Soybean Straw, Corn Stover and Sunflower Stalk as Possible Substrates for Biogas Production in Croatia: A Review

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Biomass availability is one of the key factors for biogas production in the future. The current status and possibilities for utilizing harvest residues (soybean straw, corn stover and sunflower stalk) in Croatia for biogas production is given. In the last few decades, different pretreatment methods have been developed for the degradation of different lignocellulosic biomass, but many of them are environmentally unfriendly and sometimes very expensive. More research and development is necessary in order to find both economically and environmentally friendly pretreatment methods. This paper provides a review on the mechanical, physical, and biological methods used for different lignocellulose material pretreatment. Harvest residues are usually left in the field, but with the improvement of the pretreatment process along with soil protection, they could be used for the production of huge amounts of energy in the future.

Key words:
biodegradation, biogas, harvest residues, lignocellulosic biomass, pretreatment

Introduction

Overall pollution and the need to reduce greenhouse gas emissions, issues related to human and animal health and food safety, the constantly growing trend in fossil fuel consumption and fast-growing economies, are warning signs of an energy and human society crisis.[1–3] The Kyoto Protocol, the EU Renewables Directive 2001/77/EC, and the European Biomass Action Plan are concerned about these world problems striving to encourage the development of the renewable energy sector and consequently reduce waste production and greenhouse gas emissions as well as increase energy efficiency, which would all lead to a more sustainable future.[2] With its full EU membership, Croatia is committed to achieve the aforementioned goals, and is therefore obliged to adopt a National Renewable Energy Action Plan. This document states that, in 2020, solid biomass (wood biomass and biomass from agriculture) will play the main role in total renewable energy for the production of thermal energy in Croatia.[4] As Croatia's import dependence on energy supply increases each year, the utilization of alternative energy sources becomes a major issue for future development. Renewable energy technologies have many benefits, like reduced greenhouse gas emissions, decreased fossil fuel use and energy resource diversification. Agricultural biomass exploitation is favorable in the Slavonia and Baranja and Vukovar-Srijem Counties, in the eastern part of Croatia where the highest biomass energy potential is estimated through thorough analysis.[5,6]

Out of Croatia's total area, around 52 % is agricultural land[7]. Agricultural land refers to land that is arable, under permanent crops, or under permanent meadows and pastures.[8,9] Almost 1/3 of the arable land is under corn, soybean and sunflower production.[7] Harvested areas and production of corn, soybean and sunflower for a period of 5 years (2010–2014) in Croatia is presented in Table 1. These three crops generate considerable amounts of residues, and are therefore an important source of energy.[10] It has been estimated that, based on a 10-year-period (2002–2011), 367 million tons of total agricultural residues are annually produced in the EU, whereas 62 million tons is contributed from corn production, 9 million tons from sunflower production, and 2 million tons from soybean production.[11] If one-third of the residues should remain in

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Table 1 – *Harvested area and production of corn, soybean and sunflower in Croatia for a 5-year period*

		2010	2011	2012	2013	2014
Corn	Harvested area (ha)	296 768	305 130	299 161	288 365	252 567
	Total production (t)	2 067 815	1 733 664	1 297 590	1 874 372	2 046 966
Soybean	Harvested area (ha)	56 456	58 896	54 109	47 156	47 104
	Total production (t)	153 580	147 271	96 718	111 316	131 424
Sunflower	Harvested area (ha)	26 412	30 041	33 534	40 805	34 869
	Total production (t)	61 789	84 960	90 019	130 576	99 489

*Source: Croatian Bureau of Statistics, 2015

the field to maintain soil moisture, protect soil carbon, nutrients and soil structure, and to reduce erosion, and one-third is mainly left for other uses like animal feeding and bedding, then around 122 million tons of residues are currently available for bioenergy in the EU.[12]

Considering the possibility of bioenergy production in Croatia (Table 2), the technical potential of corn stover is estimated at 0.37 million tons, soybean straw at 0.02 million tons, and sunflower at 7.8 thousand tons. An average value for a 5-year (2010–2014) production was used for calculating total production based on harvest index. Harvest index is the term used to quantify the yield of a crop species (grain, tuber, or fruit) versus the total amount of biomass that has been produced, and is defined as the ratio of yield to total plant above ground biomass. There is a wide variation in the data because yields and above ground biomass can vary widely from year to year and by soil type.[13] For this calculation, recommended harvest indices were used for all three plants.

In order to determine the estimation of residues production based on harvest index (marked as A), a 5-year average production was multiplied by the harvest index value*. Thirty percent of A was assumed to remain in the field for soil protection (data marked as B). Moreover, if the difference between A and B is multiplied by 0.3 (assumption that 30 % of residues could be used for technical potential), the amount of residues that could be used as technical potential is obtained (marked as C). The rest is needed for livestock support.

The world production of corn, soybean, and sunflower for the period 2014–2015 was 1009.68, 318.57, and 39.62 million tons, respectively.[14] According to the recommended harvest indices, annual residues of corn, soybean and sunflower for that period were determined as 1009.68, 318.57, and 15.85 million tons, respectively.

*Calculations are based on the recommended harvest index: for corn 1.0, soybean 1.0, and sunflower 0.4.

Utilization of slurries and manures from pigs, cattle and other domestic animals (resource easily available on many farms) together with the aforementioned agricultural residues, through anaerobic co-digestion creates biogas, a renewable source of energy.[15,16] Anaerobic co-digestion of agricultural wastes and residues is supposed to be one of the main alternatives in the energy sector because it is considered a complete waste-to-energy transformation.[1]

Biogas plants can be categorized according to the type of digested substrates, according to the technology applied or according to size. In Europe, there are many agricultural biogas plants and they usually co-digest manure and energy-rich co-substrates, like different plant extracts, plants, weeds, crop residues, and ensiled materials that are available naturally in the surroundings.[17,18] Manure is rich in nitrogen but lacks carbon, so using manure alone may not represent the most efficient way to produce biogas. Therefore, a high carbon content plant material is usually added as co-substrate to improve the C/N ratio and decrease the risk of ammonia inhibition.[19,20] Common plant materials which are mostly used in European biogas plants are crops and silages, and they present first generation biogas.

However, crops are the most important source of food and feed in the world, and the food demand

Table 2 – *Average production of corn, soybean and sunflower in Croatia for a 5-year period (2010–2014) and average technical potential of their residues*

	Corn	Soybean	Sunflower
5-year-average production (t)	1804.081	128.061	93.366
Estimate of residues production based on harvest index (t) A	1804.081	128.061	37.346
30 % of residues needed for soil protection (t) B	541.224	38.418	11.204
30 % of residues for technical potential (t) C	378.857	26.893	7.843

is expected to increase in the future. Additionally, using crops as feedstock for biofuels production may have a huge impact on biodiversity and land use, but the main problem is the food *vs.* fuel controversy. As a replacement, one way to avoid the negative effects of producing biofuels from food supplies is to use lignocellulosic biomass. In other words, second-generation feedstocks should be favored. These second-generation feedstocks are lignocellulosic agro-industrial byproducts which have no market and are destined for landfills or remain in the fields after harvesting. However, current technologies for processing these feedstocks are not cost effective and are still being developed, because there are a number of technical barriers that need to be overcome.[21,22]

Currently, there are 13 biogas plants in Croatia (according to the Croatian Chamber of Economy report of March 2015[23]), and 10 of them are using agricultural feedstock (mostly manures as the base substrate, and silage as the co-substrate) in the process. None of them co-digests harvest residues like straws and stovers.

According to the European Biogas Association's (EBA)[24] Biogas Report 2016, there were 17 376 biogas plants in Europe by late 2015. Most of them are producing biogas from agricultural feedstock like energy crops, agricultural residues, catch crops, and animal manure. Usually, this is performed by anaerobic co-digestion of animal manure and agricultural feedstock. Only a few biogas plants are producing biogas using harvest residues.[25] The potential from agriculture is still largely unexplored and unexploited, and this sector is expected to have huge growth rates in the coming years.[26]

The objective of this paper was to provide a) an overview of the annual production of corn, soybean, and sunflower, and their harvest residues in the world and in Croatia; b) information on lignocellulose-rich material chemical composition, and c) an overview of different environmentally friendly pretreatment methods for bioconversion of harvest residues in order to achieve higher biogas yields via anaerobic digestion (AD).

Agricultural lignocellulosic biomass

The term "lignocellulosic biomass" refers to higher plants, softwood or hardwood. The composition of agricultural lignocellulosic biomass depends on its source, but typically is comprised of about 40–50 % cellulose, 20–30 % hemicellulose, and 10–25 % lignin.[27,28]

Cellulose is the main component of lignocellulose cell walls, which gives a plant hardness and chemical stability. It is a linear polysaccharide polymer made of long chains of cellobiose units linked via β-1,4 glycosidic linkages. In the cellulose chains, a number of hydroxylic groups are presented leading to the formation of hydrogen bonds, while cellulose chains are interlinked by hydrogen bonds and van der Waals forces. Because of different orientations throughout the structure, cellulose molecules have different levels of crystallinity – low crystallinity (amorphous regions), and high crystallinity (crystalline regions).[29] The crystalline form prevails in the major part of the cellulose and is hardly hydrolyzed in comparison to amorphous form. It is therefore expected that high-crystallinity cellulose will be more resistant to enzymatic hydrolysis, but reduction of crystallinity will increase the degradability.[30]

Hemicellulose is a term used to represent a family of polysaccharides, such as pentoses (xylose and arabinose), hexoses (glucose, galactose, mannose and/or rhamnose), and acids (glucuronic acid, methyl glucuronic acid, and galacturonic acid).[27,29,31] The dominant component of hemicelluloses from hardwood and agricultural plants is xylan, while in softwoods glucomanan dominates. Hemicelluloses have a lower molecular weight than cellulose and are more amorphous, random, and branched with little strength that makes it highly susceptible to biological, thermal, and chemical hydrolysis.[29,32]

Lignin is the most complex polymer in nature.[27] It is a large and complex aromatic and hydrophobic amorphous heteropolymer consisting of three different phenylpropane alcohols: *p*-coumaryl, coniferyl and sinapyl, and their quantity varies according to species, maturity, and the space localization in the cell. Lignin gives the plant a structural rigidity, impermeability, and resistance against microbial attacks and oxidative stress. It is insoluble in water and optically inert, and therefore very difficult to degrade. The higher the lignin content, the greater is the resistance of the biomass to degradation. Lignin is a major barrier in the lignocellulosic biomass bioconversion process.[29,32]

Harvest residues could be a good source for AD, due to large availability of biomass. However, agricultural biomass like sunflower stalk, corn stover, and soybean straw contain complex structure of lignocellulose, and does not contain easily fermentable free sugars (Table 3). Therefore, its biotransformation to biofuels cannot be easily conducted.[33–36]

However, these lignocellulosic biomasses contain soluble, fermentable sugars (Table 4), natural intermediates in conversion to biofuels, but access to sugars is hindered by the recalcitrance of plant cell walls. Therefore, deriving sugars from this material requires mechanical, physical or chemical disruption.[51]

Table 3 – *Chemical composition of lignocellulosic biomass*

Lignocellulosic biomass	Parameter	Content (%)	References
Sunflower stalk	Total solids	94–96	36,37
	Volatile solids	88–89	36,37
	Cellulose	34–42	37–40
	Hemicellulose	19–33	37–40
	Klason lignin	12–30	34,37,38,40
Corn stover	Total solids	94–97	41,42
	Volatile solids	88–92	41,42
	Cellulose	31–41	32,40,41,43–45
	Hemicellulose	19–34	32,40,41,43–45
	Klason lignin	14–18	40,41,45
Soybean straw	Total solids	87–88	46,47
	Volatile solids	91	48
	Cellulose	25–49	49,50
	Hemicellulose	12–29	49,50
	Klason lignin	18	50

*All values are shown on a total solids basis (expect TS)

Pretreatments of lignocellulosic biomass as a crucial step in biogas production

Pretreatment is a crucial process step for the bioconversion of lignocellulosic biomass into biofuels. There are a number of different pretreatment technologies developed, but there are also technical barriers that make them expensive.[27] Pretreatment methods should be economically and practically viable[57], should improve the formation and avoid the loss or degradation of carbohydrates, avoid the formation of byproducts that are inhibitory to the hydrolysis and fermentation processes, and avoid consumption of chemicals.[58]

The goal of the pretreatment process is to: (a) increase the surface area and porosity of the biomass, (b) alter lignin structure, (c) depolymerize hemicellulose, (d) remove lignin, and (e) reduce the crystallinity of cellulose.[27,58]

Pretreatment methods can be divided into different categories: mechanical, physical, chemical, biological and various combinations of these.[27,29,32] Further in the text, the most common pretreatment methods used for corn, soybean and sunflower harvest residues (or the residues similar to them according to the chemical composition) are discussed in more detail. To our knowledge, the AD of soybean straw and sunflower stalk has not been studied in detail so far. Therefore, there is not much information on their degradability and possibility of utilization for biogas production. Generally, only a few authors have conducted research on these feedstocks regarding biofuels production. In contrast, there is much more research conducted using corn stover. Pretreatments that are quite expensive and aggressive to nature have mostly been studied so far. The aim of this paper was to present pretreatment methods that do not apply aggressive chemicals and agents, and are not harmful to nature, as well as to emphasize the need for their further development and improvement.

Mechanical pretreatment

Mechanical pretreatment is considered one of the most expensive processing steps in lignocellulose biomass conversion. However, it is also a crucial step which greatly contributes to the increase in hydrolysis efficiency and consequently higher biogas yields[59,60] It could be carried out easily by mills or shredders in every agro-biogas plant.[61]

The energy requirements of mechanical pretreatment depend on the type of the mill, initial and final particle sizes, material characteristics (amount, composition and moisture content).[62] The choice of the right comminution device depends particularly on the moisture content in the material.[60] Colloid mills and extruders are suitable for comminuting of wet materials with moisture contents of more than 15–20 % (wet basis), while different milling devices (hammer mills, knife mills, two-roll mills, attrition mills) are suitable for comminuting of dry materials with moisture contents of up to 10–15 % (wet basis). The ball or vibratory ball mills, as universal types of comminuting devices, can be used for either dry or wet materials.[30]

Chipping, milling or grinding lead to the reduction of the particle size increasing the accessible surface area, reducing the degree of cellulose crystallinity and the degree of cellulose and hemicellu-

Table 4 – *Polysaccharides composition in corn, soybean and sunflower harvest residues*

Agricultural residue	Glucan (%)	Xylan (%)	Arabinan (%)	Galactan (%)	Mannan (%)	References
Corn stover	26.5–40.9	14.8–25.8	1.6–6.1	0.7–3.0	0–1.8	32,44,45,52,53
Soybean straw	34.09	11.4	1.0	1.8	1.8	54
Sunflower stalk	31.5–39.0	14.8–24.4	0.66–3.1	1.3–2.0	–	34,55,56

*All values are shown on a total solids basis

loses polymerization.[29,32] By breaking the large structures, the efficiency of the hydrolysis increases.[59] It is well documented that smaller particles are better digested in biogas production particularly if combined with some other pretreatment method.[30] Sharma *et al.*[43] conducted experiments with different particle sizes (0.088, 0.40, 1, 6 and 30 mm) of forest and agricultural residues, and found that the highest biogas yield was obtained using the smallest substrate particles (0.088 and 0.40 mm). Zheng *et al.*[64] examined different particle sizes of corn stover and concluded that smaller particles (53–75 μm) are more susceptible to hydrolysis than larger particles (425–710 μm). Xiao *et al.*[65] obtained higher methane yields by reducing particle sizes of alkaline pretreated corn stover from 5–20 mm to 0.075–5 mm. In their pilot-scale experiment, Schell and Harwood[66] showed that lignocellulose particle size of 1 to 2 mm is effective for hydrolysis. Menardo *et al.*[67] conducted various mechanical and thermal treatments prior to AD of four agricultural byproducts. An net electrical energy balance was also completed to analyze the feasibility of the pretreatments according to energy input and output. Mechanical treatment included particle size reduction to 5.0, 2.0, 0.5, and 0.2 cm, whereas size reduction to 0.5 resulted in the increase in methane yield and electrical energy balance. Mshandete *et al.*[68] investigated the effect of sisal fibre particle size reduction on biogas production. The sisal fibres were reduced to 2, 5, 10, 30, 50, 70 and 100 mm particle size and anaerobically digested in mesophilic batch reactors with sisal wastewater sludge used as inoculum during 65 days. The results showed that the methane yield was inversely proportional to particle size, with respect to a best result obtained from 2 mm particle size which resulted in 23 % higher methane yield (0.22 m^3 kg^{-1} VS) compared to untreated sisal fibres (0.18 m^3 kg^{-1} VS). Liu *et al.*[69] conducted steam explosion pretreatment of corn stover with particle sizes at 2.5, 2.0, 1.5, 1.0, and 0.5 cm in order to improve its enzymatic digestibility. The results showed a higher amount of byproducts and lower sugar recoveries for the larger biomass particles (2.5 cm) during pretreatment, while sugar conversions and yields were higher during enzymatic hydrolysis. According to these results, larger corn stover particles would be more suitable for steam explosion pretreatment, reducing process costs at the same time.

Physical pretreatment

There are many different methods that are classified in this group, like steam explosion, hydrothermolysis, extrusion, and irradiation.[29,30] According to Mtui,[70] temperature and irradiation are the most successful physical treatments used in the processing of lignocellulosic biomass.

In the process of steam explosion or autohydrolysis, the lignocellulosic material is heated to high temperatures (160–260 °C) with high-pressure saturated steam (0.69 to 4.83 MPa) for a short time (a few seconds to a few minutes), and then the pressure is promptly reduced to complete the reaction, which causes the material to explode. This method is one of the most common pretreatment methods for lignocellulosic material and is commercially available.[29] Sunflower stalks were subjected to steam explosion pretreatment, in order to optimize pretreatment temperature in the range 180–230 °C, accompanied by enzymatic hydrolysis. The highest glucose yield was obtained at 220 °C, while the highest hemicellulose recovery was obtained at 210 °C.[39] Bondesson *et al.*[71] pretreated corn stover using steam explosion with and without addition of sulphuric acid as catalyst, and examined the effect of residence time and temperature on glucose and xylose recovery. The highest glucose yield was achieved after pretreatment at 210 °C for 10 min without the addition of catalyst and followed by enzymatic hydrolysis. The highest yield with the addition of catalyst was achieved at 200 °C for 10 min. The highest methane yield was obtained from the material pretreated with acid.

Hydrothermolysis or pretreatment in liquid hot water and high pressure is highly effective for enlarging the accessible surface area of cellulose, for improvement of cellulose degradability and for enhancement of sugar extraction.[29] Mosier *et al.*[72] pretreated corn stover in liquid hot water and reported optimal conditions at 190 °C and 15 min, in which 90 % of cellulose was converted by subsequent enzymatic hydrolysis. Chandra *et al.*[73] pretreated wheat straw using hydrothermolysis which resulted in 9.2 % higher biogas yield and 20 % higher methane yield compared to untreated wheat straw substrate.

Extrusion is a process that combines multiple operations, like high shear, temperature (60 to 300 °C), and pressure (up to 30 MPa).[29,74] Extrusion causes depolymerization of cellulose, hemicellulose, lignin, and protein, and sometimes also thermal degradation of sugars and amino acids. Hjorth *et al.*[75] tested five agricultural biomasses (straw, fresh grass, solid fraction of manure, and deep litter from cattle) for the biogas production by using extrusion as pretreatment. Extrusion accelerated the degradation of the majority of organic compounds which in turn increased methane yield by 18–70 % after 28 days of AD, and 9–28 % after 90 days of AD. The rate of biogas production from extruded materials was faster in comparison to untreated materials, especially when straw was used.

Irradiation includes ultrasound, microwaves, gamma-rays, electron beam, and electrokinetic disintegration.[29,30,74] Like in all other methods, when applying irradiation it is important to prevent the formation of inhibitors (e.g. phenolic compounds and furfural) by choosing the optimal process conditions.[29]

Microwave technology is the most studied irradiation pretreatment method.[29] It is effective in reducing the lignin ratio and the proportion of cellulose and hemicellulose, but usually combined with some chemical which is not favored.[76–78] Deepanraj *et al.*[59] suggested autoclave and microwave methods rather than thermal pretreatment of biomass material.

Ultrasound pretreatment disrupts cell wall structure and reduces the degree of polymerization. There is evidence that this pretreatment method cannot disintegrate lignocellulosic material, but it can improve accessibility to cellulose. It is usually used for pretreatment of water, industrial wastewater, sludge, manure, and different liquid effluents.[74,79] Liqian[80] compared the performance of different pretreatment methods (thermal, chemical and ultrasound) on agricultural biomasses. Ultrasound had a positive effect on the methane yield (increase up to 40 %) but considering the high energy input, it was stated as not profitable pretreatment.

Electric field or electroporation is used for a variety of processes in modern biotechnology but still has not been extensively studied, and the effect on lignocellulose is still not completely explained.[74] According to Kumar *et al.*,[58] pulsed electric field can affect the structural changes in plant tissue increasing the mass permeability and mechanical rupture of the plant tissue. This method is currently of interest to the food industry.[81] It is used for diffusion of soluble substances, juice extraction, and dehydration.[82–85] In biogas production high electric field strengths in the range of 5–20 kV cm^{-1} are used, causing the rupture of cells and creating pores in the cell membrane, making intracellular content available for fermentation. Electroporation also facilitates the entry of enzymes in the cell, causing the breakdown of cellulose and hemicellulose into their constituent sugars which are fermentable. Lindmark[86] studied the influence of electroporation on lay crop silage for biogas production and concluded that it holds the greatest potential for improving the efficiency of a biogas plant.

Biological pretreatment

Biological pretreatments mainly include fungal pretreatment, pretreatment by microbial consortium, and enzymatic pretreatment. The most commonly used microorganisms are white, brown, and soft-rot fungi, but actinomycetes and bacteria can be used for this purpose as well. Biological methods require low energy input and are performed under mild process conditions. However, the reaction rate of polymer hydrolysis using biological methods are usually very low and those methods require strict control of microorganism growth conditions, which limits their application for commercial purposes.[27,29,87,88]

Wood-rotting fungi that are commonly found in nature are among a number of organisms that can degrade lignocellulose components to various extents, and are generally grouped into soft-rot, brown-rot, and white-rot fungi.[89] White-rot fungi can degrade and mineralize all three major wood polymers: cellulose, hemicellulose, and lignin, whereas lignin can be degraded extensively resulting in a bleached appearance of degraded wood.[90] This ability is due to the fact that white-rot fungi produce a variety of enzymes, such as lignin peroxidases, manganese-dependent peroxidases, and laccases that degrade the lignin.[91] Planinić *et al.*[92] treated lignocellulose waste from the agro-, food and wood industries for 7 days with *T. versicolor,* which resulted in lignin conversion up to 71 %. Tišma *et al.*[93] studied *Trametes versicolor* growth on glucose, fructose, and sucrose, and developed a mathematical model of the process composed of sucrose hydrolysis catalyzed by intracellular enzyme, and microbial growth on glucose and fructose. Tišma *et al.*[94] used diverse media (industrial waste) for *T. versicolor* MZKI G-99 submerged cultivation with the aim of enzyme laccase production. Waste from the paper industry showed the highest potential for laccase production. It was proved a safe and inexpensive substrate for commercial production of laccase. However, fungal degradation of lignocellulose waste so far has not been an approach of commercial significance. Phutela *et al.*[95] pretreated paddy straw using *Trichoderma reseei* MTCC 164 and *Coriolus versicolor* MTCC 138 at different time intervals, and then anaerobically digested straw. Paddy straw pretreated with *T. reesei* showed 20.8 % enhanced biogas production, while straw treated with *C. versicolor* showed 26.2 % enhanced biogas production with a maximum of 19.1 % reduction in lignin. Liu *et al.*[96] pretreated corn stover silage by *Phanerochaete chrysosporium* in solid-state fermentation to enhance methane production via AD. It was found that *P. chrysosporium* degraded cellulose, hemicellulose, and lignin up to 19.9, 32.4, and 22.6 %, respectively. Consequently, pretreated corn stover silage achieved up to 23 % higher methane yield than the untreated corn stover silage. Liu *et al.*[97] pretreated yellow corn stover and corn stover silage with white-rot fungi to enhance biogas production. The pretreatment of yellow corn stover was accompanied by 38.3 % cellulose, 42.2 % hemicellulose, and 39.1 % lignin degradation, while the

pretreatment of corn stover silage was accompanied by 9.9 % cellulose, 23.2 % hemicellulose, and 15.2 % lignin degradation. The reducing sugar yield of pretreated corn stover and corn stover silage after enzymatic hydrolysis was 195.8 mg g^{-1} and 67.7 mg g^{-1}, respectively, which indicated that much more corn stover was degraded in comparison to pretreated corn stover silage. The results also showed 29.2 % higher methane production of pretreated corn stover silage after 21 days of AD in comparison to untreated corn stover silage, and 73.1 % higher methane production after 60 days of digestion. Higher biogas yield of pretreated corn stover was not achieved. Some other lignocellulosic biomass like wheat straw[98–100], Japanese cedar wood[101], and rice straw[102,103], have also been successfully degraded using white-rot fungi, which ultimately affected the increase in the production of biogas.

Microbial consortium consists of microbes screened from natural environments in which rotten lignocellulosic material is the substrate. In contrast to fungal pretreatment, which is mainly applied for lignin degradation, a microbial consortium usually has high ability to degrade cellulose and hemicellulose.[29] Kangrang *et al.*[104] investigated the effect of microbial consortia obtained from cattle and horse manure, and decomposed wood for production of cellulase, and further enhancement of biogas production from rice straw. To select the most efficient consortium, cellulase enzymes were extracted and

Table 5 – *Literature review of research for corn stover pretreatment methods*

Pretreatment method	Process	Pretreatment conditions	Results	References
Mechanical	Size reduction (knife mill)	Particle size: 0.5–2.5 cm	Up to 100 % glucan recovery, and 83 % xylan recovery	109
	Size reduction (scissors, food mixer-cutter and knife mill)	Particle size: 0.2–5.0 cm	Reduced organic matter degradation time; no significant improvement in methane production (up to 272 dm^3_N kg^{-1} VS)	67
	Size reduction (grinder)	Particle size: 2–20 mm	Decrease in the organic solid content by nearly 80 %, up to four-fold reduction in total solids after AD	110
Physical	Thermal treatment	Autoclave, T = 90 and 120 °C, t = 30 min	No significant improvement in the methane yields (up to 267 dm^3_N kg^{-1} VS)	67
	Thermal treatment	Fluidized bed-pyrolysis reactor, T = 180, 200 and 220 °C, t = 1 s	Up to 33 % reduction in lignin; 10 % improvement in biogas yield	111
Biological	Fungal treatment	*Pleurotus ostreatus* and *Trametes versicolor;* inoculated in sterile polypropylene bags with membrane that permitted gas exchange, T = 20 °C, t = 1–4 months	Changes in chemical composition of corn stover were not beneficial to the feed value of the crop and resulted in high losses of dry matter	112
	Enzymatic treatment	Commercial cellulase – Accellerase 1500, and Novozyme 188, T = 50 °C, t = 168 h	Enzymatic hydrolysis was conducted after mechanical pretreatment and subsequent steam explosion; up to 99 % glucan conversion, and up to 82 % xylan conversion; lignin recovery around 75 %	109
	Enzymatic treatment	Cellulase (Spezyme CP) and Multifect xylanase; 1-dm^3 glass reactors in walk-in incubation room, T = 37 ± 1 °C, t = 30 days	Around 37 % cellulose removal, and 30 % hemicellulose removal; up to 135 dm^3 kg^{-1} VS of total methane yield	113
	Fungal treatment	Flasks, *Phanerochaete chrysosporium; T* = 28 °C, t = 30 days	55 % degradation of cellulose, 64 % of hemicellulose, and 61 % of lignin; no significant influence on biogas production	114
	Enzymatic treatment	NS81210 cellulase complex and NS81220 protease	Up to 11 % higher biogas yield; up to 9 % higher methane yield	115
	Enzymatic treatment	Laccase, manganese peroxidase, and versatile peroxidase; anaerobic air-tight batch reactors, V = 250 dm^3, T = 30 °C; t = 6 and 24 h	No evidence of inhibitors, high yield; laccase increased methane yield by 25 %, and peroxidase increased methane yield by 17 %; no sinergy between enzymes detected; up to 16 % increased methane yield after treatment with both enzymes	116

their activities were analyzed. The results suggested that microbial consortium obtained from cattle manure is the best candidate for biogas production, and the highest cumulative biogas yield was 104.6 dm^3 g^{-1}. Yan *et al.*[105] cultivated mesophilic lignocellulolytic microbial consortium BYND-5 and applied it to enhance the biogas production from rice straw. The results showed degradation efficiency of BYND-5 for rice straw of more than 49 % after 7 days of cultivation at 30 °C.

Enzymatic pretreatment is applied prior to or in the AD of biomass in order to increase biogas production. These are cellulases and hemicellulases, hydrolytic enzymes, which are too expensive, and enhancement in biogas production is minimal. Therefore, their application in AD is limited.[29] Spajić[106] in his doctoral research, tested different substrates from agriculture and food industry (pig manure as base substrate, and cheese whey, brewery yeast, slaughter waste and corn silage as co-substrates) for biogas potential. Before anaerobic co-digestion, ultrasound and enzymatic pretreatments (using enzyme Spezyme CP) were conducted on all samples. After ultrasound pretreatment and subsequent anaerobic codigestion, up to 34 % higher methane yield was achieved, whereas enzymatic hydrolysis did not have effect on methane yield increase. Boussaid and Saddler[107] showed that higher enzyme loadings are needed for lignin substrates as the adsorption of enzymes to lignin is more difficult, and when using commercial enzyme mixtures because of the lower specific enzyme activity. Therefore, Gao *et al.*[108] conducted the "in-house" developed enzyme cocktail optimization for degradation of corn stover, instead of using expensive commercial enzymes. The results showed high glucose (around 80 %) and xylose (around 70 %) yields with moderate enzyme loading (~20 mg protein g^{-1} glucan).

As mentioned previously, there is limited literature information available on the soybean straw and sunflower stalk usage in biogas production. The results on corn stover degradation, using different pretreatment methods, with the aim of its further application in biogas production, are presented in Table 5.

Conclusion

Biogas is a renewable energy source the production of which depends on availability and type of biomass. By using biomass for energy production, productive land is destined to supply energy, not food or feed, which could have a huge impact on biodiversity and land use. However, the main problem is the food *vs.* fuel controversy. Therefore, utilization of crops for biogas production should be substituted with lignocellulosic residual biomass, which originates after harvest or crops processing. These byproducts have no market and are destined for landfills or remain in the fields after harvesting. Their chemical structure is complex and hard to degrade, which represents a challenge. Therefore, the pretreatment step of lignocellulosic biomass is crucial in their usage for biogas production. However, the pretreatment step is considered as rate-limiting step and governs the final cost of products.

Croatia recognizes the biogas potential but it is still poorly utilized compared to other EU states. Regarding lignocellulosic residues potential, especially of these three crops (corn, soybean and sunflower) that are of huge importance for Croatia, the situation is promising. However, methods that are used as pretreatment of lignocellulosic biomass are still too expensive and not cost-effective. They are still under development and the goal is to find technologies that protect and care for the environment and are not expensive. The point is not to produce as much energy as possible by any means, but to produce energy in a sustainable manner that will benefit all.

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List of symbols

AD – anaerobic digestion
VS – volatile solids
T – temperature, °C
t – time, min
V – volume, dm^3

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