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Complex transformation of acid hydrolysates of primary and secondary biomass to bioenergy

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In the current paper a comparative study of bioenergy (biofuels) yields from models of primary and secondary biomass - grass and potato peels is done. Acidic hydrolysis was used as a pre-treatment of these raw materials. The pre-treatment of the two types of biomass was conducted by autoclaving for 20 min at 121 °C in the presence of 1M HCl. The hydrochloric acid hydrolysates obtained from both biomasses had basic parameters for the grass hydrolysate 0.23 g reducing sugars/ g dry matter and COD 45.76 g O_2/ L, and for potato peels – 0.59 g reducing sugars/ g dry matter and COD 35.74 g O_2/ L. Both hydrolysates were found to be suitable substrates for bioethanol generation, where 12.48 mg ethanol/g dry matter was produced from grass hydrolysate and 180 mg ethanol/g dry matter from potato peels hydrolysate. The potential of both hydrolysates to biomethane generation was also studied. From the grass hydrolysate 0.196 L CH_4/ g dry biomass was obtained and from potato peels - 0.41 L CH_4/ g dry biomass. The results demonstrated the higher energy potential of potato peels compared to grass biomass. This was probably due to the high starch content typical for this type of waste.

Keywords: BMP, grass, potato peels, bioenergy, bioethanol, hydrolysis

INTRODUCTION

The conversion of lignocellulosic biomass into biofuel requires three steps, including pre-treatment, hydrolysis and fermentation [1]. Biofuels currently provide approximately 1.5 % of the global transport fuel as a result of the rapidly increasing production over the last decade [2].

Pre-treatment is usually used before anaerobic digestion to increase biodegradability of biomass. Therefore, various methods based on biodegradation and dissolution of lignin and hemicelluloses have been developed to achieve efficient hydrolysis and facilitate biogas production [3]. Pre-treatment should overcome the structural limitations of lignocellulose and its polymers (cellulose and hemicellulose), making them susceptible to microbiological treatment, leading to increased biomass and biogas yield [4]. The most commonly used methods are biological, chemical, physical or mixed.

Compared to other methods, chemical pre-treatment is considered much more promising. These methods can be quite effective in degrading more complex structured substrates. Major reactions during alkaline pretreatment include dissolution of lignin and hemicellulose and deesterification of intermolecular ester bonds. Dilute acids (< 4 % w / w) are usually used in acid pre-treatment. Often these methods are combined with high temperatures (> 100 °C). Concentrated acids are not preferred because they are corrosive and need to be recovered to make pre-treatment economically viable [5, 6].

Potatoes are starchy crops that do not require complex pre-processing. Although a high-quality crop, 5 % to 20 % of the potatoes grown remain as by-products that can be used to produce bioethanol. In addition, during potato processing, especially in potato chip production, approximately 18 % is generated as waste. Therefore, potato waste can be used as a growth medium (economically viable carbon source) for fermentation processes in ethanol production, as it has high starch content. In particular, it has great potential for bioethanol production due to the high starch content. The most used are potato pulp, potato processing water, peels and waste potato pulp [7]. In addition to producing bioethanol, potato peels are used in the production of biogas.

The sustainable use of forest biomass for fuels and chemicals, instead of fossil fuels and petroleum products, can significantly reduce carbon dioxide emissions. The conversion of wood and non-wood lignocelluloses into biofuels and renewable intermediates was investigated. In conventional ethanol fermentation, yeast or bacteria can only ferment hexoses (C6 sugars). Various bacteria are capable of metabolizing and fermenting both hexoses and pentoses, but all produce a mixture of fermentation products. Biogas can be derived from

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lignocellulosic biomass by its degradation [8].

According to the literature, hydrochloric acid is usually used for complete hydrolysis of the plant origin carbohydrates to simple reducing sugars, with no adverse effects on the material [9]. Chemical pretreatment is considered much more promising, as these methods can be quite effective in degrading more complexly structured substrates. Cellulose and hemicellulose, which are polymers of various sugar monomers, can be separated from lignin and extracts and hydrolyzed to their monomer units by acidic, alkaline or enzymatic hydrolysis.

The aim of this study was to compare the production of bioethanol and biogas (mainly biomethane) from model primary and secondary biomass - grass and potato peels. Acid hydrolysis with hydrochloric acid was used for pretreatment of these raw materials.

MATERIALS AND METHODS

Substrates

Fresh grass mix (perennial ryegrass *Lolium perenne* and cocksfoot *Dactylis glomerata*) was collected at Park Studentski in Sofia and then was cut to small pieces. The potatoes *Solanum tuberosum* were purchased from a large grocery store and were washed, peeled and blended.

Preparation of hydrolysates

The pre-treatment of both types of biomass was conducted by autoclaving them for 20 min at 121 °C with 1M HCl. For further analyses, the resulting hydrolysates were centrifuged and filtered using a 0.45 μm pore size filter. After separation the solid residues (53.1% for grass and 21.4% for potato peels) were discarded and only liquid fractions were used in the study. The obtained solutions were then refrigerated at 4 °C.

Methanogenic consortia

Methanogens were obtained as activated sludge from a factory producing bioethanol “Almagest”, Verinsko village, Bulgaria.

Analytical methods

The chemical oxygen demand (COD) was determined according to APHA, 1992 [10]. Reducing sugars were determined as glucose using dinitrosalicylic acid (DNS) reagent by the method described by Miller, 1959 [11]. Gas production rate measurements were performed using a manual constant pressure liquid displacement system. The biogas composition was estimated using the absorptive method as was described previously by Lalov *et al.*, 2015 [12] and using the gas analyzer Optima 7 biogas, MRU-Germany. Biochemical methane potential was determined by the batch process described by Velichkova *et al*., 2017 [13].

Ethanol fermentation

Hydrolysates obtained by both substrates (grass and potato peels) were subjected to ethanol fermentation by *Saccharomyces cerevisiae* under anaerobic agitated conditions in a 250 ml Erlenmeyer flask with fermentation trap. Forty milligrams of lyophilized yeast were hydrated with 2 ml of distilled water at a temperature about 30 °C for 20-30 min. They were then added to 50 ml of hydrolysate. The process conditions were: temperature around 25 °C, fermentation time 4-5 days (or lack of new bioethanol produced).

Calculation of biochemical methane potential (BMP)

The obtained results were used in the final determination of the real energy potential of grass and potato peels hydrolysates. BMP was determined according to the following eq. (1):

$$BMP = \frac{V_{biogas} \cdot C_{methane}}{V_{sub} \cdot COD_{sub}} \tag{1}$$

where:

BMP – biochemical methane potential, LCH_4 / gCOD; V_{biogas} – volume of produced biogas, L; $C_{methane}$ – methane concentration, %; V_{sub} – volume of the substrate used in the BMP-test, L; COD_{sub} – chemical oxygen demand of substrate, gO_2 / L.

RESULTS AND DISCUSSION

Characteristics of the obtained hydrolysates

In order to characterize the obtained hydrolysates as substrates for a bio-refinery platform and to study their full energy potential, the most important characteristics were examined - content of reducing sugars and chemical oxygen demand. The results are summarized in Table 1.

Table 1. Main characteristics of the obtained hydrolysates

	Reducing sugars, g / g dry matter	COD, g O_2/ L
Grass hydrolysate (GH)	0.23	45.76
Potato peels hydrolysate (PPH)	0.59	35.74

The data in Table 1 show that the amount of reducing sugars is higher in potato peels hydrolysate (PPH) *vs*. grass hydrolysate (GH). This is also a prerequisite for the higher production of bioethanol from PPH. The COD shows an inverse relationship. However, the values are very close. The results show that hydrolysates from both biomasses have a good potential for liquid (bioethanol) and gaseous (biomethane) biofuels production. This potential was then explored by biomethanation and fermentation.

Biogas production and BMP determination

The methane content under the conditions of biogas collection reached 93% for GH and 95% for PPH, respectively. The biochemical methane potential of the obtained hydrolysates was then determined by equation 1 and recalculated per gram of dry biomass. A batch process of biomethanation at 35°C was repeated three times. The results are summarized in Figure 1.

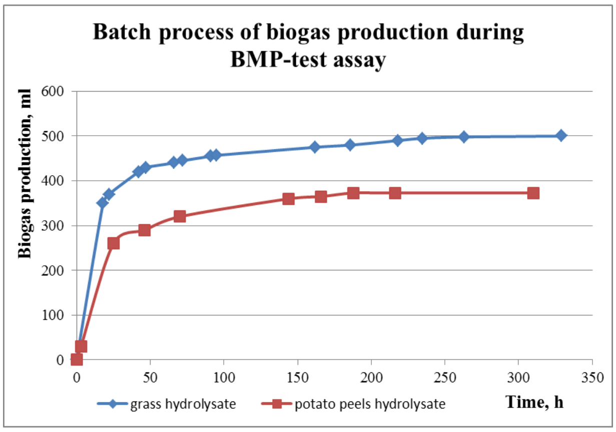

Figure 1. Batch process of biogas production from grass and potato peels hydrolysates.

BMP for PPH was 0.410 L CH_4 / g dry biomass and for GH – 0.196 L CH_4 / g dry biomass. The amount of biogas produced is higher for GH compared to PPH but the potential of potato peels as a feedstock for biomethane generation is higher. Maybe that's because they contain starch which degrades more readily than cellulose in the grass by acid hydrolysis. Potato peels waste can produce biogas about 0.55 L / g of dry matter according to the literature [14], which corresponds to our results.

Bioethanol production

The treated primary and secondary raw materials were fermented. Bioethanol with concentration 12.48 mg ethanol/g dry matter from GH and 180 mg ethanol/g dry matter from PPH was produced. Such a significant difference in the amount of bioethanol produced (compared to the amount of reducing sugars found in the different hydrolysates) can be explained mainly by the difference in the composition of the two raw materials. It is well known that the main product of the acid hydrolysis of a starch-containing raw material such as potato peels will be glucose. This compound can be easily and almost completely transformed into ethanol by the yeast culture used in the process. On the other hand, the typically high content of hemicelluloses in the composition of lignocellulosic raw materials usually leads to the formation of a broad spectrum of products, especially monosaccharides other than glucose (xylose, arabinose, galactose, mannose, etc.). Of course, such monosaccharides will increase the amount of the "reducing sugars" detected in the hydrolysate but they are non-fermentable (cannot be converted into ethanol) under the conditions of our process. Furthermore, acid hydrolysis of lignocellulosic biomass can result in formation of some inhibitory compounds such as furfural that is key derivative of xylose for example [15].

Generally, it can be assumed that the results prove once again the advantage of starch-containing raw materials over those of lignocellulosic composition.

CONCLUSION

Both hydrolysates (PPH and GH) were found to be suitable substrates for bioethanol production and had good potential for biomethane generation. The results demonstrated the higher potato peels energy potential compared to grass biomass. This was due to the high starch content typical for this type of waste. Combining the two bioenergy generation methods (biogas and bioethanol production) would expand the spectrum of generated fuels.

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