Overview of 4-oxopentanoic (levulinic) acid production methods – an intermediate in the biorefinery process

Andrzej FRANKIEWICZ* – Liquid Fuels and Bio-economy Department, Automotive Industry Institute, Warsaw, Poland

Introduction

The civilization progress causes the increase in energy and propellants demand. Depleting natural sources such as coal, crude oil, natural gas, and changing world geopolitical situation caused, that the humanity started to turn to alternative energy sources. Biofuels (fuels resulting from the biomass processing) are a kind of these sources.

The first generation biofuels consists of biofuels produced from sugar, starch, vegetable oil or animal fat. This biofuels type includes: biodiesel, bioalcohols, biogas and pure vegetable oils. Controversies appear in connection with the fact that this raw material is a food for people and animals or it is used for food production.

The second biofuels generation consists of biofuels produced from raw materials, which are not used for food production like lignocellulose or solid municipal waste. This group includes inter alia biohydrogen, biomethanol or biodiesel produced from non-edible oilseeds.

The third generation biofuels are biofuels generated from plants modified by genetic engineering methods to improve biomass conversion into biofuels. Some authors [1] count biofuels produced from algae to the third generation biofuels, but it is not correct. As a result of various algae conversion processes, biodiesel and bioethanol are obtained.

There is a concept of the fourth generation biofuels, in which the key issue is the carbon capture and storage. CO_2 formed in these processes is sequestered geologically (e.g. into declining oil fields), mineral (in the form of carbonates) or captured by crops, which reduce the greenhouse gases emission.

Levulinic acid as a biomass processing product

Levulic acid (LA) is 4-oxoacid. It fits into the biorefinery concept [2], because it is obtained from biomass and it is a material for other compounds syntheses. LA is produced from hexoses resulting from lignocellulose acid hydrolysis, hence from various industrial waste (e.g. agricultural), containing carbohydrates [3]. The most popular catalysts for these processes are mineral acids: hydrochloric, sulphuric, orthophosphoric [4]. Many of laboratory research were conducted and lots of articles were written in the field of heterogeneous catalysts usage, mainly due to fewer problems with the catalyst separation from post-process mixture [5].

LA is a raw material for interesting compounds production [6 – 8], e.g. buthyl, ethyl and methyl levulinates, 5-methyloxacyclopentan-2-on and methyltetrahydrofuran (which may be used as Diesel oil biocomponents), 5-aminolevulinic acid (used as biodegradable herbicide), diphenolic acid (bisphenol A replacement in plastics industry), butanedioic acid (raw material in many syntheses).

In the industrial scale, LA is being obtained in the Biofine process, in which lignocellulose is a raw material for the production. Initially, the material has to be shredded, (particles dimensions are: 0.5–1 cm), what enables more efficient hydrolysis into monosaccharides, occurring with the mineral acid participation.

Corresponding author:
Andrzej FRANKIEWICZ, e-mail: a.frankiewicz@pimot.eu

In the first step of this process, the raw material hydrolysis into various, soluble in the reaction medium intermediates (e.g. hydroxymethylfurfural) occurs. This stage takes place in the plug flow reactor, at (210…220)°C, 25 bar and reaction time of 12 s. The raw material is mixed with the catalyst (H_2SO_4) before transferring into the reactor, 1.5–3 wt.% with respect to the raw material.

In the second step, occurring in the back mix reactor, the first stage products hydrolysis takes place, which leads to formation of LA. The conditions at the second step are milder than at the first one. Temperature is (190…200)°C, pressure 14 bar, reaction time 14 minutes. Some volatile products are released at this stage. The mixture containing LA and process residues is passed into the gravity separator, then into dewatering column. LA is isolated from the mixture under reduced pressure, what allows to obtain a product with a purity of 98%. The catalyst is separated from the reaction mixture during the last stage, regenerated and recycled to the beginning of the process.

Theoretically [8], maximal LA yield in this process is 71.6 wt.%. However, practically, we can achieve 70–80 % of the maximal yield.

Studies on alternative raw materials and sources

Belaviqua et al. [10] investigated rice husks as the material for levulinic acid production. These husks were grounded to the diameters from 0.18 to 0.30 mm, selected with the use of an appropriate sieve, washed with distilled water and dried for 24 h in 50°C. 5 pre-treatment methods were used with the test of their influence on the yield of LA. Soxhlet extraction in aqueous phase, the one in organic phase (benzene – ethanol 1:1), pre-treatment with 1% H_2O_2, with 2% $NaClO_2$ + 0,4% CH_3COOH and with 0.1 M ethanedioic acid were chosen. It was shown, the best extraction way was the Soxhlet extraction in aqueous phase.

1.00 g of rice husks were transferred into the reactor and 10 ml of the catalyst (diluted HCl or H_2SO_4) was added. The tested reaction conditions were: 60 minutes and 170°C, 70 minutes and 160°C, 90 minutes and 170°C. The highest LA yield was reached for 4.5 vol.% of HCl as the catalyst, during the reaction in 160°C, with the reaction time 60 minutes and with the use of the Soxhlet extraction in aqueous phase as a pre-treatment method. This yield was 16.7 g/l; cellulose conversion was 54.4 wt.%. The best conditions for LA production with the use of H_2SO_4 as the catalyst were: 4.5 vol.% of the catalyst, 170°C, 60 minutes. This yield was 14.0 g/l; cellulose conversion was 45.7 wt.%. For all the tested temperature and reaction time, the highest yield was achieved for the acid catalyst concentration of 4.5 vol.%.

Ya'aini et al. [11] investigated how LA yield changes with the use of hybrid catalysts consisted of $CrCl_3$ and HY zeolites, mixed in weight ratios 1:1, 2:1 and 1:2. The 1:1 catalyst was prepared in the following way: 10 g of zeolite powder were being mixed with 10 g of 10 vol.%. $CrCl_3$ for 2 h at room temperature. Later, this mixture was dried overnight in 120°C and then calcinated for 24 h at 400°C. These steps were repeated for the other two catalyst ratios. The reaction was conducted in the following way: glucose was mixed with deionized water (1,0 %) and then stirred with the catalyst at the 1:1

ratio. The reactor was immersed in the oil bath at desired temperature, at atmospheric pressure, at 300 rpm of stirring speed. At once after the end of the reaction, 10 ml of deionized water was added and the mixture was stirred to dissolve water-soluble reaction products. The samples were filtered through the 0.45 μm membrane filter of the syringe and the products were analysed by HPLC.

The range of tested reaction temperature was: 100, 120, 140, 160 and 200°C; the reaction time was 180 minutes. Theoretically [12], formic and levulinic acid are obtained in the same molar ratio. However, it was observed during the tests, formic acid yield was lower than in the theory. There exists the concept, that formic acid decomposed to CO_2, H_2, CO and H_2O by heating and presence of stronger acids [13].

The highest LA yield was achieved for the 1:1 catalyst components ratio and the temperature of 160°C: 63 %. Glucose conversion was 100 % since reaching 140°C. Above 160°C there was a clear, rapid decrease of LA yield to 15 % at 200°C. For the hybrid catalyst in the ratio 2:1, the highest yield was achieved at 160°C and it was 47 %. Glucose conversion at this temperature was 90 %, total conversion was reached at 200°C. For the catalyst 1:2, maximal LA yield was achieved at 140°C: 38 %. Glucose conversion was 90 %, total conversion was obtained at 160°C.

Fang et al. [14] investigated sorghum usage. Reactions were conducted in the reactor situated in a bath oil. They tested the temperature of 160 and 200°C, 3 various sulphuric acid (catalyst) concentrations: 2, 5 and 8 %, 3 raw material loadings: 10, 20 and 30 %. The reaction time at 160°C was 30 minutes. The reaction time at 200°C was 40 minutes. For all the catalyst concentrations, LA yield was higher at 200°C than at 160°C. The higher catalyst concentration, the higher LA yield at the same temperature. LA yield decreased with increasing raw material loading. The best conditions for LA synthesis was: the reaction time of 40 minutes, the temperature of 200°C, the catalyst concentration of 8 %, the raw material loading of 10 %. The maximal yield was 32.6 %.

Ramli et al. [12] tested Fe/HY zeolites as the catalysts used for receiving LA from glucose. The first catalyst preparation step was changing zeolite cations from Na^+ to NH_4^+ by a contact with 2 M NH_4Cl, mixing components for 2 h, at room temperature. The precipitate was then washed with distilled water, dried overnight at 120°C and calcinated at 500°C for 5 h. These processes led to HY zeolite preparation. Next, $FeCl_3$ solution and HY zeolite powder were mixed at appropriate weight ratio (5%, 10 % and 15 % Fe/HY) and contacted by the stirrer for 2 h at room temperature. After that, the mixture was dried overnight at 120°C and calcinated for 5 h at 400°C.

Glucose conversion was carried out by dissolving 1 g of glucose in 50 ml of distilled water and by mixing it with 1 g of catalyst. The solution was heated in the reactor at desired temperature, with stirring speed of 200 rpm. After the reaction end, the mixture was cooled to the room temperature, the samples were filtered and analysed by the liquid chromatograph. The catalyst influence was tested by the reaction temperature changes from the values of: 120, 140, 160, 180, 200°C and by using the catalysts prepared in 3 various Fe/HY ratios. The reaction time was 180 minutes and it was determined basing on the previous HY zeolite tests. For all the catalysts, the highest LA yield was achieved at 180°C. The maximal yield was reached using 10% Fe/HY and it was more than 60%. Total glucose conversion was achieved at 180°C for all the catalysts.

For the 10% Fe/HY catalyst, influence of its loading and reaction time on the glucose conversion and LA yield was investigated. Five loadings were tested: 0.2 g, 0.5 g, 1 g, 1.5 g and 2g. Already for 1 g of the catalyst, glucose conversion was 100 % and remained at this level for next loadings. LA yield slightly increased between 1 and 1.5 g of the catalyst and slightly decreased for 2 g (compared with 1.5 g). The reaction time of 60, 120, 180 and 240 minutes was tested. It was also

researched, what influence on LA yield would have a catalyst recycling. It was turned out, LA yield decreased with the recycle numbers increase. The catalyst recovery from the runs also decreased.

Chang et al. [15] researched the application of wheat straw as a raw material. The straw was dried, milled and then, the particles with the size lower than 0.5 mm were selected and homogenized. The reaction was carried out at the temperature: 190, 210 and 230°C, at the reaction times: 15, 30 and 45 minutes, the catalyst concentration 1, 3 or 5% and the liquid/solid ratios 10:1, 15:1, 20:1 wt.%. The highest yield (19.60%) was reached when reaction conditions consisted of middle values from given above.

Sun et al. [16] investigated lysine functional heteropolyacids as glucose conversion catalysts. 0.4 g of glucose and 0.6 g of choline chloride was mixed in the flask at 130°C. Then, 0.016 mmol of the catalyst was added. The reaction time was 30 minutes. For the next research Ly_2HPW and $Ly_{0.5}H_{2.5}PW$ was chosen. Yield for the first catalyst was 47.9 %, for the second: 52.6 %. The temperature influence was also researched, using the following values: 110, 120, 130, 140°C, as well as glucose/choline chloride ratio influence, using values: 2:6, 3:6, 4:6, 5:6. For both catalysts, the yield increased with the temperature increase to 130°C and decreased with the glucose/choline chloride ratio increase. There was also tested how the yield changes, with the raw material change from glucose to saccharose, cellobiose, cellulose. The reaction conditions were as follows: 0.4 g of raw material, 130°C, 0.016 mmol of catalyst, reaction time of 30 minutes. Lower yields were achieved for the Ly_2HPW catalyst, using changed raw materials than using glucose. For the $Ly_{0.5}H_{2.5}PW$ catalyst, higher yield was obtained with the use of saccharose than glucose as a raw material (57.7%). It was also tested how the raw materials conversion changes with the use of catalyst recycling. It was turned out, that conversion after the sixth run was slightly lower than for the fresh catalyst.

Ren et al. [17] investigated cellulose depolymerization catalyzed by acidic ionic liquid. Appropriate amounts of cellulose, deionized water and ionic liquid were transferred into the reactor. The reaction time influence on LA yield was tested at 160, 170 and 180°C. 1-methyl-3-(3-sulfopropyl)imidazoliumhydrogen sulfate was used as the catalyst. The tested reaction time was (0,5…5) h. The loading was 1.000 of catalyst, 2.000 g of water and 0.250 g of cellulose. The tests showed, that at 170 and 180°C, the yield significantly increased (until reaction time of 1 h) and then had less variation. For 160°C the LA yield clearly increased until reaching the reaction time of 2 h and then slightly changed. The maximal yield was achieved for this temperature: 53,7 %. In the following tests series, the added water amount influence was investigated. The conditions was the same as previously; the reaction time was 5 h. The tested amounts was in the range of 2–7 g; the difference between those amounts was 1 g. For 170 and 180°C, the LA yield increased for 2–6 g of loading and next decreased. For 160°C, LA yield increased for 2–4 g of loading and then decreased. The maximal yield achieved for 170°C, 6 g of water loading: 62.1 %. The quantity of cellulose influence was also tested. The temperature, the catalyst and its loading were the same as earlier, the reaction time was 5 h, water loading was 3.000 or 6.000 g. Cellulose amount was 150–550 mg. For the all tested conditions, it was noticed, LA amount decreased with the cellulose loading increase. The maximal yield was reached at 170°C, for cellulose loading of 150 mg, water loading of 6 g and it was 64.3%.

Kang et al. [18] researched Gelidium amansii red algae influence on LA yield. In the first step, 15 g of algae was hydrolysed in sulphuric acid at the solid/liquid ratio 1:6, the catalyst concentration was 1, 5 or 9 wt.%, the temperature was 60, 70 or 80°C, the reaction time was 24, 48, 72 h. The solid residue was separated with the use of centrifuge and then washed with distilled water to pH 6.5–7. The algae was dried at 45°C (to their complete drying) and then at 105°C. In the second stage, the liquor obtained in the previous

step was used. 5 ml of the liquor was added to every reactor. The reaction time was 20, 40 or 60 h. The highest LA yield was reached at 180°C, for the catalyst concentration 3 wt.% and the reaction time 40 h. This yield was 45.84%.

Mukherjee et al. [19] give an extensive list of LA synthesis laboratory methods from different raw materials, with reaction conditions, material conversion and amount of LA obtained.

Summary

LA is still a promising substrate not only for biocomponents production and also for other chemicals. A lot of research on new raw materials application for LA production was conducted, also in the field of homogeneous catalysts replacement by heterogeneous ones, which could significantly simplify the technological production process.

While searching for new LA sources, we should consider if we could develop wasted parts of raw materials used in food, agricultural, wood industry. This action would not only allow us to find new LA sources, but also could upgrade the value of some waste and could enable new, effective utilization, bringing us more advantages.

Increasing energy, fuel, chemicals demand causes the need to turn into renewable, unconventional, alternative raw materials, which include biomass. It is important to conduct many research on the use of different raw materials, in terms of their usefulness for the production of biofuels, as well as valuable intermediates used for the synthesis of high added value compounds. The biorefinery concept is supported by the European Union, which is reflected in the research programs subjects, on which the European Union dedicates its resources. New biomass sources which are cheap, easy in processing and have the ability for rapid renewal are looked for. The example could be plants, which do not have high soil and microclimate requirements, have valuable chemical composition and have the ability to relatively rapid growth.

Looking for alternative fuel and energy sources comes down to searching for the new production methods and technological solutions and to upgrading of existing ones for process efficiency, selectivity and economy increase, with the least possible negative impact on the environment in terms of harmful substances emission.

Taking this type of actions is very important because of coal, crude oil and natural gas depleting resources and the existence of industrial processes waste, which lay on landfills and their potential is not used.

Literature

1. Alam F., Mobin S., Chowdhury H. G.: *Third generation biofuel from Algae.* Procedia Engineering 105 (2015), 763–768
2. Pandey A., Larroche Ch., Ricke S. C., Dussap C. –G., Gnansounou E.: *Biofuels. Alternative Feedstocks and Conversion Processes.* Chapter 1: Principles of Biorefining, Elsevier, 2011, 3–24
3. Qi F., Milford A. H.: *Experimental studies for levulinic acid production from whole kernel grain sorghum.* Bioresource Technology 81 (2002), 187–192
4. Tarabanko V. E., Chernyak M. Yu., Aralova S. V., Kuznetsov B. N.: *Kinetics of levulinic acid formation from carbohydrates at moderate temperatures.* Reaction kinetics and catalysis letters 75 (2012), 117–126
5. Hongzhang Ch., Bin Y., Shengying J.: *Production of levulinic acid from steam exploded rice straw via solid superacid.* S2O82-/ZrO2-SiO2-Sm2O3, Bioresource Technology 102 (2011), 3568–3570
6. Bozell J. J., Moens L., Elliott D. C., Wang Y., Neuenscwander G. G., Fitzpatrick S. W., Bilski R. J., Jarnefeld J. L.: *Production of levulinic acid and use as a platform chemical for derived products.* Resources, Conservation and Recycling 28 (2000), 227–239
7. Jenkins R. W., Munro M., Nash S., Chuck Ch. J.: *Potential renewable oxygenated biofuels for the aviation and road transport sectors.* Fuel 103 (2013), 593–599
8. Hayes D. J., Ross J., Hayes M. H. B., Fitzpatrick S.: The Biofine Process: production of levulinic acid, furfural and formic acid from lignocellulosic feedstocks, Biorefineries: industrial processes and products, Wiley, Weinheim, 2006, 139–159
9. Patent Application, US5608105 A, United States, 1997
10. Bevilaqua D. B., Rambo M. K. D., Rizzetti T. M., Cardoso A. L., Martins A. F.: *Cleaner production: levulinic acid from rice husks.* Journal of Cleaner Production 47 (2013), 96–101
11. Ya'aini N., Amin N. A. S., Endud S.: *Characterization and performance of hybrid catalysts for levulinic acid production from glucose.* Microporous and Mesoporous Materials 171 (2013), 14–23
12. Ramli N. A. S,. Amin N. A. S.: Fe/HY zeolite as an effective catalyst for levulinic acid production from glucose: Characterization and catalytic performance, Applied Catalysis B: Environmental 163 (2015), 487–498
13. Saunders G. J., Kendall K.: *Reactions of hydrocarbons in small tubular SOFCs.* Journal of Power Sources 106 (2002), 258–263
14. Fang Q., Hanna M. A.: *Experimental studies for levulinic aicd production from whole kernel grain sorghum.* Bioresource Technology 81 (2002), 187–192
15. Chang Ch., Cen P., Ma X.: *Levulinic acid production from wheat straw.* Bioresource Technology 98 (2007), 1448–1453
16. Sun Z., Wang S., Wang X., Jiang Z.: *Lysine functional heteropolyacid nanospheres as bifunctional acid–base catalysts for cascade conversion of glucose to levulinic acid.* Fuel 164 (2016), 262–266
17. Ren H., Girisuta B., Zhou Y., Liu L.: *Selective and recyclable depolymerization of cellulose to levulinic acid catalyzed by acidic ionic liquid.* Carbohydrate Polymers 117 (2015), 569–576
18. Kang M., Kim S. W., Kim J. -W., Kim T. H., Kim J. S.: *Optimization of levulinic acid production from Gelidium amansii.* Renewable Energy 54 (2013), 173–179
19. Mukherjee A., Dumont M. -J., Raghavan V.: Review: *Sustainable production of hydroxymethylfurfural and levulinic acid:Challenges and opportunities.* Biomass and Bioenergy 72 (2015), 143–183

*Andrzej FRANKIEWICZ – B.Sc., graduated from The Faculty of Civil Engineering, Mechanics and Petrochemistry, Warsaw University of Technology Branch in Płock (2015), where he is currently a M.Sc. student. He works in Automotive Industry Institute. He is the author of 2 publications. Scientific interests: fuel, biofuel and their alternative sources.

e-mail: a.frankiewicz@pimot.eu

Zmiany w składzie Zarządu Grupy LOTOS SA

13 kwietnia 2016 r. Rada Nadzorcza Grupy LOTOS SA zdecydowała o odwołaniu ze składu Zarządu Spółki Pana Pawła Olechnowicza, Prezesa Zarządu oraz Panów Zbigniewa Paszkowicza i Marka Sokołowskiego, Wiceprezesów Zarządu. W Zarządzie pozostali Panowie Maciej Szozda oraz Mariusz Machajewski. Rada Nadzorcza zdecydowała o czasowym delegowaniu do pełnienia obowiązków Prezesa Zarządu Pana Roberta Pietryszyna. Pan Pietryszyn będzie pełnił obowiązki Prezesa Zarządu Grupy LOTOS SA bez wynagrodzenia.

W celu uzupełnienia składu Zarządu Rada Nadzorcza podjęła decyzję o wszczęciu konkursu na stanowiska Prezesa Zarządu, Wiceprezesa ds. Operacyjnych, Wiceprezesa ds. Korporacyjnych oraz Wiceprezesa ds. Strategii i Rozwoju.

(inf. Biura Komunikacji Grupa LOTOS SA, 13.04.2016)