Russian Chemical Reviews **82** (7) 616 – 623 (2013) © 2013 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2013v082n07ABEH004393

Green chemistry: development trajectory

I I Moiseev

Contents

I.	Sources of raw materials	616
II.	Ethanol. Production and use	618
III.	Electricity from renewable resources	620
IV.	High fatty acid triglycerides	620
V.	Succinic acid	621
VI.	Glycerol	622
VII.	Isoprene	622
VIII.	Conclusion	622

Abstract. Examples of applications of green chemistry methods in heavy organic synthesis are analyzed. Compounds, which can be produced by the processing of the biomass, and the criteria for the selection of the most promising products are summarized. The current status of the ethanol production and processing is considered. The possibilities of the use of high fatty acid triglycerides, glycerol, succinic acid, and isoprene are briefly discussed. The bibliography includes 67 references.

In summer 2012, a series of articles dealing with problems of the waste management were published in *Science* known for its publications on fundamental aspects.[1 – 14] Such a volley of information untypical of this journal is evidence of the public interest in environmental protection problems. The matter concerns not only the waste reduction in production processes and the resource and energy saving but also the new paradigm of the development of the fuel sector of industry and the basic organic synthesis as a whole. The works devoted to this issue are published also in other leading scientific journals.[15, 16]

The present review briefly illustrates applications of green chemistry methods in heavy organic synthesis (mainly in the last two years).

I. Sources of raw materials

In 2004, the US Department of Energy (DOE) chose about a dozen compounds which were at the focus of attention of researchers. The list of these compounds includes succinic, fumaric, maleic, furan-2,5-dicarboxylic, 3-hydroxypropionic, aspartic, glucaric, glutamic, itaconic and levulinic acids, 3-hydroxybutyrolactone, glycerol, sorbitol and xylitol.[17] The list of these compounds was subsequently named DOE's Top 10 although the number of compounds changed from time to time. All these compounds are produced from carbohydrates of biomass by chemical or biological methods. These basic products were chosen based on the following criteria.[18]

1. The compound or the technology is widely covered in the literature.

2. Examples of the wide use of the product in the chemical engineering are known.

3. Examples of the direct replacement of petrochemical industry products by those produced from renewable resources are reported.

4. Approaches to the large-scale production are developed.

5. The selected compounds serve as a platform for the manufacture of a broad spectrum of products.

6. The scaling-up of the production to a pilot, demonstration or industrial scale presents no difficulties.

7. The product generated from biomass is of high demand by market.

8. The produced compound can be used as a basic intermediate for the chemical production.

9. The commercial-scale production from renewable carbon is well known.

Methods for the processing of carbohydrates substantially differ from procedures for the utilization of other biomass components, such as lignin, oils and proteins. The left (first) column in Fig. 1 lists biomass components, which are of industrial interest as raw materials. The right (last) column presents the final products of the biomass processing. The above-listed building blocks for DOE's Top 10 compounds are produced directly from carbohydrates, primary basic products (*1*, ammonia synthesis, hydrogenation products; *2*, methyl ethers, formaldehyde, acetic acid, diethyl ether, dimethyl carbonate, methylamines, methyl-*tert*-butyl ether, alkenes, petroleum benzine; *3*, linear and

I I Moiseev I M Gubkin Russian State University of Oil and Gas, Leninsky prosp. 65, 119991 Moscow, Russian Federation.
E-mail: iimois@igic.ras.ru

Received 11 March 2013
Uspekhi Khimii **82** (7) 616 – 623 (2013); translated by T N Safonova

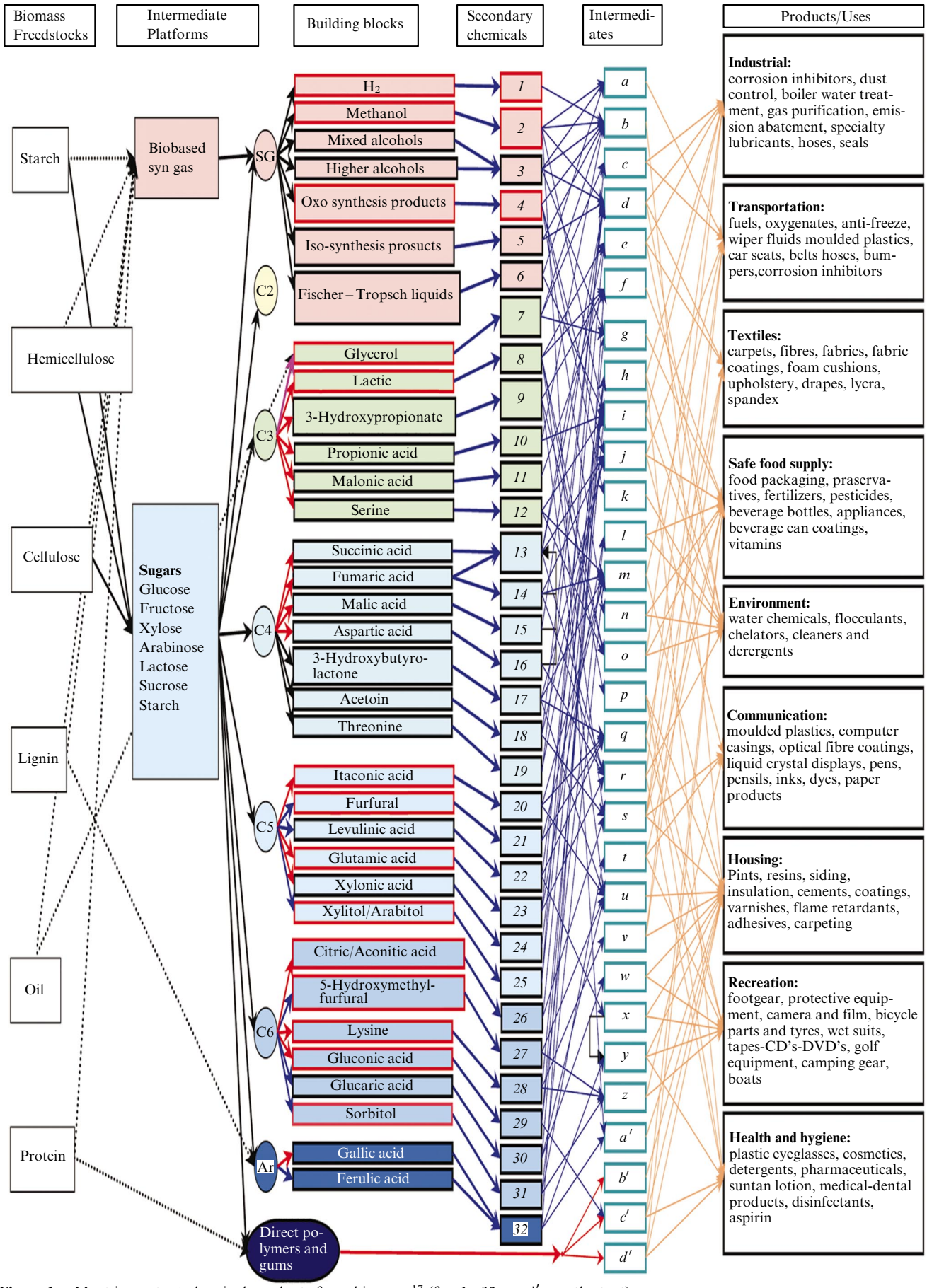


Figure 1. Most important chemical products from biomass [17] (for *1*–*32*, *a*–*d′*, see the text).

branched primary alcohols, a mixture of higher alcohols; *4*, hydroformylation products of alkenes: aldehydes, alcohols, acids; *5*, iso-C_4-compounds, isobutene and its derivatives; *6*, α-alkenes, petroleum benzine, paraffins, diesel fuel; *7*, fermentation products, propylene glycol, malonic acid, propane-1,3-diol, dicarboxylic acids, propyl alcohols, dialdehydes, epoxides; *8*, acrylates, L-propylene glycol, dioxanes, polyesters, lactides; *9*, acrylates, acrylamides, esters, propane-1,3-diol, malonic acid, *etc.*; *10*, propanol, acrylates; *11*, pharmaceutical intermediates; *12*, 2-aminopropane-1,3-diol, 2-aminomalonic acid; *13*, THF, butane-1,4-diol, γ-butyrolactone, pyrrolidones, esters, diamines, bionole, hydroxybutyric acid; *14*, unsaturated succinates; *15*, hydroxy-substituted succinates, hydroxybutyrolactone; *16,* amino-substituted succinates; *17*, hydroxybutyrates, epoxy-γ-butyrolactone, butenoic acid; *18*, butanediols, butenols; *19*, diols, keto derivatives; *20*, metyl succinate derivatives, unsaturated esters; *21*, furan derivatives; *22*, δ-aminolevulinates, 2-methyltetrahydrofuran, 1,4-diols, esters, succinates; *23*, amino diols, glutaric acid, substituted pyrrolidones; *24*, lactones, esters; *25*, ethylene glycol, propylene glycol, glycerol, lactates, hydroxyfurans, sugar-derived acids; *26*, pentane-1,5-diol, itaconic acid derivatives, pyrrolidones, esters; *27*, furan derivatives, succinates, esters, levulinic acid; *28*, caprolactam, diamino alcohols, 1,5-diaminopentane; *29,* glucolactones, esters; *30*, dilactones, monolactones, *etc.*; *31*, glycols (ethylene glycol, propylene glycol), glycerol, lactates, isosorbitol; *32*, phenols, food additives; *a*, fuel oxygenates; *b*, building blocks for reactants; *c*, antifreezing agents, deicing agents; *d*, solvents; *e*, green solvents; *f*, special chemical intermediates; *g*, emulsifying agents; *h*, chelating agents; *i*, amines; *j*, plasticizers; *k*, polyvinyl acetate; *l*, pH-controlling agents; *m*, cross-linking agents for resins; *n*, polyvinyl alcohol; *o*, polyacrylates; *p*, polyacrylamides; *q*, polyethers; *r*, polypyrrolidones; *s*, polyphthalates; *t*, polyethylene isosorbitol terephthalate; *u*, polyhydroxy esters; *v*, Nylons (polyamides); *w*, polyhydroxyamides; *x*, bisphenol A substitutes; *y*, polycarbonates; *z*, polyurethanes; *a′*, phenol formaldehyde resins; *b′*, polyhydroxyalkanoates; *c′*, polysaccharides; *d′*, polyamino acids).

II. Ethanol. Production and use

Sugar cane still serves as the main source of ethanol. The scale of this industry is so vast that the annual production capacity of green polyethylene (Braskem, Brazil) and polyvinyl chloride (Solvay, Belgium) can be about hundreds of tonnes.

According to the assessments of Direvo, the cost of ethanol produced from carbohydrates would be expected to be reduced by using advances in the genetic engineering, optimizing the fermentation process and finding an efficient way to remove by-products and ethanol from the wash.[19] This will lead to the reduction of production costs for one litre of ethanol from 3.5 to 0.45 US dollars by 2016, apparently, without taking into account economic benefits from the use of wash (vinasse) as an energy source.

Bagasse is an additional natural energy source for the ethanol production from sugar cane.† The energy consumption for the production of ethanol is about 12 kW h per tonne of the raw material. Approximately the same amount of energy can be generated by burning bagasse. This fact alone can make the sugar cane processing autothermal. The fermentation of bagasse can be used to produce biogas.[20, 21]

Currently, the production of energy sources based on the processing of plant materials contributes little to the world power engineering.[22, 23] The fermentation of exhaust gases from metallurgical and coal-tar chemical processes yielding a number of products of basic organic synthesis has attracted attention in recent years. Thus, LanzaTech uses exhaust gases from metallurgical or coal-tar chemical processes as a source for the manufacturing of ethanol and other products of basic organic synthesis.[24, 25] Hydrogen and CO serve as sources of energy; both natural and genetically modified enzymes are used. In addition to ethanol and acetic acid, propan-2-ol, acetone, butanediol, n-butanol, succinic acid and isoprene are mentioned as possible products. The potential annual ethanol output of the available pilot plant exceeds hundreds of billions of gallons. An important advantage of the new technology is the use of absolutely non-food resources and the efficient engineering of the process.

Tests of this process in China showed the successful continuous run of the pilot plant with an output of 15 000 gallons per year during more than two years. The plant showed the satisfactory practical performance and insensitivity to any impurities and changes in the gas composition. The process can be scaled up.

Bacteria used by LanzaTech were modified so that they can be used for the selective production of butanol, acetone, propan-2-ol and succinic acid from exhaust gases. The next step in the development of this process will be the use of CO_2 and hydrogen as the starting materials.

In Fig. 1, the group of compounds C2 included in the section building blocks is only mentioned but not discussed. However, ethanol is a very important compound that is formed in the processing of carbohydrate materials. It is currently widely used as a fuel additive and continues to find new applications in chemical engineering. The reduction of the costs for biomass cultivation and processing would be expected to lead to the renaissance in the area of chemistry based on ethanol processing. The ethanol dehydration was widely used for the production of ethylene in the 20th century. The vapour-phase dehydration of ethanol at 400 °C over a fluidized layer of activated Al_2O_3 affords ethylene with selectivity >99% and the conversion of 99.5%.[26] The conversion of ethanol to butadiene, dehydrogenation to form acetaldehyde, *etc.* were also important processes.

The new chemistry of ethanol, such as the conversion of this alcohol to isobutene in the presence of nanosized $Zn_xOr_yO_z$, is in progress (Scheme 1).[27]

Scheme 1

$$MeCH_2OH \longrightarrow MeCHO + H_2$$
$$2\,MeCHO + H_2O \longrightarrow MeC(O)Me + CO_2 + 2\,H_2$$
$$3\,MeC(O)Me \longrightarrow 2\,iso\text{-}C_4H_8 + CO_2 + H_2O + H_2$$
$$3\,MeCH_2OH + H_2O \longrightarrow iso\text{-}C_4H_8 + 2\,CO_2 + 6\,H_2$$

Since the time of V N Ipatiev isobutene has been used for the alkylation of paraffins to prepare components of high-octane fuels. Isoprene is produced on the industrial scale from isobutene and formaldehyde.[28] The copolymerization of isobutene and isoprene is used to produce butyl rubber.

† Bagasse is a fibrous residue remaining after the extraction of juice from the crushed stalks of sugar cane (or another plant). In the fresh form, it can serve as a fodder; in the dry form, as a fuel.

In petrochemistry, isobutene is produced from products of catalytic or thermal cracking of oil products (C_4 fraction).

Metal catalysts are known[29–32] to be able to convert aliphatic alcohols C_2-C_5 to alkanes with at least a double number of carbon atoms compared to the length of the alkyl backbone of the starting alcohol. This reaction is called the reductive dehydration of alcohols (RDA) (Scheme 2).

Scheme 2

$$m\,C_nH_{2n+1}OH + 2[H] \longrightarrow C_{mn}H_{2mn+2} + m\,H_2O$$

$n > 1, m > 2$

The results of the study of this reaction were unexpected.[32] It appeared that prolonged exposition of the well-known industrial aluminium platinum catalyst $Pt/\gamma\text{-}Al_2O_3$ under an atmosphere of a reducing agent at >450 °C leads to a change in the composition of the ethanol conversion products (Fig. 2).[29, 30, 33]

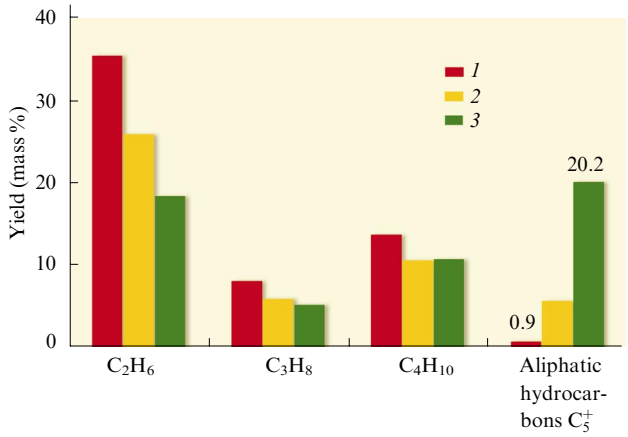


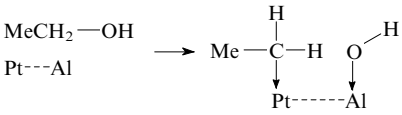
Figure 2. Effect of the temperature on the selectivity of the aluminium platinum catalyst in the reductive dehydration of ethanol.[33]
Temperature /°C: 100 (*1*), 300 (*2*), 450 (*3*).

The EXAFS and XANES studies of a modified catalyst prepared by prolonged heating suggested that the preheating causes the aluminium and platinum atoms to come closer to each other resulting in the formation of nanosized clusters of the composition Pt_2Al.[33] The formation of such clusters was observed both under the conditions similar to those used for the thermal treatment of the aluminium platinum catalyst and in the direct synthesis of the clusters from elements.[34–39]

Other important observations made in the study[33] are that the acidity of the active sites increases in the course of the treatment and that the addition of diethyl ether, which is a good ethylene donor, to the reaction mixture leads to the acceleration of the reaction. Moreover, the feeding of ethylene to the reactor also leads to an increase in the reaction rate, although, in seeming contradiction with the above facts, ethylene does not undergo oligomerization in the absence of ethanol. It is interesting that linear oligomers prevail among the reaction products of ethanol.

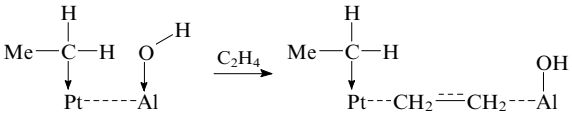
All the above facts, including the participation of Pt_2Al clusters in the reaction and high acidity of the catalyst after the treatment with a reducing agent, can be described in terms of the following mechanism. Apparently, the first step of RDA involves the oxidative insertion of an alcohol molecule into the Pt–Al bond *via* the C–O bond cleavage (Scheme 3).

Scheme 3



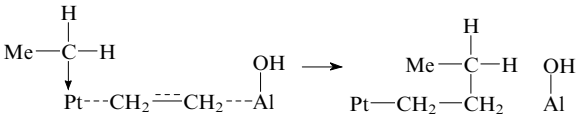
In the next step, a molecule of ethylene that is fed to the reactor or is generated upon dehydration of alcohol or diethyl ether is inserted between the platinum and aluminium atoms (Scheme 4).

Scheme 4



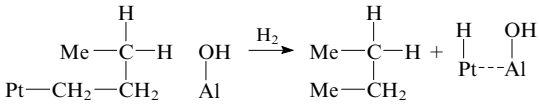
The transfer of the alkyl cation from the platinum atom to the bridging (μ^2-coordinated) ethylene affords a structure, in which the platinum atom is linked to the new carbocation (Scheme 5).

Scheme 5



The hydrogenolysis of the Pt–C bond completes the reaction yielding the final product (Scheme 6).

Scheme 6



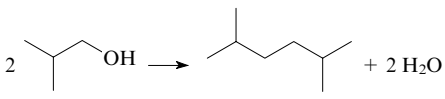
The starting form of the catalyst is recovered by the elimination of H^+ and OH^- ions and this, apparently, requires high temperature (300–400 °C) and 5–50 atm of Ar.

Evidently, this mechanistic scheme should be confirmed by additional experimental data.

The reaction with the participation of μ^2-coordinated ethylene generated from diethyl ether (an intermediate in this reaction) or alcohol leads to the carbon chain growth.

Under the conditions of RDA, ethanol gives a broad fraction of alkanes C_3-C_{16}, whereas the reactions of 2-methylpropan-1-ol and 3-methylbutan-1-ol afford 2,5-dimethylhexane and 2,7-dimethyloctane, respectively, as the major products, *i.e.*, compounds, in which the alkyl moieties of alcohols are dimerized (Scheme 7).

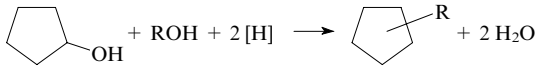
Scheme 7



Monohydric alcohols, which differ by the nature of the hydrocarbon residue, can be involved in the cross-conden-

sation to give hydrocarbons with the carbon backbone built up from fragments of the starting alcohols. Thus, the cross-condensation of acylic and alicyclic alcohols provides a direct route to valuable alkylcycloalkanes (Scheme 8).[32]

Scheme 8



A part of the alcohol which is involved in the competitive dehydrogenation serves as a source of hydrogen consumed in the reactions shown in Schemes 2, 7 and 8.[33, 34] The reactions presented in Schemes 2 and 7 afford alkanes with an even number of carbon atoms as the major products.

Glycerol and acetone (or its reduction product, propan-2-ol) are involved in the reductive dehydration of ethanol thus increasing the yield of the products (from 30 mass % to 46 mass %) and substantially increasing the fraction of alkanes with an odd number of carbon atoms (Table 1).

Table 1. Conversion of ethanol and mixtures of ethanol with glycerol and acetone to alkanes.

Products	Yield (mass %)		
	EtOH	EtOH + 20% $C_3H_5(OH)_3$	EtOH + 20% Me_2CO
H_2	0.3	0.1	0.2
C_1	5.6	4.7	7.6
C_2	12.3	11.3	14.0
C_3-C_{12}	30.6	41.4	46.3
$CO+CO_2$	45.2	35.5	29.4
Oxygenates	5.1	5.8	1.6
Aromatic hydrocarbons	0.5	0.6	0.7
Cyclic hydrocarbons	0.4	0.4	0.2
Σ	100.0	100.0	100.0

The yield of alkanes with an odd number of carbon atoms (2 + 3, 4 + 3, *etc.*) produced in the reactions of ethanol in a mixture with acetone or glycerol is much higher than that in the conversion reactions of individual ethanol (Fig. 3). An increase in the yield of alkanes with an odd number of carbon atoms is indicative of the involvement of acetone and glycerol molecules in the carbon chain growth.

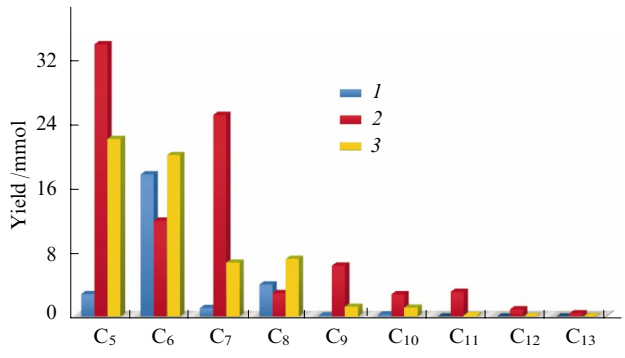


Figure 3. Composition of the products of the reductive dehydration of ethanol and the cross-condensation of mixtures of ethanol with acetone and glycerol.[33]
(*1*) EtOH, (*2*) EtOH + 20% Me_2CO, (*3*) EtOH + 20% $C_3H_5(OH)_3$.

The discovered reactions are the previously unknown examples of the one-step formation of C–C bonds in the reactions of ethanol with ketones or trihydric alcohols. They suggest a new route to producing fuel components based on by-products of such large-scale processes as the production of biodiesel (glycerol is the by-product) and the cumene-to-phenol process (acetone is the by-product).

III. Electricity from renewable resources

The design of mobile energy systems based on fuel cells for the independent energy supply of various local social service institutions, as well as of petrochemical and oil production plants is one of topical problems in power engineering. Russian chemists of Moscow and Ekaterinburg[40–44] proposed using mixtures of products of biomass fermentation without the separation and fine purification for the production of electric power. In the context of the research supported by Federal programmes in institutes of the Russian Academy of Sciences (Institute of High Temperature Electrochemistry of the Ural Branch of the Russian Academy of Sciences, A V Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences, Institute of Structural Macrokinetics and Materials Science of the Russian Academy of Sciences), modern modifications of solid-oxide fuel cells were developed for the electric power generation and membrane-catalytic systems, which exhibit high activity in the steam, carbon dioxide and combined carbon dioxide and steam reforming of conversion products of biomass to syngas with a specified composition. These works served as the basis for the joint research aimed at creating a small-scale energy power plant, in which the membrane catalytic converter is integrated with a solid-oxide fuel cell (SOFC). The use of new technologies for the production of SOFC made it possible to achieve the current density of about 300 mA cm^{-2} and the power density higher than 150 mW cm^{-2} in the course of testing. The following good mass-size characteristics of the cell battery were achieved: the specific volume was 3.3 litre kW^{-1} and the specific mass was 1.6 kg kW^{-1}. The setup was tested within the pilot plant. Methane, ethanol and a mixture that mimics a fermentation product without the isolation of the organic substrate were used as the primary fuel. The characteristics of SOFC operating with all kinds of fuels were virtually the same. Based on new technologies and in collaboration with Rosatom's enterprises (LLC Electrochemical Converter Plant, Novouralsk; OJSC Chepetsk Mechanical Plant, Glazov) and CJSC URALINTEKH (Ekaterinburg), a SOFC-based electrochemical generator with a power of 1.5 kW is under development assigned and funded by LLC Gazprom Transgaz Ekaterinburg. The available results provide the basis for the design of serial autonomous small-scale and mobile energy setups.[40–44]

IV. High fatty acid triglycerides

High fatty acid triglycerides (FATG) are main components of lipids in microalgae.[45] They are subjected to methanolysis, and the resulting high fatty acid esters are used as diesel fuel additives (biodiesel) or are deoxygenated to make higher-calorific fuel (green diesel). Since it is necessary to

overcome problems associated with the recirculation of methanol taken in excess and the associated significant energy costs, as well as the loss of methanol and lipid carbon in the course of the conversion of biodiesel to green diesel, an essential task for chemists and biotechnologists is to shorten the route from biomass to products, whose properties are identical to those of the standard fuel.[45–50]

The deoxygenation of fatty acid methyl ester and triglycerides in the presence of Pt, Pd, Rh, Ru or Ir supported onto ZrO_2-CeO_2, as well as of catalysts for hydrocracking and reforming of oil raw materials, such as Ni/Al_2O_3, $NiCo/Al_2O_3$ and CoW/Al_2O_3,[50,51] affords alkanes up to C_{18}, with hepta- and octadecanes predominating. Heptadecane is formed by decarboxylation of acids, whereas octane is produced through the reduction of their carboxyl groups,[50,51] where the length and structure of the carbon chains remain unchanged.

In the presence of metal-containing zeolite catalysts (pentasil), FATG are decomposed to form a broad spectrum of products, with aromatic compounds predominating.[52–55]

An industrial aluminium platinum catalyst pretreated according to the above-described procedure radically changes the selectivity of the reductive deoxygenation of FATG by hydrogen at 400–600 °C to give a rather narrow fraction of alkanes, in which the carbon chain length of the major component is equal to the length of the alkyl moiety of the acyl group in the main component of the starting oil. This fact attests to the reduction of the carboxyl group of FATG.

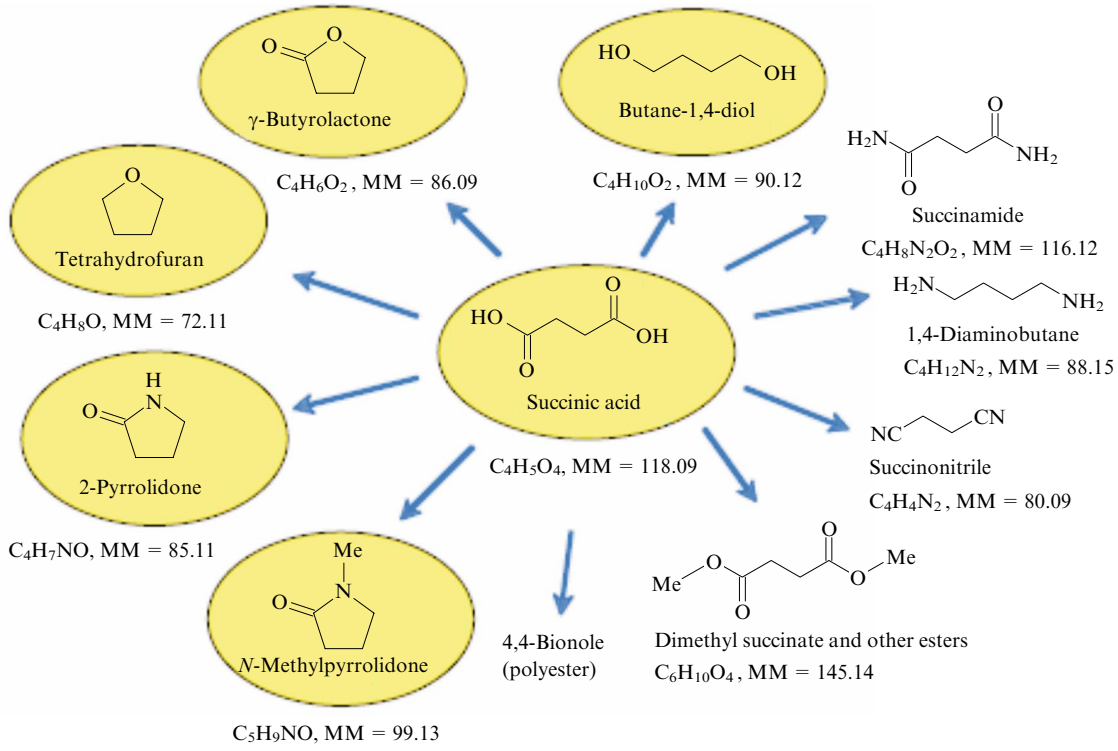
V. Succinic acid

In handbooks of chemical engineering and basic organic synthesis, data on succinic acid were lacking until recent years. Trace amounts of this compound were obtained during the oxidation of cyclohexane involved as a step in the production of adipic acid.[56] The possibility of the industrial synthesis of this compound from saccharides has brought about a revolution in the chemistry of polymer materials. Scheme 9 shows possible applications of succinic acid (here and in Scheme 10 products which have commercial significance and are produced on the industrial scale are enclosed in ovals).

The fermentation of succinic acid opens up a route to cheap butane-1,4-diol, which is used in the production of polyurethanes, polyesters (condensation with terephthalic acid gives polybutylene terephthalate) and efficient plasticizers for thermoplastics, as well as for the production of γ-butyrolactone. Butane-1,4-diol is of importance as a plasticizer and a wetting agent for gelatin, cellophane, special types of paper and tobacco. Earlier, butane-1,4-diol was produced in ~90% yield mainly *via* the condensation of acetylene with formaldehyde (Reppe process) on a copper bismuth catalyst (90–100 °C; 0.5–0.6 MPa) followed by the hydrogenation of the resulting but-2-yne-1,4-diol on a copper nickel chromium catalyst (150–160 °C; 20 MPa). A substantial drawback of this method is the use of acetylene as a source. The acetylene production is the energy-intensive and multistep process. The production of formaldehyde is equally technology-intensive. As a result, petrochemical butane-1,4-diol is expensive and unacceptable from the environmental point of view. The green chemistry proposed a way out of this difficult situation.

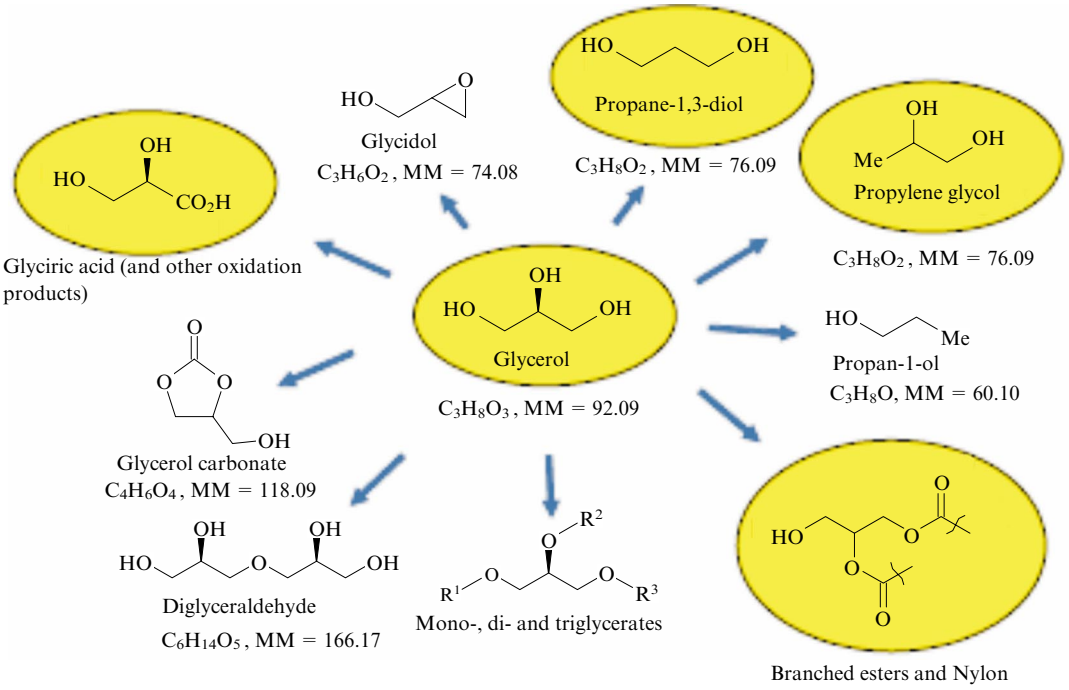
Genomatica and Novamond plan to produce 40 million pounds of butane-1,4-diol from succinic acid using modified *Escherichia coli* bacteria. The production of butane-1,4-diol was upscaled by Genomatica to the 3000-litre fermentation.[57]

Scheme 9



MM is the molecular mass

Scheme 10



VI. Glycerol

In the mid-20th century, attempts were made to produce glycerol on the industrial scale by the hydrogenation of saccharides. However, these attempts were not successful because of the low selectivity of the process. Currently, glycerol is produced by the hydrolysis of lipids and the fermentation of saccharides. Glycerol, not being a carbohydrate, is among the most important chemical products derived from biomass. The possible ways of its processing are shown in Scheme 10.[17]

Propylene glycol is produced on the commercial scale from glycerol with the selectivity of nearly 90%; the conversion is 65%.[58] Biochemists proposed a number of systems (*E. coli* bacteria and genetically modified *Clostridium acetobutylicum*) for the generation of propane-1,3-diol from glycerol in the production of the Sorona polymer (DuPont), which is used in the textile industry and the carpet manufacturing.[59]

VII. Isoprene

Isoprene is a favourite building block in nature and occurs in many long-known compounds. Natural rubber is built up of isoprene. Russian chemists (OAO Nizhnekamskneftekhim, Vniineftekhim, SPS Eurochim) substantially improved the well-known[60] synthesis of isoprene from isobutene and formaldehyde, which was commercialized in the USSR in 1960–1970s.[61, 62] The new process made it possible not only to reduce raw material and energy costs but also to decrease the specific consumption of sewage water, as well as the discharge of hazardous substances into the air.

The new inexpensive procedure for the production of isoprene from resources that are thick on the ground is very attractive. In this context, the recent Danisco invention of the enzymatic synthesis of isoprene from lignocellulosic biomass is of considerable importance.[63] Danisco assesses the global market for isoprene at 1–2 billion US dollars and plans to invest 50 million US dollars in the further development of this project during the next year. In November 2009, Goodyear, one of the world's leading tyre companies, and Genencor, a division of Danisco, announced their fusion. It should be noted that the production volume of mechanical rubber items, primarily, tyres, is among indicators used to assess the development level of chemical industry.[22, 64, 65]

The synthesis of bioplastics based on renewable resources has attracted considerable attention of a wide range of chemists.[66, 67]

VIII. Conclusion

The green chemistry has been initially focused exclusively on the fuel synthesis. However, over time it became clear that the crop yield of cultures serving as sources for the new field of industry is the bottleneck in the solution of problems of the fuel-energy complex. On the one hand, this gave impetus to the search for new resources, for example, such as exhaust gases from metallurgical plants and factories. On the other hand, works are in progress on the application of biochemical methods to the synthesis of compounds, whose production by traditional petrochemical methods is energy and resource intensive. It is noteworthy that the chemistry of natural compounds, which, until recently, has provided a basis for the drug design and the manufacturing of perfumery compounds and other fine chemistry products, is looking for and has already found applications in the new field, the heavy organic synthesis.

In one of the presentations, the German chemical giant LANXESS showed a photo of a car of tomorrow. This car will be made of renewable materials and, hence, it will be rather light in weight. The car will be powered by fuel of tomorrow produced from renewable non-food resources and, consequently, it is environmentally safe. The word LANXESS is a combination of the French word 'lancer' (meaning 'to launch') and the English word 'success'. Nowadays, chemical giants set new chemistry in motion.

This review has been written with the financial support of the Council on Grants at the President of the Russian Federation (Programme for State Support of Leading Scientific Schools of the Russian Federation, Grant NSh-5232.2012.3) given to young members of my research team.

References

1. J Mervis *Science* **337** 668 (2012)
2. J Mervis *Science* **337** 670 (2012)
3. G Vogel *Science* **337** 673 (2012)
4. E Pennisi *Science* **337** 674 (2012)
5. E Pennisi *Science* **337** 675 (2012)
6. R F Service *Science* **337** 676 (2012)
7. G Miller *Science* **337** 679 (2012)
8. S B Grant, J-D Saphores, D L Feldman, A J Hamilton, T D Fletcher, P L M Cook, M Stewardson, B F Sanders, L A Levin, R F Ambrose, A Deletic, R Brown, S C Jiang, D Rosso, W J Cooper, I Marusic *Science* **337** 681 (2012)
9. B E Logan, K Rabaey *Science* **337** 686 (2012)
10. B K Reck, T E Graedel *Science* **337** 690 (2012)
11. C O Tuck, E Pérez, I T Horváth, R A Sheldon, M Poliakoff *Science* **337** 695 (2012)
12. M Xanthos *Science* **337** 700 (2012)
13. Z Bian, X Miao, S Lei, S Chen, W Wang, S Struthers *Science* **337** 702 (2012)
14. J G Hering *Science* **337** 623 (2012)
15. O Jacquet, C das Neves, M Ephritikhine, T Cantat *J. Am. Chem. Soc.* **134** 2934 (2012)
16. B E Logan, M Elimelech *Nature (London)* **488** 313 (2012)
17. *Top Value Added Chemicals from Biomass. Results of Screening for Potential Candidates from Sugars and Synthesis Gas* Vol. I (Eds T Werpy, G Petersen) (U.S. Department of Energy, 2004)
18. J J Bozell, G R Petersen *Green Chem.* **12** 539 (2010)
19. G Luli, B Wood, B Yang, C Wyman, S Zou, Y Qian, L Ingram *The 25th Symposium on Biotechnology for Fuels and Chemicals, Brechenridge, CO, 2003* Presentation SpTB-01
20. EP P. 2167672 (2013)
21. US P. 20120111514 (2012)
22. *Energy Technology Perspectives. In Support of the G8 Plan of Action. Scenarios and Strategies to 2050* (OESR, International Energy Agency, 2008)
23. S Chu, A Majumdar *Nature (London)* **488** 294 (2012)
24. US P. 20100323417 (2010)
25. H N Abubackar, M C Veiga, C Kennes *Biofuels, Bioproduct, Biorefiner* **5** 93 (2011)
26. A Morschbacker *Polym. Rev.* **49** 79 (2009)
27. J Sun, K Zhu, F Gao, C Wang, J Liu, C H F Peden, Y Wang *J. Am. Chem. Soc.* **133** 11096 (2011)
28. H J Prins *Chem. Weekblad* **16** 1072 (1919); *Chem. Abstr.* **13** 3155 (1919)
29. RF P. 2220940 (2004); *Byull. Izobret.* (1) (2004)
30. RF P. 2220941 (2004); *Byull. Izobret.* (1) (2004)
31. M V Tsodikov, V Ya Kugel', F A Yandieva, G A Kliger, L S Glebov, A E Gekhman, I I Moiseev *Kinet. Katal.* **45** 904 (2004) [a]
32. M V Tsodikov, F A Yandieva, V Ya Kugel, A V Chistyakov, A E Gekhman, I I Moiseev *Catal. Lett.* **121** 199 (2008)
33. F A Yandieva, M V Tsodikov, A V Chistyakov, V Ya Kugel', Ya V Zubavichus, A A Veligzhanin, L E Kitaev, V V Yushchenko, A E Gekhman, I I Moiseev *Kinet. Katal.* **51** 572 (2010) [a]
34. T Chattopadhyay, K Schubert *J. Less-Common Met.* **45** 79 (1976)
35. J H Kang, L D Menard, R G Nuzzo, A I Frenkel *J. Am. Chem. Soc.* **128** 12068 (2006)
36. K Hayek, H Goller, S Penner, G Rupprechter, C Zimmermann *Catal. Lett.* **92** 1 (2004)
37. P Stadelmann *Ultramicroscopy* **21** 131 (1987)
38. X Zhong, J Zhu, J Liu *J. Catal.* **236** 9 (2005)
39. A Pietraszek, P D Costa, R Markues, P Kornelak, T W Hansen, J Carma, M Najbar *Catal. Today* **119** 187 (2007)
40. RF P. 2325219 (2008); *Byull. Izobret.* (15) (2008)
41. RF P. 2375114 (2009); *Byull. Izobret.* (34) (2009)
42. RF P. 2414954 (2011); *Byull. Izobret.* (9) (2011)
43. RF P. 2424974 (2011); *Byull. Izobret.* (11) (2011)
44. Appl. for Utility Model RF 2012146204 from 30 10 2012
45. M Edwards *Green Algae Strategy: End Oil Imports and Engineer Sustainable Food and Fuel* (Tempe, AZ, 2008)
46. B Smith, H C Greenwell, A Whiting *Energy Environ. Sci.* **2** 262 (2009)
47. I Senol, E-M Ryymin, T-R Viljava, A O I Krause *J. Mol. Catal. A: Chem.* **268** 1 (2007)
48. A S Berenblyum, V Ya Danyushevskii, E A Katsman, T A Podoplelova, V R Flid *Neftekhimiya* **50** 317 (2010) [b]
49. V O Dundich, V A Yakovlev *Khim. Inter. Ustoich. Razvitiya* 527 (2009) [c]
50. J Hancsók, M Krár, Sz Magyar, L Boda, A Holló, D Kalló *Microporous Mesoporous Mater.* **101** 148 (2007)
51. J Hancsók, Sz Magyar, A Holló *Chem. Eng. Trans.* (11) 41 (2007)
52. Y S Prasad, N N Bakhshi *Appl. Catal.* **18** 71 (1985)
53. US P. 4300009 (1981)
54. A G Dedov, A S Loktev, L Kh Kunashev, M N Kartasheva, V S Bogatyrev, I I Moiseev *Khim. Tekhnol.* (8) 15 (2002) [d]
55. A G Dedov, A S Loktev, A N Kharlanov, I Yu Kartashev, D A Udal'tsov, I I Moiseev *Zh. Fiz. Khim.* **78** 1980 (2004) [e]
56. K Weissermel, H-J Arpe *Industrial Organic Chemistry* (2nd Ed.) (Weinheim: VCH, 1993)
57. H Yim, R Haselbeck, W Niu, C Pujol-Baxley, A Burgard, J Boldt, J Khandurina, J D Trawick, R E Osterhout, R Stephen, J Estadilla, S Teisan, H B Schreyer, S Andrae, T H Yang, S Y Lee, M J Burk, S Van Dien *Nat. Chem. Biol.* **7** 445 (2011)
58. M A Dasari, P P Kiatsimkul, W R Sutterlin, G J Suppes *Appl. Catal., A* **281** 225 (2005)
59. US P. 5686276 (1997)
60. T Laue, A Plagens *Named Organic Reactions* (New York: Wiley-VCH, 2000)
61. I I Moiseev, V M Busygin, Kh Kh Gil'manov, A S Dykman, E V Fedortseva *Ekonom. Upravlenie* **70** (8) 29 (2011)
62. A A Lamberov, Kh Kh Gil'manov *Modernizatsiya Katalizatorov i Tekhnologii Sinteza Izoprena na OAO 'Nizhnekamskneftekhim'* (Modernization of Catalysts and Isoprene Production Process at the OAO 'Nizhnekamskneftekhim') (Kazan: Kazan University, 2012)
63. US P. 8173410 (2010)
64. *Strategiya Razvitiya Khimicheskoi i Neftekhimicheskoi Promyshlennosti Rossii na Period do 2015 g.* Prikaz Minpromenergo Rossii ot 14 Marta 2008 g. No 119 (Strategy of Development of the Chemical and Petrochemical Industry of Russia for the Period to 2015. The Order of the Ministry of Industry and Energy of Russia from 14 March 2008 No. 119); http://www.minprom.gov.ru/activity/chem/strateg/0
65. A V Artemov, A V Brykin, M N Ivanov, O V Shelyakov, V A Shumaev *Ros. Khim. Zh.* **52** (4) 4 (2008) [f]
66. *International Business Directory for Innovative Bio-based Plastics and Composites* (2nd Ed.) iBIB 2012/13. Published by nova-Institute GmbH and Bioplastics MAGAZINE; http://www.bio-based.eu/iBIB-Download
67. K Kimura, Y Horikoshi *Fujitsu Sci. Technol. J.* **41** 173 (2005)

[a] — *Kinet. Catal. (Engl. Transl.)*
[b] — *Petrol. Chem. (Engl. Transl.)*
[c] — *Chem. Sust. Develop. (Engl. Transl.)*
[d] — *Theor. Found. Chem. Eng. (Engl. Transl.)*
[e] — *Russ. J. Phys. Chem., Ser. A (Engl. Transl.)*
[f] — *Mendeleev Chem. J. (Engl. Transl.)*