

Michał RYMS¹, Witold M. LEWANDOWSKI¹, Ewa KLUGMANN-RADZIEMSKA¹
Katarzyna JANUSZEWICZ¹ and Krzysztof CIUNEL¹

METHODS OF LIQUID BIOFUEL PRODUCTION - THE BIOETHANOL EXAMPLE

METODY PRODUKCJI BIOPALIW CIEKŁYCH NA PRZYKŁADZIE BIOETANOLU

Abstract: Ethanol is used in chemical and food industry, mainly either in the synthesis or as a solvent. The newest application of ethanol is as a fuel. This alcohol, produced on an industrial scale from crop waste, is widely known under the name bioethanol. It could be used as a fuel by itself or in a mixture with gasoline. Today, there are several technologies for bioethanol production known. The relatively simple method of obtaining bioethanol is through the mechanism of fermentation. There is an interest in use and improvement of this and other production mechanisms. Given the increasing demand for alternative fuels, ethanol today is one of the most supported research and implementation issues in the fuel sector. This paper summarizes the current knowledge on the subject. In this article, data from the largest producers of ethanol in the world and an analysis of use of biofuels in each country are presented. Identified characteristics of bioethanol production and its mechanism for the main technologies of production are presented. The paper contains a forecast on the future use of biofuels - the construction of a new generation of biorefineries.

Keywords: biofuels, bioethanol, technology of production

Introduction

Ethanol is used in chemical and food industry, mainly in the synthesis or as a solvent. Its relatively new application is utilizing as a liquid fuel. In this case, the popular solution is to use ethanol as a supplement of gasoline, because of the fact that the pure ethanol can be used in specially modified engines. Bioethanol has excellent oxidizing properties, causes limited emission of toxic gases (such as carbon and nitrogen oxides) and increases the fuel's octane number. On the other hand, if we use addition of ethanol, it is necessary to use others compounds. They reduce its volatility and limited tribological properties of the fuel, in order to counteract increased friction and rapid wear of the engine [1].

Ethanol can be produced from crops containing both monosaccharides and polysaccharides. In Poland, the most amount of ethanol is derived from potatoes and ryes. In future ethanol could be made from cellulosic materials, especially waste materials [1]. Production of bioethanol is still developing, the main direction of research aims at developing new techniques, lowering productions costs, lowering environmental pollutions, activation of agriculture, and, in a larger scale, reduction of oil import.

Poland has a considerable amount of excess biomass and experience in ethanol production. However, there's a problem with insufficient amount of the existing distilleries and spirit plants. Therefore, thinking about the future use of ethanol as a fuel, requires construction of new plants.

¹ Gdansk University of Technology, ul. G. Narutowicza 11/12, 80-233 Gdańsk, phone 58 347 23 22, email: smyr@plusnet.pl

The world production of ethanol

The world production of ethanol is about 31-33 mln m³ (24.5-26 mln Mg), 93% of which is generated by alcohol fermentation, the rest through chemical synthesis. The main part of production is located in Brazil and USA (65%). In Asia, the percent of production is about 18% and in Europe - 15%. Nowadays, production of ethanol as a fuel covers 2/3 of total world production. In Brazil, 95% of ethanol in circulation is utilized in form of fuel, in USA over 60%, in EU only 5%.

The largest company in Europe, which produces bioethanol, is Spanish Abengoa. Other large companies include: French confectionery Tereos and German: Crop Energies AG and Südzucker. An important place in the ranking is reserved for SEKAB, a Swedish company specializing in bioethanol production technology from lignocellulose, utilizing wood waste from paper industry (pulp), and excess of alcohol (wine). The guidance of the European Commission, which adjudicated on the possibility of managing the surplus of the product in the wine industry, encouraged company to use in the production wine stocks. SEKAB planned for 2008, invest in the production of bioethanol in Hungary. The plan was to build a four modern bioethanol plants for 380 million Euros, with a total production of 600 million liters (raw materials are mainly maize and wheat). By-product of this is over 460 000 Mg of animal feed [2]. Unfortunately, market verified the plans. The increasing prices of raw materials (cereals) in combination with reduced harvest of corn in Hungary (compared with the expected), also possibility of changes in European Union standards (for biocomponent), effectively discouraged investors. The company projects SEKAB are suspended due to lack of funds and so far there's little possibility to change this situation [4]. Hungary is now forced to cover their demand for bioethanol imports from Slovakia. SEKAB currently focused on promoting the new E-tech technology-based on bioethanol production from cellulose. The first stage of the raw material is subject to dilute acid (sulfuric acid or sulfur dioxide) and heat, which converts hemicellulose into sugar [5]. Other parts of the process are similar to any other processes of bioethanol production from lignocellulose.

The country, which strongly promotes the use of hydrated ethanol, is Brazil where pure ethanol is available at 26 thousand different fuel stations. The total number of cars, which are modified to use ethanol is more than 3 million. In recent years in the USA a significant increase in sales of E10 fuel has been observed - but still it is only 12% of total sales of gasoline.

The characteristic of bioethanol

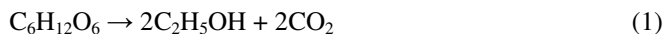
Bioethanol is defined as 99% ethyl alcohol derived from biomass. In trade, as an alternative fuel, it can be used in pure form or as an additive to gasoline at different volume ratios. It is accepted that the name of bioethanol determining the percentage of ethanol in biofuel preceding them with the letter E (eg E 85). According to the European standard for diesel fuel (DIN EN 228), the ethanol concentration in gasoline may not exceed 5% (E5). The use fuel with higher levels of ethanol in the vehicle inaccessible to the bioethanol may result in the loss of warranty. Bioethanol has a higher (by almost 10 units) octane number than gasoline, this can improve engine performance by increasing the degree of compression in the cylinder, however the use of pure fuel - 95% ethanol - requires special

engine construction. The standard also permits the use of other additives in the form of ethyl-t-butyl ether (ETBE - 47% ethanol and 53% of isobutene) in an amount not exceeding 15%. ETBE has also a high octane number, and adding it to gasoline improves the resistance to explosive combustion. However, the raw material for the production of ETBE is also ethanol [6].

Mechanism of alcoholic fermentation

One of the main methods of bioethanol production is a alcoholic fermentation, which is a hydrolytic decomposition of monosaccharides like: (glucose (honey), fructose (fruits), saccharose (beets, sugar cane)). Ethanol could be generated in a enzymatic decomposition of polysaccharides - starch (*eg* from corn and cereals) to monosaccharides in the hydrolysis process. Research is being conducted on a method of ethanol production from cellulose and hemicellulose from wood and straw. In this method, the raw materials are not food biomass but waste biomass and in future this production may become competitive to other technologies.

In the fermentation process, glucose is decomposed to alcohol and CO₂ by using yeast enzymes (zymase), according to the following reaction:



From a biochemical point of view, the alcoholic fermentation is a process of anaerobic sugar decomposition. This makes it possible for organism to thrive in anaerobic conditions (bacteria *eg* milk fermentation, cells of striated muscle in a effort, erythrocyte etc.). Alcoholic fermentation has three stages, one and two are similar like in milk fermentation - named glycolysis.

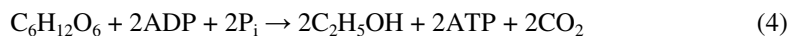
In the first stage, a glucose molecule, driven by ATP in the in the process of hexokinase, through gluco-6-phosphorane (glucose-fructose isomerase) is transformed with another ATP molecule into fructo-6-phosphorane which in turn causes the formation of 1,6-fructosediphosphate.

In the second stage, the diphosphat decomposes into 3-phosphogliceryne aldehyde or phosphodihydroxyacetone. These two compounds can be converted into each other by mechanism of tri-phosphate isomerase. The two molecules of 3-phosphogliceryne aldehyde undergo transformations involving oxidation and phosphorylation, and the reactions are accompanied by the creation of four molecules of ATP and two molecules of pyruvic acid (CH₃COCOOH) [7, 8].

In the third stage, a decarboxylation of two molecules of pyruvic acid occurs, through pyruvate decarboxylase. From two molecules of acetaldehyde (CH₃CHO) by alcoholic dehydrogenase with NAD, two molecules of ethyl alcohol are generated.



These three stages can be presented in simplified terms by cumulative reactions:



Bioethanol production technologies

Fermentation of ethanol is one of the oldest techniques of biotechnology. It uses microorganisms, usually yeast: *Saccharomyces cerevisiae* capable of anaerobic conversion of monosaccharides to ethanol. The process of ethanol production can be divided into three main stages:

- preparation of raw material - enzymatic degradation of carbohydrate (starch, cellulose) into monosaccharides (glucose) by hydrolysis,
- ethanol fermentation - the processing of sugar conversion to alcohol, with emission of CO₂,
- separation of the product - distillation, ethanol dehydration and rectification.

Two different methods of preparation of raw material - wet or dry milling are used in ethanol production on an industrial scale. Before the fermentation process is carried out, the wet process requires the separation of raw material (separately on the germ, fiber, protein and starch). In modern distilleries, the grinding process of raw materials is carried out, followed by their enzymatic hydrolysis. In older agricultural distilleries, fermentation is carried out periodically, which in case of the new fermentation processes has been replaced by continuous extraction with ethanol or diffuse discharges. The use of vacuum extraction of fermentation products provides higher efficiency. These methods, due to their high cost and complexity, are not applied on an industrial scale yet.

The fermentation of broth is the primary microbial process. The yeast are need to carry out processes - these include: *Saccharomyces cerevisiae* and *Saccharomyces carlsbergensis* in the upper fermentation, or *Saccharomyces bayanus*, wine yeast, baking, and wild yeast (a mixture of many cultures) in case of lower fermentation.

Yeast used in brewing ferment at low temperatures 5-10°C for about 1-2 weeks providing 2.5-5% vol. alcohol. Optimum fermentation temperature is 25-30°C and is used in distilling, where it takes 2-3 days, giving the mash content of 7-12% alcohol, but also a large amount of pollutants. Pollutants are disposed of by refining, rectification and using activated carbon adsorption. The turbulent and secondary fermentation of wine is carried out at lower room temperature, and therefore takes longer: 1-2 months (maturing for several years), but the resulting product has only trace amounts of fusion, giving it a special flavor and taste, specific for the vineyard.

Ethyl alcohol is separated from the fermentation residues using the distillation, and the boiling temperature difference using the two others components (ethanol boils at 78.3°C). Unfortunately, ethanol and water form an azeotrope mixture, which has a boiling point of 95.6% ethyl alcohol, about 4% water and the rest (higher alcohols, esters, ethers and acids). Even a small amount of water is unacceptable, because it can cause the presence of water in the fuel mixture. Therefore, only anhydrous alcohol (99.5-99.9%) should be used as a fuel.

The agricultural distilleries are used as distillation columns, designed for continuous work, the shelves separate raw spirit of broth digestate [9].

In distilleries, a 95.6% mixture of ethanol and water is produced, commonly known as spirit. It is in fact an azeotropic mixture and the pure ethanol could not be generated from it. In order to obtain the pure ethanol (100%), azeotropic distillation is conducted in the ethanol-water-benzene system. After adding a small amount of benzene, initially there is a threefold process of boiling azeotrope benzene-ethanol-water, then ethanol-benzene

azeotrope, and finally the process of distilling to pure anhydrous ethanol. It is possible to bound water with 95.6% ethanol by adding calcium oxide or anhydrous magnesium sulphate(VI) or sodium sulphate(VI). Absolute ethanol is hygroscopic and absorbs water from the air, so it should be stored in hermetic containers. Completely anhydrous ethanol (water content < 100 ppm) is obtained by distillation from over magnesium ethoxide in the system protected from air [10, 11].

The distillery produces low wine, containing about 90-92% ethanol. It is processed in rectification plants to the anhydrous or consumption alcohol. To obtain anhydrous alcohol, molecular sieves are used (sorption of water in a suitable sorbent) [1].

Iogen technology

Bioethanol production technology proposed by Iogen company is based on a combination of thermal, biomass chemical and biochemical conversion into a fuel called cellulosic ethanol [12]. Cellulosic ethanol is produced in an amount of more than 340 liters per Mg of fiber.

Lignin, present in plant's fibers is processed and used as fuel for process steam and electricity. This eliminated the need of additional coal or natural gas, and also reduced CO₂ emissions. In the process of pretreatment, which is to increase the surface and "availability" of plant fibers to the enzymes, special water vapor injection systems are utilized. It improves the performance of both the pretreatment and ethanol production, which provide lower cost of the fuel. The company has also developed its own cellulose enzyme groups and delivers them worldwide to pulp, paper, textiles and animal feed industries.

ICM technology

Technology adopted by ICM uses dry milling process in which grain is grinded for sharps. The starch contained in it is easier and faster converted into ethanol by fermentation process [13, 14].

Silos for the storage of grain are sufficient to supply the production line for 7-10 days. From the tray material goes to the hammer mills, preceded by a set of screens designed to remove residual stems, stones and ground, which could hinder the process of grinding. The ground grains are mixed with: process water (with pH of about 5.8) and enzyme (α -amylase). The slurry is then heated to a temperature of 82-88°C for 30-45 minutes to reduce its viscosity and pumped pressurized steam injector, which also heats the mash to the 105°C. After 5 minutes, the mash is cooled in the tank with air at reduced pressure to a temperature of 82-88°C and left for 1-2 hours to make sugar from starch into short concatenation dextrin.

After the initial stage of saccharification and addition of a second enzyme - glucoamylase, the mash is pumped into fermentation tanks.

In the glucoamylase fermentation process, dextrin is broken down into simple sugars, then yeast is added, which provides the conversion of sugar into ethanol and carbon dioxide. The mash is allowed to ferment for 50-60 hours, resulting in the final mixture containing about 15% ethanol, also solid residues from grain and yeast. The fermented mash is pumped into the distillation columns, which provides additional warmth. Product leaving the distillation columns contains about 95% (by volume) ethanol. The residue from

this process (containing raw materials and water) is pumped from the bottom of the column to the centrifuges.

The resulting ethanol, containing still 5% of water, is directed to a molecular sieve to physically separate the water and ethanol, based on the difference in particle size between those substances. After going through this stage anhydrous ethanol is obtained. Small amounts of denatured alcohol are added before storage tanks. This contamination prevents distribution and use of this alcohol as a consumer product. Most of the tanks in the factory of ethanol are so capacious that they allow the storage of the product (as in the case of material) for 7-10 days.

The process of fermentative production of ethanol creates two by-products: carbon dioxide and stillage (cereal, potato). CO₂ can be captured and treated in a scrubber, and then launched to sold of agri-food processing, *eg* for aerating beverages. While the stock is headed to the centrifuges, where is separated into two fractions: a rare (liquid containing 5-10% solids) and a *thick wet solid residue* (WDG). Some of thin stillage is recycled to the process, which reducing the demand of process water. The rest is directed to a system of evaporators, where it is concentrated to a syrup having a concentration about 25-50%. This syrup, high in protein, yeast, sugar and fat, is used to enrich WDG. This could be perfect fodder for farm animals. Many bioethanol plants are not near the farmers to take advantage of all the WDG produced. Long term storage of such products is not a solution, because of the short life span of wet stillage (because of rapid biodegradation). In this case, the additional drying system is used, which removes moisture and prolongs its life span. Dry stillage (DDG) is used as high-protein feed ingredient of cattle, pigs, poultry and fish.

Technology using supercritical water

A new, exciting technology for the production of bioethanol is developed at Kyoto University [15]. Lignocellulose in biomass is subjected to the water in the supercritical state ($T > 374^{\circ}\text{C}$, $p > 22.1 \text{ MPa}$). The hydrothermal reaction of oxidative reforming, forming the fraction soluble in water and methanol, other soluble fraction only in methanol and lastly an insoluble residue. Hydrolysis products of carbohydrate derivatives, dehydrated, and shredded products and organic acids are the water-soluble substances. The residue is a mixture of glucan (polysaccharide) and lignin, which are insoluble in water, but are soluble in supercritical water, soluble in methanol part is derived from lignin.

The use of supercritical water allows the pretreatment of lignocellulose, involving the rupture of it long, chemically stable, chains for simple sugars, which are already subject to fermentation in the traditional production of ethanol [15].

The biomass resilient to ethanol fermentation (wood, straw, Lety, cake, *etc*), that contains lignocellulose is transported into reactor for hydrothermal decomposition with supercritical water. Products of hydrothermal decomposition, after the cold water addition, are pumped to the extractor, where the separation of water-soluble products from the methanol-soluble products occurs. The first of these fractions, containing products of cellulose and hemicellulose decomposition, is subjected to saccharification processes in an enzyme hydrolyser, then after the fermentation, distillation and rectification is generating the product which is bioethanol. The remaining, soluble in methanol, fraction containing aromatic compounds, derived from hydrothermal decomposition of lignin, is converted into

other useful products (solvents, intermediates and chemical reagents). A team of researchers from Kyoto is still conducting research to optimize this technology [16, 17].

Usefulness of water in the under or supercritical state as a solvent, reagent and catalyst of acid / alkaline in recent years is the subject of intensive research, which tends to use it in: chemical synthesis reactions, conversion processes, gasification, biomass processing, and wastewater treatment [18].

Biorafineries as a perspective for development of bioethanol

Main research aiming at improving efficiency of bioethanol production is conducted in the following areas: raw material acquisition in form of waste or biomass, which does not undergo alcoholic fermentation, developing methods for pretreatment of biomass, the use of carbon dioxide and ammonia for decomposition of biomass and synthesis of more efficient enzymes.

In these studies, special emphasis was placed on the acquisition and use of more diverse material in the production of bioethanol, for example, waste from wood, crop residues, firewood from the forests, plants and municipal waste. The chemical structure of this potential raw material is much more diverse than traditional distilling material to which ethanol is the main source of starch or sugar. However, this requires solving many technological and chemical processes [19].

Summary

In this study, a collection of examples of modern technologies allows obtaining ethanol has been presented. It systemizes knowledge in the field of liquid biofuels, based on the alcoholic fermentation. Proposed future solution, in the form of biorefineries is setting new trends and gives hope for further development and implementation of research in this area over the next decade.

References

- [1] Szewczyk KW. Outline of the possibility of using ethanol as a renewable energy source. [In Polish] <http://www.mi.gov.pl/files/0/1791041/etanoljakoodnawialnerdoenergii.pdf>
- [2] Creating Markets for Renewable Energy Technologies European Renewable Energy Technology Marketing Campaign - Bioethanol Production and Use. Project: RESTMAC. www.erec.org/fileadmin/erec_docs/.../Brochure5_Bioethanol_low_res.pdf
- [3] Main actors in biodiesel and bioethanol production in the EU. Biofuels Platform. ENERS Energy Concept. <http://www.biofuels-platform.ch/en/infos/eu-actors.php>
- [4] BiofuelsDigest - news market. <http://www.biofuelsdigest.com/blog2/2008/03/19/sekab-cancels-hungarian-ethanol-project-citing-financing-30-hungarian-ethanol-projects-now-shelved/>
- [5] SEKAB. How We Make Ethanol. <http://www.sekab.com/cellulose-ethanol/e-tech-process>
- [6] Bioethanol - Press releases. <http://www.biomotion-tour.eu/>
- [7] FNR Biokraftstoffe 2007, FNR Biokraftstoffe Basisdaten Deutschland 2008. <http://www.nachwachsenderohstoffe.de/>
- [8] Kurcek A. Glykolysis. e-Biotechnologia.pl. <http://www.e-biotechnologia.pl/Artykuly/glikoliza/>
- [9] Alcoholic fermentation, e-Biotechnologia.pl, <http://www.e-biotechnologia.pl/Artykuly/Fermentacja-alkoholowa/>
- [10] Preparation of common solvents and reagents. Ethanol [In Polish]. <http://www.trimen.pl/witek/ciecz/rozpuszczalniki.html#etanol>
- [11] Vogel AI. Textbook of Practical Organic Chemistry. Warsaw: WNT; 1984
- [12] Iogen Corporation. http://www.ioegen.ca/cellulosic_ethanol/what_is_ethanol/process.html

- [13] Jakóbiec J, Wolszczak J. Prospects, barriers to growth and technical conditions for use of biofuels. Conference on Alter-Motive project. Poświętne: Nov. 4, 2010. <http://www.alter-motive.org/>
- [14] ICM Gasification Technology. http://www.icminc.com/ethanol/production_process/
- [15] Saka S, Phaiboonsilpa N, Nakamura Y, Masuda S, Lu X, Yamauchi K, Miyafuji H, Kawamoto H. Eco-Ethanol Production from Lignocellulosics with Hot-Compressed Water Treatment Followed by Acetic Acid Fermentation and Hydrogenolysis. The 31st Symposium on Biotechnology for Fuels and Chemicals. San Francisco, CA: May 3-6, 2009.
- [16] Phaiboonsilpa N, Lu X, Yamauchi K, Saka S. Chemical conversion of lignocellulosics as treated by two-step hot-compressed water. Green En Tech. 2010;III:166-170. DOI: 10.1007/978-4-431-99779-5_25.
- [17] Ehara K, Saka S. Decomposition behavior of cellulose in supercritical water, subcritical water, and their combined treatments. J Wood Sci. 2005;51:148-153. DOI:10.1007/s10086-004-0626-2.
- [18] Pińkowska H, Wolak P, Złocińska A. Hydrothermal decomposition of alkali lignin in sub- and supercritical water. Chem Eng J. 2012;187:410-414. DOI: 10.1016/j.cej.2012.01.092.
- [19] Lewandowski WM, Ryms M. Biopaliwa - proekologiczne odnawialne źródła energii. Warsaw: WNT; Forthcoming; 2013.

METODY PRODUKCJI BIOPALIW CIEKŁYCH NA PRZYKŁADZIE BIOETANOLU

Katedra Aparatury i Maszynoznawstwa Chemicznego, Politechnika Gdańska

Abstrakt: Etanol, poza wykorzystaniem w przemyśle spożywczym oraz chemicznym, gdzie służy jako rozpuszczalnik i substrat syntezowy, w ostatnich czasach zyskał również ważne zastosowanie w branży paliwowej. Produkowany jest na skalę przemysłową, głównie z substratów nienadających się do spożycia, i występuje pod zwyczajową nazwą bioetanol, pełniąc funkcję biopaliwa lub dodawanego do benzyny w różnych proporcjach biokomponentu. Z uwagi na stosunkowo prosty sposób produkcji, wykorzystujący mechanizm fermentacji, znanych jest dziś kilka technologii produkcji bioetanolu, a zainteresowanie ich wykorzystywaniem i ulepszaniem jest wciąż znaczne. Biorąc pod uwagę rosnące zapotrzebowanie na paliwa alternatywne, bioetanol jest dziś jednym z najbardziej nośnych tematów badawczych i wdrożeniowych w sektorze paliwowym. Niniejsza praca stanowi podsumowanie dotychczasowej wiedzy w tym obszarze. Przytoczono w niej dane, dotyczące największych producentów etanolu i bioetanolu na świecie oraz analizę wykorzystania tego biopaliwa w poszczególnych krajach. Przedstawiono charakterystykę bioetanolu, mechanizm jego produkcji i schematycznie zaprezentowano najważniejsze technologie produkcji. Praca zawiera również opis najbardziej prawdopodobnego przyszłego wykorzystania biopaliw - budowę biorafinerii nowej generacji.

Słowa kluczowe: biopaliwa, bioetanol, technologie produkcji