Biofuels – have we exhausted all the possibilities?

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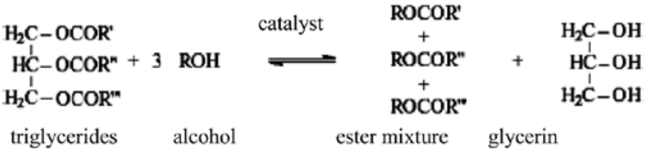
Our living environment requires constant heating, lighting for a big part of the day and huge amounts of energy which is consumed by the economy. The anticipated increase of world energy consumption in the years 2001÷2025 equals 54% [1]. Up to now, the energy needs of the world have been met mainly by carriers obtained from mineral sources – coal, petroleum and natural gas. Currently, approx. 80% of the world's primary energy consumption is obtained from fossil fuels, out of which 56% is consumed by the transportation branch [2]. It is commonly known that mineral energy carrier resources are being systematically exhausted which brings about an increase in their price. Currently verified world reserves of petroleum equal 169 billion t, coal – 847 billion t, and natural gas – 177 quintillion m^3. These reserves, as of 2007 and with currently observed trends, will last 42 years in the case of petroleum, 60 years in the case of natural gas and 133 years in the case of coal [3]. The peak of petroleum recovery is anticipated for the '40s of the 21st century. Taking into account a several-percent annual increase of demand in highly and moderately developed countries, the maximum recovery will take place with a considerably higher as compared to the present one. The situation is slowly becoming dramatic. World transportation is almost entirely based on mineral fuels – gasoline, diesel fuel, liquid gas and compressed natural gas, almost entirely refinery-based.

What, if any, are the chances of substituting conventional energy sources with renewable ones?

In 2002 the participation of renewable energy in the world energy consumption balance equaled 14%, out of which 11% came from biomass or waste [4]. A common-sense analysis of potential renewable energy and raw material sources shows that with the current state of knowledge only biomass has the potential to satisfy, to a large degree, the energy demands of the world and it may also be an efficient source of raw materials for the chemical industry. In the nearest future, four fuel sources may be taken into account as strategically significant: biofuels, hydrogen, biogas and synthesis gas (syngas) from the gasification of renewable sources and bituminous coal; in addition, biofuels are considered to be the most eco-friendly [5]. They are nontoxic, biodegradable and free from sulfur and carcinogenic compounds [6].

Biofuels

The notion of biofuels pertains to liquid and gaseous substances as well as to solid fuels produced from biomass. They are substances of different types. Biofuels include ethanol, methanol, dimethyl ether, biodiesel, diesel fuel from Fischer-Tropsch synthesis, hydrogen or methane [5]. The term 'biodiesel' denotes transesterified vegetable oils used for engines with self-ignition. Oil transesterification is the most popular method used for decreasing the viscosity of vegetable oils. Because of their viscosity, vegetable oils and animal fats (waste from meat processing) cannot be used as direct fuel in the majority of Diesel engines. During transesterification, fatty acid glycerides contained in vegetable plants are processed against acidic or basic catalysts into fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE) in reactions with methanol or ethanol (Fig. 1).



$$\begin{matrix}H_2C-OCOR' \\ HC-OCOR'' \\ H_2C-OCOR'''\end{matrix} + 3\ ROH \xrightleftharpoons{catalyst} \begin{matrix}ROCOR' \\ + \\ ROCOR'' \\ + \\ ROCOR'''\end{matrix} + \begin{matrix}H_2C-OH \\ HC-OH \\ H_2C-OH\end{matrix}$$

Fig. 1. Transesterification reaction equation

The byproduct of the process is glycerin whose management transfers considerably onto the efficiency and profitability of using biodiesel. The solution to the problem of glycerin is to substitute oil transesterification with cross esterification using methyl (ethyl) formate or methyl (ethyl) acetate. The byproduct of the reaction – glycerin triformate (triacetate) – does not have to be separated from FAME or FAEE as a valuable fuel constituent. This not only simplifies the technological process of obtaining bioesters but also enhances the quality of the end product (Fig. 2 [7]).

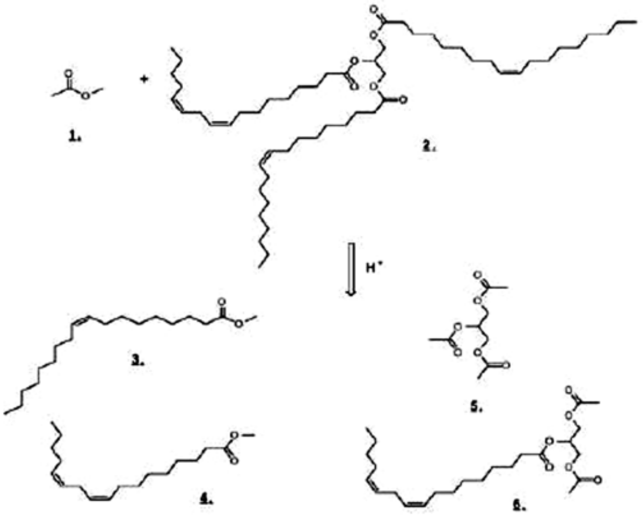


Fig. 2. Diagram of obtaining Gliperol®: 1. methyl acetate; 2. glycerin and fatty acid ester; 3., 4. fatty acid methyl esters; 5. triacetylglicerol; 6. Diacetylmonoacylglicerol [7]

In 1991, the world production of biodiesel was estimated at 2.9 million gallons, while the production of bioethanol equaled over 4318 million gallons. Over a span of a dozen or so years the production of biodiesel increased over a hundred times while the production of bioethanol just doubled (in 2003, 467 million gallons of biodiesel and 7593 million gallons of bioethanol were produced [8]). The main producers of ethanol are Brazil and the United States of America. The third manufacturer with large potential is China which adopted a plan anticipating that in 2012 the production of ethanol will be at a level of 6.3 billion liters and that half of the fuel consumed in China will be enriched with a 10% addition of ethanol [9]. The production of biodiesel is concentrated especially in the European Union. The biggest manufacturer is Germany which, together with France, produces nearly 80% off biodiesel in the world [4]. In 2007, the European Parliament adopted a resolution stating that in 2020 the energy balance of the EU will include 20% of energy from renewable sources while the minimum target will be for all member states to achieve a 10% share of biofuels in the transportation branch by 2020 [10]. In Poland, the National Index Target assumed 5.75% for 2010 (the target was achieved), while for the years 2011, 2012 and 2013 it is 6.20%, 6.65% and 7.10%, respectively [11]. The solution used in many countries, including Poland, which involves adding a few-percent biodiesel additive to mineral diesel has also a practical use because biodiesel has a larger lubricating ability than mineral diesel fuel that has sulfur compounds added to it in order to increase lubricity. The limits of sulfur emission are constantly tightened; therefore, it may be expected that supplementing mineral fuel with biodiesel will become a necessity [12]. The existing and developing technologies of producing biofuels were presented in Figure 3 [5].

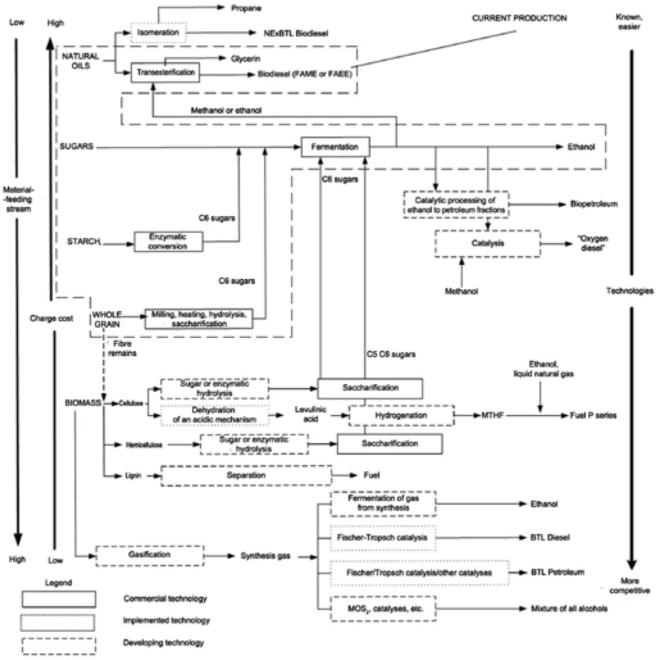


Fig. 3. Methods of biofuel production [5]

Primary and secondary first generation biofuels

The basic way of classifying biofuels is their division into primary and secondary. Primary biofuels are used in an unprocessed form, usually for heating, cooking or generating power. Primary biofuels include firewood, shavings, granulated wood flour or animal waste [5]. Secondary biofuels are products of processing biomass and include ethanol, FAME and DMA mentioned earlier. They are used mainly as motor fuels in vehicles and stationary engines. Currently, already three generations of secondary biofuels are mentioned. First generation biofuels are produced from materials containing starch or vegetable oils. These may include seeds, grain, fruit, stems, roots or bulbs. From the point of view of the applied processes, obtaining first generation biofuels is relatively easy. In the case of materials containing starch (wheat, oats, corn, potatoes) or simpler sugars (sugar beets, sugar cane), ethanol or n-butanol are produced in the fermentation process. In the classic fermentation process the first step is hydrolysis of starch to glucose, while in the subsequent – as a result of the work of enzymes from yeast – a conversion occurs of the hexacarbon molecule to the bi-carbon ethanol molecule.

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

The last step is distillation and dehydration. In the case of materials containing vegetable oils (rape-seed, soybean, sunflower, palm and other types), the product is biodiesel obtained as a result of transesterification. First generation biofuels arouse much controversy because of using vegetable oils as the material for producing food or fodder for farm animals as well as for the fact that in the production of biofuels only small fragments of plants are used (mainly seeds or grains), while the major part of the plant becomes waste. This is waste of acreage and energy invested in plant cultivation. The use of plants utilized in food production as materials for obtaining energy chemicals has led to a rapid increase in the prices of these plants and, consequently, to the increase of food prices. The world index of food prices is the highest in 20 years – in the period from October 2010 to January 2011 these prices have increased on average by 15% (it is assumed that, depending on the adopted model, 20-40% of the increase in these prices is due to the demand related to biofuel production). Such a situation urges agricultural producers to expand their crop areas of plants whose cultivation renders high profits which leads to a considerable limitation in cultivating other plants used for food purposes. The result of the last increase in food prices was pushing approximately 44 million people into poverty [13].

Second generation biofuels

The conflict between the production of food and industrial production has resulted in the search for other solutions which use inedible parts of plants for production. This led to second generation biofuels. The material for their production is lignocellulosic biomass coming either from inedible plant parts constituting plant waste or from entire inedible plants grown for the purpose of obtaining energy. The production of second generation biofuels requires more sophisticated technological equipment, larger outlays on the production unit and a considerably larger scale. The most important directions of lignocellulosic biomass production include:

- fermentation processes (ethanol fermentation, butanol fermentation, anaerobic fermentation which leads to the creation of methane or fermentation in which the obtained products are short-chain carboxylic acids)
- gasification of biomass using steam and oxygen (synthesis gas is obtained from which diesel oil is obtained from the Fischer-Tropsch synthesis, methanol, dimethyl ether)
- thermolysis (depending on the process conditions it leads to light gases of oil fractions).

Thermochemical conversion of biomass requires the application of considerably more severe conditions (temperature, pressure) than biochemical conversion. A serious limitation of the fermentation method is that – putting aside the enzymes which are unsuitable for broad implementation because of their high price – to this day an effective industrial method of cellulose hydrolysis has not been created. On the other hand, in the case of thermolysis the liquid fraction consists of oil mixed with water which contains numerous oxygen compounds (alcohols, esters, ethers and short-chain carboxylic acids) and tarry substances which requires the application of a very complicated process of transforming it into the form of propellant. The most realistic solution in the long-term perspective seems to be the process of gasifying biomass to synthesis gas. Further processing of gas will take place using known and proven processes with large technological perfection (such as methanol synthesis), further processing or obtaining synthetic diesel fuel.

Third generation biofuels

The use of waste from agriculture and other economy branches for the production of second generation biofuels will perhaps allow for the minimization of the conflict between food processing and the industrial use of plants; however, it will not solve the problem of too small agricultural acreages in relation to the growing demands of the modern world. The solution to this problem should be third generation biofuels; here, the material includes algae and seaweed out of which ethanol, biodiesel and hydrogen can be obtained. The undeniable advantages of algae include: all-year production, obtaining crops in a continuous way, high efficiency of obtaining oil from algae, even 10 times higher than in the case of cultivated plants [14] with a high content of oil (20-50% of dry mass), the possibility of carrying cultivation even in areas considered as wasteland, quick increase and small requirements (the medium may be waste and the cultivation does not require the use of pesticides). These are undeniable advantages; however, third generation biofuels remain a solution of the distant future and they will probably not remain the target solution. The area of wasteland which may be used for growing seaweed in open ponds is as limited as the growing acreage while cultivating algae in open waters seems to exclude the possibility of a worldwide ecological catastrophe.

Summary

Nigam and Singh [5] postulate 4 conditions for optimizing the production process of balanced biofuels:

1. The process of enzymatic hydrolysis of agricultural products must be perfected. This can be obtained by using initial enzymes which are cheaper or of a higher specificity, through their production in a cheaper process and by using a new technology of carrying out processes with a large number of solids.
2. It is necessary to develop microbiological strains which, apart from desirable qualities as fermenting microorganisms, will be characterized by a higher resistance to inhibitors present in hydrolyzates used as materials. The sought after strains should also have the capability to ferment all sugars occurring in the hydrolyzate, high efficiency and they should resist high concentration of the product in the solution.
3. It is necessary to apply a strategy aimed at integrating the processes and, consequently, at decreasing the number of intermediate stages.
4. For all byproducts and waste generated during the production process, a 3-R strategy (*Recycling, Reduction and Reuse*) should be applied in order to decrease the energy costs and to protect the environment.

The use of biomass for biofuel production has great potential and will be developed in the future. The advantages of such a solution cannot be overestimated – biomass is renewable and during its production solar energy is used in such an effective way that is impossible to achieve by humans. Moreover, biomass is available almost everywhere and, contrary to mineral materials, does not lead to the division of the world into more and less privileged parts. The production processes of biomass and biofuel are not toxic; they are eco-friendly and do not generate carbon dioxide. However, it is rather definite that biofuels will never fulfill the entire energy needs of humans. This is illustrated by the report drawn up in April 2005 [15] whose aim was to determine whether the United States of America are capable of realizing the assumed goal: using energy from biomass to fulfill 30% of the country's energy needs in 2030 – in order to achieve this, the United States would have to produce approximately a billion tons of dry biomass. In the report it was estimated that by fulfilling various conditions it is possible for USA to achieve biomass production at a level of approximately 1.3 billion tons of dry biomass per year. This means that by 2030 the country would be able to realize its assumed goals and obtain 1/3 of energy from biomass. However, in consequence this also means that it will be difficult to reach beyond that goal; the achieved 30% constitutes the limit of possibilities in terms of fulfilling energy demands. Perhaps with time new methods will be created for increasing crop efficiency or for growing new, more energetic types of plants; on the other hand, this will also increase the energy demand. With the current and presently anticipated state of knowledge it should be assumed, that even in a country as highly-developed as the United States, biomass may provide only approx. 1/3 of energy demand coverage.

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Marta KIJEŃSKA - Ph.D., in 2004 she graduated from the Faculty of Chemistry of the University of Warsaw; in 2005 she finished studies in biotechnology at the Faculty of Biology of the University of Warsaw. In 2010 she defended her doctoral dissertation in chemical technology at the Faculty of Chemistry of the Warsaw University of Technology. Since 2005 she has been employed at the Industrial Chemistry Research Institute. Her scientific interests revolve around the chemical use of plant materials. She also deals with the strategy of applying renewable sources in power engineering and industry.

Jacek KIJEŃSKI – Prof. dr Jacek KIJEŃSKI. Outstanding expert in the field of chemistry and chemical processing, particularly in the lines and strategy of chemical industry development, catalysis, industrial organic synthesis and recycling of plastic waste. Professor of the Warsaw University of Technology, member of the Senate of the Warsaw University of Technology from 1996 to 2006. Since 2008 Dean of the Faculty of Civil Engineering, Mechanics and Petrochemistry and Vice-Rector for the School of Engineering and Social Sciences in Płock. From 1987 to 1990 Dean of the Faculty of Chemistry of the Warsaw University of Technology. From 2002 to 2007 Director of the Industrial Chemistry Research Institute in Warsaw. Since 2002, now for the third tenure, President of the Association of Chemical Industry Engineers and Technicians. Vice-President of the Committee on Chemistry of the Polish Academy of Sciences. Prof. Jacek Kijeński, as an experienced manager and expert on the development of chemical processing, has been appointed by the Minister of Economy, Labour and Social Policy to work with the Interministerial Group for Ownership Transformations of R&D Organisations and with the Trilateral Group for the Chemical Sector. President of the Centre of Advanced Technology „Chemistry for Economy" CHEMCAT, from 2003 to 2008 Co-ordinator of the Polish Hydrogen and Fuel Cell Technology Platform, founder and member of the Steering Committee of the Polish Biofuels and Biocomponents Technology Platform. Member of the Standing Committee of the Chemical Technology Congresses, Association of Inventors, Polish Association of Plastic Processors, and programme boards of technical magazines: "Przemysł Chemiczny", "Chemik", "Polimery", "Wiadomości Chemiczne" (up to 2007), "Rynek Chemiczny" and "Ochrona przed Korozją". Former representative of the Minister of Economy at the UN European Economic Committee, member of the World Association of Industrial and Technological Research Organisations (WAITRO), Associate Member of the Committee on Chemistry and Industry of the International Union of Pure and Applied Chemistry (IUPAC), member of the German Society for Chemical Engineering and Biotechnology DECHEMA, American Chemical Society, Network for Industrial Catalysis In Europe (NICE) and European Federation of Chemical Engineering (EFCE). Awarded with the Gold Cross of Merit, Knight's Cross of the Order of Polonia Restituta, Officer's Cross of the Order of Polonia Restituta, Medal of the Commission of National Education and Officer's Cross of the Order of Invention of the Kingdom of Belgium. He was honoured with the title of an Outstanding Inventor and with the WIPO (World Intellectual Property Organization) Gold Medal, Golden Badge of Honour of NOT (Polish Federation of Engineering Associations), Golden Badge of the Wrocław University of Technology, Badge of Honour of SITPChem (Association of Chemical Industry Engineers and Technicians), Prof. Świetosławski Medal. Honorary Member of SITPChem. Five times laureate of awards of the Minister of Science and Higher Education and of the Minister of National Education. His inventions were awarded many times on world and international exhibitions of inventions. One of them, Gliperol® biofuel, was awarded gold medals on exhibitions in Geneva, Brussels, Seoul, Nuremberg, Moscow, Warsaw, Gdańsk and Częstochowa. Prof. Jacek Kijeński is author and co-author of more than 170 publications, more than 200 conference papers, 8 monographs and 35 patents. Prof. Jacek Kijeński is an outstanding propagator of engineering and technological knowledge. His extremely popular lectures delivered during open sessions, anniversary meetings and conventions are imbued with humanistic and philosophical content and present a holistic vision of the world, where exact sciences and technology provide the prime impulse for spiritual development of society and civilisation. Prof. Jacek Kijeński is one of the originators and inspirers of the "Sunny Chemistry" Programme, harmonised with IYC'2011, which is a far-flung effort to change the social image and perception of chemistry by implementing an educational and promotional programme by Associations of Chemical Industry Engineers and Technicians, publishers of the CHEMIK monthly, with the participation of most eminent authorities on chemistry, chemical processing and modern chemical industry. Besides having great scholarly and engineering accomplishments, Prof. Jacek Kijeński is an outstanding humanist, erudite, deeply interested in literature, art and history of civilisation.

Unusual crystal patterns win chemistry Nobel

The discovery of a crystal whose atoms are packed in a pattern that never repeats has won Israeli scientist Daniel Shechtman the 2011 Nobel Prize in chemistry. The structures in quasicrystals, as they are known today, are similar but never exactly identical. This patterning is found in 800-year-old Islamic tiling and described in the mathematical sets of English mathematician Roger Penrose, but was thought to be forbidden in matter. Quasicrystals are exceedingly strong and are found in particular blends of steel used to make razor blades and surgical instruments. These crystals are also slippery like Teflon and scientists are investigating them for use in coatings for frying pans. Poor conductors of heat, quasicrystals may prove also useful as heat insulators for engines or in devices such as light-emitting diodes. Shechtman, 70, of the Technion–Israel Institute of Technology in Haifa, made the discovery one April morning in 1982 while investigating a mix of aluminum and manganese. At the time Shechtman was working at the U.S. National Bureau of Standards (now the National Institute of Standards and Technology). Many in the scientific community scoffed at the initial discovery, and the research wasn't accepted for publication in a scientific journal until 1984. Most states of matter are either well behaved and orderly or a disordered mess. Quasicrystals are peculiar because they fall in between — they are regular but never repeating. When Shechtman made his discovery he had just quickly cooled a glowing hot metal, which should have yielded disorder among the atoms. But when he looked at the diffraction pattern created when electrons scattered off his material, he saw something orderly.

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