

THE ROLE OF MAIZE HYBRIDS IN CURRENT TRENDS OF BIOETHANOL PRODUCTION

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Abstract

Bioethanol is a biofuel that is mostly used as a replacement for fossil fuels worldwide with yearly production reaching nearly 110 billion liters in 2019. Trends of producing this alternative fuel are rising and maize is considered as one of the best renewable raw materials for the production of fuel ethanol due to the high content of starch in the grain. Taking into account that Serbia is one of the most prominent maize producers in Europe, the surpluses of this crop could be directed towards bioethanol production. Even though there is no organized production and consumption of bioethanol as an automotive fuel in Serbia, the Serbian Government has recently introduced some new regulations regarding biofuels. However, due to the reduction of economic activities since the onset of COVID-19 pandemic in 2020, the global demand for crude oil has fallen sharply, negatively affecting the gasoline demand, and thus for bioethanol, which makes the future of this alternative fuel production notably uncertain.

Keywords: bioethanol, environment, fuel, maize

Introduction

The modern era has brought about a number of global changes such as the depletion of fossil fuel resources and the environmental pollution increase. Bioethanol, an alternative fuel that can be obtained by fermentation of sugars present in the biomass, accounts for the majority of biofuels used worldwide, either as a fuel or gasoline enhancer. Renewable and biodegradable feedstocks, such as maize hybrids are currently in focus due to their potentials in biofuels production, namely bioethanol (Gohain et al., 2021; da Silva et al., 2021; Garcia et al., 2020). The total world bioethanol production has reached 109.9 billion liters in 2019 (Table 1), with the United States at the top of the list as the largest bioethanol producers (RFA, 2020).

The importance of bioethanol for the environment is reflected in the reduction of total

emissions of CO₂, one of the greenhouse gases that affect global warming. The total balance of CO₂ in the process of bioethanol combustion equals zero because during the process of photosynthesis plants consume the amount of this gas identical to that produced during the combustion of bioethanol (Mojović et al., 2007). Bioethanol is most commonly used as a substitute for motor gasoline in mixtures (E5, E10, E15, E85), as pure alcohol (in specially designed engines) or it can be converted to ETBE (ethyl tertiary butyl ether) and as such added to gasoline or diesel fuel in concentration up to 15%. Only highly purified - absolute ethanol is used as a fuel additive (Thangavelu et al., 2016). Bioethanol intended for mixtures with fossil fuels must have a minimum purity of 99.5% to 99.8% vol. depending on the standard of the country in which it is produced (Semenčenko, 2013).

Review Paper (Pregledni naučni rad)

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Table 1. Annual world bioethanol production in millions of liters*
 Tabela 1. Godišnja proizvodnja bioetanolu u milionima litara

Region	2015	2016	2017	2018	2019	Share of World Production (%)
United States	56.050	58.344	60.324	60.910	59.718	54
Brazil	27.255	25.589	25.286	30.321	32.441	30
European Union	5.250	5.212	5.300	5.413	5.451	5
China	3.077	3.199	3.255	3.975	3.407	3
Canada	1.650	1.650	1.779	1.817	1.893	2
India	738	1.041	795	1.514	2.006	2
Thailand	1.264	1.219	1.401	1.476	1.590	1
Argentina	798	999	1.098	1.098	1.098	1
Rest of World	1.480	1.855	1.567	2.078	2.271	2
Total	97.562	99.108	100.805	108.602	109.875	

*Source: RFA. 2020

Raw materials for bioethanol production can be divided into five basic groups:

- 1) sugary, such as sugar beet (*Beta vulgaris*), sugar cane (*Saccharum officinarum*), sorghum (*Sorghum bicolor*), fruit, etc.),
- 2) starchy (maize (*Zea mays* L.), wheat (*Triticum aestivum* L.), rice (*Oryza sativa*), potato (*Solanum tuberosum* L.), cassava (*Manihot esculenta* Crantz), sweet potato (*Ipomoea batatas* (L.) Lam.), barley (*Hordeum vulgare* L.), etc.),
- 3) lignocellulosic (wood, agricultural surpluses, municipal waste, etc.),
- 4) by-products of various technological processes and 5) algal biomass.

Bioethanol produced from sugary and starchy feedstock can also be classified as a first-generation biofuel, lignocellulosic and by-products form the second generation, while algal biomass is used for the third generation bioethanol production (Bioenergy and Biofuels, 2018; Semenčenko 2013).

Maize is one of the most important raw materials used in North America and Europe for the production of bioethanol due to the high starch content in the grain (about 70%). In the world today, there is great interest in the cultivation of maize hybrids, the application of which would accelerate the production of bioethanol (Zabed et al., 2017; Bertrand et al., 2016). Previous studies have shown that high yields of ethanol can be achieved from grains

that contain more starch and less protein and lipids. This means that grain composition and starch structure are crucial factors in predicting the yield of bioethanol from maize. Maize hybrids with a higher content of fermentable sugars have been developed, and work is underway to create hybrids with modified starch characteristics (Zabed et al., 2017a; Gumienka et al., 2016; Nikolić, 2009). Two large seed companies in the United States, Pioneer and Monsanto, have created commercial maize hybrids specifically for bioethanol production that can produce up to 4% higher yields of this alternative fuel than standard hybrids kernel chemical composition of (which would mean an increase in profit of 1-2 million dollars for the production of ethanol of 150·10⁶ l per year) (Srichuwong et al., 2009).

Bioethanol production in Serbia

Currently, there is no organized production and consumption of bioethanol as an automotive fuel in Serbia. According to the data of the Statistical Office of the Republic of Serbia, the annual bioethanol production in the period from 2009 to 2016 was about 60,000-65,000 hl, less than half compared to the amount produced in the period 2005-2008 (about 145,000 hl per year), which indicates that part of the production capacity is currently underutilized (Dodić et al., 2018). Despite the significant

potential, Serbia is not producing bioethanol as an energy source. In Serbia, ethanol is produced in several plants (“Panon”, Crvenka; “Ada Vrenje”, Belgrade; “Lukas”, Bajmok; “Reahem”, Srbobran and “Alpis -SLC”, Kovin), mainly medical alcohol and for use in the pharmaceutical industry or as a disinfectant. Molasses and cereals are mainly used as raw materials in these factories. Due to the recent COVID-19 pandemic, some of the plants have increased their production capacities, mainly for the production of 70% ethanol for disinfection (Blic, 24.04.2020.; Telegraf, 28.03.2020).

In the National Action Plan, the goals for the use of renewable sources are determined based on energy needs, economic opportunities and obligations of the Republic of Serbia undertaken by ratified international agreements (Zakon o energetici, 2018).

In order to harmonize the legal regulations related to the consumption and production of biofuels with the laws of the European Union, several regulations have been recently introduced by the Government of the Republic of Serbia. These regulations include Regulation on biofuel sustainability criteria (Uredba o kriterijumima održivosti biogoriva, 2019), Regulation on the share of biofuels on the market (Uredba o udelu biogoriva na tržištu, 2019), Regulation on monitoring the quality of oil and biofuel derivatives (Uredba o monitoringu kvaliteta derivata nafte i biogoriva, 2017), and Regulation on marking of oil derivatives (Uredba o obeležavanju (markiranju) derivata nafte, 2017).

Despite the fact that a new type of fuel derivative is being introduced in order to reduce fuel import dependence, Serbia does not have domestic production of biofuels. Starting from January 1, 2021, the application of the Regulation on the share of biofuels on the market will begin, so that the sale of gasoline with added bioethanol, or euro diesel with added biodiesel should start at gas stations across Serbia. It is a fuel that drivers are already accustomed to in the countries of the European Union (Bonenkamp et al., 2020). Granted that both petrol and diesel will bear the previous names, additional markings which will indicate the percentage of biofuel that is mixed into the appropriate oil derivative should be introduced on the gas stations (Petrović-Stojanović, 2019).

It is important to emphasize that despite the currently very low level of industrial production of ethanol, in Serbia today there are basic preconditions for the development and improvement of the production of this alcohol thanks to great potential in terms of raw materials, tradition and professional staff (Mojović et al., 2013).

The crop that is currently the most suitable for the production of bioethanol in Serbia is maize. Serbia, one of the most prominent maize producers in Europe, had the total annual production of 6.96 million tons with the average grain yield of 7.7 tons per hectare in 2018 (Statistical Yearbook of the Republic of Serbia, 2019). Annual maize yields in Serbia over the past few years have generally been around seven million tons, which fully meets the needs for maize in the food and feed industry (estimated

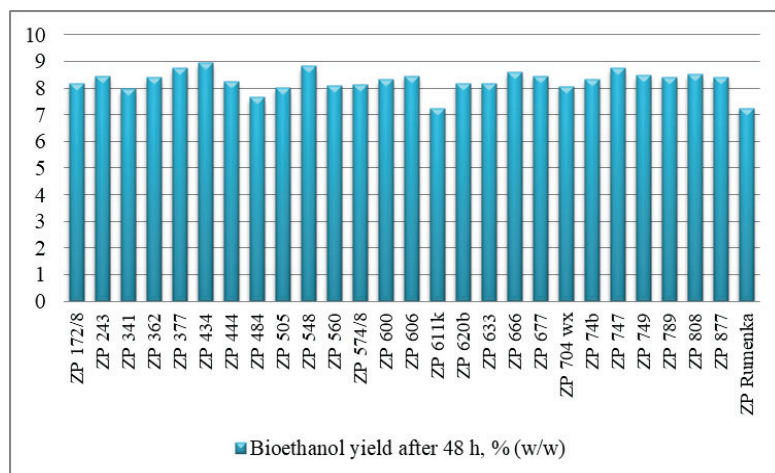


Figure 1. Bioethanol yields in percentages of the theoretical yields after 48 h fermentation of the wholegrain flour 27 ZP maize hybrids (Semenčenko, 2013)

Grafikon 1. Prinos bioetanola u odnosu na teorijski prinos nakon 48 h fermentacije integralnog brašna 27 ZP hibrida kukuruza (Semenčenko, 2013)

needs are between 4 and 4.5 million tons). Given that maize production in Serbia exceeds domestic needs, the surplus could be utilized for the production of this alternative fuel, which would free our country from importing about 2.5 million tons of oil per year (Mojović et al., 2013).

In the Maize Research Institute “Zemun Polje”, on domestic raw materials and thanks to the multitude of different maize hybrids, research has been conducted with the possibility of a further contribution to the development of ethanol production (Semenčenko, 2013; Semenčenko et al., 2013; Radosavljević et al., 2009). For the investigated hybrids, different degrees of fermentability were determined based on the yield of bioethanol in the fermentation process (Figure 1). Yellow dent kernel hybrids with standard chemical composition showed better fermentative characteristics than hybrids with specific properties such as popcorn, waxy, white and red kernel hybrids. Hybrid ZP 434 had the highest yield of bioethanol which was 94.5% of the theoretical content of bioethanol in the process of separate hydrolysis and fermentation (SHF). The high bioethanol yield of this hybrid is attributed to the high starch content in its kernel, as well as the high proportion of the soft fraction of endosperm which is more susceptible to the effect of enzymes that hydrolyze starch and decompose starch granules during hydrolysis. Due to its high yield, i.e. yield per hectare, the hybrid ZP 434 requires less arable land for cultivation, which also contributes to the environment conservation (Semenčenko, 2013). The possibilities of conducting further research that would show the potentials of ZP maize hybrids for the production of bioethanol from grain or lignocellulosic biomass are currently being investigated.

A study conducted by Bojic et al. (2018) showed that maize stover currently represents the most abundant and highly suitable feedstock for lignocellulosic bioethanol production in Serbia. Mapping of potentials showed that most of these raw materials are concentrated in the Province of Vojvodina, where it is expected to have supply radius up to 70 km, which would enable positive effects of supply costs and GHG emissions (Bojic et al., 2018). However, to our knowledge, there are still many issues that need to be considered, mostly regarding transport costs, production facilities and implementation of new technologies.

By-products of the maize bioethanol industry

Dry distillers grains with solubles (DDGS) is an important by-product of the bioethanol industry and distillery plants. During the production of bioethanol, per 1000 kg of consumed maize with 12% moisture and 65% starch (calculated on the dry matter), 229 kg of DDGS with 90% dry matter can be obtained, while producing 293 l of bioethanol. Apart from being a valuable source of proteins, water-soluble vitamins and minerals, DDGS contains a range of complex organic macromolecules, mostly polysaccharides. (Chatzifragkoua et al., 2015; Liu, 2011; Mojović et al., 2007).

Fresh stillage can be used for animal feed on farms in the immediate vicinity of the bioethanol factory because it is very susceptible to spoilage. In contrast, the dried product is stable and can be used as a component of animal feed throughout the year. DDGS is relatively cheap, available in large quantities but has limited industrial application. This by-product of the bioethanol industry is an excellent source of protein and energy for animals and is, therefore, most commonly used as a component of feed mixtures for farm animals. DDGS contributes significantly to the overall economy of the maize dry-mill processes, together with carbon dioxide and ethanol (Ferreira et al., 2018).

Cereal by-products from the bioethanol and food industries such as DDGS, bran, and brewer's spent grain, represent a constant source of components with a nutritive value that could be used as innovative raw materials for secondary production of value-added commodities providing simultaneously economic benefits and waste reduction for bioethanol plants (Roth et al., 2019; Chatzifragkoua et al., 2015; Liu, 2011). Apart from being exploited as animal feed, stillage from bioethanol production on different substrates (maize, wheat, triticale or waste bread) in form of distillery wastewater, DDGS, or wet distillers' grains (WDG) can be used as a substrate for methane, hydrogen and single-cell protein production. The possibility of lactic acid production from cereal-based by-products has already been demonstrated in distillery silages and wastes from bioethanol and beer production (Djukić-Vuković et al., 2016; Djukić-Vuković et al., 2015).

During the research conducted at the Maize Research Institute on samples of DDGS obtained by bioethanol production from ZP maize hybrids, it was found that all samples of tested hybrids showed favourable characteristics in terms of physical properties, chemical composition, presence of minerals, digestible and metabolic energy content as and the percentage of dry matter digestibility. The high content of both digestible and metabolic energies of the investigated samples indicated that these DDGS samples can be classified as both protein and high-energy feeds. The share of protein in DDGS has more than doubled concerning wholegrain maize flour as a starting material. Quality DDGS obtained from ZP maize hybrids can be used for the preparation of complete and concentrated mixtures for feeding different types and categories of domestic animals (Semenčenko et al., 2015, Semenčenko, 2013).

The use of DDGS for animal nutrition in Serbia could generate income in the amount of 14% of the total revenues from bioethanol production. DDGS as a by-product of the grain-based bioethanol industry could positively influence the development of bioethanol production by being used in the nutrition of domestic animals as a component of mixtures in a percentage higher than previously practised in the world and our country (Semenčenko, 2013).

Possibilities of maize agro residues utilization

Agroresidues are classified as waste by-products of agricultural crops and agro-industry. The constant generation of these waste materials leads to environmental and economic problems. These issues could be addressed by using these waste materials to produce other value-added products. (Sindhu et al., 2020)

Second-generation biofuels are produced from lignocellulosic raw materials that can include crop and forestry waste, other agricultural by-products such as manure, municipal, and waste that arises from industry, i.e. raw materials that are not traditionally used as food. Agroresidual waste, such as lignocellulosic biomass, consists mainly of cellulose, hemicellulose, and lignin. Given that up to 18 billion tons of lignocelluloses are readily avail-

able every year, excessive research has been focused on the production of ethanol from these substrates. The introduction of efficient production of bioethanol from lignocellulosic raw materials would be of great importance in the production of alternative fuels and the simultaneous use of agricultural waste (Ferreira et al., 2018; Semenčenko et al., 2011; Lin and Tanaka 2006).

Residues and waste from agriculture such as straw, corn cobs, stems, grain, and husks, are forms of biomass that can be used as an alternative energy source (Gupta and Verma, 2015). After the maize is harvested, maize stalks with leaves, cobs and husks remain on the cultivated land. Since the average grain-to-mass ratio (so-called harvest ratio) is 53%: 47%, it follows that there is approximately as much biomass as there is grain. If grain and cob are separated, then their ratio is on average 82%: 18%, i.e. 0.89 t of maize biomass is obtained per 1 t of maize grain produced, which makes 0.71 t of maize grain and 0.18 t of cob. Although it is indisputable that the resulting biomass must primarily be returned to the soil, ploughing between 30 and 50% of that mass is recommended, which means that at least 30% remains for energy use (Semenčenko et al., 2009).

Although raw materials for the production of second-generation bioethanol, like maize agro residues, are significantly cheaper and are not traditionally used for human and animal consumption, demanding technological procedures during the preparation of these raw materials for fermentation and high prices of enzyme preparations make it difficult to introduce second-generation biofuels into commercial production (Schwab et al., 2016).

Energy and economic aspects of maize bioethanol production

The energy values of bioethanol obtained per kilogram of maize vary between 7.87 and 9.47 MJ before purification to the degree of purity prescribed by fuel composition standards (minimum 99.5% ethanol). Refinement causes loss of about 17% of the initial fuel energy when the bioethanol yield is about 8.5% (w/w).

The profit made by selling one litre of bioethanol could be higher than from selling a kilogram of maize grain. Considering that the

production of one litre of bioethanol requires an average of 2.5 kg of maize grain, the calculation leads to the conclusion that production of bioethanol per hectare of arable land is more profitable than the production of mercantile maize. However, in the real case, it is not to be expected that all maize, intended primarily for human and animal consumption, will be used for biofuel production (Semenčenko, 2013).

Impact of COVID-19 pandemic on bioethanol production

Due to the reduction of economic activities since the appearance of COVID-19 virus in China at the end of 2019 and its rapid expansion around the world, the demand for crude oil has fallen sharply, which has led to a large drop in crude oil prices. At the same time, the average monthly price of bioethanol fell from \$ 1.32 per gallon in December 2019 to \$ 0.82 in March 2020. The decline in economic activity resulting from social distancing has negatively affected the gasoline demand, and thus for bioethanol. The current predictions are that bioethanol producers will either reduce production levels or, in some cases, simply close their plants. Since a large portion of maize produced in USA (about 38%) is used to obtain bioethanol (and DDGS), this situation is expected to cause a large drop in maize demand (Taheripour and Mintert, 2020).

Conclusion

The results presented in this paper highlight the importance of maize hybrids for bioethanol production worldwide. Apart from being used for food and feed, maize hybrids play an important role in the biofuel industry. By-products such as DDGS used for animal feed production also contribute to the significance of this raw material. Never the less, the production of a certain percentage of bioethanol from maize in Serbia could potentially be profitable, therefore, it would be recommendable to design the production in a way that an adequate measure can be found between the needs of the food and alternative fuel industries. However, the COVID-19 virus pandemic negatively affected the gasoline demand, and thus for bioethanol, which makes

the future of this alternative fuel production currently uncertain.

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ULOGA HIBRIDA KUKURUZA U AKTUELNIM TRENDOVIMA PROIZVODNJE BIOETANOLA

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Sažetak

Bioetanol je biogorivo koje se uglavnom koristi kao zamena za fosilna goriva širom sveta, a godišnja proizvodnja dostigla je gotovo 110 milijardi litara u 2019. godini. Trendovi proizvodnje ovog alternativnog goriva rastu, a kukuruz se smatra jednom od najboljih obnovljivih sirovina za proizvodnju bioetanolu zahvaljujući visokom sadržaju skroba u zrnu. Uzimajući u obzir da je Srbija jedan od najistaknutijih proizvođača kukuruza u Evropi, viškovi useva ove poljoprivredne kulture mogli bi se usmeriti ka proizvodnji bioetanolu. Iako u Srbiji ne postoji organizovana proizvodnja i potrošnja bioetanolu kao transportnog goriva, Vlada Republike Srbije nedavno je usvojila nekoliko novih uredbi u vezi sa stavljanjem u promet, obeležavanjem i potrošnjom biogoriva. Međutim, zbog smanjenja ekonomskih aktivnosti od početka pandemije virusa COVID-19 tokom 2020. godine, globalna potražnja za sirovom naftom naglo je opala, što je negativno uticalo na potražnju za benzinom, a time i za bioetanolom, zbog čega je budućnost proizvodnje ovog alternativnog goriva za sada u velikoj meri neizvesna.

Ključne reči: bioetanol, gorivo, kukuruz, životna sredina

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