

Biomass – Renewable Feedstock for Organic Chemicals (“White Chemistry”)*

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Limited resources compel us to turn to renewable sources, new and old, that are capable of supporting sustainable development of the human society, and satisfying the demand in energy and materials. Plant life is far from being depleted; while its potential in supporting sustainable and renewable feedstock for organic material is great. This review is devoted to the use of biomass in production of basic organic chemicals, and to the main technological directions of biomass processing. These processes mainly involve transformation of cellulose and carbohydrates into final products by chemical or fermentation technologies. Some processes are already applied in industry, while their field of application is permanently growing. A number of chemical products can be isolated from plants directly including genetically modified species. Progress in chemical technology and biotechnology enables an almost 50–70 % substitution of oil feedstock with biomass.

Key words: *Biomass, organic chemicals, cellulose, carbohydrates, lipids, processing*

Introduction

The existence of our human civilization is closely connected with natural biological processes. Starting from the transformation of carbon oxides into biomass and oxygen, bioprocesses and bioproducts have always been the main resources for mankind. For many centuries, wheat and rice, cotton and silk, rubber and spices, tea and coffee, and many others like fish, meat and milk were and still are staple products of everyday life. The chemistry of these numerous plant and animal substances (organic matter) was formulated as “Organic Chemistry” at the turn of the 19th Century (J.-B. Dumas, Ch. Gerhardt, A. Laurent and other famous scientists)¹.

Wöhler’s synthesis of acetic acid in 1824 and then urea initiated active development of the synthetic routes to organic chemicals. Technical revolution in the second half of the 20th century, progress of science and technology, the huge resources of oil and natural gas, converted our society into “synthetic” and “oil-dependent”. Synthetic materials – numerous synthetic polymers, fibers, dyes, lubricants and solvents that can be produced easily from gas and oil in considerable volumes, quickly forced out and almost fully replaced natural products. Synthetic rubber, dyes and other synthetic materials alternatives to natural rubber and cellulose are examples of this tendency. Of course, in many cases the human society gained new materials with principally new useful properties required for new techniques and technologies. Moreover, the process of seeking and creating new materials will continued for further progress of society.

Contradictions between depletion of resources and growing demands of society, continuously volatile oil and gas prices, growth of CO₂ concentration in the atmosphere and other problems require revision of existent life practice. Limited resources compel us to return to renewable sources, new and old, that will enable us to realize sustainable development of the human society and satisfy the demand for energy and materials. Of course, availability, prices and desired properties of those materials have to be competitive with products derived from fissile carbon. In order to solve the existing problems, the plant potential is far from depleted and, taking into account the progress in biotechnology, opens excellent possibilities to serve the sustainable feedstock for organic material family.

Naturally, the first task is to compensate some quantity of organic fuels with “biofuel”. Energy demand in a developing world and problems arising from traditional energy sources at the end of last century (fossil fuel, discussions on nuclear energy use, pollution from thermal power plants and climate changes, etc) induced the high interest of various nations for renewable energy sources – wind, solar and “biofuels”. Talking about “biofuel”, we mean mainly products such as ethanol and unsaturated fatty acid esters from plant oils, generally called “biodiesel”.^{2,3} Some countries try to solve partly the liquid fuel demand for transportation by increasing production of ethanol and biodiesel, in order to reduce the dependence on foreign oil producers and to ensure national energy stability.^{4,5,6}

Could the “green world” be sufficiently productive in satisfying the demand of human society for foods and feedstock production to substitute oil?

Plant potential

Today nearly 1.5 billion ha, or 11 % of the total land on Earth’s is involved in agricultural cultivation. The photo-

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synthetic product of plants and trees in an energy equivalent is estimated at around 3150–4000 EJ, 10 times more than total energy consumption. The light conversion into plant biomass by photosynthesis theoretically may amount to 9%, but due to attendant metabolic processes the final effectiveness decreases 2–4 times. Agricultural lands yield from 3 to 22 t/ha annually⁷. If biomass yield is assumed 5 t/ha in average from arable lands, it is possible to have approx. 7–10 billion tons of biomass from agriculture.⁸ For instance, USA agriculture is the source of about 1 billion t of dry biomass, from which 428 Mt are agricultural wastes and 377 Mt are tailings of perennials.⁹ Forests occupy about 30 % of Earth's territory with biomass amounts of up to 420 Bt; they are an important source of energy, wood and biomass.¹⁰ For example, USA forests annually can yield 368 Mt dry material in comparison to 148 Mt produced today. Existing technology is considered to be able to collect 75 % dry plant biomass. Probably, in future we will use also more biomass from ocean flora and algae cultivation. Thus, to compare the productivity of ploughed lands and consumption of staple foods mentioned,⁷ it is possible to think about the considerable perspective of biomass production for both foods and feedstock for chemical industry.

Plants are an important source of primary materials such as fibers, first of all – cotton, jute and flax, which have been used by man for over 5,000 years. By many parameters, natural fibers compete with synthetic materials, and their wastes are biodegradable. Production of plant fibers, substantially diminished after the offensive of synthetic materials, can again become useful and an attractive sources of raw materials in the production of numerous semi-synthetic composites.^{11,12} Natural rubber is one of the best examples – modern technology cannot refuse using natural rubber and hevea plantations occupy significant areas in Asia and Africa.⁷ Natural rubber (9 Mt in 2004) accounts for an average of 40 % in total rubber consumption (natural and synthetic) because it is a required ingredient in the production of high quality radial tires for tracks and planes. No doubt that today's high prices of oil will be a stimulus for additional demand for natural rubber. Moreover, a rebirth of synthetic rubber production from ethanol that have been used the last century would be expected.

Perspectives of plant biomass as raw material are closely associated with modern progress in genetic engineering and biotechnology.¹³ To provide necessities of our civilization we should create such sorts of plants, in which the useful matter content will correlate with economic parameters acceptable in order to use them as feedstock. Perennials deserve special attention as a long-term source of raw material. The other task is to double biomass production relative to the present level by promoting photosynthetic productivity in plants. Major hopes are here associated with the success of genetic modification and possible use of photosynthetic bacteria genes. On average, the photosynthesis process of plants uses about 2 % of light energy, but there are pre-conditions to promote efficiency of the process with the use of cyanobacteria genes, to multiply absorption of CO₂ and, accordingly, biomass production. There are other perspective ideas to increase biomass accumulation, for example, to activate the plants genes that provide firmness to stress conditions or improve the cellulose – lignin ratio. In some cases, it is possible to regulate biosynthesis of the secondary plant metabolites with industrial interest.

Basic organic chemicals

The total production volume of basic organic chemicals is around 270–320 Mt annually. Taking into account some losses in processing, the volume of oil/gas as raw materials for their production it is possible to estimate them at 380–420 Mt (nearly 1/10 of total oil produced).

Comparison of these figures with the volume of accessible biomass leads us to conclude that a valid possibility exists to replace a major part of oil as feedstock with biomass, if the proper technologies with competitive parameters will be created. The main direction of oil use (accounting for 3/4 of all feedstock) is the production of organic chemicals, transformation of oil hydrocarbons into solvents, monomers and polymers, additives, surfactants, pharmaceuticals, etc. If we substitute the oil as feedstock for organic chemicals with biomass, it can save a significant part of oil for other purposes and, moreover, we will provide resource sustainability for the chemical industry.

Table 1 – Production of basic organic chemical (thousand tons)¹⁴

Tablica 1 – Proizvodnja bazičnih (osnovnih) organskih kemikalija (u tisućama tona)

	Europe Europa		USA SAD		World Svijet
	2000	2007	2000	2007	
acetic acid octena kiselina	754	876			5 000
acetone aceton	1 325	1 235			3 000
benzene benzen	4 565	6 150	9 156	7 979	30 000
butadiene butadien	2 097	2 182	2 009	1 805	5 000
butanol butanol	67	452			
ethylene etilen	19 444	21 408	25 113	25 682	110 000
ethylene glycol etilen-glikol	637	1 256			9 000
methanol metanol	1 148	2 531			32 000
styrene stiren	3 215	4 383	5 405	5 100	18 000
synthetic fibers sintetska vlakna	2 227	3 015	4 460	3 472	
cellulose fibers celulozna vlakna	627	636	158	27	

Among all basic organic chemicals ethylene and propylene (170–180 Mt annually) are leaders due to production polymers and monomers for other plastics. Indeed, ethylene is used to synthesize vinyl chloride and polyvinyl chloride, butadiene and synthetic rubbers, ethylene oxide, ethylene glycol and some other products. Next position is occupied by methanol and benzene, which are also basic chemicals in the production of numerous monomers, solvents and other chemicals (Table 1).

Biomass as feedstock for chemicals

The first chemicals from biomass produced by man were ethanol and acetic acid as food products and then chemicals and fuel. During the 1940s nearly 30 % of industrial chemicals were produced from plant feedstock. We have some examples of well-developed technology for biomass conversion.

Modern cellulose production is sufficiently optimized and integrated. Lignin and hemi-cellulose are mainly used as fuel to produce energies and surfactants. The effective technology is applied for starch – it is hydrolyzed to glucose, which is converted into fructose and by hydrogenation into sorbitol, or it is directed to produce other chemicals – ethanol, lactic acid, citric acid. The technology resembles the processes of living cells, which convert the nutrients in pro-

ducts necessary for life, energy and numerous secondary metabolites, and is similar to the “green” low-wastes natural process. New biomass processing into organic chemical products can also be optimized on principles of low-waste and ecologically sound processes.

Today in the chemical industry 7–10 organic chemicals are basic. It is possible to define the same base in the case of biomass use as feedstock. Recently USA scientists selected 20 chemicals that may be produced from biomass and are perspective as feedstock for the modern products of the chemical industry.¹⁵

The first “long” list counted almost 300 “candidates” and the final has 20 compounds. Among them are 12 base chemicals – blocks for the subsequent synthesis that can be produced from sugar biomass, such as 1,4-dicarboxylic acids – succinic, maleic and fumaric acids, 2,5-furandicarboxylic acid, 3-hydroxypropionic acid, aspartic acid, glucaric and glutamic acids, levulinic acid, 3-hydroxybutyrolactone, glycerol and sorbitol. It is possible to add ethanol, furfural and fatty acids from plant oil to this list (Fig. 1).

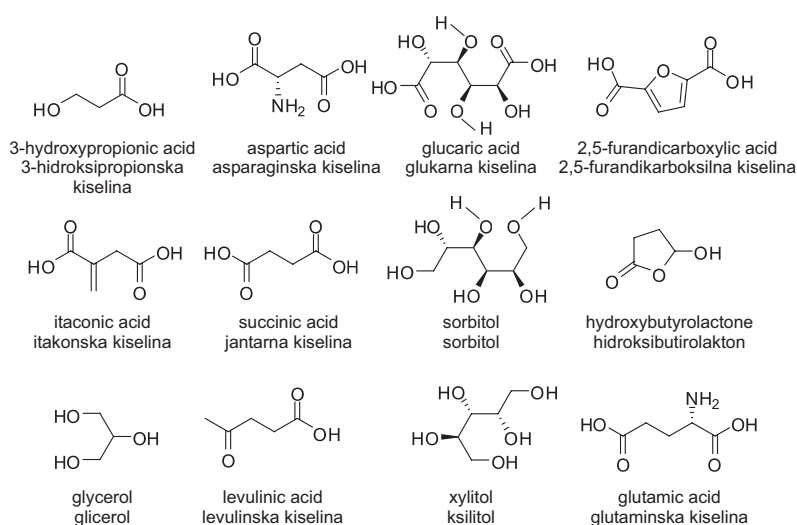


Fig. 1 – Organic compounds – “candidates” to be basic organic industrial chemicals

Slika 1 – Organski spojevi – “kandidati” za pripremu bazičnih (osnovnih) industrijskih kemikalija

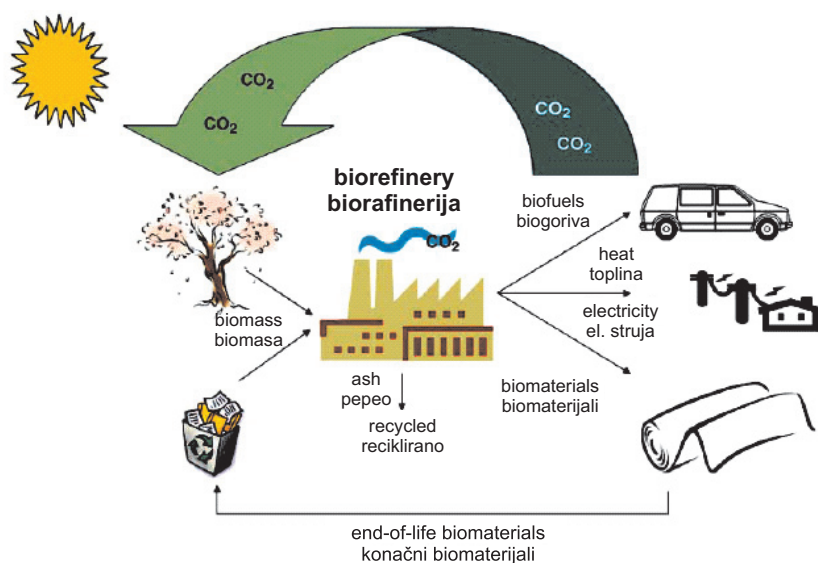


Fig. 2 – D. Elliott's Conception of Biorefinery

Slika 2 – D. Elliott: Koncept biorafinerije

D. Elliott has formulated the “Concept of Biorefinery” (Fig. 2) as a model of integrated technology to process biomass into chemical products with maximal use of material and energy. In such processes biomass is separated into main components, then the components are transformed into products by catalytic or biochemical processes in scales which provide sufficient efficiency.¹⁷ The economic indexes of the production must be competitive with petrochemical production. Some processes that use biomass to a certain extent already use this concept.^{3,17}

Some technology to process biomass already exists: fermentation of sugars into alcohols and acids, hydrolysis of carbohydrates, hydrogenation or oxidation, pyrolysis or gasification with partial oxidation, conversion into synthesis-gas with further processing in some products.¹⁸ By these technologies it is possible to obtain some basic chemicals. Also, it is needed to create new competitive technologies to produce chemicals and also to introduce new products on the market which can replace the already existing ones. By estimations about 2/3 of oil could be substituted with renewable biomass feedstock and products from biomass could satisfy the market demand.¹⁵ The DOE (USA) in 1998 offered to produce 10 % basic chemical blocks to 2010 from renewable sources and to reach 50 % in 2050. This new direction in chemical production is presented in numerous excellent reviews published last years.^{17–20}

Chemical technologies of biomass processing into basic organic chemicals

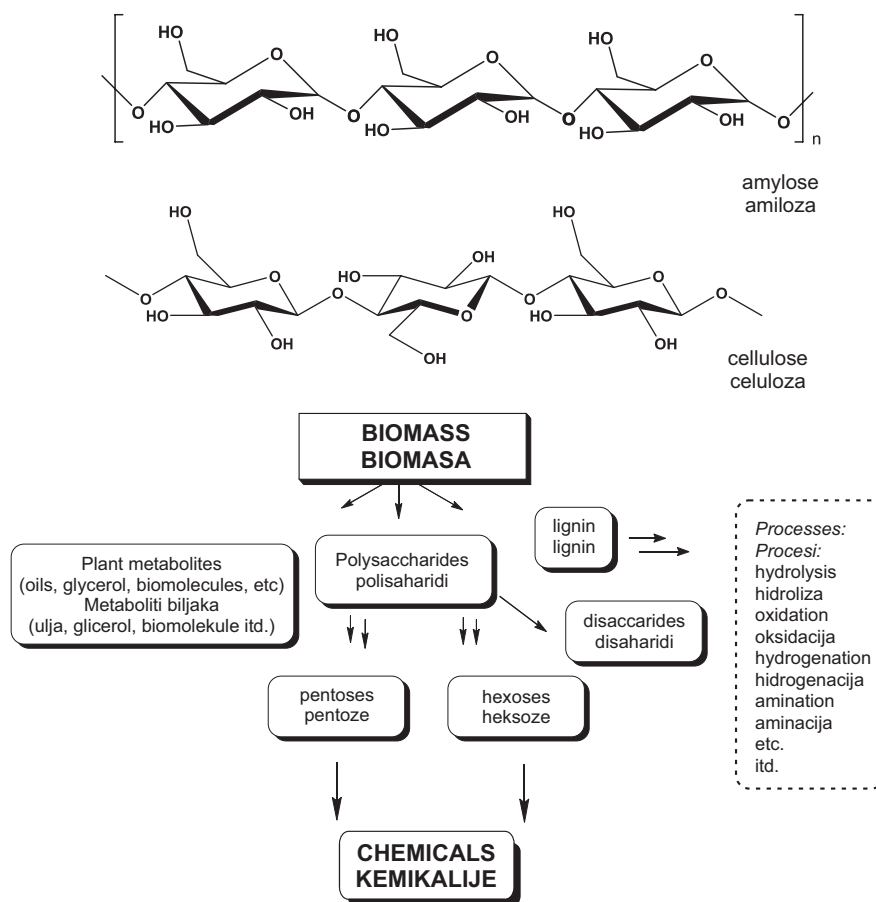
Biomass is constituted by three main types of organics – hexoses (glucose) and pentoses (xylose) types of $C_nH_{2m}O_m$ carbohydrates and lignin (polyphenolic compounds). One of the simplest technologies to process biomass is deep destruction into syngas, which by a well-known technology can be conver-

ted into numerous basic organic chemicals and products. New pyrolysis technology converts biomass into liquid fuel or syngas.²¹ The partial oxidation of biomass with oxygen or steam gasification gives fuel gas as mixture of CO, CO₂, H₂, CH₄ and tar with a heating value gas of 12–20 MJ/m³. “Old” biomass pyrolysis technology yielded methanol, acetic acid and acetone, hydroxyacetone, formaldehyde and ketones as well as oil-fraction with phenol content. In fast pyrolysis around 500 °C biomass decomposes to generate mostly vapours and some charcoal. The rapid cooling of the pyrolysis vapours gives the bio-oil that it is obtained up to 75 % yield on dry feed basis. The technology can be applied to process any form of biomass. Food flavourings are commercially produced from wood pyrolysis products in many countries.

The main biomass units are **C-5- and C-6-carbon** sugars of general formula C_nH_{2m}O_m (Scheme 1). The first consideration of chemical composition of sugars allows imagining their transformation into the numerous oxygen containing organic products. Depolymerization of polysaccharides results in disaccharides, which can invert to the mixture of glucose and fructose. More complex polysaccharides, for example cellulose, may also be hydrolyzed to monosaccharides. The modern arsenal of organic chemistry allows introducing sugars into the various reactions in order to prepare the desired chemicals. The main problem of biomass processing is destruction of lignocellulosic structures in order to prepare solubilized mono-sugars suitable for further tran-

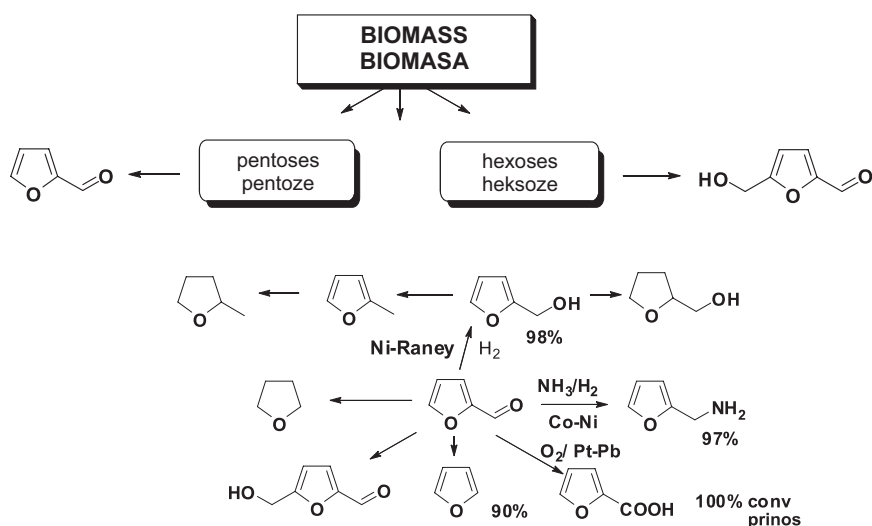
sformations. Two technologies are generally used, i.e. acid hydrolysis and enzymatic hydrolysis by cellulases. Obviously, pretreatment of biomass is the necessary procedure before hydrolysis. Numerous studies of the problems are directed to improve an efficiency of hydrolysis, selectivity and cost of the process. For example, “double” acid hydrolysis of lignocellulosic waste with 1 wt. % HCl and H₂SO₄ combination was shown to result in 76 % yield of monosaccharides with low energy consumption.²²

The acid hydrolysis of carbohydrates affords the products of sugar degradation with formation of furfural from **5-carbon** and hydroxymethylfurfural from **6-carbon** sugars (Scheme 2). Dehydration of pentoses yields furfural as the main product (Quaker Oats and Petrole-chimie processes), dehydration of hexoses gives hydroxymethylfurfural and then – levulinic acid. The pentose fraction of lignocellulosic biomass is dehydrated in acid medium with good conversion and selectivity. From 1 t of dry biomass it is possible to obtain up to 160 kg (6–17 % by weight against an origin of biomass). The main studies in the area are devoted to finding new effective catalysts, including zeolites or polymeric nature, and to optimize the process.¹⁸ As a rule, starting material is wastes of corn processing, and such technology even survived “petrochemical” competition. Furfural is used to produce plastics, furan and tetrahydrofuran, for some time it has been used in preparation of adiponitrile to produce nylon. Reductive amination of furfural yield furfurylamine



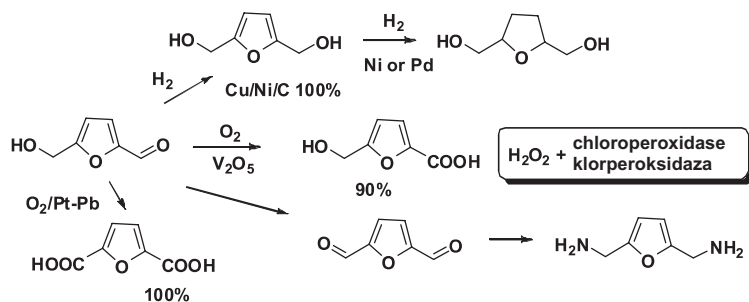
Scheme 1 – Some structural units of biomass for further transformations

S h e m a 1 – Neke strukturne jedinice biomase za daljnje pretvorbe



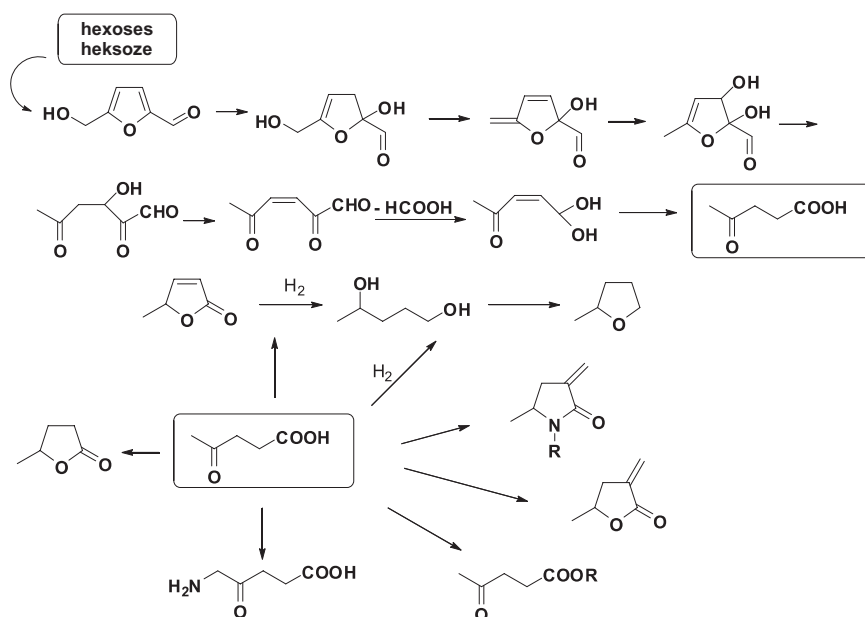
S c h e m e 2 – Biomass acid hydrolysis and some furfural transformations into chemicals

S h e m a 2 – Kisela hidroliza biomase i neke transformacije furfurala u kemikalije



S c h e m e 3 – Some useful organic chemicals prepared from hydroxymethylfurfural

S h e m a 3 – Neke korisne organske kemikalije iz hidroksimetilfurfurala



S c h e m e 4 – Transformation of hydroxymethylfurfural into levulinic acid and some useful chemicals

S h e m a 4 – Prevođenje hidroksimetilfurfurala u levulinisku kiselinu i druge korisne kemikalije

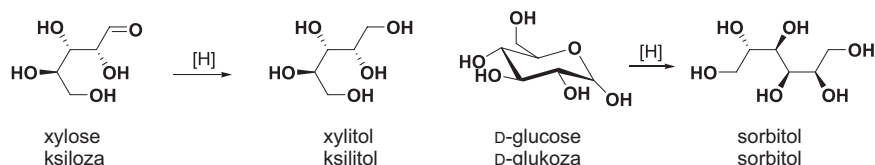
which is used in production of pharmaceuticals and pesticides. 2-Methyltetrahydrofuran, which is commercially available by two-step hydrogenation of furfural, was proposed as new bulk solvent in organometallic reactions with properties similar to THF or Et₂O²³ (Scheme 2).

Hydroxymethylfurfural (HMF) is sometimes called the “sleeping giant” of feedstock because it can be converted into numerous chemicals – solvents, monomers, intermediates, etc (Scheme 3). HMF may be prepared from wood biomass, cellulose and starch and then be transformed into levulinic acid that is the useful representative of 6-carbon blocks. Levulinic acid is starting compound for synthesis of γ -valerolactone used in monomers and solvents production (pyrrolidinones), pentaediol for production of polyester plastics, methyltetrahydrofuran – useful solvent and diesel fuel or oxygen additive to petrol. Levulinic acid can be converted into acrylic or succinic acids, used in polymers similar to polyacrylates and polycarbonates. Introduction of amino group results in aminolevulinic acid that it is natural insecticide and herbicide attractive to use in agriculture. (Scheme 4).

The first commercial-scale plant to produce levulinic acid (3,000 t/y) from tobacco bagasse and paper mill sludge by Biofine process has been built in Italy. The Biofine process uses dilute sulfuric acid at 220 °C to hydrolyze cellulose from any plant source into sugars. Key to the processes is a two-stage reactor design that favours formation of levulinic acid over a series of other possible products in 70 % yield with formic acid and furfural as by-products.²⁴ γ -Valerolactone (GVL), a naturally occurring chemical in fruits and a frequently used food additive, which could be synthesized from levulinic acid, was proposed as sustainable liquid, renewable, easy and safe to store.²⁵

2,6-Furandicarboxylic acid is synthesized by oxygenic dehydration of C-6 sugars on Pt/C or SiO₂ at 333 K in 100 % yield. Other perspective technology is based on direct oxidation of fructose on bi-functional catalyst with 70 % yield and high selectivity. The compound is perspective to produce polymers for packing materials similar to polyethylene terephthalate and by reduction-amination to synthesize also diols and diamines similar to those that are used in production of polyamide and polyester fibres. Taking into account high demand on polyesters and polyamides a production of new polymers completely from natural feedstock is very attractive.

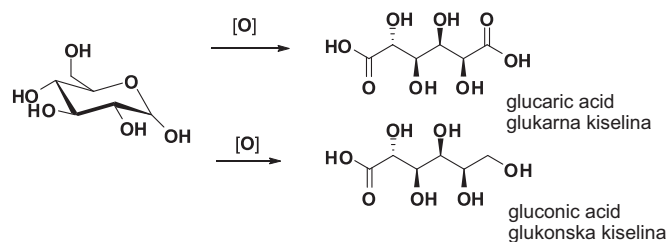
Hydrogenation of biomass sugars results in various natural alcohols in particular sorbitol from glucose, xylitol from xylose, lactitol from lactose, etc (Scheme 5). All of them are used in food industry and have numerous useful properties. The hydrogenation processes can be regulated in order to prepare sorbitol or xylitol together with ethylene glycol and glycerol. Polyhydroxy alcohols from biomass are perspective starting material products for new polymers, solvents and additives as well as components of composite materials. As example, some sugar alcohols increase hardness of polyethylene terephthalate polymers for containers and bottles.



Scheme 5 – Polyhydroxylated alcohols from xylose and glucose

S h e m a 5 – Polihidroksialkoholi iz ksiloze i glukoze

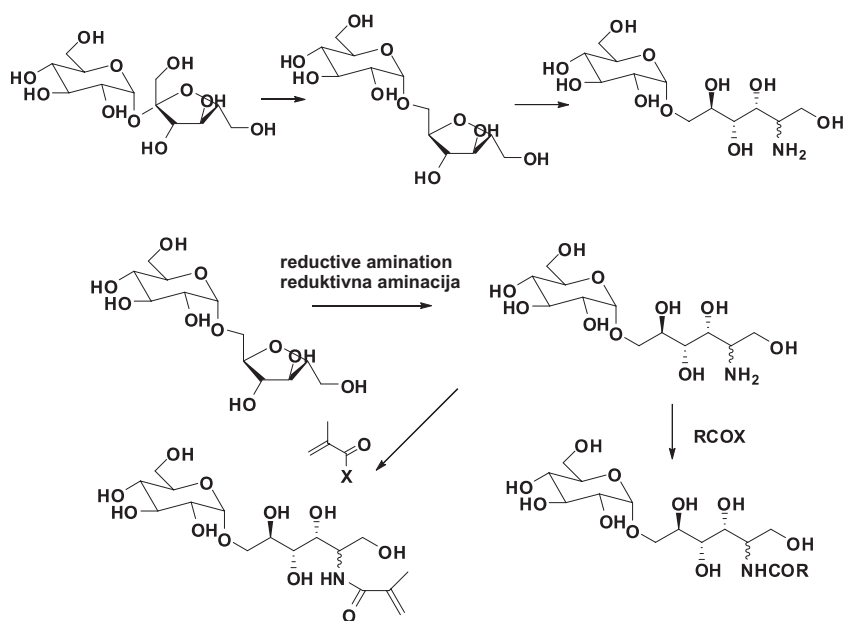
World production of sorbitol reaches 700 000 t/year. By catalytic hydrogenation of fructose it is produced the second important polyol, mannitol that it demonstrates excellent mechanic properties and low hygroscopicity. Xylitol, which has sweetness as sucrose, can be obtained by hydrogenation from wood pulp. New Ru catalysts enable to increase selectivity on xylitol up to 99 %. Recently, Dumesic has demonstrated that combination of a series of aldol condensation, hydrogenation and dehydration reactions enables conversion of carbohydrates into liquid alkanes $\text{C}_7\text{--}\text{C}_{15}$.²⁶



Scheme 6 – Chemicals from oxidation of glucose

S h e m a 6 – Kemikalije dobivene oksidacijom glukoze

Oxidation of glucose yields **6-carbon** hydroxy acids – gluconic and glucaric perspective for polyester synthesis of polyamide type similar to hydroxylated nylon with increased hydrophilic character (Scheme 6). From glucaric acid it is possible to synthesize various solvents, surfactants etc. The compound begin to use in polyester composition and also is perspective in polyamide synthesis similar to nylon with higher hydrophilicity. The presence in the molecule of a few hydroxy groups enables easily to introduce additional components, e. g. active dyes or other useful residues. Today glucaric acid is prepared by oxidation of starch glucose and there are technological perspectives to synthesize it from xylose and arabinose as less expensive raw material. Keto-gluconic acid is applied in fermentative vitamin C production.



Scheme 7 – Isomalt by disaccharide transformation. Carbohydrate containing monomers from disaccharides.

S h e m a 7 – Izomalt dobiven transformacijom disaharida. Ugljikohidrat s monomerima iz disaharida.

Chemistry of disaccharides has also wide synthetic perspectives.²⁷ Besides selective transformation with conservation of structure it may be possible to open one of the sugar cycles and to introduce a new functionality. For instance, sucrose is converted by rearrangement of 1,2- to 1,6-glycoside bridge into isomaltulose and following hydrogenation gives isomalt (Scheme 7). Both isomaltulose and isomalt are perspective key compounds to syntheses of various useful

composite materials and heterocycles with sugar moiety (e. g.²⁸).

Recently it was shown that C–O–C glycoside bond of cellobiose can be selectively broken with C-6-alcohol formation quantitatively via selective hydrogenation with Ru nano-cluster catalyst under pressure. Cellulose can also be converted to C-6 alcohols with Ru catalyst in $[\text{bmim}]\text{Cl}$ ionic liquid with low conversion (15 %) for the present.²⁹

Enzyme technologies of biomass processing into chemical products

The second scale approach to yield organic chemicals from biomass is the biotechnology.³⁰ By projection for Europe in 2050 the “white” biotechnology of biobased bulk chemicals could be reached 38 % to all organic chemicals production. Biotechnology is also considered as the important part in the development of a biorenewables industry in USA.^{31,32} Fermentation is used for production of ethanol, butanol, acetone, citric and lactic acids. In 1999 ethanol was produced in USA plants about 7 Mm³ and 16 M m³ in 2006 from corn and wastes of starch production and lately – from the pulp by-products. Brazil produced over 15 million m³ ethanol annually, Europe – more than 1.5 million m³. In 2007 world production of ethanol has reached about 51,000 m³; about 73 % of produced ethanol corresponds to fuel ethanol, 17 % to beverage ethanol and 10 % to industrial ethanol.³³ Ethanol could also be obtained from syngas catalytically, but the process has numerous problems with selectivity.^{34,35} Nevertheless, the first of six new USA government-supported commercial-scale cellulosic ethanol biorefineries will be built in Soperton. Range Fuels facility will produce 40 million gal of ethanol per year from wood biomass by proprietary thermochemical (syngas) conversion technology.³⁶

“Tree” of ethanol processing into other chemicals is well known (Fig. 2); ethanol can be used to yield acetic acid, acetaldehyde, butadiene and ethylene, various esters and ethers. From these “primary” chemicals it is possible to synthesize numerous “secondary” ones, e. g. ethyl and vinyl acetates, butanol and other solvents, pyridine etc. These processes have been applied in the past, as for example, synthesis of butadiene and synthetic rubber; most of them in new conditions would be economically attractive even now. For example, Dow Chemical is projected in Brazil to produce 350,000 t of polyethylene annually from ethylene made from ethanol. Braskem, Brazilian chemical company, plans by the end of 2009 to build a 200,000 t plant ethanol-based polyethylene, which it named “green polyethylene”.³⁶ Developing countries continue to use the production of chemicals from “bioethanol”; for example, in India and Brazil some plants produce acetaldehyde, ethyl acetate, acetic anhydride and cover the country demand in the chemicals.

Genetic engineering has enabled substantial reduction of the cost of ethanol production by fermentation. Plant wastes of agricultural and wood contain xylose and arabinose to 30 % by sugar mass, but these sugars are poorly processed by fermentation. Therefore, efforts are directed to find new genetically modified microorganisms, which will enable conversion of pentosane components from straw and other wastes into ethanol. Another direction is the use of microorganisms, that are able to convert sugars into acetaldehyde that has a boiling temperature 21 °C and can be easily evaporated from the reaction mixture. Then acetalde-

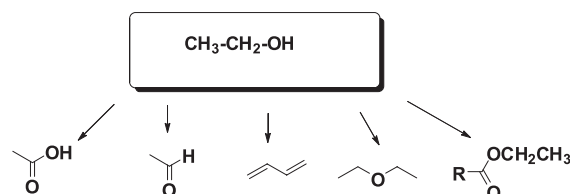


Fig. 2 – “Classical” ethanol transformations into bulk organic chemicals

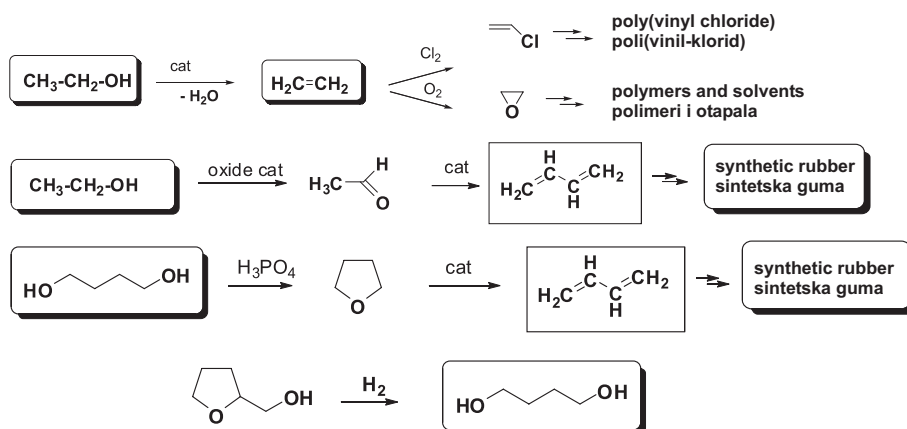
Slika 2 – “Klasična” transformacija etanola u više organskih kemikalija

hyde is oxidized into acetic acid or reduced to ethanol with the substantial energy efficiency in comparison with distillation of alcohol from water solution. The use of *Zymomonas mobilis* enables to obtain acetaldehyde in 55 % yield from glucose.³⁷

As mentioned, production of ethylene and butadiene for synthetic rubber was firstly based on ethanol as raw material (Scheme 8). Dehydration of ethanol on acid catalysts gives ethylene in 90 % yield. Butadiene is obtained from ethanol on oxide catalyst with an output to 50 % (Lebedev method), though low selectivity of the process is the negative side of the technology. Another route is ethanol transformation into butadiene by two-stage Ostromyslensky method through acetaldehyde formation. Both methods of butadiene synthesis have been industrial to the second half of the 20th century. Butadiene can be obtained from butanediol prepared from biomass through furfural.

Acetic acid can be prepared by fermentation directly from glucose with 75–80 % yield (Scheme 9). The thermophilic anaerobic microorganisms *Clostridium thermoaceticum* and *Acetogenium kivui* enable to consume fructose, glucose and xylose with vinegar acid yield to 85 % from sugar. By fermentation it is possible to have propionic acid by applying *Propionibacterium* microorganism.

Lactic acid (α -hydroxypropionic acid) is an industrial chemical to produced polylactate – the polymer with a growing market (Scheme 10). Lactic acid is produced by fermentation of carbohydrates with *Lactobacillus* cultures. Fermentation mixture contains 10 % lactic acid, which is separated as calcium salt. For example, lactic acid is produ-



Scheme 8 – Butadiene and monomers prepared from ethanol

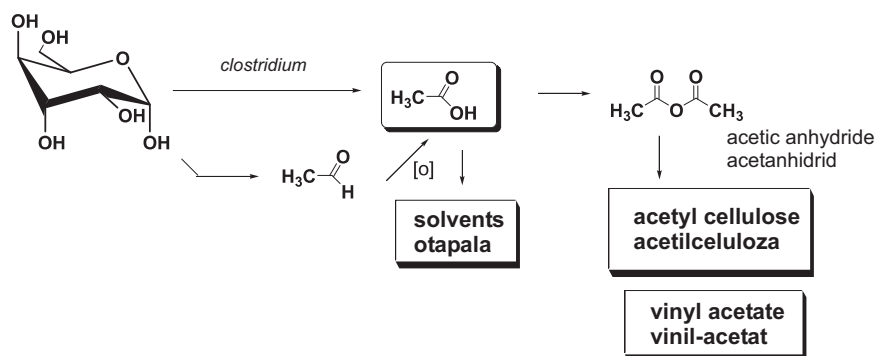
Slika 8 – Butadien i monomeri pripravljeni iz etanola

ced from bagasse cellulose by simultaneous saccharification and fermentation in a media containing a cellulase enzyme and cellobiose utilizing *Lactobacillus delbrueckii* mutant Uc-3. A maximum lactic acid concentration of 67 g/l was produced from a concentration of 80 g/l of bagasse cellulose.³⁹ Then by dehydration the acid can be transformed into lactide, dimer of acid, which is polymerized in polylactate.

No doubt, lignocellulose is most attractive to produce lactic acid. For this purpose, special technology was developed; lignocellulose of straw or softwood is processed with dilute acid to release sugars from biomass and then is directed on fermentation with thermophilic *Lactobacillus* cultures.³⁹ Lactic acid bacteria can produce either L(+) or D(-) or racemic mixture of lactic acid. Significant advantage of lactic acid production by biotechnology is cheap raw materials such as whey, molasses, starch waste, beet, cane sugar and other carbohydrate rich materials.⁴⁰ Polylactate is first "natural" biotechnologically produced multi-functional versatile organic chemical which is produced in large scale. For example, Cargill built plant on 140 000 t/y. From polylactate Danone company is producing biodegradable packing. Market of polylactate for packing materials, textile filaments and medical wares is estimated at 540–590 thousand t annually. The lactic acid is consumed as additive in the food and beverage sector, cosmetic products, pharmaceutical compositions etc. Lactic acid can be converted into non-toxic solvents and monomers also. Ethyl lactate is used as solvent alternative ethylene glycol and substitute of toxic chlorinated hydrocarbons.

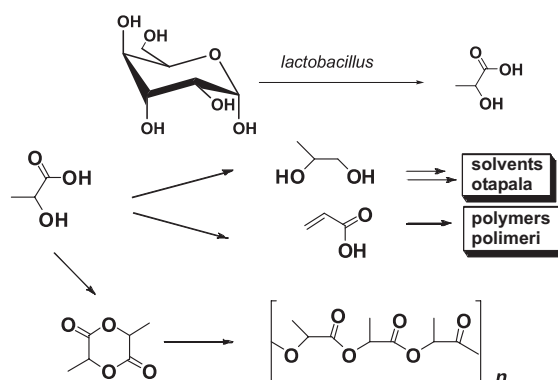
3-Hydroxypropionic acid is also a perspective chemical when prepared by fermentation (Fig. 3). This compound can be reduced into 1,3-propanediol or converted into acrylic acid and acrylonitrile. But all these processes require development of new catalysts and improving fermentation technology.

Polyhydroxy butyric acid is considered a perspective chemical which is obtained by the bacterium of *Alcaligenes eutrophus* and produced firstly by ICI company (Scheme 11). There are a lot of patents on polymer application for films, packing materials and fibers. Using new genetic engineering cultures the PHB concentration in plants reached 14 % by weight of dry biomass. In order to improve the polymer characteristics it was proposed to combine PHB with polyhydroxy valerate, because the mixture of these two polymers gives already materials with acceptable properties. The forest industry wastewater contains large amounts of fermentable organic matter and could be considered suitable as a feedstock for polyhydroxyalkanoates (PHAs) pro-



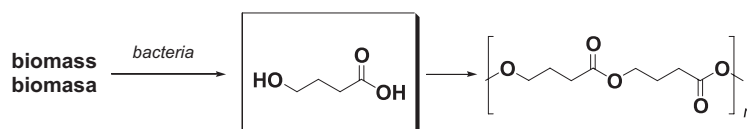
Scheme 9 – Acetic acid from glucose and its derivatives

Shema 9 – Octena kiselina iz glukoze i njezinih derivata



Scheme 10 – Lactic acid and some applications of the compound

Shema 10 – Mliječna kiselina i neke njene primjene



Scheme 11 – Polyhydroxyalkanoates from biomass

Shema 11 – Polihidroksialkanoati iz biomase



Fig. 3 – 3-Hydroxypropionic acid and derivatives.

Slika 3 – 3-Hidroksipropionska kiselina i derivati

duction. Production of PHAs in activated sludge treating wastewater represents an economic and ecologically promising alternative to pure culture fermentations. In experiments the PHAs mixture of 31–47 mol % hydroxybutyrate and 53–69 mol % hydroxyvalerate was obtained in 48 % yield of the sludge dry weight.⁴¹

6-Carbon sugars by fermentation with *Actinobacillus succinogenes* and *Anaerobiospirillum* microorganisms can be transformed into succinic acid, **4-carbon** molecules^{15,32} (Scheme 12). Succinic acid is an attractive source for producing polymers and plasticizers, solvents, lubricants, cosmetics or reagents for the pharmaceutical industry with the

hydroxy and epoxy groups, heterocyclic fragments, cyclopropane units, etc.⁴⁴ A barrier for direct technical application is that plant oils are the mixture of fatty acids ethers of a different structure. It is difficult to separate these mixtures, especially in the case of compounds with similar structure. Castor oil from *Ricinus communis* is the rare example of high selectivity. It contains over 80 % solely fatty acid that is already acceptable to the chemical industry. Oleic acid $\text{CH}_3(\text{CH}_2)_7\text{-CH=CH-(CH}_2)_7\text{-COOH}$ is dominant in olive and canola oil. Linoleic acid and linolenic acid is found in flax, maize, soy-bean and sunflower oils. Plant oils of some species contain unusual and saturated fatty acids as major component. In recent years, genetic engineering has demonstrated possibilities to optimize the ratio of fatty acids in desired direction.⁴⁵

Unsaturated plant oils are a valuable feedstock to produce useful chemical products (Fig. 5). They may be transformed into epoxides – polymer components, adhesives and polymers for medicine. For example, oxidation of oleic acid results in formation of epoxides and dihydroxy derivatives. Ozonation gives destructed molecules as a mixture of aldehydes, alcohols and hydroxy acids. From ricinoleic acid – main component of castor oil it is possible to prepare sebacic acid that is used in nylon production. 9-hydroxynonanoic acid, which is a precursor to the desired monomer, can be obtained in high yield and purity from oleic acid using cost efficient catalysts and mild reaction conditions and has been converted into the dilactone, monomer for potentially useful polyester materials.⁴⁶ Cross-metathesis of unsaturated fatty acid derivatives, e. g. the cross-metathesis with ethylene, offers the opportunity to obtain desired chemicals in high yields for the sustainable production of a variety of polymers, including polyesters, polyamides, polyethers, as well as polyolefins. Methyl acrylate (MA) as a cross-metathesis co-reactant is useful for the direct synthesis of α,ω -dicarboxylic acid derivatives. This approach opens a direct access to desirable monomers and detergent intermediates in high yields.⁴⁷

Plant oil has a very broad spectrum of practical application, such as lubricants, paints and coatings, adhesives and monomers etc. The hydraulic liquids prepared from plant oil are perspective to use in numerous mechanisms. Sixty percent of the losses of such liquids, which are usually produced from oil occur through the breaks and poor connections, and contaminate the environment.⁴⁸ Therefore, the use of biodegraded hydraulic liquids produced from plant oil is extremely attractive. The European market of hydraulic “bioliquids”, by expert estimations, will grow at a rate of 5–10 % annually. The liquids, prepared from soy-bean oil by Agri-Lube Company, has demonstrated the same characteristics as synthetic ones in the indexes of viscosity and low inflam-

mability. U.S. Agricultural Research Service and Caterpillar have developed and tested over 50 samples of new liquids from plant oils. Soya oil can be used to prepare new elastomers having properties from soft to hard rubbers by copolymerization with cyclopentadiene and divinylbenzene and other biobased soft materials^{49,50} (Scheme 15).

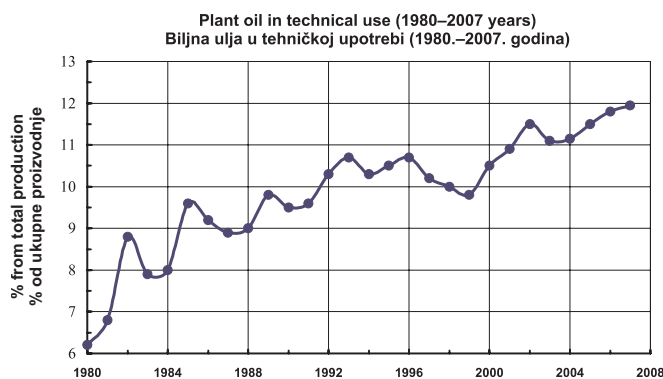


Fig. 4 – Trends of technical usage of plant oils
Slika 4 – Trendovi tehničke upotrebe biljnih ulja

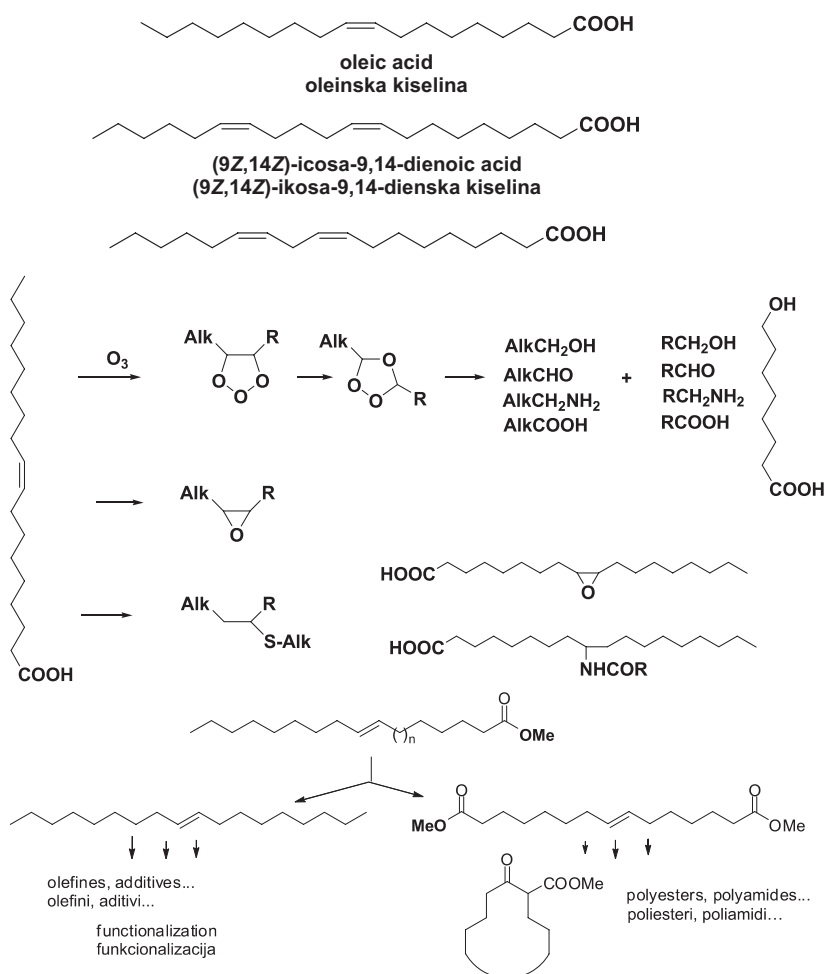
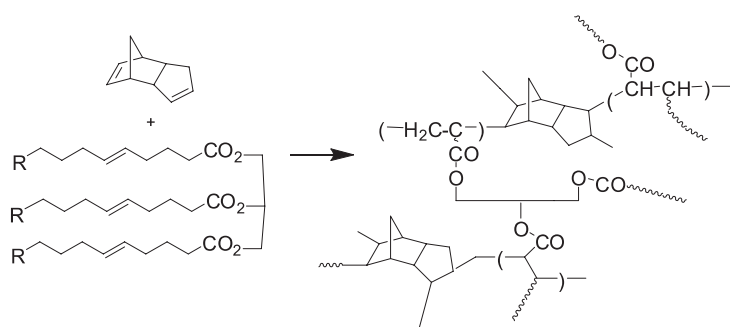


Fig. 5 – Unsaturated fatty acids of plant oils and some their transformations into industrial chemicals

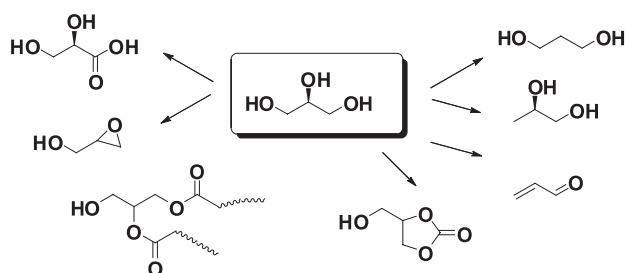
Slika 5 – Nezasićene masne kiseline iz biljnih ulja i neke njihove pretvorbe u industrijske kemikalije



S c h e m e 15 – Polymers and elastomers based on unsaturated fatty acids

S h e m a 15 – Polimeri i elastomeri iz nezasićenih masnih kiselina

Fatty acids are only one important part of glycolipids, the second is glycerol. Glycerol also comes as a basic chemical due to hydrolysis of plant oils into biodiesel. Indeed, in the USA nearly 75 % of production of glycerol is built upon biomass. Naturally, price-cutting on glycerol and production growth will cause a development of new directions of application of glycerol as starting chemicals (Scheme 16). Now from glycerol it is already obtained propanediol that can be used for production of various condensed products and carboxylic acids.¹⁵ Glycerol, as was recently found, may be transformed into 1,2-propanediol with selectivity to 100 % useful for polyester polymers. Hantsman Corp. decided to produce propylene glycol from glycerol.⁵¹ Dow Chemical announced a plan to use their own process to make propylene glycol from glycerol and to build a plant in China to make epichlorohydrin from glycerin for the epoxy resin. Solvay recently completed an epichlorohydrin plant in France that is based on glycerin and is planning a larger scale plant in Thailand. Glycerol could be converted into acrolein in 80 % selectivity and 90 % of glycerol conversion.⁵² Monoglycerides obtained by partial hydrolysis of triglycerides are used as polyol segments in polyurethane materials.



S c h e m e 16 – Glycerol as basic industrial chemical

S h e m a 16 – Glicerol kao osnovna (bazna) industrijska kemikalija

Starch at the beginning of the 1970s became the object of various modifications to apply for polymers. For example, if prices of amylase were the same as those of starch, polymers from amylase ethers could replace polyethylene and polystyrene in numerous applications, where biodegradation is required. On the basis of starch a new series of composites was created, which combine wonderful thermostability together with moistening.

Applications of cellulose are well known. The use of biomass for production of cellulose pulp requires delignification, i. e. separation of cellulose from lignin. Separated lignin, which consists of 15 to 30 % biomass of lignocellulose, is mainly directed to produce energy for processing of cellulose.³ There are new approaches to separation, for example, application of ionic liquids that yields the purest cellulose.⁵³ From BASF data, the ionic liquids allow substantial decrease of the amount of wastes in the separation. It is possible to use cornhusk cellulose, which has characteristics intermediate between cotton and flax. By calculations it is possible to use over 9 Mt annually of such cellulose fibres, to shorten cotton plantation and to replace a share of synthetic fibres. Numerous possibilities exist for chemically modifying hemicelluloses, for example, to use in packaging films and coatings for foodstuffs as well as biomedical applications and other potential applications, including selective membranes.⁵⁴

Biomass is also examined as the most accessible source of hydrogen.⁵⁵ Some processes of pyrolysis and reforming can be applied to produce hydrogen from municipal and agricultural organic wastes. The biological methods of hydrogen production from biomass take advantage of thermolysis or chemical methods by energy parameters. To obtain hydrogen it is proposed to use biophotolysis of water by water-plants and photo-fermentation.

Some directions of IBPC NASU activity on biomass usage

Ukraine is well known as the country with rich soil and agricultural resources. This year, the grain crop in Ukraine is predicted to be about 40 Mt of corn. Thus, Ukrainian agriculture can also be a significant producer of biomass from the sector – straw, wastes of corn and sunflower processing. Another source of biomass is the municipal sector, which produces about 40–50 Mt of waste every year. The main component of these wastes is organic materials, paper etc, that could be useful feedstock for industry. Ukraine also has a developed chemical industry which produces both basic inorganic and organic chemicals. Unfortunately, in the last decade the production of organic chemicals – methanol, acetic acid, vinyl monomers, olefins, polymers and solvents has significantly declined due to various reasons. One of them is the limits of national resources of oil and gas and high prices on the world market. In order to solve the problem with feedstock for the organic chemical industry, Ukraine has real possibilities to use the organic matter of plants, first of all – wastes from agriculture and wood processing that could supply about 20–30 Mt of dry biomass. National agriculture can also increase production of so-called “technical” plants which are notable for high content of lipids and plant oils, increased biomass crop, high content of starch. This year, numerous Ukrainian farmers started to cultivate rape thinking about the biodiesel international market.

Taking into account the experience gained in the production of ethanol from sugar beet and corn by fermentation, Ukraine has a “good starting position” in the use of the cellulosic wastes from agriculture for “bioethanol” production by fermentation or pyrolysis to “syn-gas” and then to etha-

nol. Bioethanol could be an important feedstock for various organic chemicals produced by the national chemical industry. The Ukrainian chemical industry used oil for many years as a basic feedstock in the production of ethylene and propylene, and natural gas in the production of methanol and acetic acid. To use bioethanol, Ukraine will have sustainable feedstock for production of chemicals and solvents based on ethanol, especially, basic monomers such as ethylene and butadiene, which are starting materials for tire-rubber industry, styrene and polystyrene compositions, polyvinylchloride and copolymers.

In 2006, the Institute of Bioorganic Chemistry and Petrochemistry NASU (IBPC) started some studies on biomass conversion to fuel components and chemicals using experience in oil processing. At the end of the 1980s, in Ukraine there were 5 operating plants converting corn-cobs into furfural by acid hydrolysis. From 1 t of dry biomass it is possible to obtain up to 160 kg (6–17 % by dry weight against an origin of biomass). In order to avoid or to reduce significantly the mineral acid use we applied various salt systems as co-catalyst of the reaction and showed that 3 % NaCl – 12 % aq. HCl mixture at 400 K produced furfural from corn-cob with 14.6 % yield from dry biomass. The ion-exchange resin KU-2-8 as solid acid catalyst can also be applied to the process especially in the presence of salt co-catalyst which significantly accelerates the reaction from hours to minutes. The last method could be used for renovation of furfural production from agricultural wastes in Ukraine because the technology avoids using large volumes of inorganic acids as catalyst. Other raw material for the process could be the sediments from wastewater treatment of the paper industry which can also be hydrolyzed to furfural in 5–5.2 % (by dry mass) by the proposed method.⁵⁶

Transfer of some elements of petrochemical technology can also be useful tools for biomass sugar conversion into useful chemicals. We proposed to combine the catalytic hydrocracking process and hydrated proton flow to obtain chemicals from biomass. The methodology results in significant decreasing of the process temperature and improving productivity and chemical selectivity due to reactions of hydrogenation. A suspension of biomass in water is directed to the reaction vessel (Fig. 6) where it comes into contact with the catalyst and hydrated proton flow at regulated temperature. At high temperature of the process (1000–1300 °C), the reaction product is syngas. At lower temperature of the process, 200–300 °C, some hydrocarbons (fuel components) and various chemical products are yielded.

The main constructive element of the reactor is the high temperature proton-conducting membrane on ceramic basis. A catalyst of hydrocracking is deposited on one side of the membrane. The low temperature plasma is obtained by a classic variant by an injection of water or carbohydrates into arc. The membrane is the transport tool for selective extraction of hydrated protons from low temperature plasma.

The reactor enables;

- destruction of cellulose to a mixture of carbon oxide and hydrogen in 1 : 4.5 mole ratio that is ready to be used directly for synthesis of dimethyl ether in one step or to separate hydrogen for other applications;

- at moderate temperature, it is possible to hydrogenate biomass components and obtain fuel substances.

This reactor was used in hydrogenation of furfural obtained from cellulose. The final products of hydrogenation were 2-methylfuran and pentane in 90 % yield.⁵⁷

Prof. G. Kovtun⁵⁸ proposed the use of the fuel cell as a chemical reactor that produces electricity and chemicals simultaneously by biomass oxidation. The design concept of the reactor – fuel cell is shown in Fig. 7. Electrode materials are graphite or graphite with catalyst layer. Various sugar-containing materials were introduced in the cell, such as glucose, arabinose, xylose, starch in water, glycogen, C₂–C₄-alcohol mixture (from starch fermentation), cellulose hydrolysis products (mixture), lactic acid... As catalysts some clusters and nano-clusters of Fe, Co, Sn and Pd organometallic compounds are used (Table 2). The catalysts accelerate glucose oxidation in the reactor space to produce electricity and chemical – products of glucose oxidation. At 25 °C the fuel cell in 75 % efficiency generated a current of 0.36 V and 15 mA/cm². The battery of 9 cells generated a current of 3.5 V and 250mA/cm². Chemical products of the process were hydroxy acids (gluconic, glucaric and gluconic acids), aldehydes and some others compounds. Different catalysts enable to change the structure and yield of major oxidation products than could be used in production of some chemicals with commercial interest.

By a general scheme, rape oil is separated and refined from byproducts – oil fuses, soap stock and phosphatidic concentrate. The technology chain of plant oils processing starts typically from catalytic transesterification of glycerides with ethanol or methanol to corresponding esters, their further transformation to fatty alcohols and amines and fi-

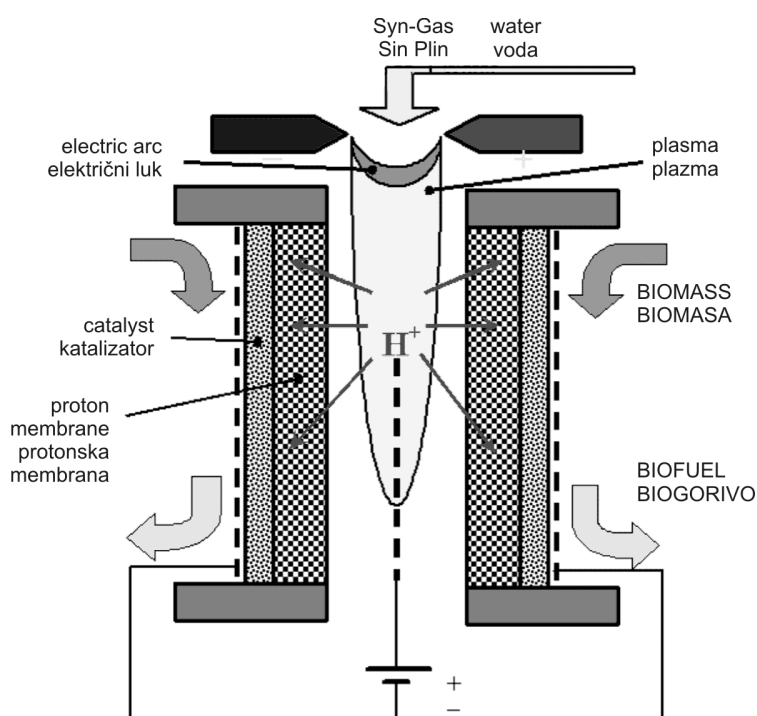


Fig. 6 – Principal scheme proton membrane reactor
Slika 6 – Shema protonskog membranskog reaktora

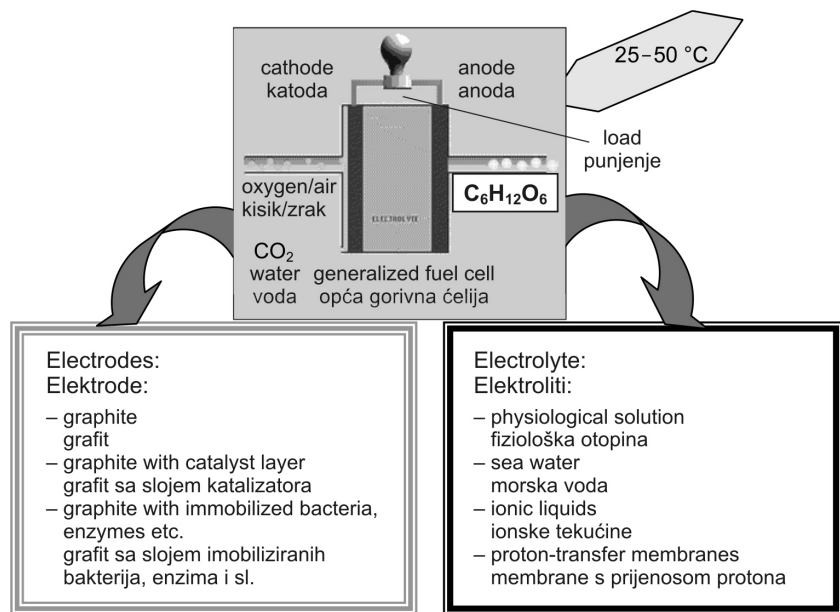
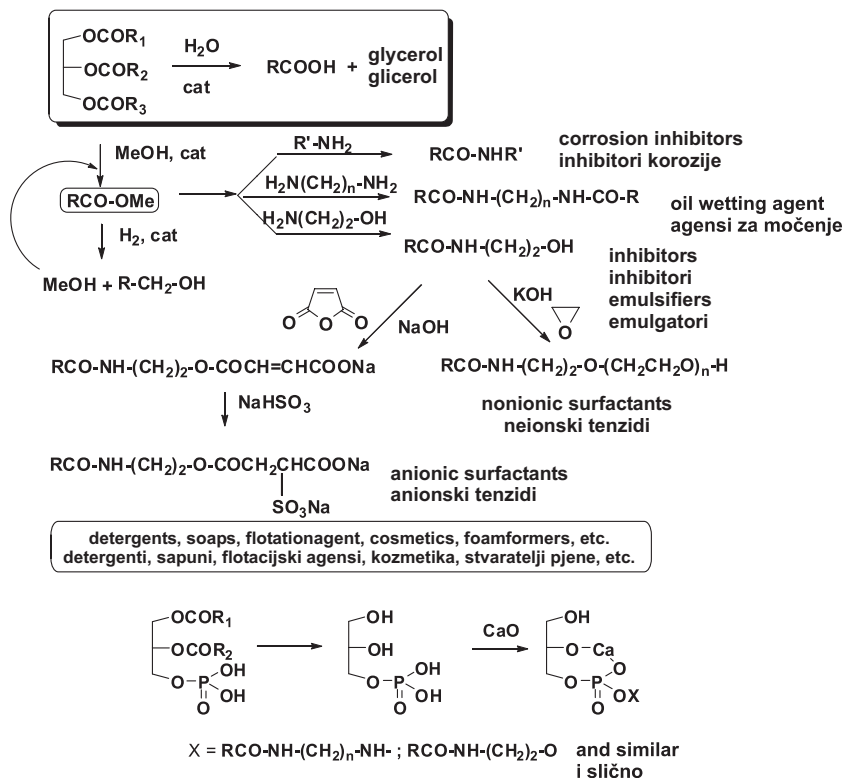


Fig. 7 – Fuel cell as chemical reactor
Slika 7 – Gorivna ćelija kao kemijski reaktor

Table 2 – Catalysts used in fuel cell on graphite electrodes

Tablica 2 – Katalizatori na katodnim elektrodama u gorivnoj ćeliji

Structure of catalyst Struktura katalizatora	Formula Formula
homo open-chain homo otvoreni lanac	$ISn(C_6H_5)_2-[Sn(C_6H_5)_2]_7-C_6H_5)_2SnI$
cyclic ciklički	$Co_3(\mu_3-CCH_3)(CO)_9$ $Fe_3(\mu-NC_6H_5)_2(CO)_9$ $Cu_4[\mu_3-S(S)P(OC_3H_7-i)_2]_4$ $Co_4(acac)_4(CH_3OH)_4[\mu-(OCH_3)_4]$
cage kavezasti	$[Fe_5Co(\mu^{BH}-C)(CO)_{16}]^{2-}$ $[Fe_6C(CO)_{16}]^{2-}$ $Co_6(\mu^{BH}-C)(CO)_{12}(\mu-S)_2$
nanoclusters nanoklasteri	$[Co_8(\mu^{BH}-C)(CO)_{18}]^-$ $Pd_{561}Phen_{60}(OAc)_{180}$ $Pd_{561}Phen_{60}(OAc)_{60}(PF_6)_{60}$ $Pd_{1415}Phen_{60}(O)_n$



Scheme 17 – Surfactants from plant oil feedstock
Slika 17 – Površinski aktivne tvari iz biljnih ulja

nally – to anionic, cationic or nonionic surfactants (Scheme 17). Triglycerides are hydrolyzed to a mixture of fatty acids that are converted to methyl esters. Methyl esters can be hydrogenated under pressure to high fatty alcohols from which nonionic surfactants are synthesized by oxyethylation.

A mixture of fatty acids is introduced in amidation by fatty amines (prepared from fatty acids), diamines or amino alcohols at 120–130 °C. In this process free fatty acids may also be used. The obtained products with amino – or hydroxyl groups are the starting material for preparation of anionic and nonionic surfactants by sulfation, oxyethylation or esterification with maleic anhydride.

Prof. Pope proposed to use also by-products of plant oil refining, namely phosphatide fuses from which a series of surfactants have been synthesized. Some of these new products demonstrated excellent properties as corrosion inhibitors of oil-and-gas production equipment, emulsifier-stabilizer of disperse system and inhibitors of wax accumulation. New technology based on these surfactants was developed for killing of wells with low steam pressure, renewal of wells and cleaning of well bottom zone.

Conclusions

Petrochemistry and the fermentation technology have both some similarities and substantial differences. Oil and gas can be easily concentrated and delivered to the processing plants. Processing is mostly carried out with the use of continuous technology and large volume reactors, and gives the monofunctional product. Unlike the sources of oil and gas, biomass as a rule is dispersed, it needs to be reared and

collected, concentrated and delivered saving needed quality. The biomass fermentation technology uses, as a rule, dilute solutions and requires the substantial increase of productivity in order to be competitive with petrochemistry. But fermentation results in transformations of multifunctional compounds with saving main functional groups; high stereoselectivity of fermentation processes is the greatest advantage in synthesis of special chemicals and pharmaceuticals. The fermentation process is realized in water solutions and, as a rule, at ambient temperatures. To extract a useful product from the reaction mixture, well developed technologies are applied, such as extraction or filtration, and standard processes of purification. In modern petrochemistry, 70 % of energy is used on product separation. The same percentage of energy, obviously, is needed to separate products in fermentation processes. Therefore, the increase in concentration of the final product in fermentation reaction medium is a very important task that, together with application of membrane technologies and other principles of separation, will allow substantial reduction of energy input as well as achieve corresponding efficiency. It is necessary to note that petrochemical technologies have improved over the decades, and that the industrial chemical fermentation technology has only begun its development. The biomass use in combination with fermentative technologies has an advantage also because by-products and wastes are ecologically acceptable and easily biodegraded in the environment.

Obviously, in the near future, chemical production of organic materials and chemicals will be based on three sources of raw materials: hydrocarbons, carbohydrates and products of plant metabolism. The share of organic chemicals produced from biomass by chemical and fermentation technology will grow quite fast. Such chemicals will include organic acids, alcohols and diols, amino acids, solvents, products of fine synthesis (special chemical), and others. Plants will be used as the source of eco-friendly pesticides and dyes, pharmaceuticals and others. Attention to the problem to replace oil with biomass will induce a new active search for new technology and new products from starch and cellulose, fatty acids and alcohols. Maybe some "old" products from cellulose and plant fibres that were forced out by synthetic products will find their way back to the market. No doubt that active researches on biomass conversion technologies and application of "new" biobased chemicals will result in competitiveness with "classic" oil-gas processing and chemical products.

Natural life exists due to the well concerted processes of interconversion, communication and matter-energy cycle that are the best principles of sustainability. Perfection of our knowledge on biological processes and the use of the rich possibilities of the Biosphere – is the basis of the human society's sustainable development.

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SAŽETAK

Biomasa – obnovljiva sirovina za organske kemikalije ("Bijela kemija")

V. P. Kukhar

Ograničeni prirodni resursi prisiljavaju nas da se okrenemo obnovljivim izvorima, starim i novim, koji mogu osigurati održivost ljudske zajednice i zadovoljiti naše potrebe za energijom i materijalima. Biljni svijet ima ogroman potencijal kao sirovina za proizvodnju organskog materijala. Ovaj pregled posvećen je upotrebi biomase za proizvodnju nekih osnovnih organskih kemikalija te glavnim smjerovima razvitka tehnologije za preradu biomase. To su uglavnom procesi koji pretvaraju celulozu i ugljikohidrate u finalne proizvode kemijskim ili fermentacijskim procesima. Neki se procesi već primjenjuju u industriji, međutim njihov opseg primjene stalno raste. Brojni kemijski proizvodi mogu se izravno izdvojiti iz biljaka, uključujući i genetski modificirane vrste. Napredak u kemijskoj tehnologiji i biotehnologiji omogućuje gotovo 50–70 postotnu zamjenu nafte kao sirovine biomasom.

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