

# Environmental friendly method of the epoxidation of limonene with hydrogen peroxide over the Ti-SBA-15 catalyst

Agnieszka Wróblewska\*, Mariusz Malko, Marika Walasek

West Pomeranian University of Technology, Szczecin, Faculty of Chemical Technology and Engineering, Institute of Organic Chemical Technology, Pulaskiego 10, 70-322 Szczecin, Poland,

\*Corresponding author: e-mail: agnieszka.wroblewska@zut.edu.pl

This work presents the studies on the epoxidation of limonene to 1,2-epoxylimonene with hydrogen peroxide and over the titanium-silicate Ti-SBA-15 catalyst. The main object of the research was a solvent effect on the epoxidation process. The influence of solvents, such as: methanol, toluene, propan-2-ol (isopropyl alcohol), acetonitrile and ethanol has been studied. Furthermore, the influence of temperature in the range of 0–120°C and the reaction time in the range of 0.25–48 h have been investigated. Gas chromatography and iodometric titration methods were used to establish the products of this process and amount of the unreacted hydrogen peroxide. 1,2-Epoxy limonene, 1,2-epoxylimonene diol, perillyl alcohol, carvone and carveol have been determined as the main products of this process. All these compounds are very valuable raw materials for organic syntheses, medicine or cosmetic and food industry.

**Keywords:** Limonene epoxidation, 1,2-epoxylimonene, 1,2-epoxylimonene diol, perillyl alcohol, Ti-SBA-15 catalyst, titanium-silicate catalysts, hydrogen peroxide.

## INTRODUCTION

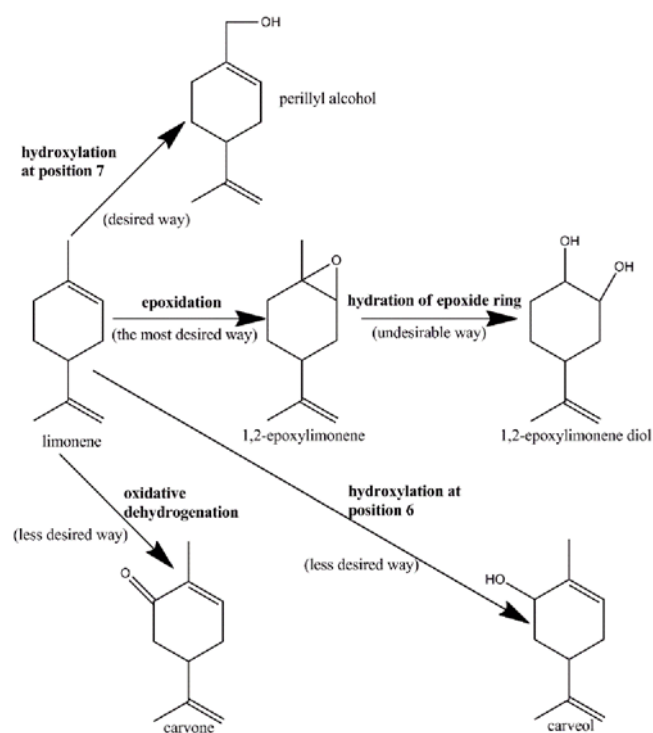
Recently, the epoxidation of limonene became a very popular topic. The process owes its popularity to many valuable products formed in this reaction. The most desired product of limonene oxidation is 1,2-epoxylimonene. It can be used in a production of poly(limonene carbonate) – as a great alternative for polystyrene<sup>1</sup>, or in a pharmaceutical industry as a component of medicines used in the treatment of schistosomiasis<sup>2</sup>. Furthermore, products such as: 1,2-epoxylimonene diol, perillyl alcohol, carvone, and carveol are equally important by-products of this process. They are formed by such side reactions, as: hydration of epoxide ring, hydroxylation and oxidative dehydrogenation (Fig. 1). All from these products have

many applications, for example in pharmacy (perillyl alcohol is a well-known anticancer agent especially against Glioblastoma multiforme<sup>3,4</sup>), in a food industry (carvone is widely used as a fragrance and flavor agent<sup>5</sup>) and in a cosmetic industry<sup>6</sup>.

The literature analysis showed, that it can be distinguished few ways of limonene oxidation. First of all, as oxidants in this process aqueous solution of H<sub>2</sub>O<sub>2</sub><sup>7–10</sup>, t-butyl hydroperoxide<sup>11–13</sup>, sodium periodate<sup>14</sup> and iodosylbenzene<sup>15</sup> have been used so far. This process may occur in homogeneous medium, where the catalyst can be for example: systems based on silicotungstates<sup>16</sup>, tungstophosphates<sup>17</sup>, vanadyl cationic complexes<sup>18</sup>, or ionic liquids<sup>19</sup>, and heterogeneous, catalyzed by: Fe-doped MoO<sub>2</sub> nanosheets<sup>20</sup> or Fe/nanoporous carbon materials<sup>21</sup>, but the most common catalysts used in this process are titanium silicates, such as: Ti-MCM-41<sup>22</sup>, TS-1<sup>8</sup> and Ti-SBA-15<sup>23</sup>. A great advantage associated with use of this kinds of catalysts can be the easiness of its separation, further regeneration and the possibility of obtaining interesting products with high selectivity.

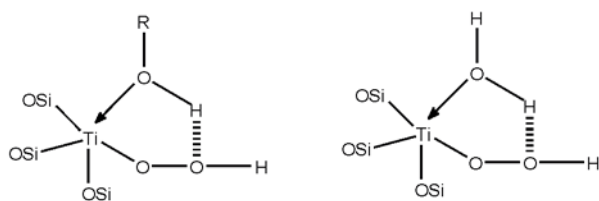
Herein, we applied an aqueous solution of hydrogen peroxide as an oxidant and Ti-SBA-15 mesoporous material as a catalyst. The combination of H<sub>2</sub>O<sub>2</sub> solution and titanium silicate catalysts allow to design environment-friendly process, especially when Ti-SBA-15 is used. This mesoporous material is synthesized with the presence of a biodegradable copolymer – Pluronic P123 (copolymer of ethylene oxide and propylene oxide), which is used as a template in such process. In contrary to other titanosilicates, the process of its preparation does not involve any ammonium compounds, thus the crystallization is deprived of smell and toxicity of amines, which are formed during the calcination process<sup>22</sup>.

The challenge is to develop a process, which is more selective for epoxidation products, such as 1,2-epoxylimonene and less selective for hydroxylation products (e.g. perillyl alcohol and carveol). For the creation of products of hydroxylation can be responsible strong hydrophilic character of Ti-SBA-15 material. It was pro-



**Figure 1.** Possible reaction pathways in the oxidation of limonene with aqueous solution of hydrogen peroxide

ven, that the hydrophilicity of the catalyst is associated with the presence of hydroxyl groups and that in turn, can be a reason of lower selectivity to epoxides<sup>24-27</sup>. By selecting appropriate parameters and suitable medium for this process we can limit the products of undesirable reactions associated with the presence of -OH groups in reaction environment. Furthermore, Corma et al.<sup>29</sup> demonstrated the significant role of a solvent in the epoxidation processes with  $H_2O_2$  over titanium-silicates. They presented the results of solvent influence on the epoxidation of 1-hexene over the Ti-Beta catalyst. It was shown, that the catalyst activity increases with solvent polarity in both, aprotic and protic solvents, but for aprotic solvents the increase was more pronounced and reached higher values. Such a phenomenon can be explained by the formation of unstable complexes with Ti atoms in nonprotic media, in which water, instead of alcohol (like in case of protic solvents) is the ligand of Ti (Fig. 2). According to the fact, that water has lower donor properties, the unstable complex formed in aprotic medium have a higher electrophilic character, and hence higher reactivity to epoxidation, then the stable alcohol complex in protic medium.



structure formed in protic medium    structure formed in aprotic medium  
**Figure 2.** Possible complexes formed during epoxidation with hydrogen peroxide over titanium-silicate catalysts in different media

On the other hand, in protic medium, five-membered cyclic structure has protic molecule – ROH, which stabilizes the Ti-peroxo complex through hydrogen bonding and can be modified by basics and acids. Therefore, the formation of this complex can be the reason of successful epoxidation reactions in protic environment when titanium-silicate materials are used as catalysts.

Given the above under consideration, the aim of our work was to study the influence of chosen solvents (polar aprotic, polar protic and nonpolar) on the oxidation of limonene with hydrogen peroxide over the Ti-SBA-15 catalyst. To this end, we have determined all of the products of the reaction and this gave us a clue in which direction the reaction occurred. Moreover, we investigated the influence of temperature and time of reaction for each studied environment. Thanks to the use of gas chromatography method, we have determined in the reaction medium five products of limonene oxidation: 1,2-epoxylimonene, 1,2-epoxylimonene diol, perillyl alcohol, carvone and carveol. Mechanisms of obtaining these compounds were described in our previous paper<sup>23</sup>. The proposed method of limonene oxidation can be beneficial taking into account the possibility of utilization of limonene derived from waste orange peels. Also application of hydrogen peroxide as oxidizing agent is environmentally friendly.

## EXPERIMENTAL

We have studied the influence of temperature, reaction time and effect of solvent on the epoxidation of limonene with 60 wt% solution of hydrogen peroxide in water and over the titanium-silicate catalyst Ti-SBA-15. The effect of solvents, such as: propan-2-ol, acetonitrile, toluene, methanol and ethanol were examined. These solvents can be divided into three groups depending on their chemical and physical properties: nonpolar (toluene,  $\epsilon_r = 2.4$ ), polar aprotic (acetonitrile,  $\epsilon_r = 37.5$ ) and polar protic (methanol,  $\epsilon_r = 32.7$ ; ethanol,  $\epsilon_r = 24.5$ , and propan-2-ol,  $\epsilon_r = 18$ ). Temperature was studied in the following range: 0–120°C and the reaction time was studied in the range from 15 min to 48 h. Other parameters remained unchanged in the entire studies and amounted respectively: catalyst content – 3 wt% (in relation to the mass of the reaction mixture), solvent concentration – 80 wt% (in relation to the mass of the reaction mixture), intensity of stirring 500 r.p.m and limonene/hydrogen peroxide molar ratio 1:1.

Ti-SBA-15 material has been previously synthesized using the method described by Berube et al.<sup>22</sup>. The molar ratio of Si/Ti in the gel before crystallization was 40:1. Thanks to the instrumental analysis of catalyst samples (XRF method), we have determined the Ti content in this catalyst, which was 2.46 wt%, the size of pores was about 5.0 nm, the specific surface area (622 m<sup>2</sup>/g) (BET method) and the shape and size of particles (which had shape of the rods with the width of about 3–4 nm and the length of 15 nm and were composed with smaller particles with the width of 0.54 nm and the length of 0.76 nm) (SEM method). The detailed description of Ti-SBA-15 catalyst was presented in our previous works<sup>25-27</sup>.

All of the epoxidation processes were carried out in glass reactors (50 ml) immersed in a thermostatted bath, equipped in a reflux condenser, magnetic stirrer and thermocouple. We have used the iodometric titration method in order to determine the amount of consumed hydrogen peroxide, and the gas chromatography method to determine qualitatively and quantitatively products of the reaction. Also tests without the catalyst were performed and reaction did not proceed. As the most important functions describing the process we have chosen: conversion of hydrogen peroxide ( $C_{H_2O_2}$ ) – the number of moles of  $H_2O_2$  that undergoes reaction divided by the initial amount of  $H_2O_2$ , the whole is multiplied by 100% – the value is expressed in mole%, conversion of limonene ( $C_L$ ) – the number of moles of limonene that undergoes reaction divided by the initial amount of limonene, the whole is multiplied by 100% – the value is expressed in mole%, selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed, understood as efficiency of hydrogen peroxide ( $E_{H_2O_2}$ ) – the amount of moles of hydrogen peroxide that has been converted into organic compounds divided by the amount of moles of hydrogen peroxide that has reacted, the total is multiplied by 100 and expressed in mole%, and selectivity of main product (mainly 1,2-epoxylimonene) – the amount of moles of limonene that has been converted to the chosen product divided by the number of moles of limonene that has reacted, the whole is multiplied by 100 and expressed in

mole%. Such functions helped us in choosing the most favorable conditions and the most beneficial medium for the epoxidations of limonene.

In the GC analyses the Focus apparatus equipped with the Restek RTX column (0.53 mm x 30 m x 1.0  $\mu$ m film (polyethylene glycol 20,000 Da)) was used. The carrier gas was helium, at a flow rate of 1 mL/min. Column temperature was initially 60°C for 2 min, then gradually increased to 240°C at 4°C/min. For GC-MS (Restek RTX column) an electron ionization system was used with an ionization energy of 70 eV.

## RESULTS AND DISCUSSION

### Acetonitrile as polar aprotic solvent

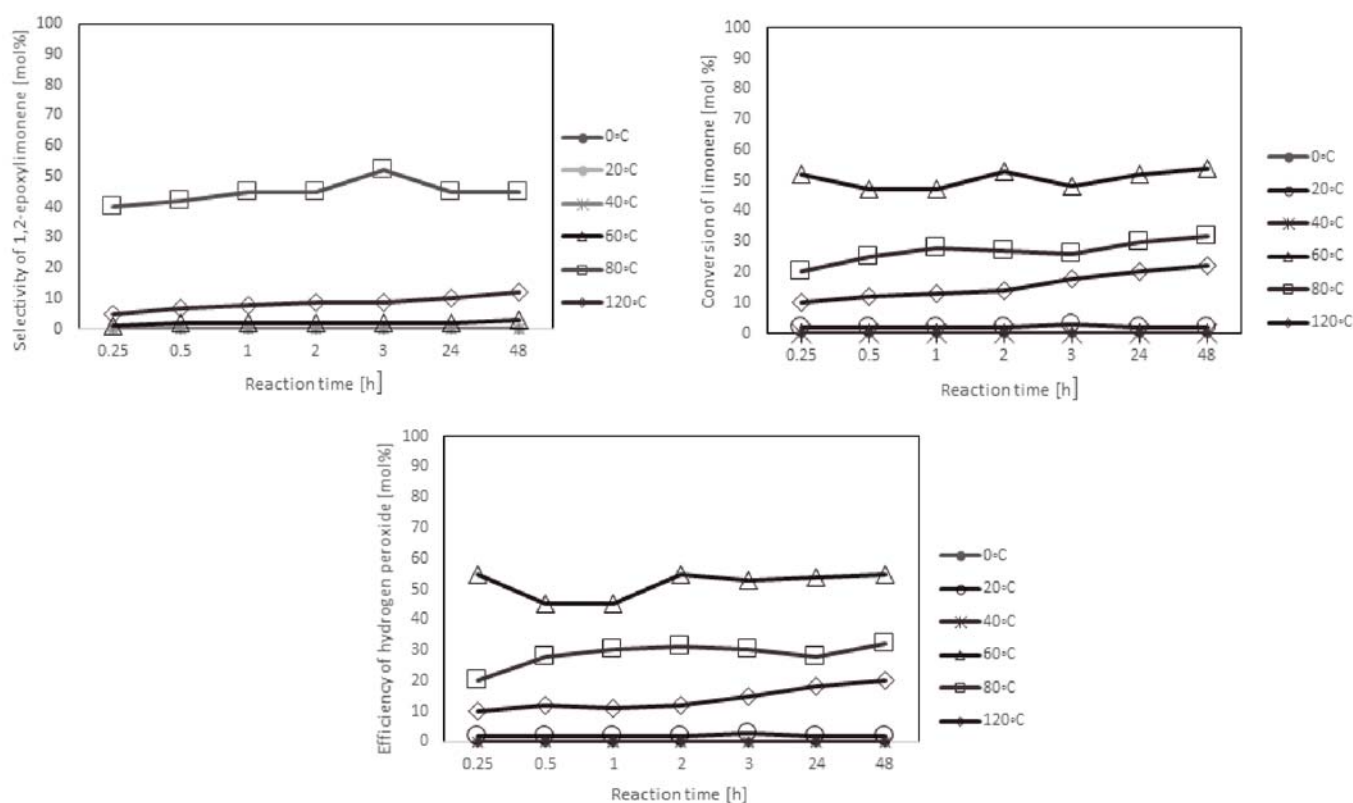
The effect of the acetonitrile as a solvent was investigated. From the results given in the Fig. 3. it can be concluded, that the process of limonene epoxidation does not occur at the temperatures below 60°C. Selectivity of 1,2-epoxylimonene (Fig. 3a) was comparable in the whole range of studied reaction time and amounted respectively: for the temperature of 80°C – 43.8 mol% (after 15 minutes), and for the temperature of 120°C – 11.9 mol% (after 24 hours). As the most beneficial temperature – the temperature of 80°C and as the best reaction time – the time of 0.25 hour were chosen for studied process. In these conditions, the selectivity of main epoxidation product – 1,2-epoxylimonene was 43.8 mol%. Moreover, we have detected perillyl alcohol in the post-reaction mixture, only when the reaction was carried out at 60°C and its selectivity reached the highest value after 2 hours and amounted to 22.5 mol%. Other by-products were detected at temperatures above 60°C

and the selectivities of these products at the most beneficial conditions reached following values:  $S_{1,2\text{-epoxylimonene diol}}$  – 10.6 mol%,  $S_{\text{carvone}}$  – 20.2 mol%, and  $S_{\text{carveol}}$  – 25.4 mol%. For the temperature of 120°C and after 24 hours all of the by-products reached values as follows:  $S_{1,2\text{-epoxylimonene diol}}$  – 20.9 mol%,  $S_{\text{carvone}}$  – 38.6 mol%, and  $S_{\text{carveol}}$  – 28.7 mol%.

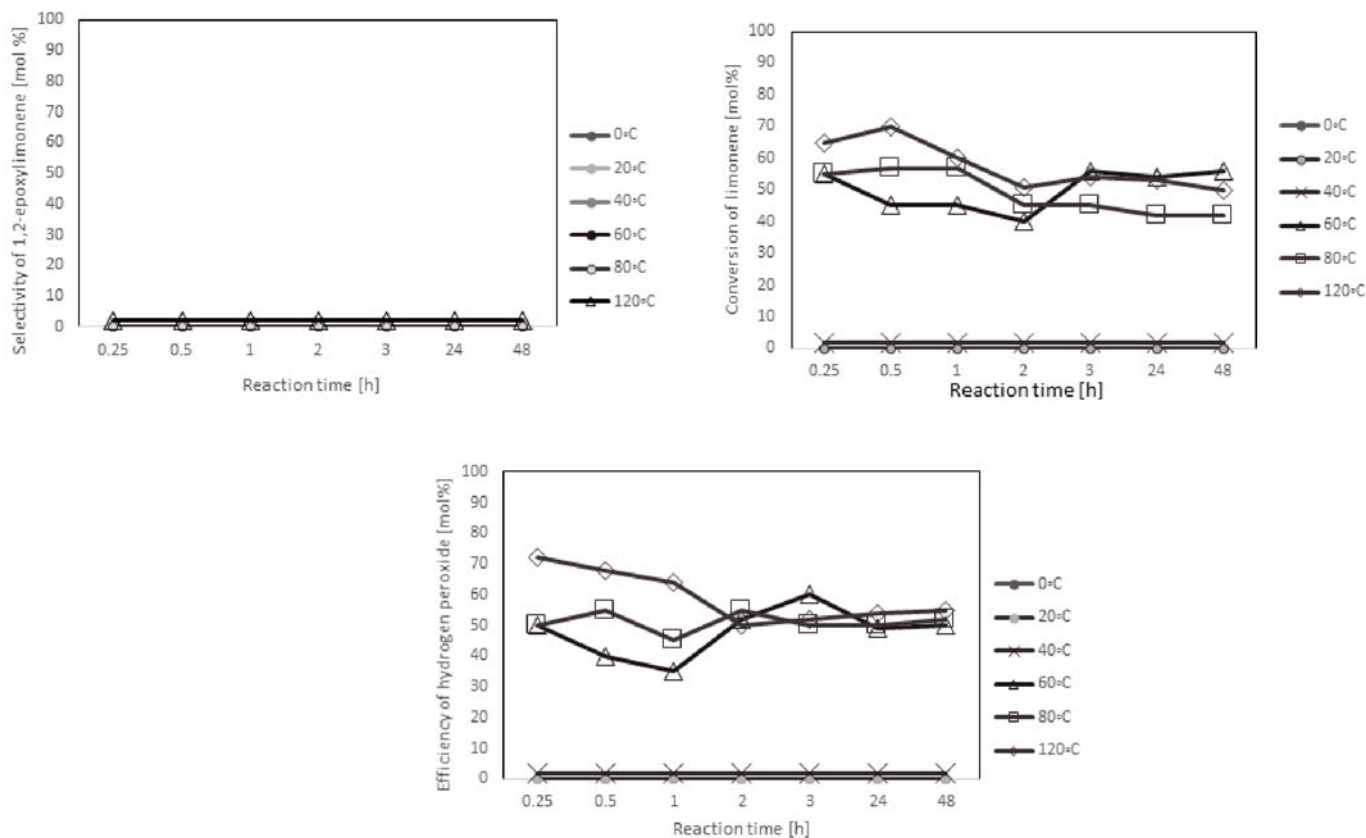
The conversion of limonene (Fig. 3b) increases with the increasing the reaction time and reached at 80°C and after 0.25 h – 19.8 mol%. Similarly, was in the case of hydrogen peroxide efficiency. This function at 80°C and after 0.25 h reached 20.0 mol%.

### Ethanol as polar protic solvent

During the studies on ethanol effect it was observed, that the presence of this solvent in reaction mixtures cause formation of hydroxylation products (Fig. 4). We have not detected any epoxidation products in the reaction mixtures (Fig. 4a). The value of perillyl alcohol selectivity was the highest from all of the detected products. It remained constant throughout the whole range of tested time at temperature above 80°C and amounted about 64.5–68.6 mol% at 80°C and 67.4–71.2 mol% at 120°C. The selectivities of other by-products reached at 80°C and after 24 hours following values:  $S_{1,2\text{-epoxylimonene diol}}$  – 14.2 mol%,  $S_{\text{carvone}}$  – 4.2 mol%, and  $S_{\text{carveol}}$  – 16.5 mol% and at 120°C after 24 hours:  $S_{1,2\text{-epoxylimonene diol}}$  – 7.7 mol%,  $S_{\text{carvone}}$  – 5.7 mol%, and  $S_{\text{carveol}}$  – 20.5 mol%. Furthermore, the values of limonene conversion (Fig. 4b) were high throughout the whole range of studied temperatures (above 60°C) and ranged at different temperatures respectively: 60°C: 39.6–54.9 mol%, 80°C: 45.3–58.9 mol% and 120°C: 48.7–68.5 mol%. The hydro-



**Figure 3.** The most important functions describing the process of limonene epoxidation in acetonitrile medium in the appropriate ranges of the reaction time and temperature (with Ti-SBA-15 amount of 3 wt% in reaction mixture, solvent concentration in reaction mixture – 80 wt%, intensity of stirring 500 r.p.m and limonene/H<sub>2</sub>O<sub>2</sub> molar ratio – 1/1



**Figure 4.** The most important functions describing the process of limonene epoxidation in ethanol medium in the appropriate ranges of the reaction time and temperature (with Ti-SBA-15 amount of 3 wt% in reaction mixture, solvent concentration in reaction mixture – 80 wt%, intensity of stirring 500 r.p.m and limonene/H<sub>2</sub>O<sub>2</sub> molar ratio – 1/1)

gen peroxide efficiency (Fig. 4c) reached at the highest point 71.5 mol% at 120°C and after 0.25 h.

#### Propan-2-ol as polar protic solvent

The results obtained in the epoxidation of limonene in propan-2-ol medium are very like those achieved in ethanol medium (Fig. 5). In such process, we have not detected any epoxidation products (Fig. 5a). Nevertheless, perillyl alcohol was determined with slightly higher values. It is obtained with a selectivity of 74,1 mol% and 68,2 mol%, when the temperature equals respectively 80°C and 120°C, and the time of reaction was 48 hours. Selectivity of by-products, such as: limonene-1,2-diol, carvone and carveol amounted to respectively – 14.2 mol%, 4.2 mol%, 16.5 mol% at 80°C and 7.7 mol%, 5.7 mol%, 20.5 mol at 120°C (after 24 hours). The conversion of limonene and efficiency of hydrogen peroxide (Fig. 5b–c) were higher in a comparison to the results obtained in ethanol medium. The highest value of conversion was reported at 120°C and after 0.5 hour and amounted to about 70 mol%. On the other hand, the highest value of hydrogen peroxide efficiency was reported at 120°C after 0.25 hour.

#### Methanol as polar protic solvent

During the studies of methanol influence it has been shown that this medium is less conducive for hydroxylation reactions (Fig. 6a). The values of by-products selectivities were the lowest in comparison to other solvents and reached at 80°C and after 24 hours as follows:  $S_{1,2\text{-epoxylimonene diol}}$  – 12.2 mol%,  $S_{\text{carvone}}$  – 3.9 mol%, and  $S_{\text{carveol}}$  – 13.5 mol%. Results of limonene conversion and H<sub>2</sub>O<sub>2</sub> efficiency (Fig. 6b–c) are slightly lower, then

in case of other solvents. The efficiency of hydrogen peroxide reached the highest value (55.9 mol%) at 80°C and after 48 hours and the conversion of limonene reached 56 mol% in the same conditions. The selectivity of perillyl alcohol was the lowest of all tested solvents and reached 57.5 mol% (48 h, 80°C). As in the case of other protic solvents, epoxidation process products have not been detected.

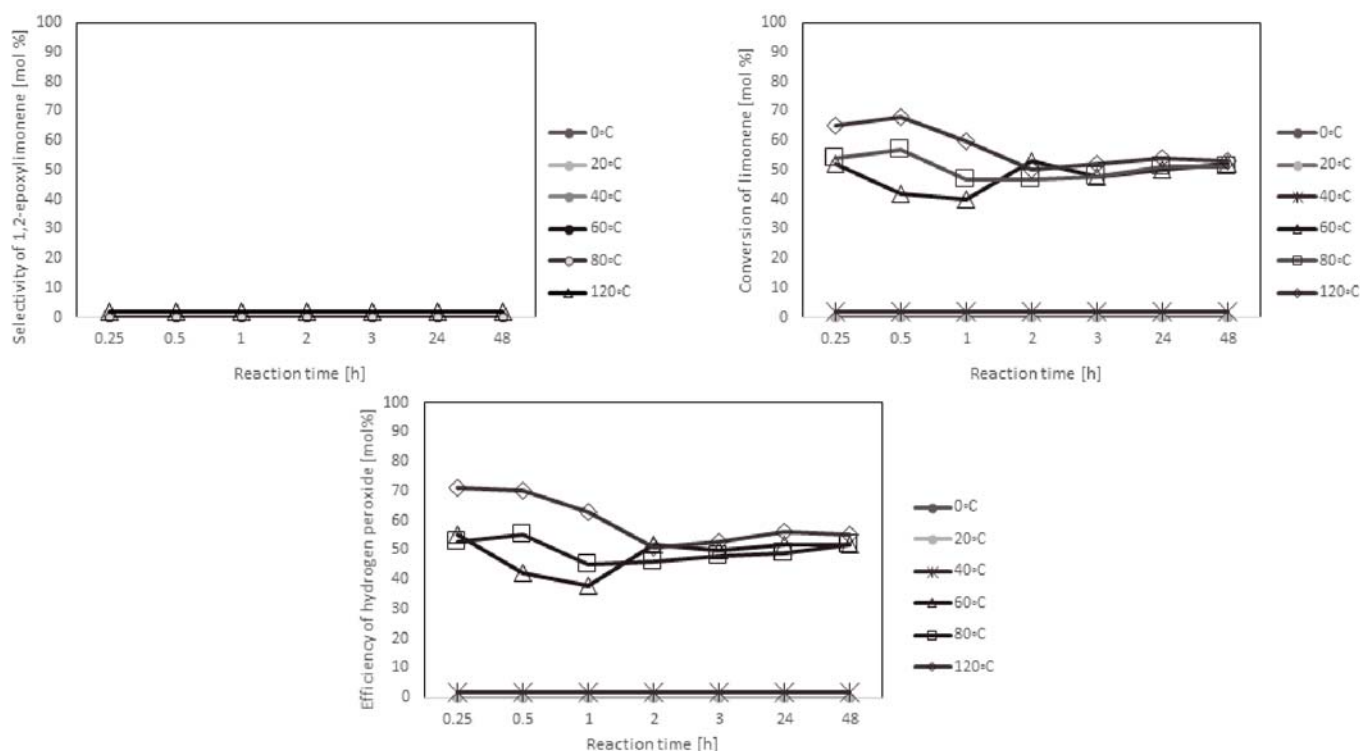
#### Toluene as nonpolar solvent

In the entire range of studied temperatures and time in toluene medium did not occur any process, neither epoxidation nor hydroxylation. Throughout the whole range of studied parameters, the values of the most important functions describing the process amounted to 0.0 mol%. We have not detected any product of this process.

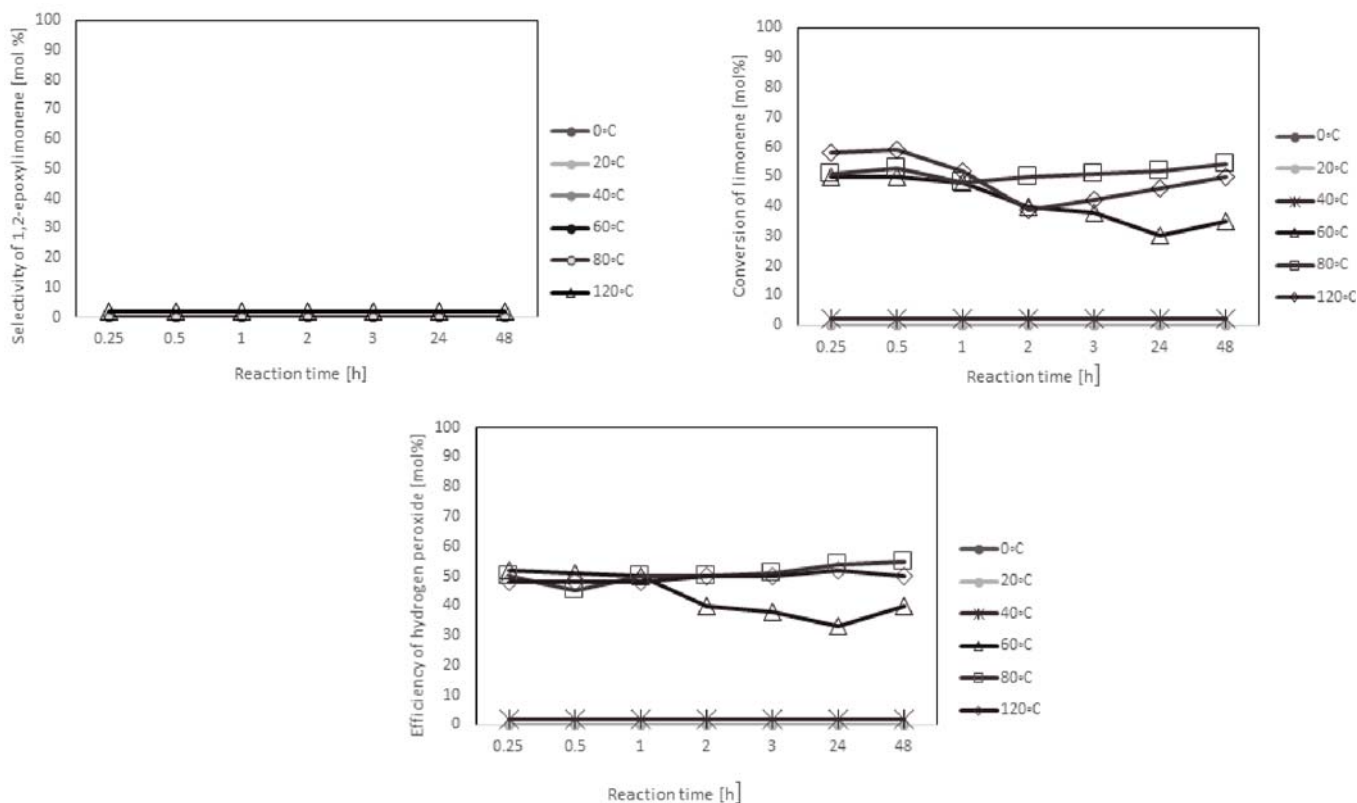
## CONCLUSIONS

The influence of solvents, such as: methanol, ethanol, propan-2-ol, toluene and acetonitrile on the epoxidation of limonene with hydrogen peroxide and over the Ti-SBA-15 catalyst has been studied. The basis for determining the most advantageous medium were three the most important functions describing the process: selectivity of 1,2-epoxylimonene, limonene conversion and efficiency of H<sub>2</sub>O<sub>2</sub>. Additionally, the selectivity of perillyl alcohol was designated in order to determine the progress of hydroxylation process in different media.

Analysing the obtained results, it can be concluded, that aprotic medium (acetonitrile) is suitable for epoxidation process. In protic and apolar media the epoxidation did



**Figure 5.** The most important functions describing the process of limonene epoxidation in propan-2-ol medium in the appropriate ranges of the reaction time and temperature (with Ti-SBA-15 amount of 3 wt% in reaction mixture, solvent concentration in reaction mixture – 80 wt%, intensity of stirring 500 r.p.m and limonene/H<sub>2</sub>O<sub>2</sub> molar ratio – 1/1)



**Figure 6.** The most important functions describing the process of limonene epoxidation in methanol medium in the appropriate ranges of the reaction time and temperature (with Ti-SBA-15 amount of 3 wt% in reaction mixture, solvent concentration in reaction mixture – 80 wt%, intensity of stirring 500 r.p.m and limonene/H<sub>2</sub>O<sub>2</sub> molar ratio – 1/1)

not occur. In acetonitrile, the value of 1,2-epoxylimonene selectivity was the highest at 80°C and after 3 hours. In such conditions, it reached 48.7 mol%. Furthermore, other parameters (conversion of limonene and hydrogen peroxide efficiency) reached respectively:  $C_L = 49.9$  mol% and  $E_{H_2O_2} = 28$  mol%.

On the other hand, it can be stated, that the competitive reaction for limonene epoxidation is its hydroxylation, in which perillyl alcohol is obtained. It is especially visible for such solvent as: ethanol ( $\epsilon_r = 24.5$ ) and propan-2-ol ( $\epsilon_r = 18$ ). Moreover, by selecting the appropriate parameters, other by-products of this process can be obtained

with relatively high selectivity. 1,2-Epoxy limonene diol, carveone and carveol can be obtained with selectivity amounted to 20.9 mol%, 38.7 mol% and 28.7 mol% respectively in acetonitrile medium, at the temperature of 120°C and after 24 hours.

Apolar medium (toluene) is not suitable neither for epoxidation nor hydroxylation reactions.

The comparison the influence of temperature and reaction time on the course of limonene oxidation in the appropriate solvents showed that in acetonitrile (polar aprotic solvent) temperature had influence on the course of epoxidation. There was temperature below the epoxidation did not proceed (60°C) – at higher temperatures epoxidation proceeded but selectivity of 1,2-epoxy limonene decreased. Moreover, in acetonitrile prolongation the reaction time increased the conversion of limonene and efficiency of hydrogen peroxide conversion, but increase in temperature caused decrease in values of these functions – probably because the ineffective decomposition of hydrogen peroxide at higher temperatures and polymerization of limonene. In polar protic solvents epoxidation of limonene did not proceed, mainly formation of perillyl alcohol was observed. Prolongation the reaction time decreased slightly the conversion of limonene and efficiency of hydrogen peroxide conversion but the increase in temperature caused increase in values of these two functions.

## LITERATURE CITED

- Auriemma, F., De Rosa, C., Di Caprio, M.R., Di Girolamo, R., Ellis, W.C. & Coates, G.W. (2015). Stereocomplexed Poly(Limonene Carbonate): A unique example of the cocrystallization of amorphous enantiomeric polymers. *Angew. Chem. Int. Ed.*, 54, 1215–1218. DOI: 10.1002/anie.201410211.
- Nunes, L.C.C., De Almeida, A.A.C., De Carvalho, R.B.F., Cardoso, L.T., De Moraes, J.N.E., De Souza, D.P. & De Freitas, R.J. (2012). BR Patent No 102012006336.
- Yapa, A.S., Wang, H., Pyle, M., Shrestha, T.B., Troyer, D.L., Wendel, S.O. & Bossmann, S.H. (2016). Abstracts, 51st Midwest Regional Meeting of the American Chemical Society, Manhattan, KS, United States, October 26–28, 312.
- Chen, T., Levin, D. & Pupalli, S. (2016) Patent WO No US17543, PCT Int. Appl.
- De Carvalho, C.C.C.R. & Da Fonseca, M.M.R. (2006). Carvone: Why and how should one bother to produce this terpene, *Food Chem.* 95:413–422. DOI: 10.1016/j.foodchem.2005.01.003.
- Panda, H. (2005). *The Complete Technology Book on Herbal Perfumes & Cosmetics*, 234–248, Delhi : National Institute of Industrial Research.
- Nadealian, Z., Mirkhani, V., Yadollahi, B., Moghadam, M., Tangestaninejad, S. & Mohammadpoor-Baltork, I. (2013) Selective oxidation of alkenes using [BMIM]<sub>5</sub>[PW<sub>11</sub>ZnO<sub>39</sub>]<sub>3</sub>H<sub>2</sub>O hybrid catalyst. *J. Iran. Chem. Soc.* 10(4), 777–782.
- Wróblewska, A., Makuch, E. & Miadlicki, P. (2016). The studies on the limonene oxidation over the microporous TS-1 catalyst. *Catal. Today*, 268, 121–129. DOI: 10.1016/j.cattod.2015.11.008.
- Granadeiro, C.M., Barbosa, A.D.S., Ribeiro, S., Santos, I.C.M.S., De Castro, B., Cunha-Silva, L. & Balula, S.S. (2014). Oxidative catalytic versatility of a trivacant polyoxotungstate incorporated into MIL-101(Cr). *Catal. Sci. Technol.* 4: 1416–1425. DOI: 10.1039/C3CY00853C.
- Hua, L., Chen, J., Chen, C., Zhu, W., Yu, Y., Zhang, R., Guo, L., Song, B., Gan, H. & Hou, Z. (2014). Immobilization of polyoxometalate-based ionic liquid on carboxymethyl cellulose for epoxidation of olefins. *New J. Chem.* 38, 3953–3959. DOI: 10.1039/C4NJ00270A.
- Serra, S. (2015). MnO<sub>2</sub>/TBHP: A versatile and user-friendly combination of reagents for the oxidation of allylic and benzylic methylene functional groups. *Eur. J. Org. Chem.* 29, 6472–6478. DOI: 10.1002/ejoc.201500829.
- Silvestre-Alberó, J., Domine, M.E., Jordá, J.L., Navarro, M.T., Reya, F., Rodríguez-Reinoso, F. & Corma, A. (2015). Spectroscopic, calorimetric, and catalytic evidences of hydrophobicity on Ti-MCM-41 silylated materials for olefin epoxidations. *Appl. Catal. A*, 507, 14–25. DOI: 10.1016/j.apcata.2015.09.029.
- Fernandes, C.I., Carvalho, M.D., Ferreira, L.P., Nunes, C.D. & Vaz, P.D. (2014). Organometallic Mo complex anchored to magnetic iron oxide nanoparticles as highly recyclable epoxidation catalyst. *J. Organomet. Chem.* 760, 2–10. DOI: 10.1016/j.jorganchem.2014.01.035.
- Tangestaninejad, S., Moghadam, M., Mirkhani, V., Mohammadpoor-Baltork, I. & Saedi, M.S. (2010). Efficient epoxidation of alkenes with sodium periodate catalyzed by reusable manganese(III) salophen supported on multi-wall carbon nanotubes. *Appl. Catal. A*, 381, 233–241. DOI: 10.1016/j.apcata.2010.04.013.
- Lima, L.F., Cardozo-Filho, L., Arroyo, P.A., Márquez-Alvarez, H. & Antunes, O.A.C. (2005). Metal(salen)-catalyzed oxidation of limonene in supercritical CO<sub>2</sub>. *React. Kinet. Catal. Lett.* 84, 69–77. DOI: 10.1007/s11144-005-0192-7.
- Ma, B., Zhao, W., Zhang, F., Zhang, Y., Wu, S. & Ding, Y. (2014). A new halide-free efficient reaction-controlled phase-transfer catalyst based on silicotungstate of [(C<sub>18</sub>H<sub>37</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>N]<sub>3</sub>[SiO<sub>4</sub>H(WO<sub>5</sub>)<sub>3</sub>] for olefin epoxidation, oxidation of sulfides and alcohols with hydrogen peroxide. *RSC Adv.* 4: 32054–32062. DOI: 10.1039/C4RA04036H.
- Santos, I.C.M.S., Gamelas, J.A.S., Duarte, T.A.G., Simoes, M.M.Q., Neves, M.G.P.M.S., Cavaleiro, J.A.S. & Cavaleiro, A.M.V. (2017). Catalytic homogeneous oxidation of monoterpenes and cyclooctene with hydrogen peroxide in the presence of sandwich-type tungstophosphates [M<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sub>n</sub>–, M = Co<sup>II</sup>, Mn<sup>II</sup> and Fe<sup>III</sup>. *J. Mol. Catal. A: Chem.* 426, 593–599. DOI: 10.1016/j.molcata.2016.10.021.
- Nunes, C.D., Vaz, P.D., Veiros, L.F., Moniz, T., Rangel, M., Realista, S., Mourato, A.C. & Calhorda, M.J. (2015). Vanadyl cationic complexes as catalysts in olefin oxidation. *Dalton Trans.*, 44, 5125–5138. DOI: 10.1039/C4DT03174A.
- Nadealian, Z., Mirkhani, V., Yadollahi, B., Moghadam, M., Tangestaninejad, S. & Mohammadpoor-Baltork, I. (2013). Selective oxidation of alkenes using [bmim]<sub>5</sub>[PW<sub>11</sub>ZnO<sub>39</sub>]<sub>3</sub>H<sub>2</sub>O hybrid catalyst. *J. Iran. Chem. Soc.* 10, 777–782. DOI: 10.1007/s13738-012-0212-2.
- Bento, A., Sanches, A., Vaz, P.D. & Nunes, C.D. (2016) Catalytic Application of Fe-doped MoO<sub>2</sub> Tremella-Like Nanosheets. *Top. Catal.* 59, 1123–1131. DOI: 10.1007/s11244-016-0631-x.
- Wróblewska, A., Makuch, E., Młodzik, J., Koren, Z.C. & Michalkiewicz, B. (2017). Fe/nanoporous carbon catalysts obtained from molasses for the limonene oxidation process. *Catal. Lett.* 147, 150–160. DOI: 10.1007/s10562-016-1910-7.
- Cagnoli, M.V., Casuscelli, S.G., Alvarez, A.M., Bengoa, J.F., Gallegos, N.G., Samaniego, N.M., Cribello, M.E., Ghinoe, G.E., Perez, C.F., Herrero, E.R. & Marchetti, S.G. (2005). “Clean” limonene epoxidation using Ti-MCM-41 catalyst. *Appl. Catal. A: General*, 287(2), 227–235. DOI: 10.1016/j.apcata.2005.04.001.
- Wróblewska, A. (2014). The epoxidation of limonene over the TS-1 and Ti-SBA-15 catalysts. *Molecules*. 19, 19907–19922. DOI: 10.3390/molecules191219907.
- Berube, F., Kleitz, F. & Kaliaguine, S. (2008). A comprehensive study of titanium-substituted SBA-15 mesoporous materials prepared by direct synthesis. *J. Phys. Chem.* 112(37), 14403–14411. DOI: 10.1021/jp803853m.

25. Makuch, E. & Wróblewska, A. (2013). Preparation of titanium-silicate catalyst Ti-SBA-15. *Chemik*, 67,811–816.
26. Wróblewska, A. & Makuch, E. (2014). Regeneration of the Ti-SBA-15 catalyst used in the process of allyl alcohol epoxidation with hydrogen peroxide. *J. Adv. Oxid. Technol.* 17, 44–52. DOI: 10.1515/jaots-2014-0106.
27. Wróblewska, A. & Makuch, E. (2012). The utilization of Ti-SBA-15 catalyst in the epoxidation of allylic alcohols. *Reac. Kinet. Mech. Cat.* 105, 451–468. DOI: 10.1007/s11144-011-0405-1.
28. Melero, J.A., Iglesias, J., Arsuaga, J.M., Sainz-Pardo, J., de Frutos, P. & Blazquez, S. (2007). Synthesis and catalytic activity of organic–inorganic hybrid Ti-SBA-15 materials. *J. Mater. Chem.* 17, 377–385. DOI: 10.1039/B610868G.
29. Corma, A., Esteve, P. & Martinez, A. (1996). Solvent effects during the oxidation of olefins and alcohols with hydrogen peroxide on Ti-beta catalyst: the influence of the hydrophilicity–hydrophobicity of the zeolite. *J. Catal.* 161,11–19. DOI: 10.1006/jcat.1996.0157.