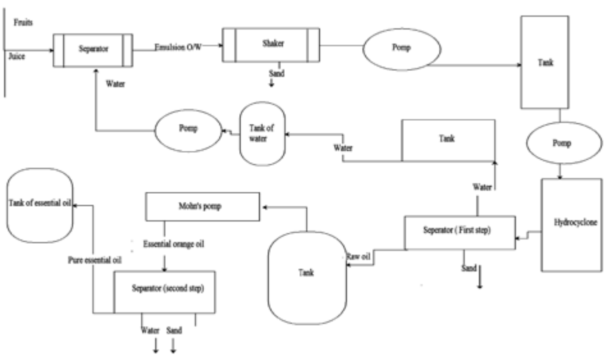

Fig. 3. The technological scheme of the orange oil production proposed by GEA Westfalia company [2]

According to the Figure 2 the orange fruits are served to the extractor, where first they are cut of and the juice is squeezed from them, later peels of the fruits are fragmented and pressed in order to obtain from them the orange oil. The resulting oil is then extracted with water. In this way the orange oil in the form of emulsion type O/W is obtained. This emulsion is then washed with water in shakers and directed into the tank. The resulting emulsion of O/W type contains 70–90 wt% of the essential oil from the orange peels. In the next stages the orange oil is separated from the water layer using the hydrocyclone and separators, and then it cleared of solid parts, such as: sand, seeds of the fruit and parts of skin. Water, which is used in the several stages of this process is recycled to the first stage of extraction. This water contains about 2–5 kg of the essential oil on the 100 kg of the used raw material, but the amount of the essential oil in water depends on the type of the fruit and the way on which they are processed. The pure product is stored in tanks. In some variations of the process of the obtaining the essential oil from the orange peels also the step of freezing is applied. It allows to separate from the essential oil waxes which are contained in this oil.

Another method of the industrial obtaining of R-(+)-limonene is a pyrolysis of used car tyres. This method has been described in many patents and articles, and it is a very good way for the recycle of this very dangerous for the environment waste. Simultaneously, it allows to obtain many valuable organic compounds, such as limonene [3]. The utilization of milder conditions during this pyrolysis, for example a low temperature, causes that during this process dangerous gases are not formed. This vacuum pyrolysis is carried out at lower temperatures in comparison to the classical pyrolysis (this difference amounts to 75–100°C), in which the product – fuel oil can have different chemical composition [4]. This oil includes: polycyclic aromatic hydrocarbons (PAHs), which are very dangerous for human health. PAHs are obtained from aliphatic hydrocarbons during the process of pyrolysis in the classical Diels-Alder reactions at the temperature of 720°C. Moreover, Cunliffe and Williams found that the content of PAHs in fuel oils after pyrolysis which was carried out at the nitrogen atmosphere increases with the increasing of the temperature of pyrolysis [5]. The utilization of vacuum pyrolysis for the pyrolysis of waste tires allows to obtain about 55 wt% of fuel oil. This oil usually contains 20–25 wt% of the gasoline fraction with the boiling point below 200°C and the paraffin fraction which usually contains 20–25 wt% of the racemic mixture of limonene [6].

Limonene – the compound with many applications

R-(+)-limonene found mainly applications in cosmetics, in medicine – including the aromatherapy in the natural medicine (relaxing, harmonizing and stabilizing the nervous system), in the perfume industry, in the food industry (flavor and fragrant additives for food) – Figure 4. R-(+)-limonene is also present in carbonated beverages which are produced by large corporations, such as: Coca–Cola Company, in fruit juices, ice creams and sweets, where limonene plays a role of a fragrant compound and a stabilizer [7]. This compound is also used in agriculture as an ecological insecticide and also as the component of feeds for poultry (Herbromix ®) [8] because it has antibacterial and disinfecting properties. Limonene is used in the syntheses of many useful intermediates for the organic chemistry and the organic industry, and also as an alternative solvent for the organic syntheses because it is a cheap, biodegradable, low toxic compound. The main disadvantage connected with the utilization of limonene in organic syntheses is its easiness to oxidation, so it can not be the solvent in oxidation reactions. This compound can also be used as a cleaner for electronic equipment due to its ability to degrease various surfaces. Limonene found also utilizations as the fragrant component of the household chemicals (detergents, and air fresheners). R-(+)-limonene is also used in the relaxing massages, and to fight against cellulite. In polymers production it the valuable monomer in production for example "fragrant" and biodegradable polymers.

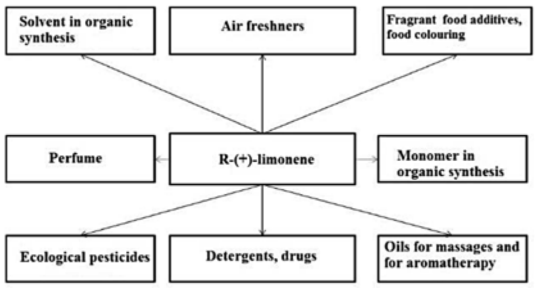

Fig. 4. The main directions of limonene applications

Wide applications of limonene in organic synthesis are related to the fact that this compound has a carbon skeleton similar to the construction of many biologically active compounds, which are used for example in medicine, and also in cosmetics or perfume industry [9]. To the group of these compounds belong: α-terpineol, carvone, carveol, perillyl alcohol, menthol and 1,2-epoxylimonene (the oxygenated derivatives of limonene) and p-cymene which is formed by the dehydrogenation of limonene [10]. The synthesis of p-cymene can be performed from 5 to 30 min by action of the microwave radiation in the presence Lewis acids on the reaction mixture. In this way the high selectivity of p-cymene is achieved – 90% – Figure 5.

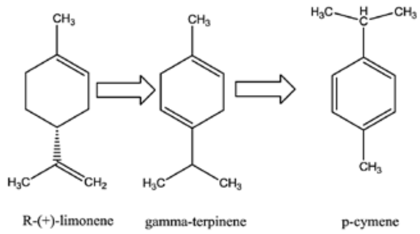

Fig. 5. The synthesis of p-cymene from R-(+)-limonene with application of the microwaves

All above mentioned oxygenated derivatives of limonene are much more valuable than limonene and were applied in the perfumery, cosmetics and food industry, as ingredients of fragrances for cosmetics, beverages and food. In addition, p-cymene is used in the production of p-cresol [11]. S-(-)-limonene, the second isomer of limonene, occurs in the bergamot and eucalyptus oils. However, in comparison to R-(+)-limonene, S-(-) isomer is less active and has a pine scent. When this isomer is used in the refreshers as a mixture with air and ozone, it effectively removes the smell of the cigarette smoke. In the textile industry, R-(+)-limonene encapsulated in the coating of polyurethane-urea has found the utilization as the fragrance compound for the production of fabrics. This compound is also used as an inhibitor of the steel corrosion process under the influence the chlorinated acids.

The applications of R-(+)-limonene has been thoroughly studied. It is toxicology is also well known. The toxicological studies on rats show that the oral lethal dose of R-(+)-limonene amounts to 4400 mg/kg. What's more, its properties are considered to be environmentally friendly, because it is biodegradable. Limonene is characterized by a good affinity to fats, thus it found applications as the cleaning agent and as the alternative solvent for petroleum derivatives and also chlorinated compounds. Today, the products containing in the composition of R-(+)-limonene are used in industrial plants for the cleaning of surfaces made of different materials. Moreover, it is applied in the production process in the aviation, automotive and electronic industry as the alternative solvent for chlorinated compounds [12]. Limonene can be easily mixed with surfactants. It causes formation of environmentally friendly aqueous cleaning preparations with a low flammability, and cable to clean dirty surfaces in many kind of the industry (for cleaning concrete and ship body's, and for removing inks and adhesives) [13]. The basic and well known preparation which contains 90% of R-(+)-limonene is LimoSol-90. This preparation is used as the solvent, varnish remover and cleaning agent having unique antibacterial anti-insecticide properties. Another preparation from this family is LimoSol-10 – it is a transparent microemulsion, which is used as a pesticide in agriculture to protect crops against insects. As a solvent, (R)-(+)-limonene found applications instead of n-hexane in the microwave extraction of oils from olives and other fats – this process is used by the Milestone Group [14].

Very interesting application of limonene on an industrial scale is its utilization as a compound which improves the process of outputting and purification of the crude oil from the oil sand (bitumen) [14].

From the medical point of view, R-(+)-limonene is a very good solvent for cholesterol [15]. It is also used in a clinical treating for the removal of gallstones. It also can neutralize the stomach acids, thus it is used in the drugs reliving heartburn. R-(+)-limonene also shows an activity against certain types of cancers, for example it hinders the development of the breast and colon cancers [16]. Ten years ago, the team of Keinan from Israel has identified the antiasthmatic properties of (R)-(+)-limonene. However, the main disadvantage of R-(+)-limonene are its allergic properties. In addition, R-(+)-limonene under the influence of oxygen undergoes oxidation to hydroperoxides, which irritate the skin [17].

Thanks to the presence of two double bonds in the structure and the six-membered ring, R-(+)-limonene is a good raw material for the production of many valuable products. It can easy undergo the following processes: isomerization, epoxidation, addition and hydrogenation. Very valuable is the utilization of R-(+)-limonene in the production of advanced polymers, which have specialist applications, for example: biologically active polyesters (R)-(+)-limonene and 5-hydroxymethylfurfural, which can be used as coatings for window glasses, indicating good permeability and stability to light [18, 19]. The received films are biodegradable and biocompatible in contact with food [18]. These films are used as containers for food.

From the point of view of chemical technology a special attention is directed to the following reactions: isomerization, oxidation, acetoxylation, aromatization and epoxidation of R-(+)-limonene. The Figure 6 shows the products of R-(+)-limonene.

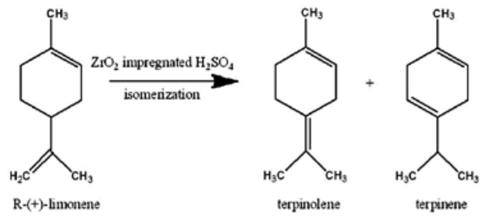

Fig. 6. The products of R-(+)-limonene isomerization

The process of R(+)-limonene isomerization was carried out at a temperature of 60°C and in the presence of the impregnated with H_2SO_4 zirconium oxide (ZrO_2). As a result of this isomerization the mixture of terpinene and terpinolene was obtained [19]. During this process the side reactions were observed, such as hydration, which leads to terpineols formation and aromatization of the cyclic ring, which causes cymene formation.

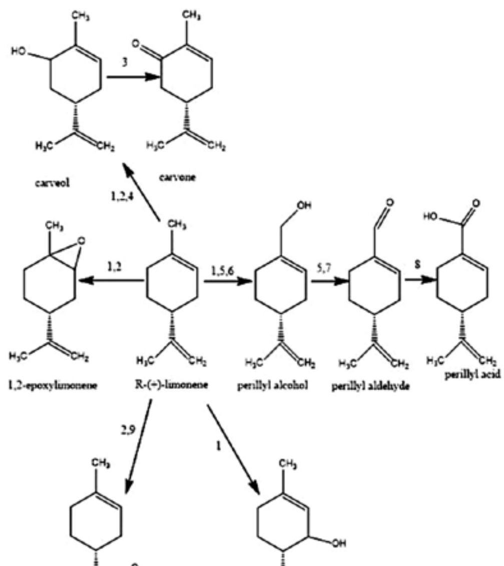

Fig. 7. Biotransformation of monoterpenes with utilization of bacterial monooxygenases and deoxyhydrogenases: 1: CYP101A1 (P450cam) from *Pseudomonas putida*; 2: CYP102A7 from *Bacillus licheniformis*; 3: CYP111A2 from *Novosphingobium aromaticivorans*; 4: P450cin from *Bacillus cereus*; 5: monooxygenase from *Bacillus stearothermophilus BR388*; 6: CYP153A6 from *Mycobacterium sp. PYEHOLE-1500*; 8: Ogee from *Pseudomonas putida*; 9: CymB from *Pseudomonas putida*;

It has been shown in the literature many modifications of the process of R-(+)-limonene oxidation. An example can be the utilization in the oxidation of R-(+)-limonene enzymes produced by the appropriate strains of bacteria's. Figure 7 shows ways of R-(+)-limonene transformation under the influence of the appropriate enzymes. The utilization of the appropriate enzymes allowed to obtain valuable oxygenated derivatives of R-(+)-limonene, such as: perillyl alcohol perillowy, 1,2-epoksylimonene and carveol.

Another very interesting application of R-(+)-limonene is the synthesis of lavandulol. This compound founds utilizations in the cosmetics industry in the Bayer-Villiger oxidation process, which proceeds in the presence of such microorganisms as *Acremonium roseum* [20]. Figure 8 shows the scheme of reactions (simplified due to many-staged process) lavandulol synthesis from R-(+)-limonene. This process undergoes in two stages and with the reconstruction of the carbon skeleton. In the reaction with a Grignard reagent two carbon atoms are linked to the structure, and in the next stage the loss of two carbon atoms in Baeyer-Villiger oxidation reaction is observed.

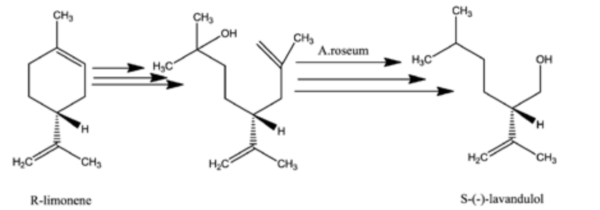

Fig. 8. The synthesis of S-(-)-lavandulol from R-(+)-limonene with help of *Acremonium roseum*

The epoxidations of (R)-(+)-limonene in the presence of both kind of catalysts, homogeneous and heterogeneous, are widely described in the literature. For the epoxidation of this compound the following catalysts have been used: porphyrins, ruthenium and cobalt complexes, mesoporous titanium silicalite catalysts and hydrotalcites ($Al_2Mg_6(OH)_{16}CO_3 \cdot 4H_2O$) [21]. In epoxidation of (R)-(+)-limonene the following oxidants were used: hydrogen peroxide, molecular oxygen, t-butyl hydroperoxide and cumene hydroperoxide. Figure 9 shows the possible reactions that can proceed during the epoxidation R-(+)-limonene.

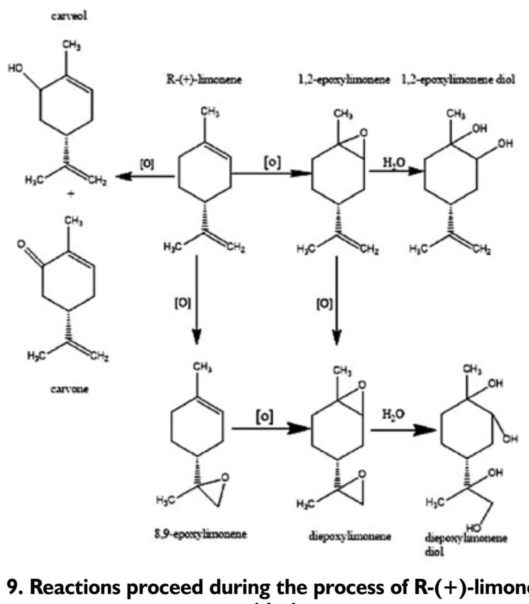

Fig. 9. Reactions proceed during the process of R-(+)-limonene epoxidation

Mariano at al. [22] have studied the process of limonene epoxidation at the temperature of 70°C, in the glass reactor fitted with a reflux condenser, thermometer and magnetic stirrer. In the post-reaction mixtures the presence of: carvone, carveol, diepoxylimonene and diols was detected. It was found during the studies that the selectivity of the transformation of hydrogen peroxide to the organic compounds was lower than 100%. It was connected with the decomposition of hydrogen peroxide at the conditions at which the reaction was carried out. Moreover, it was shown that during the studies at which the molar ratio of organic substrate/hydrogen peroxide was 1 or above 1 no leaching of Ti from the structure of the catalyst was observed.

Berlini at al. [23] have studied the processes of epoxidation of the organic unsaturated compounds (including terpenes) on the Ti-MCM-41 catalyst. The epoxidations were carried out in the glass reactor and at the temperature of 85°C. Acetonitrile and ethyl acetate were used as the solvents and as the oxidizing agent t-butyl hydroperoxide was applied. The molar ratio of oxidant/organic reactant amounted to 1:1 and amount of the catalyst in relation to the organic reactant was 30 wt%. In acetonitrile conversion of limonene reached 62 mol% and the selectivity of 1,2-epoxylimonene amounted to 79 mol%, while in ethyl acetate values of these functions were as follows: 68 mol% and 62 mol%.

Chicker at al. studied the epoxidation of R-limonene on the specially prepared Ti-SBA-15 catalyst [24]. The studies were carried out in acetonitrile as the solvent and at the temperature of 70°C. The quantitative analyses of the post reaction mixtures were made after 24 hours. It results from those studies that worse results were obtained for hydrogen peroxide as the oxidant, as the conversion of limonene amounted to 40 mol%, and the selectivity of the epoxide compound 100 mol%. In case of t-butyl hydroperoxide conversion of limonene was 97 mol%, and the selectivity of the epoxide compound amounted to 100 mol%.

In other methods of R-(+)-limonene epoxidation were used: zincochromate and zincophosphorate molecular sieves, ionic liquids and ion exchange columns [25]. The epoxidation of limonene in the presence of molecular sieves relied on the hydrothermal synthesis of molecular sieves in the first stage and next the epoxidation with hydrogen peroxide as the oxidizing agent oxidizer and in butane-1-ol as the solvent was carried out. At the temperature of 60°C the selectivity of 1,2-epoxylimonene amounted to 70 mol% was obtained.

The process of R-(+)-limonene epoxidation in the presence of ionic liquid underwent in the different way. The first such epoxidation process was performed in the presence of the Jacobsen catalyst (immobilized manganese complex), which was dissolved in 3-buthyl-1-methylimidazolium tetrafluoroborate [26]. In this epoxidation hydrogen peroxide was used as the oxidant. The epoxidation of limonene was performed 1 hour, and after this time the conversion of limonene amounted to 50–90 mol%. The considerable advantage of this process is its lower influence of ionic liquids on the natural environment in comparison to organic solvents such as toluene or benzene.

During our research on the process of R-(+)-limonene epoxidation as the oxidizing agent 60 wt% water solution of hydrogen peroxide was used. The process was carried out at the range of temperatures from 0 to 120°C and in the presence of the mesoporous Ti-MCM-41 catalyst. The studies on the composition of the post-reaction mixtures showed the presence of carvone, carveol, perillyl alcohol, 1,2-epoxylimonene and its diol in those mixtures. We were used in our studied 5 doff rent solvents: ethanol, methanol, isopropanol, acetonitrile i toluene. The studies showed that the medium of the reaction, the temperature, and the reaction time considerably affected the composition of the post-reaction mixtures, and the selectivity of products changed depending on the solvent used. The conversion of hydrogen peroxide achieved 90–95 mol%, while the conversion of limonene was 20-30 mol%.

Summary and conclusions

The presented in this article numerous applications of limonene show that very important is developing the modern, efficient and ecofriendly technologies of the obtaining and utilization of this compound. Especially, because this compound is not produced in Poland. One of the ways of the utilization of this compound can be the epoxidation of limonene over the mesoporous titanium silicate catalysts in the presence of the "ecological" oxidizing agent – hydrogen peroxide. The production of R-(+)-limonene allows to recycle the biomass in the form of orange peels which are waste from the fruit jounces industry.

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