

Coupled action of ozone and UV radiation towards obtaining adipic acid from cyclohexane/one

Adam A. Marek*, Dawid Lisicki

Department of Chemical Organic Technology and Petrochemistry, Silesian University of Technology, Krzywoustego 4 street, 44-100 Gliwice, Poland

*Corresponding author: e-mail: adam.a.marek@polsl.pl

A lot of research is constantly underway in the world to develop new or improve the current processes of the chemical industry to make them more effective and environmentally friendly. The described research on the oxidation of cyclohexane or cyclohexanone to adipic acid with a coupled action of UV radiation and oxygen–ozone mixture, instead of the currently used oxidation with HNO_3 , is part of this trend. Gas chromatography was used to determine process indicators, such as cyclohexane conversion and selectivity to AA, which exceeded 50% at 25 °C, after 16 h. This method can also be used for the preparation of other dicarboxylic acids from cycloalkanes, which proves its universal character.

Keywords: adipic acid, oxidation, ozone, UV radiation.

INTRODUCTION

Adipic acid (AA) is the most important of the aliphatic dicarboxylic acids. Its global production is about 2.7 million tons per year, and it has been used, among others, in the production of polyamides, polyesters, and plasticizers. Industrially, AA has been obtained for about 80 years by oxidizing cyclohexanol (CH-OL), cyclohexanone (CH-ON), or a mixture thereof with HNO_3 ^{1,2}. This process is well known and described due to the formation of nitrogen oxides, mainly N_2O , a strong greenhouse gas. As a result of the production of AA, about 290–310 kg N_2O / t AA are generated³.

There are three known industrial methods for producing AA; from cyclohexane, cyclohexene and phenol³ (Figure 1, left side). Most often, AA is produced from cyclohexane as a result of its two-stage oxidation. In the first stage, cyclohexane is oxidized in the liquid phase with air to a mixture of cyclohexanol and cyclohexanone⁴. The reaction is carried out under increased pressure at a temperature of 150–170 °C in the presence of a Co(II)/Fe(II) catalyst system. The resulting mixture is then oxidized with HNO_3 at a temperature of 60–90 °C and in the presence of a further V(V)/Cu(I) catalyst system. The disadvantage of this solution, apart from the formation of N_2O , is the need to carry out cyclohexane oxidation with a low conversion of 3–7% to increase the selectivity

of the reaction. To solve this problem, you can replace cyclohexane with cyclohexene as a raw material. In the first step, cyclohexene is reacted with water to obtain cyclohexanol which is then oxidized with HNO_3 to AA. The disadvantage of this solution is the production of cyclohexene itself. It is produced by selective hydrogenation of benzene with about 80% selectivity and the remaining 20% is cyclohexane. The separation of unreacted benzene, cyclohexene, and cyclohexane is also problematic. The further path leads, similarly to the previous one, through the HNO_3 oxidation stage. The use of phenol as a raw material is also practiced on an industrial scale. Phenol, obtained by the cumene method, like cyclohexane and cyclohexene, is primarily produced from benzene. In the first stage, the phenol is hydrogenated to cyclohexanol or cyclohexanone, depending on the catalyst system used, and then the intermediate is oxidized once more with nitric acid (V). The disadvantage of this solution may be, among others low cost-effectiveness of the process, which depends on the demand for phenol.

Undoubtedly, it is desirable to develop a new technology for AA production that complies with the principles of “green chemistry” and is economically viable. In practice, it is associated with the use of commercially available raw materials, and catalysts and obtaining AA with high selectivity and conversion.

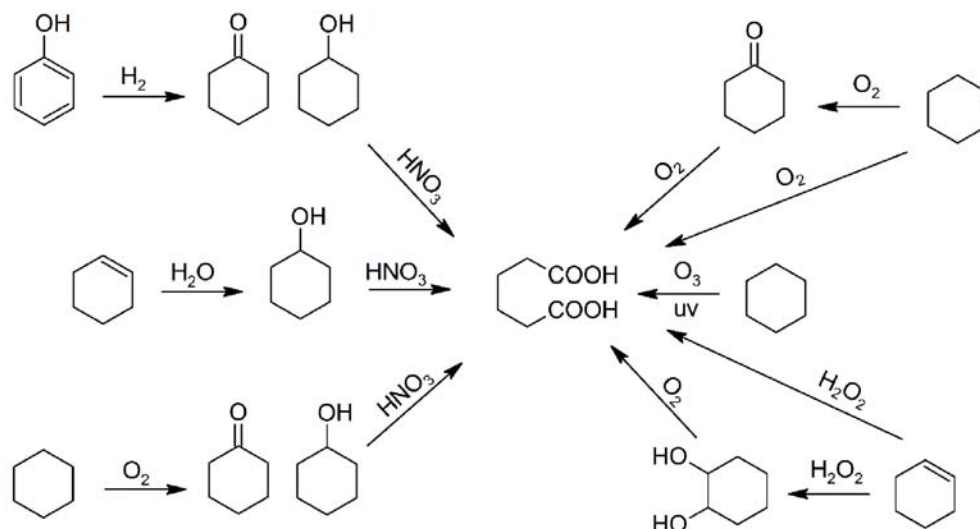


Figure 1. Overview of methods of obtaining adipic acid from petrochemical raw materials

Some alternative approaches and processes have been described in the literature from which AA can be obtained, although these have not been implemented on a large scale (Figure 1, right side). One of the solutions is direct oxidation of cyclohexane to AA^{5, 6}. Often the oxidation is carried out in a polar solvent in the presence of a catalyst system consisting of transition metal salts like Co(II)/Mn(II) and N-hydroxyphthalimide (NHPI)⁷⁻⁹. NHPI is an organo-catalyst showing catalytic activity in the oxidation of hydrocarbons¹⁰⁻¹⁴. A widely described solution is also the oxidation of cyclohexanone with oxygen or air¹⁵⁻¹⁸. These solutions seem to be self-evident to implement due to the availability of raw materials, cheap catalysts, and the use of oxygen as an oxidant. Usually, the oxidation is carried out in the presence of Co(II)/Mn(II) compounds, in AcOH as the solvent^{19, 20}. Nevertheless, in these processes, AA is obtained with relatively low selectivity in the range of 60–80%.

The preparation of AA by oxidation of cyclohexene with H₂O₂ is more and more often described in the literature²¹⁻²³. This solution allows to obtaining AA with high selectivity with high conversion of cyclohexene, but it is connected with the necessity to use large amounts of H₂O₂ in a molar ratio of even 4: 1 to the substrate. Moreover, the oxidation process is carried out in a 2-phase system (liquid / liquid), which is associated with the use of relatively expensive phase transfer catalysts. The solution to this problem may be to perform a two-stage oxidation of cyclohexene²⁴. In the first step, cyclohexene is oxidized with H₂O₂ to cyclohexane-1,2-diol, which is oxidized in the next step with oxygen to AA. This solution is more complicated, however, it is possible to reduce the amount of H₂O₂ from 4 to 1 mole in relation to the raw material and replace it with cheap oxygen gas, which significantly increases the cost-effectiveness of the solution.

We found in the literature a process of one-pot room-temperature conversion of cyclohexane to adipic acid by ozone and UV light [25]. High conversions (over 90%) and selectivity to AA over 80% were the reason for undertaking the present research in this area. However, we used a different reaction system and a different methodology for products analysis – gas chromatography.

MATERIALS AND METHODS

Raw materials and chemicals

Most of the chemical substances used in the oxidation process (cyclohexane, cyclohexanol, cyclohexanone, adipic acid, glutaric acid, cyclooctane, cyclodecane, cyclooctanone) were $\geq 98\%$ purity grade and purchased from Sigma-Aldrich. Other chemicals (acetic acid, sulfuric acid, methanol, toluene) were purchased from Chempur with analytically pure grade. All the materials were used as received.

Equipment

The processes were performed in a specially designed glass reactor with a volume of 6 and 50 mL, in which the lower part of the reactor was equipped with a heating / cooling jacket and a reflux condenser, while the reaction mixture was irradiated with a Hg lamp generating UV

radiation through the upper section (Fig. 2). Oxygen with ozone added from an ozone generator OL80F / DSTR (OzoneLab), was introduced through a bubbler at a constant rate 1.5 and 7.5 L / h with an ozone concentration of 107–146 mg/L.

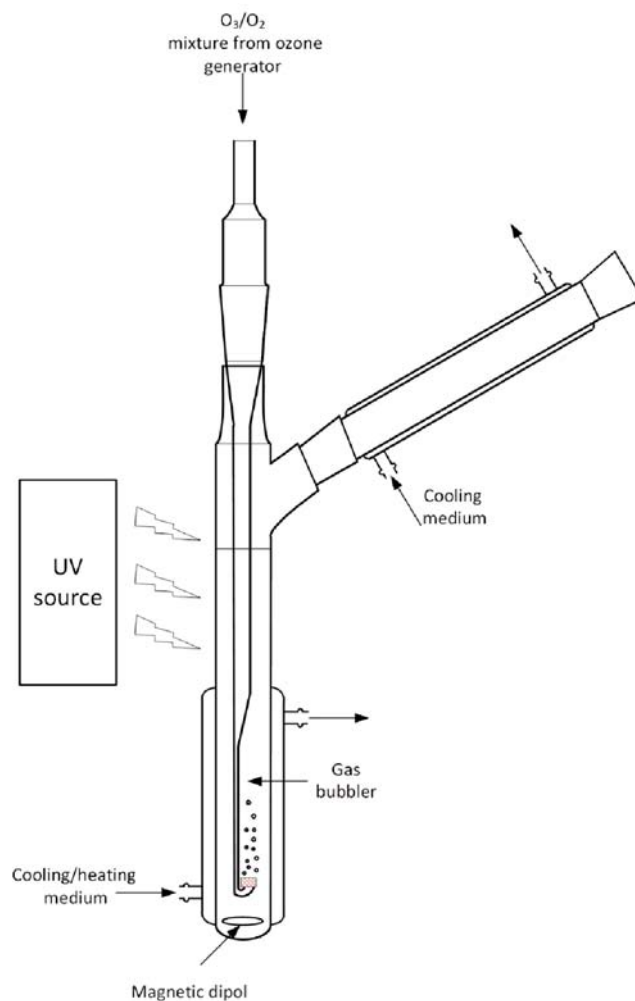


Figure 2. The reactor used in the research

Analytical methods

The composition of the reaction products was analyzed using an Agilent 5890 Series II gas chromatograph (GC) equipped with Flame Ionization Detector (FID) detector, a Zebtron ZB-5HT column (30 m x 0.25 mm x 0.25 μ m), and an autosampler. The analysis was carried out using an internal standard (toluene) method and helium as the carrier gas with a flow rate of 1 mL/min. GC analysis conditions included: injector temperature 200 °C, detector temperature 300 °C, split ratio 100:1, injection volume 1 μ L, airflow 400 mL/min, nitrogen flow 24 mL/min, hydrogen flow 30 mL/min. The temperature program was as follows: 70 °C for 10 min, a ramp of 6 °C/min to 112 °C, a further ramp of 20 °C/min to 212 °C, and a hold at 212 °C for 8 min. Each sample was analyzed twice, and the concentration of the substance was calculated based on previously prepared standard curves.

The products composition was additionally confirmed by gas chromatography coupled with mass spectrometry (GC-MS) performed using an Agilent gas chromatograph 7890C with an Agilent HP-5 MS capillary column (30 m x 0.25 mm x 0.25 μ m) and Electron Ionization (EI) (70 eV). Helium with a flow rate of 1 ml/min was used

as the carrier gas, and analysis parameters included an injector temperature of 250 °C, ion source temperature of 230 °C, and quadrupole temperature of 150 °C. The temperature program was 40 °C for 14 min, a ramp of 6 °C/min to 112 °C, and a further ramp of 20 °C/min to 212 °C. The obtained spectra were compared using the NIST/EPA/NIH Mass Spectral Library. GC/MS chromatogram of oxidation products is presented in Figure 3.

Cycloalkane, cyclic ketone, and alcohol content: 0.2 mL was taken from the reaction products and diluted with oxidized substrate to 1 mL. Then 5 mL of a solution of toluene in acetic acid (24 g/L) was added. The obtained mixture was analyzed using gas chromatography.

Content of dicarboxylic acids: 0.2 mL was taken from the reaction products and diluted with oxidized substrate to 1 mL. Then 12 mL of a solution of toluene in methanol (12 g/L) and 1–3 drops of sulphuric acid (VI) were added. The solution was stirred (200 rpm) for 24 h at room temperature to form carboxylic acid methyl esters. The solution prepared in this way was analyzed by gas chromatography to determine the amount of dicarboxylic acid dimethyl esters, related to the amount of dicarboxylic acids.

RESULTS AND DISCUSSION

Initial studies were carried out in a bubble reactor with a capacity of 6 mL to determine the basic parameters (temperature, time, ozone concentration) for the conversion of cyclohexane and the selectivity of the obtained products. The content of cyclohexanol, cyclohexanol, adipic acid, and glutaric acid was determined in the post-reaction mixture by GC method. The presence of these products was previously confirmed using GC-MS (Figure 3). The obtained results are presented in Table 1.

The processes were carried out in the temperature range of 15–25 °C for 2, 4, and 6 h. For the process carried out at 25 °C, the effect of ozone concentration in the oxidizing agent (107–146 mg/L) was determined. Based on the obtained results, it was found that it is advantageous to run the process with the maximum concentration of ozone. An increase in the CH conversion from 31.8 to 46.8% and the selectivity of the main oxidation products CH-ON and AA from 25.5 to 38.5% and from 11 to 18%, respectively, was observed, therefore, the amount of 146 mg/L. This amount was the upper limit of ozone production in the apparatus used. The lowering of the process temperature to 20 °C allowed for improvement in the process indicators and achieved

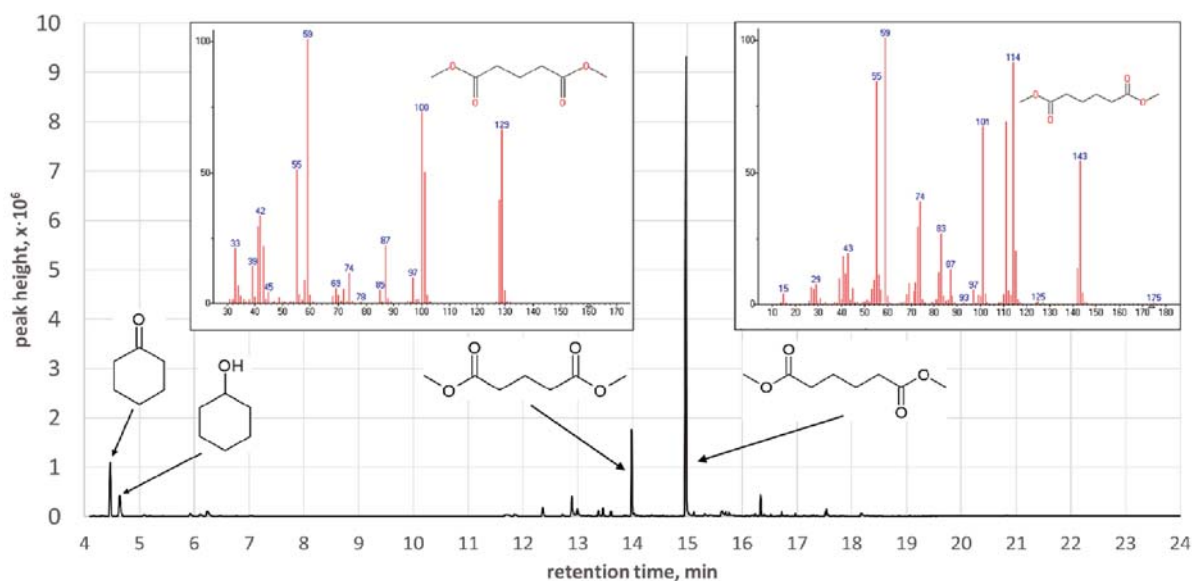


Figure 3. GC-MS chromatogram with MS spectra of main oxidation products

Table 1. Results obtained in the oxidation of cyclohexane with oxygen-ozone mixture in the presence of UV radiation in a 6 mL reactor

Time (h)	Temp. (°C)	Ozone (mg/L)	Conv. (%)	Selectivity (%)			
				CH-OL	CH-ON	AA	GA
2	25	146	14.1	1	10.5	5.5	2
4	25	146	22.2	2	32.5	11.5	3.5
6	25	146	46.8	1	38.5	18	6
2	25	135	12.6	1	10	6	2
4	25	135	16.8	1.5	23.5	7.5	4
6	25	135	40.8	1	34.5	14	8
2	25	107	13.8	1	6.5	6	4
4	25	107	11.1	1.5	14	8	2.5
6	25	107	31.8	1.5	25.5	11	4
2	20	146	9.6	0.5	7	11.5	4
4	20	146	11.1	0.2	7	14	6.5
6	20	146	56.7	1.1	54.5	21	6
2	15	146	9.6	0.5	7	11	4
4	15	146	15.0	0.5	14	10	3.5
6	15	146	22.5	0.5	32.5	20	6

Cyclohexane: 6 mL, Oxidizer flow rate: 1.5 L/h

Table 2. Results obtained in the reaction of long-term oxidation of cyclohexane and other substituted cycloalkanes with oxygen-ozone mixture in the presence of UV radiation in a 50 mL reactor

Substrates	Time (h)	Temp. (°C)	Conv. (%)	Selectivity (%)			
				CH-OL	CH-ON	AA	GA
Cyclohexane	16	25	55.6	0.3	5.8	49.5	17.0
Cyclohexanone	16	25	33.2	–	–	30.0	11.0
Cyclohexanone	16	60	67.8	–	–	62.0	15.5
Cyclooctane	16	25	29.2	–	C ₈ -ON 2.0	Octanedioic acid 38,3	–
Cyclododecane + acetic acid	16	25	32.3	–	–	Dodecanedioic acid 42.6	–
Methylcyclohexane	16	25	34.0	(CH ₃)C ₆ -OL 3.3	–	6-Oxoheptanoic acid 18.7	–

Cyclohexane: 50 mL, Oxygen Flow: 7.5 L/h, Ozone: 146 mg/L

CH conversion of 56.7% after 6 h and selectivity to CH-ON and AA of 54.5 and 21%, respectively. Another reduction of the temperature by 5 degrees resulted in a diametric worsening of the results. Two factors seem to be relevant here. On the one hand, the solubility and stability of ozone in the reaction system increases at lower temperatures, and on the other hand, the rate of the oxidation reaction behaves oppositely and slows down at low temperatures.

Cyclohexanone and several other cycloalkanes were also used as raw materials in the research. The processes were carried out in a reactor with a capacity of 50 mL, and their time was extended to 16 h.

Extending the process time to 16 hours resulted in a further increase in cyclohexane conversion and selectivity to AA, 55.6 and 49.5%, respectively. Although better results were expected, it is possible that the reason for this is the use of a larger reactor and poorer dispersion of oxygen with ozone in the system, which plays a dominant role in bubbling processes. The use of a sintered bubbler was not possible here, because on the one hand, it was observed to become clogged with the resulting adipic acid, and on the other hand, ozone decomposed on the sinter. A capillary with several fine holes was used as a bubbler.

The possibility of using other cycloalkanes as raw materials in the process was also checked (Table 2). When the process was carried out at 25 °C, after 16 h conversions of 30% and selectivity to the appropriate dicarboxylic acids of about 40% were obtained. Due to the lower vapor pressure, losses due to blowing of the raw material were avoided here, and in the case of cyclododecane it was necessary to use a solvent (acetic acid).

Quite good results were obtained for cyclohexanone. The oxidation process was carried out both at 25 °C and 60 °C. In the latter case, after 16 h, the conversion was 67.8% and the selectivity to AA and GA was 62 and 15.5%, respectively. The use of cyclohexanone as a raw material instead of cyclohexane may be important for the industry as an alternative to produce AA, moreover, there is no CH-OL in the reaction products, which facilitates the separation of the post-reaction mixture.

CONCLUSION

The obtained results confirmed the literature reports on the possibility of obtaining adipic acid by the simultaneous action of ozone and UV radiation at room temperature on cyclohexane²⁵, although the process ratios obtained in this case did not exceed 60%. The effectiveness of the

process results mainly from the concentration of ozone in oxygen and its dispersion in the reaction mixture. Research has shown that other dicarboxylic acids can also be obtained by this method.

The method described here is interesting and is a potential alternative for obtaining AA in place of the currently used industrial method of oxidation with HNO₃, in particular that CH-ON can be used instead of CH and the post-reaction mixture separation node can be simplified.

Acknowledgments

This research was funded by the National Science Center through the project NCN MINIATURA 2019/03/X/ST8/01139 and Silesian University of Technology grant No. 04/050/BKM23/0179.

CRedit authorship contribution statement

Adam A. Marek: Conceptualization, Methodology, Investigation, Data analysis, Writing – original draft, Writing – review & editing, Visualization. Dawid Lisicki: GC Analytical Methodology, Writing – original draft.

LITERATURE CITED

1. Bart, J.C.J. & Cavallaro, S. (2015). Transiting from adipic acid to bioadipic acid. 1, Petroleum-based processes. *Ind. Eng. Chem. Res.* 54(1), 1–46. DOI: 10.1021/ie5020734.
2. Bart, J.C.J. & Cavallaro, S. (2015). Transiting from adipic acid to bioadipic acid. Part II. Biosynthetic pathways. *Ind. Eng. Chem. Res.* 54(2), 567–576. DOI: 10.1021/ie502074d.
3. Rios, J., Lebeau, J., Yang, T., Li, S. & Lynch, M.D. (2021). A critical review on the progress and challenges to a more sustainable, cost competitive synthesis of adipic acid. *Green Chem.* 23, 3172–3190. 10.1039/d1gc00638j.
4. Abutaleb, A. & Ali, M.A. (2021). A comprehensive and updated review of studies on the oxidation of cyclohexane to produce ketone-alcohol (KA) oil. *Rev. Chem. Eng.* 38(7), 769–797. DOI: 10.1515/revce-2020-0059.
5. Wang, T., She, Y., Fu, H. & Li, H. (2016). Selective cyclohexane oxidation catalyzed by manganese porphyrins and co-catalysts. *Catal. Today* 264, 185–190. 10.1016/j.cattod.2015.07.034.
6. Shen, H.M., Wang, X., Ning, L., Guo, A.B., Deng, J.H. & She, Y.-B. (2021). Efficient oxidation of cycloalkanes with simultaneously increased conversion and selectivity using O₂ catalyzed by metalloporphyrins and boosted by Zn(AcO)₂: A practical strategy to inhibit the formation of aliphatic diacids. *Appl. Catal. A–Gen.* 609, 117904. 10.1016/j.apcata.2020.117904.
7. Iwahama, T., Syojo, K., Sakaguchi, S. & Ishii, Y. (1998). Direct conversion of cyclohexane into adipic acid with molecular oxygen catalyzed by N-hydroxyphthalimide combined with

Mn(acac)₂ and Co(OAc)₂. *Org. Proc. Res. Dev.* 2(4), 255–260. DOI: 10.1021/op980016y.

8. Gunchenko, P.A., Li, J., Liu, B., Chen, H., Pashenko, A.E., Bakhonsky, V.V., Zhuk, T.S. & Fokin, A.A. (2018). Aerobic oxidations with N-hydroxyphthalimide in trifluoroacetic acid. *Mol. Catal.* 447, 72–9. DOI: 10.1016/j.mcat.2017.12.017.

9. Liang, F., Zhong, W., Xiang, L., Mao, L., Xu, Q., Kirk, S.R. & Yin, D. (2019). Synergistic hydrogen atom transfer with the active role of solvent: Preferred one-step aerobic oxidation of cyclohexane to adipic acid by N-hydroxyphthalimide. *J. Catal.* 378, 256–69. DOI: 10.1016/j.jcat.2019.08.042.

10. Lisicki, D. & Orlińska, B. (2020). Oxidation of cycloalkanes catalysed by N-hydroxyimides in supercritical carbon dioxide. *Chem. Pap.* 74(2), 711–6. DOI: 10.1007/s11696-019-00937-0.

11. Talik, G., Osial, A., Grymel, M. & Orlińska, B. (2020). N-Hydroxyphthalimide on a polystyrene support coated with Co(II)-containing ionic liquid as a new catalytic system for solvent-free ethylbenzene oxidation. *Catalysts* 10(12), 1367. DOI: 10.3390/catal10121367.

12. Dobras, G., Kasperczyk, K., Jurczyk, S. & Orlińska, B. (2020). N-hydroxyphthalimide supported on silica coated with ionic liquids containing CoCl₂ (SCILLs) as new catalytic system for solvent-free ethylbenzene oxidation. *Catalysts* 10(2), 252. DOI: 10.3390/catal10020252.

13. Talik, G. & Orlińska, B. (2021). New evidence for the key role of hydrogen bonding between N-hydroxyphthalimide and halide ionic liquids in hydrocarbons oxidation. *Chem. Cat. Chem.* 13(21), 4578–90. DOI: 10.1002/cctc.202100990.

14. Dobras, G., Sitko, M., Petroselli, M., Caruso, M., Cametti, M., Punta, C. & Orlińska, B. (2020). Solvent-free aerobic oxidation of ethylbenzene promoted by NHPI/Co(II) catalytic system: The key role of ionic liquids. *Chem. Cat. Chem.* 12(1), 259–266. DOI: 10.1002/cctc.201901737.

15. Bhanja, P., Ghosh, K., Islam, S.S., Patra, A.K., Islam, S.M. & Bhaumik, A. (2016). New hybrid iron phosphonate material as an efficient catalyst for the synthesis of adipic acid in air and water. *ACS Sustainable Chem. Eng.* 4(12), 7147–7157. DOI: 10.1021/acssuschemeng.6b02023.

16. Nale, S.D., Rathod, P.V. & Jadhav, V.H. (2017). Manganese incorporated on glucose as an efficient catalyst for the synthesis

of adipic acid using molecular O₂ in aqueous medium. *Appl. Catal. A-Gen.* 546, 122–125. DOI: 10.1016/j.apcata.2017.08.008.

17. Gao, X., Zhou, Y., Gu, J., Li, L. & Li, Y. (2019). Facile synthesis of hierarchical manganese-containing TS-1 and its application on the oxidation of cyclohexanone with molecular oxygen. *Micropor. Mesopor. Mat.* 275, 263–269. DOI: 10.1016/j.micromeso.2018.08.037.

18. Zou, G., Zhong, W., Mao, L., Xu, Q., Xiao, J., Yin, D., Xiao, Z., Kirk, S.R. & Shu T. (2015). A non-nitric acid method of adipic acid synthesis: organic solvent- and promoter-free oxidation of cyclohexanone with oxygen over hollow-structured Mn/TS-1 catalysts. *Green Chem.* 17, 1884–1892. DOI: 10.1039/c4gc02333a.

19. Lisicki, D. & Orlińska, B. (2018). Oxidation of cyclic ketones to dicarboxylic acids. *Pol. J. Chem. Technol.* 20(4), 102–107. DOI: 10.2478/pjct-2018-0061.

20. Lisicki, D. & Orlińska, B. (2019). Patent PL 239347.

21. Liu, G., Chen, M., Jin, X., Song, C., He, F. & Huang, Q. (2021). Combination of H₃PW₁₂O₄₀-TiO₂ catalysts for photo-thermal oxidation of cyclohexene to adipic acid by 30% H₂O₂. *J. Environ. Chem. Eng.* 9(4), 105422. DOI: 10.1016/j.jece.2021.105422.

22. Jin, P., Wei, H., Zhou, L., Wei, D., Wen, Y., Zhao, B., Wang, X. & Li, B. (2021). Anderson-type polyoxometalate as excellent catalyst for green synthesis of adipic acid with hydrogen peroxide. *Mol. Catal.* 510, 111705. DOI: 10.1016/j.mcat.2021.111705.

23. Soares, J.C.S., Gonçalves, A.H.A., Zotin, F.M.Z., de Araújo, L.R.R. & Gaspar, A.B. (2021). Influence of reactional parameters in the adipic acid synthesis from cyclohexene using heterogeneous polyoxometalates. *Catal. Today* 381, 143–53. DOI: 10.1016/j.cattod.2020.07.052.

24. Peckh, K., Lisicki, D., Pabich, E. & Orlińska, B. (2022). Oxidation of 1,2-cyclohexanediol as a step for adipic acid synthesis. *J. Ind. Eng. Chem.* 110, 131–6. DOI: 10.1016/j.jiec.2022.02.053.

25. Hwang, K.C. & Sagadevan, A. (2014). One-pot room-temperature conversion of cyclohexane to adipic acid by ozone and UV light. *Science*, 346, 1495–98. DOI: 10.1126/science.1259684.