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CHALLENGES IN BIOETHANOL PRODUCTION: UTILIZATION OF COTTON FABRICS AS A FEEDSTOCK

Article Highlights

- The characteristics of cotton fabric as a feedstock for bioethanol production are presented
- The state and perspective of bioethanol production from cotton-based materials in Serbia
- Different pretreatment methods of cotton-based materials are described
- Hydrolysis and fermentation of corona pretreated and mercerized cotton fabrics are investigated

Abstract

Bioethanol, as a clean and renewable fuel with its major environmental benefits, represents a promising biofuel today which is mostly used in combination with gasoline. It can be produced from different kinds of renewable feedstocks. Whereas the first generation of processes (saccharide-based) have been well documented and are largely applied, the second and third generation of bioethanol processes (cellulose- or algae-based) need further research and development since bioethanol yields are still too low to be economically viable. In this study, the possibilities of bioethanol production from cotton fabrics as valuable cellulosic raw material were investigated and presented. Potential lignocellulosic biomass for bioethanol production and their characteristics, especially cotton-based materials, were analyzed. Available lignocellulosic biomass, the production of textile and clothing and potential for sustainable bioethanol production in Serbia is presented. The progress possibilities are discussed in the domain of different pretreatment methods, optimization of enzymatic hydrolysis and different ethanol fermentation process modes.

Keywords: bioethanol, cotton, lignocelluloses, pretreatment, hydrolysis, fermentation.

Currently, the primary source of energy is still non-renewable fossil fuels and sources such as natural gas, oil and coal which have been used for the production of fuel, electricity and others goods [1]. The extreme consumption of fossil fuels has caused air pollution due to release of greenhouse gases (GHGs) during the last few decades (the main GHGs being CO₂, N₂O, CH₄, SF₆ and chlorofluorocarbons). Energy production and use (including fuels used by vehicles) represent the largest source of GHGs emis-

sions worldwide - about 71% of the total in 2010. Between 1990 and 2010, net emissions of CO₂ increased by 42%, which is particularly important because carbon dioxide accounts for about three fourths of total global emissions of GHGs [2]. The transportation sector accounts for more than 70% of global carbon monoxide (CO) emissions and 19% of global carbon dioxide (CO₂) emissions [3]. Today, both renewable as well as non-renewable energy sources are consumed and due to the overconsumption and exploitation of non-renewable energy resources, eventually, all petroleum reserves will be completely depleted. The increase in the price of petroleum in the long run, the finite nature of fossil fuels, increasing concerns regarding increased GHGs emissions, and health and safety considerations are for-

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cing the search for new renewable energy sources and alternative ways to power the motor vehicles. This has led to a major interest in expanding the use of bioenergy and a carbon neutral technology which is used to convert biomass into energy [4]. Biofuels as biomass-based fuels are referred to fuels for direct combustion for electricity production, but are generally used for liquid fuels for transportation sector [5]. Biofuels encompasses three major domains of sustainable development, *i.e.*, economic, environment and social [6]. Alternative renewable biofuels must be technically feasible, economically competitive, environmentally acceptable and readily available [7]. The possibilities of substituting non-renewable oil products with

different types of biofuels are presented in Figure 1.

Renewable liquid biofuels for transportation offer many advantages over petroleum-based fuels and have recently attracted much attention in different countries all over the world because of their renewability, sustainability, common availability, regional development, rural manufacturing jobs openings, reduction of GHGs emissions, and their biodegradability [9,10]. The major benefits, as well as disadvantages, of biofuels use are presented in Table 1 [11].

The development of genetically modified crops (GM crops) for biofuel production improves production efficiency. Plant biotechnology contributes to higher yielding biofuel crops with changed biomass compo-

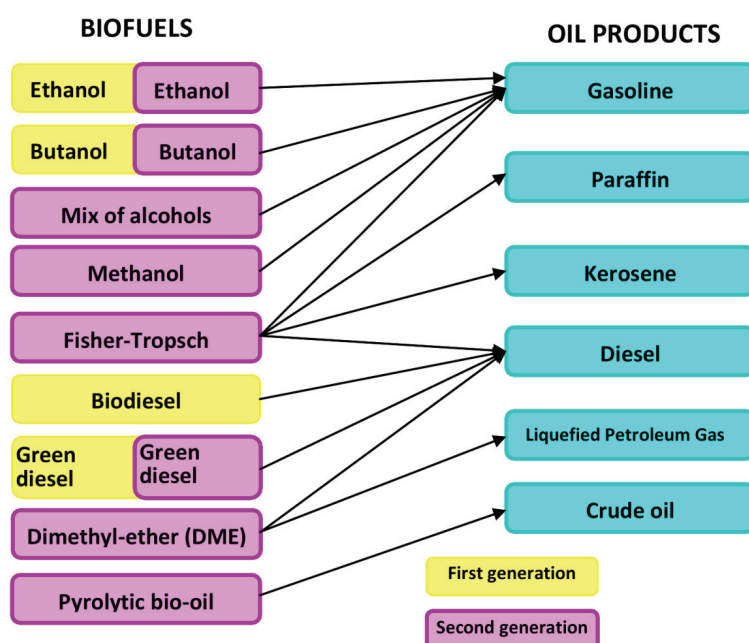


Figure 1. The possibilities of substitution of traditional fuels-oil derivatives with different types of biofuels (modified from [8]).

Table 1. Benefits and disadvantages of the use of biofuels [11]

Benefits:	<ul style="list-style-type: none"> • Decreased use and import of fossil fuels • Environmentally friendly (contain no sulfur compounds and aromatic hydrocarbons which can be detrimental to the environment) • Decreased emission of GHGs (during combustion generate less CO₂ and other GHGs compared to fossil fuels) • Biodegradable • High quality fuel (octane number > 105, cetane number > 55) • No changes are necessary on the existing distribution infrastructure or on existing engines • Contribute to sustainable development (renewable energy sources)
Disadvantages:	<ul style="list-style-type: none"> • Formation of monoculture / disappearance of biodiversity • Redevelopment of existing fields and forests for the purpose of planting crops that are used for biofuel production • Use of edible crops for mass-production of first-generation biofuels can have negative impact on the food industry and agriculture, <i>i.e.</i>, on the cost of food and its shortage • For biofuels such as bioethanol and biodiesel, the cost of production significantly depends on the type of raw material, and sometimes is greater than the price of fossil fuel production • Increasing the use of genetically modified plants^a • Contamination of soil and water caused by intensive cultivation of crops intended for biofuel production

^aThis disadvantage applies only to the European biofuels sector. Additional explanations are described in the text

sition and increased conversion efficiencies which allow production on a smaller land footprint minimizing competition with agriculture for food production and biodiversity conservation. Genetic modification improves the composition of biomass, such as the reduction in lignin content and modification of the carbohydrate components to maximize the glucose yield during biomass hydrolysis [12]. In the USA, one of the largest markets for both GM crops and biofuels, 73% of corn acreage (corn is a main feedstock for biofuel production in USA) was planted with GM seed in 2007 [13]. The GM crops have helped U.S. farmers to increase yields by 30% over the past 10 years, which should provide sufficient feedstock for the United States to meet its biofuels commitments, as set out in the Energy Independence and Security Act of 2007, which requires that biofuels account for 36 billion gallons of the US fuel supply by 2022 [14].

On the other hand, growing GM crops is prohibited by the European Union (EU), where 70% of people oppose them. This arises from two main reasons: that the foreign genes added to GM crops might escape into wild plants, and that food derived from GM crops could pose a health risk to consumers [15]. As a result, although the European Commission introduced a comprehensive regulatory regime for GM crops in 2003 (Directive 2003/30/EC), the vast majority of GM crops still have not received regulatory approval in Europe. In the EU, there is no specific need to grow GM crops for biofuels since EU member states should be able to meet the target set by the European Commission for biofuels to make up 10% of transport fuel by 2020 without GM crops. In the EU, however, not only are most GM crops not approved, but the produce from those crops, such as the grain from GM corn, are not allowed to be imported. In 2011, the EU decided to allow low levels of unapproved GM crops in animal feed. GM crops can be grown experimentally with approval from national regulators, or commercially if approved by the EU [13,15].

The global production of renewable energy has been increased rapidly, particularly after 2000. Total world production of biofuels was 127.7 billion L in 2014, which is for 10.4% more than in 2013 [16]. Large-scale production of biofuels offers an opportunity for certain developing countries to reduce their dependence on oil imports. In developed countries there is a growing trend towards employing modern technologies and efficient bioenergy conversions [17]. In EU-28 (28 Member States of EU) biofuel production is 18.6 billion L in 2014 [16]. Regulations influencing the EU biofuels market are the Biofuels Directive (2003/30), the EU Climate and Energy Pack-

age (2009/147) and the Fuel Quality Directive (2009/30). The Regulations include new “20/20/20” mandatory goals for 2020, one of which is a 20% share for renewable energy in the EU total energy mix. Part of this 20% share is a 10% minimum target for renewable energy consumed in transport (biofuels) to be achieved by all Member States [18].

Bioethanol, as a promising alternative bioenergy resource, is one of the dominating renewable biofuels in the transportation sector. Bioethanol is ethyl alcohol; its octane number of 108 is higher than gasoline. The octane number is a measure of the gasoline quality and the fuels with higher octane numbers are preferred in spark-ignition internal combustion engines ICEs. Disadvantages of bioethanol include its lower energy density than gasoline (but about 35% higher than that of methanol), its corrosiveness, low flame luminosity, lower vapor pressure (making cold starts difficult), miscibility with water, increase in exhaust emissions of acetaldehyde, and increase in vapor pressure (and evaporative emissions) when blending with gasoline [19-21]. Bioethanol can be blended with gasoline (E5, E10, E85) or used as neat alcohol in dedicated engines, taking advantage of the higher octane number and higher heat of vaporization, and also, it is an excellent fuel for future advanced flexi-fuel hybrid vehicles [22,23]. Bioethanol is most commonly blended with gasoline in concentrations of 10% bioethanol to 90% gasoline, known as E10. Bioethanol can be used as a 5% blend with gasoline under the European Union (EU) gasoline quality standard EN 228 [24]. This blend requires no engine modification and is covered by vehicle warranties. With engine modification, bioethanol can be used at higher levels, for example, E85 [25]. Bioethanol can also be used in the form of ETBE (ethyl tertiary butyl ether) as oxygenator to increase the octane number (in lower concentrations, up to 15%) and as a replacement for toxic MTBE (methyl tertiary butyl ether). Besides increasing the octane number, bioethanol and ETBE as oxygenate additives improve the thermal efficiency of the engine ignition and reduce the pollution of exhaust gases achieving better combustion in the engine [26,27]. The fact that the existing fossil fuel infrastructure, eventually with minor modifications, can be used for bioethanol distribution and utilization puts this biofuel in front of other energy alternatives. The key factor of bioethanol use is the net energy balance of biomass to bioethanol conversion. Studies have shown that corn-based bioethanol yields 20-30% more energy, typically fossil fuel energy, than is consumed in making it. On the other hand, sugarcane and cellulosic bioethanol yield

renewable energy is nine times worth the fossil energy used to produce them [28].

The production of bioethanol is increasing over the years, and has reached the level of 93 billion L during the year 2014 [29]. An increase in bioethanol production up to more than 125 billion L until 2020 has been predicted assuming the production support by governmental policies and exemptions [30]. Brazil and the USA are the two major bioethanol producing countries with 26.72 and 56.72% of the world production, respectively [31]. The EU occupies the third position with 6% of total production, which amounted to 5.47 billion L in 2014. However, although the amount of biofuels produced in the EU is growing; the quantities in general remain small compared to the total volume of mineral-based transport fuel sold. Other major ethanol producers are also China, Canada, Thailand, Argentina and India [32].

The industrial production of bioethanol mainly depends on sucrose from sugarcane in Brazil and starch, mainly from corn, in USA. Presently, bioethanol production depending upon starch and sugar substances may not be popular due to their food and feed purposes. There are several criteria for choosing crops as raw materials for bioethanol production: price and yield of raw material, bioethanol yield, starch content, pest and diseases resistance, suitability for soil and weather conditions, harvesting transportation and storage options as well as the usability of byproducts [33]. The availability of feedstocks for bioethanol production can vary considerably from season to season and depends on geographic locations [34]. However, feedstocks for bioethanol production must be sustainable and must not threaten biodiversity or food security [35]. Even though bioethanol production for decades mainly depended on energy crops containing starch and sugar (corn, sugar cane, etc.), new technologies for converting lignocellulosic biomass into bioethanol are being developed. Kim and Dale [36] reported that 442 billion L of bioethanol can be produced from lignocellulosic biomass and that total crop residues and wasted crops can produce 491 billion liters of bioethanol per year, about 16 times higher than the actual world bioethanol production. The cellulosic materials are renewable, low cost and are available in large quantities. They include crop residues, grasses, sawdust, woodchips, agro-waste etc. One major problem with bioethanol production is the availability of raw materials for the production. Since bioethanol is being produced in steadily growing volumes it is necessary to consider its production from renewable raw materials that are not currently used. However,

such a transfer requires development of new production processes that are economically feasible.

Cotton is one of the sources of agro-industrial residues that can be utilized to produce fuels and chemicals [37]. In 2014, the total world production of refined cotton fibers was 25.9 million t, with Brazil and India, the largest world producers, contributing with 1.5 and 6.7 million t, respectively [38]. Disposal cotton fabrics left after cutting and sewing in textile industry, and residues from cotton processing (cotton gin dust - CGD and cotton gin waste - CGW) can be used for bioethanol production. The major advantages of these cotton materials compared to other lignocellulosic biomass are their high cellulose content (88-96%) and the absence of lignin or hemicelluloses. However, the supporting evidence for the application of cotton fibers and residues for bioethanol production is relatively scarce in comparison to other lignocellulosic agricultural residues such as corn stover, sugarcane bagasse and wheat straw [39].

For conversion of cotton materials to cellulosic ethanol, an adequate pretreatment method is needed for separation of free cellulose from raw material and for increase of accessibility of cellulose to enzymatic hydrolysis. Besides being considered as a crucial step in the biological conversion to bioethanol, the pretreatment represents one of the main economic costs in the process [40]. The second process of enzyme hydrolysis is performed by cellulase, a biocatalyst for conversion of cellulose to glucose. Common cellulases used to perform this process include fungi such as: *Fusarium solani*, *Clostridium thermocellum*, *Trichoderma reesei* and *Trichoderma viride* [41]. The sugars obtained by prior enzymatic hydrolysis are transformed into ethanol by process of fermentation. The bioethanol fermentation is performed by microorganisms, traditionally by yeasts (*Saccharomyces* strains), although some types of engineered bacteria such as *Zymomonas mobilis*, *Escherichia coli* or *Klebsiella oxytoca* [42,43] could also be used. After the fermentation, the bioethanol is separated from the fermentation broth, conventionally by means of distillation and rectification or by using more efficient separation technologies such as pervaporation, membrane filtration or molecular sieves [44,45]. The current world bioethanol research is driven by the need to reduce the costs of production. Improvement in feedstock selection and pretreatment, application of adequate process mode, shortening of fermentation time, lowering the enzyme dosages, improving the overall cellulose hydrolysis could be the basis of cutting down the production costs.

The main aim of this review is to present a brief overview of the available and accessible technologies for bioethanol production using cotton fabrics as cellulosic raw materials.

Lignocellulosic materials as potential feedstocks for bioethanol production

The various types of biomass feedstocks potentially available for biofuels production can be categorized as following: dedicated crops (sugar crops, starch crops, oil crops, lignocellulosic crops, algae and aquatic biomass) and wastes and residues (oil-based residues, lignocellulosic residues, organic residues and others, and waste gases). Based on the feedstock used in production, biofuels may be: a) conventional (first-generation) biofuels and b) advanced (second-generation and third-generation) biofuels that are produced from feedstock that “do not compete directly with food and feed crops, such as wastes and agricultural residues (*i.e.*, wheat straw, municipal waste), non-food crops and algae” (defined by the European Commission) [46]. Conventional (first-generation) biofuels include sugar- and starch-based ethanol, oil-crop based biodiesel and straight vegetable oil, as well as biogas derived through anaerobic digestion. Typical feedstocks used in these processes include sugarcane and sugar beet, starch-bearing grains like corn and wheat, oil crops, animal fats and used cooking oils. Conventional biofuel technologies include well-established processes that are already producing biofuels on a commercial scale. Advanced biofuel technologies are conversion technologies which are in the research and development, pilot or demonstration phase, and some in commercial phase. This category includes hydrotreated vegetable oil (HVO), which is based on animal fat and plant oil, as well as biofuels based on lignocellulosic biomass, such as ethanol, Fischer-Tropsch liquids and synthetic natural gas (SNG), and algae-based biofuels [46,47]. Globally, projects such as the “Landscape Biomass Project”, Iowa State University, look at how to balance needs for food, feed, fuel and energy, by integrating advanced biofuels technologies and novel energy crops [48].

For any proposed use of biomass, a Life Cycle Analysis (LCA) needs to be applied taking into account the total cost and energy balance from the source of the feedstock to its end use. The overall economic, environmental and energy costs of collection, handling, processing and transport need to be assessed. On the other hand, a certain proportion of biomass (straw, stalks, fallen wood, etc.) has to be left in situ to maintain forest or field ecology, and to

maintain the condition of the soil, prevent erosion, provide habitat, and to promote biodiversity. In many potentially productive areas, preserving biodiversity may offer greater environmental and economic benefit than clearing forest to produce energy crops [47,49].

Previously, several studies have been conducted at the European and global level in order to assess the potentials of different biomass resources for production of biofuels. In the EEA (European Environment Agency) study “How much bioenergy can Europe produce without harming the environment?” it is estimated that the total bioenergy potential from agriculture, forestry and waste will be almost 300 Mtoe in 2030 [50]. Of this, 142 Mtoe will come from agriculture only which is obtained from 19 million ha of agricultural land. This is equivalent to 12% of the utilized agricultural area in 2030. But, the study of VIEWLS project (“Clear Views on Clean Fuels” project supported by the European Commission NNE5-2001-00619) in 2004 comes with a much higher estimate of 35–44 million ha of land available for biomass production only in EU-10 [51]. In other study [52] the authors state that if all waste and residues were converted only to biofuels in the EU, 16% of road transport fuel could be provided in 2030 (technical potential of sustainably available feedstock from waste).

Bioethanol can be produced from different kinds of raw materials, which are classified into three categories according to their chemical composition: sucrose-containing feedstocks (*e.g.*, sugar cane, sugar beet, sweet sorghum and fruits), starch materials (*e.g.*, corn, wheat, rice, potatoes, cassava, sweet potatoes and barley) and lignocellulosic materials (*e.g.*, wood, straw and grasses). Currently, because of the above-mentioned problems concerning feedstocks, there is a growing interest worldwide to find out new, abundant and economically more favorable feedstocks. However, crops such as corn, wheat and sugar cane are still dominant at the industrial level [52,54].

The productivity, energy input, and costs, as well as environmental impact vary for different feedstocks [55]. Lignocellulosic materials serve as a cheap and abundant feedstock, from which bioethanol can be produced at reasonable costs. Chemical composition of lignocellulosic materials is a key factor affecting efficiency of bioethanol production. Lignocelluloses consist mainly of cellulose, hemicellulose and lignin which build up about 90% of dry matter in lignocelluloses, with the rest consisting of mostly extractives and ash. While cellulose and hemicellulose are macromolecules constructed from different sugars, lignin is an aromatic polymer synthesized from phenylpropanoid precursors. Hemicellulose is

composed of various 5- and 6-carbon sugars such as arabinose, galactose, glucose, mannose and xylose. Lignin is composed of three major phenolic components: *p*-coumaryl alcohol (H), coniferyl alcohol (G) and sinapyl alcohol (S), Figure 2. The chemical composition of various types of lignocellulosic biomass materials that can be used as feedstock for bioethanol production is given in Table 2 [6,56,57]. The proportion of these wood constituents varies between species, and there are distinct differences between hardwoods and softwoods, as presented in Table 2. Bioethanol yield is directly related to cellulose, hemi-

cellulose, and individual sugar concentrations in the feedstock, while the lignin cannot be used for bioethanol production [6]. Therefore, only these components of lignocellulosic materials are presented in Table 2. Some cellulosic materials, such as citrus peel, are relatively easy to breakdown into substrates for bioethanol production. For more complex cellulosic materials containing greater amounts of lignin (*e.g.*, hardwood) the production route to liquid biofuels requires pretreatment and may be more challenging and costly.

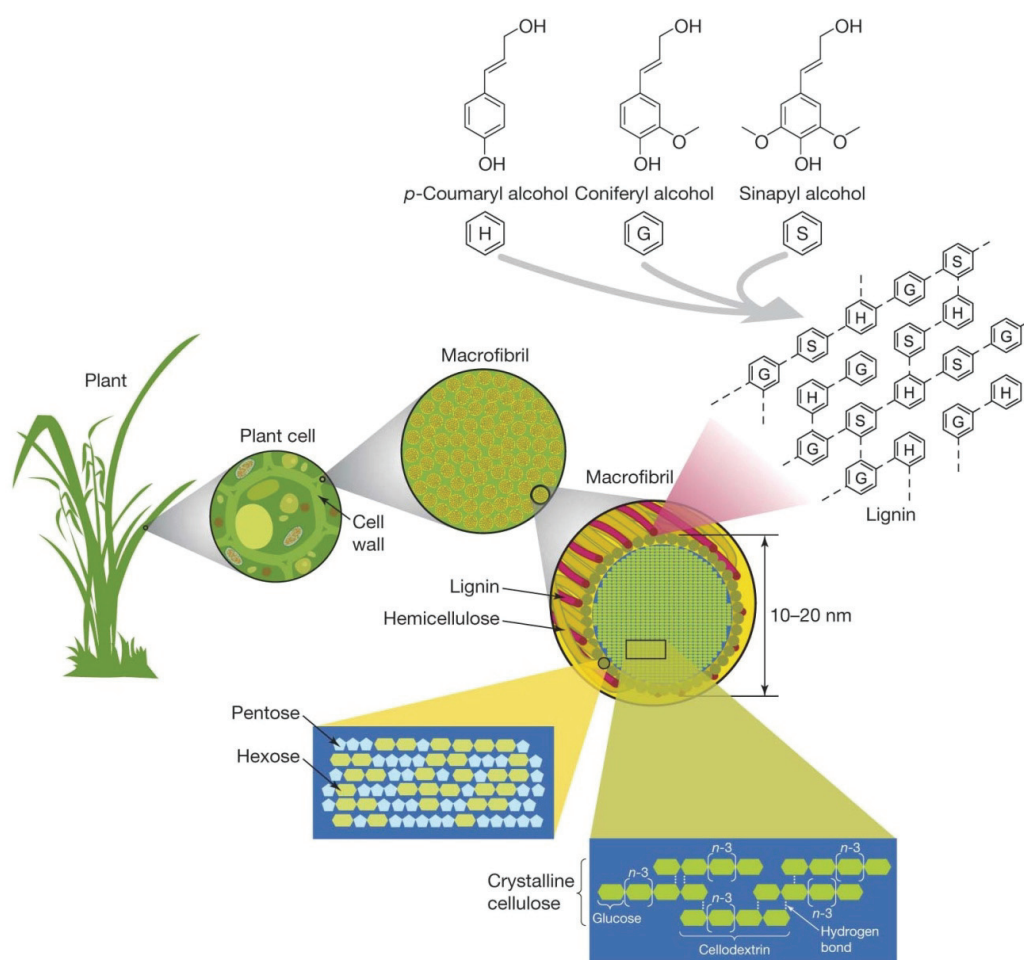


Figure 2. The structure of lignocellulosic biomass and supramolecular structure of cellulose. Adapted from [61] with permission from Nature Publishing Group.

Table 2. The composition of various types of lignocellulosic biomass materials (% of dry weight) [6,56,57]

Material	Cellulose	Hemicelluloses	Lignin
Softwood	40-50	25-30	25-35
Hardwood	40-50	25-35	20-25
Cotton seed hairs	80-85	5-20	-
Cottonseed hulls	62.1	-	20.9
Flax	92	2	4
Algae (green)	20-40	20-50	-

Table 2. Continued

Material	Cellulose	Hemicelluloses	Lignin
Grasses	25-40	25-50	10-30
Cornstalks	39-47	26-31	3-5
Corn stover	31	43	13
Wheat straw	37-41	27-32	13-15
Cereal straw	35-40	26	15-20
Rice straw	32.6	27.3	18.4
Chemical pulps	60-80	20-30	2-10
Jatropha waste	56.3	17.5	23.9
Paper	85-99	-	0-15
Switch grass	31-35	24-28	17-23

As shown in Table 2, the major advantage of the cotton fibers and cotton residues compared to other lignocellulosic materials is their high cellulose content and absence of lignin. Hence, these renewable feedstocks have been investigated for the production of bioenergy by fermentation of cellulose to ethanol or by pyrolysis, gasification, anaerobic fermentation and catalytic conversion to value-added chemicals instead of its disposal by incineration or landfilling [37].

Cotton fibers are the seed hairs of the plant of genus *Gossypium*. Raw cotton, after ginning and mechanical cleaning, is composed of approximately 96% cellulose. The noncellulosic constituents include proteins, amino acids, other nitrogen-containing compounds, wax, pectin materials, organic acids, sugars, inorganic salts and very small amount of pigments. The amounts of these constituents depend on fiber maturity, variety of cotton and environmental conditions (soil, climate, farming practices, etc.) [58]. Purification of cotton is performed by a combination of mechanical sorting steps and scouring (mild alkali treatment at elevated temperature) and followed by a bleaching process. By these methods, the cellulose content in cotton can reach 99-100% [59].

Cotton is the main supply of natural fibers for textile industries. Used clothes and surplus of textile industries (after sewing and cutting) usually end in waste collection stations. Therefore, they represent a potential and promising feedstock for bioethanol production since they are cheap waste materials, rich in cellulose, that are usually landfilled or incinerated if not used in other purposes [58]. Cotton with annual production of more than 25 million t per year stands for about 1/3 of the global market of textile fibers [38]. Innumerable products are made from cotton. From lint (the fiber separated from the seed) come the major products, chiefly textile and yarn goods, cordage, automobile-tire cord, and plastic reinforcing. Cotton hulls are used for fertilizer, fuel, and packing; fiber

from the stalk is used for pressed paper and cardboard [60].

In order to process the cotton materials to bioethanol by adequate pretreatments and hydrolysis and fermentation processes, it is necessary to know the complex structure of lignocellulosic biomass and supramolecular structure of cellulose, which are presented in Figure 2. Cellulose, the most abundant constituent of the plant cell wall, is a homo-polysaccharide composed entirely of D-glucose linked together by β -1,4-glucosidic bonds and with a degree of polymerization of up to 10,000 or higher. The linear structure of the cellulose chain enables the formation of both intra- and intermolecular hydrogen bonds resulting in the aggregation of chains into elementary crystalline microfibrils (2-20 nm in diameter) of 36 cellulose chains. Cellulose, hemicellulose and lignin form structures called microfibrils, which are organized into macrofibrils [61].

Available biomass and potential for sustainable bioethanol production in Serbia

To achieve the target proposed in the European Directive 2009/28/EC, EU members must implement various political, fiscal and technical measures and incentives. Each EU Member State should adopt a national renewable energy action plan setting out its national targets for the share of energy from renewable sources consumed in transport, electricity, heating and cooling in 2020 [62]. Serbia and other Balkan countries, which are interested in joining the EU, have accepted the obligation to follow EU policies and programs, including those that oblige them to introduce the production and use of fuels from renewable energy sources. Better coordination between institutions and academic and private sector is a very important step in order to realize cost-effective bioethanol production in Serbia. The Kyoto Protocol (adopted in Kyoto, Japan, on December 11, 1997) is an inter-

national agreement linked to the United Nations Framework Convention on Climate Change, which commits its Parties to reduce greenhouse gases emissions by setting internationally binding emission reduction targets, and in that way to fight against global warming [63]. By implementation of the Kyoto Protocol, Serbia sends to international community and the EU a clear signal of readiness to implement the concept of sustainable development and monitor of global socio-economic trends, which will improve the investment climate and increase the confidence of potential foreign investors.

However, bioethanol production in Serbia is now at a low level, even lower than the production scale at the very end of twentieth century, and it is not enough to fulfil the country's ethanol needs just for beverages, medical and pharmaceutical purposes. This is the main reason why in Serbia there is still not an organized production and utilization of bioethanol or other biofuels for gasoline substitution. Our recent analysis revealed that Serbia will need to build new bioethanol plants in order to produce enough bioethanol for use as a fuel and thus to follow the aims of the European directive 2009/28/EC. Based on the given replacement of 20% of gasoline by bioethanol by 2020 according to European directive 2009/28/EC, it has been reported [64] that it will be needed to produce 233,000 t of bioethanol until 2026. If it is assumed that the needs of the ethanol industry and pharmacy stay the same (52,000 t), total demand for bioethanol would be 285,000 t, which is 12 times the installed capacity in Serbia. It is now clear that in Serbia, it is necessary to introduce new plants for the bioethanol production - large capacity plants that besides bioethanol include the production of animal feed and carbon dioxide; or introduce a network of small plants for the production of raw bioethanol (65–70 vol.%) which would be further separated from mash using different techniques within the petroleum industry.

Annual biomass energy potential in Serbia is around 3.2 Mtoe (about 134,000 TJ). Of these, about 1.7 Mtoe (about 71,000 TJ) comes from agricultural biomass, while the energy potential of biomass from forestry and wood industries approximately 1.5 Mtoe (about 63,000 TJ) [65]. Serbia, especially province Vojvodina, is very suitable for the production of bioethanol for the following reasons: high-quality soil; excellent raw materials for bioethanol production and the possibility of production of alternative raw materials (such as grain sorghum, corn and sorghum, Jerusalem artichokes); a tradition in the production of alcohol; a tradition in the production of seed varieties and hybrids, an existing professional staff, etc.

Today in Serbia, the bioethanol production is performed in seven plants ("Panon" - new and old plant in Crvenka; "Kadaks" in Crvenka; "Vrenje" in Belgrade; "Lukas" in Bajmok; "Reahem" in Srbobran and "Alpis-SLC" in Kovin) with total production capacity of 23,225 t/year. Raw materials used in these plants are molasses and cereals. In these plants, 96% vol. bioethanol is produced, which is used mainly for alcoholic drinks and for medical and pharmaceutical purposes. The bioethanol production in Serbia was 6.32 million L in 2014, which is only around 22% of annual production capacity in Serbia. This indicates that the capacity utilization of bioethanol plants is rather small. The biggest bioethanol production of 19.17 million L was achieved in 2007 [65,66]. It is important to point out that despite current low level of industrial production of bioethanol, Serbia has the main prerequisites to develop and improve this production since it possesses a large feedstock potential, tradition and also educated human potential.

In Serbia, conventional energy crops such as starch-based raw materials are the most suitable and available agricultural raw material which can be used for industrial bioethanol production. However, a growing demand for the corn and wheat on global market are currently increasing their price and make these feedstocks less appropriate. For these reasons, cheaper substrates such as waste cotton materials, damaged crops, triticale, etc. could be used for bioethanol production [26,67].

The textile industry in Serbia represents a good base for different waste cotton materials that can be used as feedstocks. The production of textiles and clothing in Serbia during the period 2010–2014 is presented in Figure 3. The data in Figure 3 are expressed as index on industrial production, which shows the change in the volume of industrial production in the relevant year compared to the previous year on a given territory. The methodology and statistical terminology is consistent with the standards of International Energy Agency and Eurostat [65]. In 2014, the production of cotton yarn was 516 t, the production of fabrics from cotton yarn was 2,176,000 m², the production of finished textile goods (except clothes) was 2,657,000 m², the production of other technical and industrial textiles was 862 t, and the production of clothing was 22,890,000 pieces. In 2014, the overall export of textile industry of Serbia was 852.9 million dollars. The largest markets for Serbian goods are the Italian, Russian and German markets. Also in 2014, import was recorded in the amount of 1 billion dollars from the markets of China, Italy, Turkey, Bangladesh,

India and Hungary. The coverage of imports by exports was 82% [65].

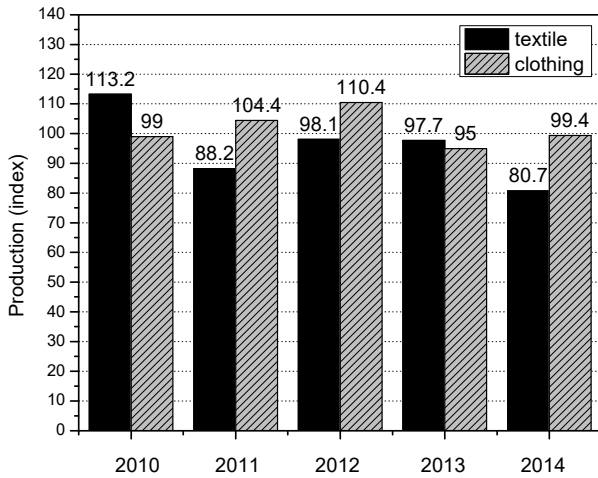


Figure 3. The production of textiles and clothing in Serbia during the period 2010-2014.

The pretreatments of cotton fabrics

Figure 4 shows the flow chart for the production of bioethanol from lignocellulosic biomass materials (modified from [68]). The basic process steps in producing bioethanol from lignocellulosic materials are: pretreatment, hydrolysis, fermentation and product separation/distillation.

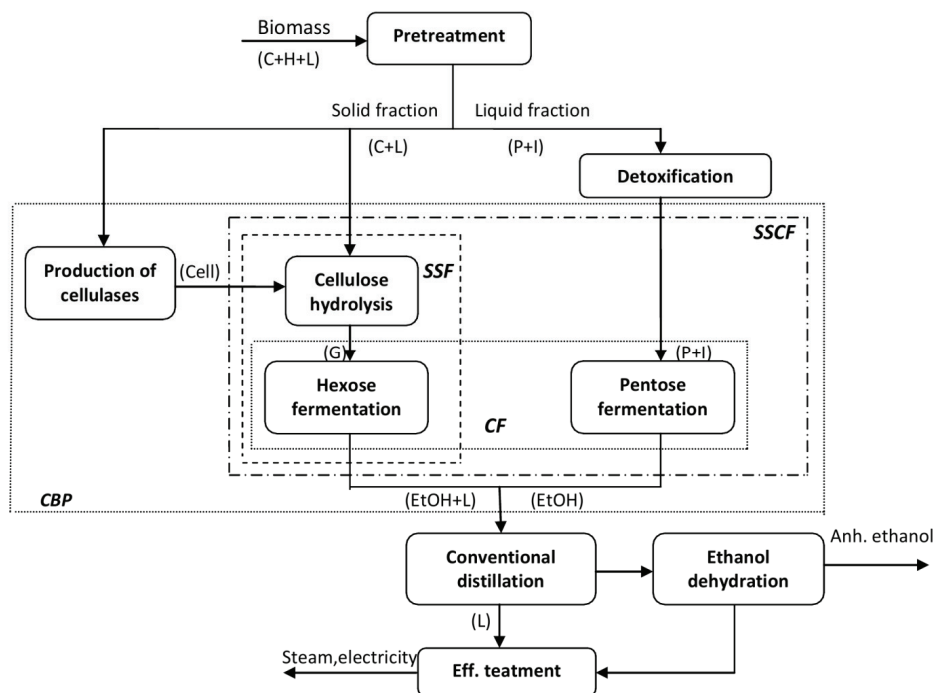


Figure 4. Generic block diagram of bioethanol production from lignocellulosic biomass. Possibilities for reaction-reaction integration are shown inside the shaded boxes: CF - co-fermentation; SSF - simultaneous saccharification and fermentation; SSFC - simultaneous saccharification and co-fermentation, CBP - consolidated bio-processing. Main stream components are: C - cellulose; H - hemicellulose; L - lignin; G - glucose; P - pentose; I - inhibitors; EtOH - ethanol, Cell - cellulase (modified from [68]).

In order to efficiently hydrolyze cellulose to fermentable monomeric sugars, an adequate pretreatment is necessary. The pretreatment changes the chemical, physical and morphological characteristics of cellulose and makes the material more accessible for the action of saccharifying enzymes. Therefore, the pretreatment includes different methods of modification, such as: physical (*e.g.*, milling, grinding), chemical (*e.g.*, alkali, dilute acid), thermal (*e.g.*, steam treatment) and biological methods (*e.g.*, wood degrading fungi), or a combination of the above. The general idea of pretreatment is to increase surface area and enzyme accessibility through changes in porosity and particle size, and to a lesser degree decrease the cellulose crystallinity. Besides being considered as a crucial step in the bioethanol production, biomass pretreatment as an energy-intensive process step represents one of the main economic costs in the process [69,70].

Over the years a number of different technologies have been developed for pretreatment of lignocelluloses, but no single technology has proven ideal or superior for all substrates. The optimal pretreatment technology should have a number of features. The digestibility and recovery of cellulose and hemicellulose should be high and at the same time, no or little lignin and hemicellulose-derived inhibitors

should be generated. Also, water, chemical and energy usage should be minimized and the method must be scalable to industrial size. In reality, it is difficult to fully accomplish all the above mentioned issues in any process. However, the last two points are important for economical and practical viability of a given industrial process [69]. A pretreatment of lignocelluloses is therefore necessary to disrupt or remove lignin from such substrates, and then increase accessibility of cellulose, but such pretreatment would increase costs, and complicate the process. Moreover, some of the delignification methods have influenced the biocompatibility of the process. As an advantage, cotton fibers due to lack of lignin in their cellulosic structure won't face with such problems,

and thus are suitable substrates for bioethanol production.

The following section is therefore focused only on cotton-based materials. Different pretreatment methods of cotton-based materials with optimal conditions and the obtained results are presented in Table 3. As shown in Table 3, the results highly depend on the material used. The chosen optimal pretreatment method should provide adequate cellulose degradation, the acceleration of hydrolysis, the enhanced release of fermentable sugars and thus high glucose yield after hydrolysis, but should also be economical and environmentally justified. In order to fully realize the potential benefits of chosen pretreatment it is necessary to scale up system designs to large batch or continuous processes.

Table 3. Types and conditions of pretreatments of cotton-based materials utilized in the production of bioethanol by various authors

Type	Conditions	Raw material	Obtained results and optimal conditions	Ref.
Alkali pretreatment	0-20% NaOH; 3h; 0,23 and 100 °C	Cotton-based waste textile	>85% glucose yield; 90% ethanol yield; 12% NaOH, 0 °C, 24h	[71]
	12% NaOH; 3h; room T	Cotton waste fibers	75.1% hydrolysis yield	[72]
	0-5% NaOH; 30 min; 121 °C	Cotton gin waste	80 mg/ml sugars	[71]
	2% NaOH; 1h; 121 °C	Cotton stalks	46% ethanol yield	[73]
	4% NaOH; 250 °C, high pressure 100 bar; 50-1450 pm	Cotton stalks	Hydrolysis efficiency 96%; 53% efficiency based on glucose; 180 °C; 45 min 100 rpm	[74]
Acid pretreatment	0.5,1 and 2% NaOH; 30, 60 and 90 min; 90 and 121 °C; 15 psi; 10% solids	Cotton stalks	65.63% cellulose conversion; 2% NaOH, 90 min, 121 °C; 15 psi	[75]
	Concentrated phosphoric acid 83~85.9%; 50 °C; 90 rpm	Cotton-based waste textile	63.4% glucose yield	[71]
	Diluted sulphuric acid 0-5%; 30 min; 121 °C	Cotton gin waste	110 mg/ml sugars	[76]
Other chemical pretreatments	Diluted sulphuric acid 0-2%, 4-20 min; 160-220 °C	Cotton gin waste	Hydrolysis yield 89%; 0.8% H ₂ SO ₄ ; 180 °C; 12 min	[39]
	73, 79 and 85% of N-methyl-morpholine-N-oxide (NMO); 90 and 120 °C; 0.5-15 h	Cotton linter	100% hydrolysis yield; 85% NMO; 120 °C; 2.5h	[77]
	0.5,1 and 2% H ₂ O ₂ ; 30, 60 and 90 min; 90 and 121 °C; 15 psi; 10% solids	Cotton stalks	Cellulose conversion 49.8%, 2%; 121 °C, 30 min	[75]
Ionic liquid pretreatment	Fenton reagent- FeSO ₄ ·7H ₂ O (0.25-1.25 mM) + H ₂ O ₂ (0.5-2.5 vol%); 40 °C; 24-120 h; pH 4.2	Cotton linter	0.5 mM Fe ²⁺ ; 2 vol% H ₂ O ₂ ; 48 h	[78]
	1-ethyl-3-methylimidazolium acetate; 30 min; 150 °C; 150 rpm	Cotton stalks	Cotton stalks conversion 82-85%; ethanol yield 74%	[73]
Ultrasound pretreatment	Dual frequency ultrasonic reactor (16 kHz and 20 kHz); 60 min	Cotton fabrics	Improvement of cellulose enzymes 35%	[79]
	Hielscher Ultrasonic Processors, 30 kHz; 10% solids	Cotton gin waste	Cellulose conversion 23%; ethanol yield 31.6% (in combination with autoclave and laccase enzymes Prima-Green® 30°C, 96 h, 150 rpm pH 6)	[80]
Microwave pretreatment	Microwave power 30-300 W; 25-170 °C; 10-60 min	Waste cotton	Hydrolysis efficiency 63%, ethanol conc 2.5 g/L; 110 °C; 195 W; 10 min	[81]

Table 3. Continued

Type	Conditions	Raw material	Obtained results and optimal conditions	Ref.
Radiation	γ -Ray irradiation in 3000 Ci ^{60}Co irradiator IGS-3, dose range 10^3 - 10^6 Gy	Commercial cotton wool and natural cotton fibers	33% glucose yield	[82]
Liquid hot water pretreatment	Autoclave - 121 °C, 1.5 atm, 1h	Pure cotton	Glucose content 2.20%, 39.00 mass%	[83]
Corona pretreatment	Atmospheric pressure 900 W	Cotton fabric	Glucose conc., 11.98 g/L; glucose yield, 0.35 g g ⁻¹ ; theoretical glucose yield of 33.70%	This study

The authors of this paper have studied the utilization of cotton fabrics for bioethanol production. The research has been conducted through TR 31017 project supported by the Serbian Ministry of Education, Science and Technological Development. The research encompassed the most of the relevant parameters and progress trends of this paper such as: a) investigation of two different cotton materials: mercerized cotton and cotton fabric, b) the choice of adequate pretreatment and optimization of the pretreatment, c) optimization of enzymatic hydrolysis and fermentation steps, etc. Different pretreatment methods of two mentioned cotton materials were investigated. The highest glucose yield of 0.35 g/g after enzymatic hydrolysis with enzyme cellulase (Celluclast[®] 1.5L) was obtained with corona pretreated mercerized cotton (Table 3). Some investigated pretreatments (ultrasound; autoclave; air, oxygen and argon plasma pretreatment) did not affect glucose concentration and yield (data not shown).

Enzymatic hydrolysis and ethanol fermentation of cotton-based materials

The hydrolysis of cellulose and hemicellulose can be carried out chemically (*e.g.*, by dilute sulfuric acid) and enzymatically by cellulolytic enzymes. This study considers only enzymatic processes. The enzymatic hydrolysis is generally accomplished by synergistic action of at least three major classes of enzymes: endo-glucanases, exo-glucanases and β -glucosidase which are usually called together cellulase or cellulolytic enzymes. These enzymes act in synergy for attacking the crystalline structure of the cellulose, removing cellobiose from the free chain-ends and hydrolyzing cellobiose to produce glucose. Cellulases are produced by fungi, mainly *T. reesei*, besides *Aspergillus*, *Schizophyllum* and *Penicillium* [41]. The enzymatic hydrolysis is usually performed under mild conditions: pH 4.5-5 and temperature 40-50 °C [84].

Due to the complexity of the cellulose substrate and the cellulase enzyme system, the mechanism of hydrolysis of cellulose is still not fully understood,

although detailed knowledge of some aspects of enzyme structure, enzyme molecular properties and the supramolecular structure of cellulose have been obtained through extensive study during the last few decades. One of the possibilities to get better insight into the biodegradation process and to present the changes in the morphology of cotton fibers affected by biodegradation is to analyze the materials by scanning electron microscopy (SEM) [85]. Enzymatic hydrolysis is influenced by both substrate- and enzyme-related factors. The substrate-related factors are: crystallinity, degree of polymerization, accessible surface area for cellulase, ratio between particle size and specific surface area and lignin distribution (lignin is not present in cotton). The enzyme-related factors are: features of enzymes from different microbes, synergism of two or more enzymes and adsorption of the enzymes [84]. Additional problems during hydrolysis occur due to substrate- or enzyme-inhibition which effect on the hydrolysis rate. In addition, during fermentation the microorganism-enzyme interaction affects the growth kinetics of the cells and their ethanol productivity, as well as potential inhibitory effects of hydrolysis products (cellobiose, glucose) and metabolites (ethanol) on enzyme and microbial activity [76].

The authors of this paper have recently studied the possibilities of enzymatic hydrolysis of bleached cotton fabric (weight: 130 g/m²) by cellulase Celluclast[®] 1.5L (Novozymes, Denmark). The enzymatic hydrolysis was carried out at 50 °C and pH 5.0 for 8 days in flasks in thermostated water bath with shaking (100 rpm). Three different initial cellulose contents (19.2, 32 and 64 g of cellulose/L of solution) were investigated. The enzyme concentration was constant at 6 ml/L, which corresponded to cellulase concentration of 18% (in cotton fabric). The results of the obtained glucose concentrations are presented in Figure 5.

As shown in Figure 5, the maximum glucose concentration of 6.17 g/L and percentage of theoretical glucose yield of 17% were achieved during hydrolysis with cellulose content of 32 g of cellulose/L of

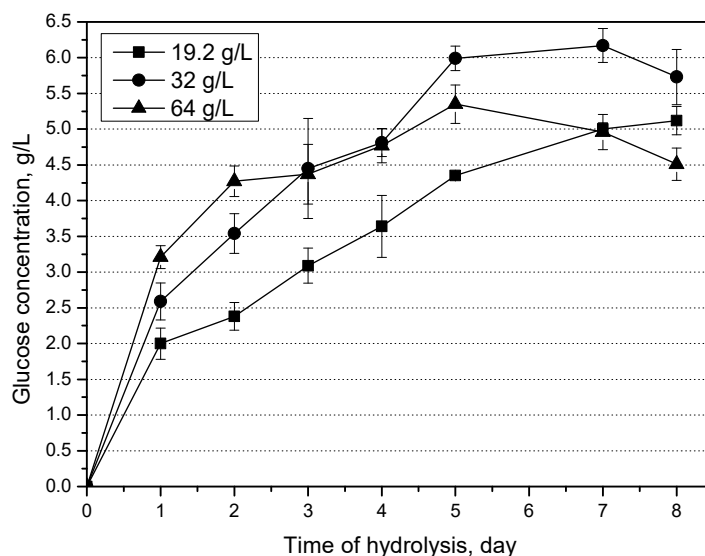


Figure 5. The glucose concentration during enzymatic hydrolysis of cotton fabrics with various cellulose contents at a constant enzyme concentration. Process conditions: 50 °C, pH 5.0, 100 rpm, 6 mL/L of Celluclast® 1.5L.

solution at 7th day of hydrolysis. During hydrolysis with cellulose content of 32 and 64 g/L, a product inhibition was noticed after 7 days of hydrolysis due to enzyme inhibition by glucose accumulation. The glucose concentrations obtained during the hydrolysis with cellulose content of 64 g/L after 3 days were much lower compared to results achieved during hydrolysis with cellulose content of 32 g/L, probably due to the substrate inhibition.

The initial substrate content had a pronounced effect on both the cellulose hydrolysis and later the ethanol fermentation. Regarding the glucose concentration, lower substrate contents are more suitable since substrate inhibition could be thus avoided. Also, one of the problems in enzymatic hydrolysis, are released sugars that can also inhibit hydrolysis reaction and cause product inhibition [84]. Accumulation of glucose during hydrolysis can significantly lower the rate of cellulose hydrolysis through inhibition by blocking the active site or preventing the hydrolyzed substrate from leaving. Compounds other than glucose, potentially present in biomass, also can be inhibitory and influence the activity of beta-glucosidases, including (but not exclusively) other simple sugars, sugar derivatives, amines, and phenols. Taking into account possible substrate and product inhibition as well as the time of hydrolysis which can significantly reduce production costs and make beneficial energy savings, an initial substrate content of 32 g of cellulose/L of solution and 5 days of hydrolysis were chosen as optimal hydrolysis parameters.

Hong *et al.* [86] reported results of enzymatic hydrolysis of cotton similar to ours. They obtained glu-

cose yield of 12.1% after 24 h of hydrolysis with cellulase concentration of 3.3 U/mL and substrate concentration of 50 g/L. Also, Jeahanipour *et al.* [77] reported that enzymatic hydrolysis of the untreated cotton fibers resulted in a rather low theoretical glucose yield of 11% after 24 h of hydrolysis.

One of the methods used to overcome the problem with product inhibition is SSF (simultaneous saccharification and fermentation) in which fermentation and enzymatic hydrolysis are performed simultaneously in the same reactor and the released sugars are directly consumed by fermenting microorganism [68,87]. The fermentation of the xylose released from the pre-hydrolysis process can be carried out in a separate vessel or in the SSF reactor using a genetically modified strain from the bacterium *Z. mobilis* that can convert both glucose and xylose. The latter method is named simultaneous saccharification and cofermentation (SSCF). Both SSF and SSCF processes are presented in Figure 4 [68]. Compared to the separate hydrolysis and fermentation process (SHF), both SSF and SSCF exhibit several advantages like lower requirement of enzyme, shorter process time and cost reduction due to economy in fermentation reactors (only one reactor compared to the multiple sets). Disadvantages include the difference between optimal temperatures for saccharification (50–60 °C) and fermentation (30 °C), inhibition of enzymes and yeast by ethanol and the insufficient robustness of the yeast in co-fermenting C5 and C6 sugars [87].

The authors of this paper also investigated ethanol fermentation from the cotton hydrolyzates by

yeast *S. cerevisiae* var. *ellipsoideus* under anaerobic conditions (pH 5.0; 30 °C; mixing rate 100 rpm) for 30 h. In our previous study [88] we reported that an inoculum concentration of 5 vol.% (which corresponds to initial viable cell number of $\sim 1.5 \times 10^6$ CFU/mL) was an optimal and the same concentration was used in this investigation. Two different cotton materials were used: bleached cotton fabric (weight: 130 g/m²), and bleached and mercerized cotton fabric (weight: 119.2 g/m²) purchased from "Tekstina d.d.", Ajdovščina, Slovenia. The maximum values of significant process parameters, such as ethanol concentration, ethanol yield (based on cellulose) and volumetric productivity achieved after 18 and 6 h fermentation are presented in Figure 6. Optimal duration of fermentation was 18 and 6 h for corona pretreated and mercerized cotton fabrics, respectively.

system was more productive. In this system, the volumetric productivity of 0.933 g/(L·h) was around four times higher than the productivity obtained after fermentation of corona pre-treated cotton fabric. The increase in the productivity can be of much greater importance in a continuous fermentation system, which will be a part of our further research.

CONCLUSIONS

Bioethanol produced from renewable biomass is expected to be one of the dominating renewable biofuels in the transport sector within the coming twenty years. The priority in global future in the bioethanol production is put on lignocellulosic processing, which is considered as one of the most promising second-generation biofuel technologies. The

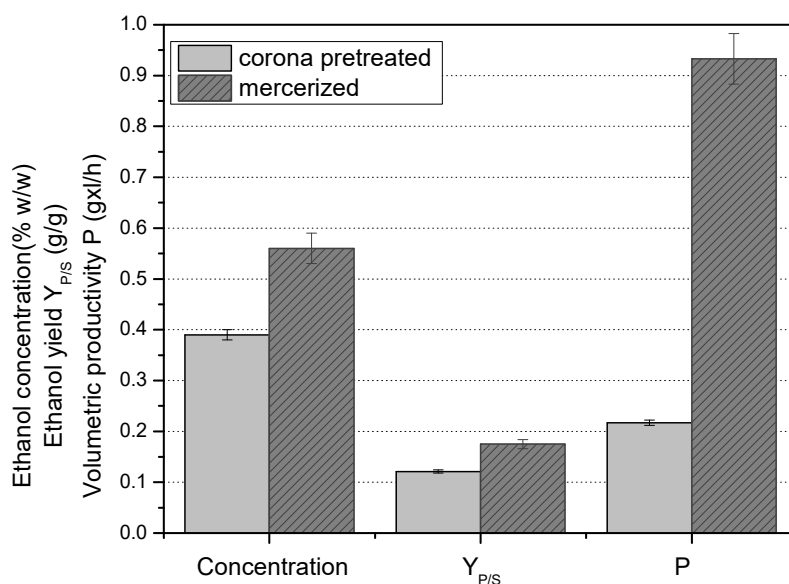


Figure 6. Maximum ethanol concentration, ethanol yield (based on cellulose) and volumetric productivity obtained after fermentation of corona pretreated unmercerized and mercerized cotton fabrics by *S. cerevisiae* var. *ellipsoideus* yeast. Duration of fermentation of unmercerized and mercerized cotton fabrics were 18 and 6 h, respectively. No pattern bar - unmercerized cotton, dashed pattern bar - mercerized cotton.

As shown in Figure 6, the maximum ethanol concentration of 0.56 mass% was achieved after 6 h of fermentation of mercerized cotton fabric. In this case, the percentage of the theoretical ethanol yield of 97.70% (based on glucose), ethanol yield of 0.175 g/g (based on cellulose) and 0.50 g/g (based on glucose) were obtained. Rather similar ethanol concentration and ethanol yield were achieved after fermentation of both materials. But, comparing the values of the obtained volumetric productivities, mercerized cotton fabric has been found to be very perspective raw material for bioethanol production. Under selected optimal process conditions, this fermentation

choice of suitable, abundant and cheap raw material is of great importance since the feedstock cost represents a major part of the production cost. Thus, different cotton-based materials present a promising feedstock for bioethanol production, since the cellulose content in cotton fabrics can reach even 100% (after bleaching and mercerization) and there is no lignin present. A significant progress and enhancement of the economy of the bioethanol production may be obtained by the optimization of feedstock pretreatment, enzymatic hydrolysis and by using appropriate process mode for ethanol fermentation (SHF, SSF and SSCF).

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NAUČNI RAD

IZAZOVI U PROIZVODNJI BIOETANOLA: KORIŠĆENJE PAMUČNIH TKANINA KAO SIROVINE

Bioetanol, kao čisto i obnovljivo gorivo sa svojim velikim ekološkim prednostima, predstavlja jedno od najvažnijih biogoriva koje se uglavnom koristi u smeši sa benzinom. Bioetanol se može proizvoditi iz različitih vrsta obnovljivih sirovina. Dok se procesi proizvodnje bioetanola prve generacije (na bazi saharida) već uveliko komercijalno koriste u velikim kapacitetima, procesi druge i treće generacije (na bazi celuloze i algi) zahtevaju dalja istraživanja i razvoj s obzirom na vrlo male prinose koji nisu ekonomski isplativi. U ovoj studiji, istraživane su i predstavljene mogućnosti proizvodnje bioetanola iz pamučnih tkanina kao značajnih celuloznih sirovina. Analizirana je i okarakterisana lignocelulozna biomasa koja se može koristiti u proizvodnji bioetanola, pogotovo materijali na bazi pamuka. Predstavljena je dostupna lignocelulozna biomasa, proizvodnja tekstila i odevnih predmeta i mogućnosti održive proizvodnje bioetanola u Srbiji. Opisane su mogućnosti napretka u domenu različitih metoda predtretmana, optimizacije enzimske hidrolize i različitih režima izvođenja alkoholne fermentacije.

Ključne reči: bioetanol, pamuk, lignoceluloza, predtretman, hidroliza, fermentacija.