

PRETREATMENT OF WHEAT STRAW FOR BIOETHANOL PRODUCTION

Lenka BLINOVÁ - Jozef FIALA - Maroš SOLDÁN

ABSTRACT

The aim of this contribution is to measure the impact of the pretreatment on lignocellulosic biomass utilization for bioethanol production. Biofuels produced from different lignocellulosic materials (f.e. wood, forest or agricultural residuals) have the potential to be a valuable substitute for, or complement to, gasoline. The

goal of pretreatment is to make the cellulose accessible to hydrolysis for conversion to fuels. The impacts of pretreatment and different conditions of pretreatment were studied. The results of study, which are focused on evaluation of reducing sugars are included in this contribution.

Key words:

bioethanol, lignocellulosic phytomass, pretreatment, reducing sugars

INTRODUCTION

The increased concern for the security of the oil supply and the negative impact of fossil fuels on the environment, particularly greenhouse gas emissions, has put pressure on society to find renewable fuel alternatives. The most common renewable fuel today is ethanol produced from sugar or grain (starch); however, this raw material base will not be sufficient. Consequently, future large-scale use of bioethanol will most certainly have to be based on production from lignocellulosic materials [1].

Bioethanol is an attractive alternative fuel since that it can be blended with gasoline or used as neat alcohol in dedicated engines, taking advantage of the higher octane number and higher heat of vaporization [2]. It can be produced from sugar crops, starch-containing and lignocellulosic biomass [3].

Lignocellulosic biomass is a sustainable and renewable source of mixed sugars and includes straw, corn stover, sugarcane residue, wood chip, waste paper, Miscanthus, and switch grass [4]. It consists of lignin, cellulose and hemicellulose fractions, which quantitatively and qualitatively vary according to the plant material [5].

Lignocellulosic biomass can be used as fuel by direct combustion or by first gasifying and then burning the gas. However, being the only renewable resource which can be converted to liquid fuel for transportation, there is a great deal of interest in converting these resources to bioethanol and other chemicals. The concept is to hydrolyze the cellulose and hemicelluloses to recover C5 and C6 sugars and then ferment the sugars to bioethanol [6].

The process of converting lignocellulose into bioethanol consists of four main parts: pretreatment, enzymatic hydrolysis, fermentation and separation [7]. Pretreatment is an important tool for practical cellulose conversion processes and it is considered as one of the most expensive processing steps in cellulosic biomass-to-fermentable sugars conversion [8]. Physical, physico-chemical, chemical and biological processes can be used for pretreatment of lignocellulosic materials. Each pretreatment has its own effect(s) on the cellulose, hemicellulose and lignin; the three main components of lignocellulosic biomass [9]. Pretreatment is required to alter the structure of cellulosic biomass to make cellulose more accessible to the enzymes that convert the carbohydrate polymers into fermentable sugars [8]. The goal of pretreatments is to remove lignin and hemicellulose, reduce cellulose crystallinity, and increase the porosity of the material. Successful pretreatment can significantly increase the quantity of reducing sugars and improve the hydrolysis [10]. Various pretreatment technologies have been extensively studied to process different biomass for cellulosic ethanol production. However, none of those can be declared a "winner" because each pretreatment has its intrinsic advantages and disadvantages [11].

METHODS AND MATERIALS CHARACTERISTICS

Pretreatment is the first and the most important step in the experiment. As pretreatment were used the physical processes (grinding, breaking, hydrothermal pretreatment) and chemical process (acid hydrolysis) and their combination. Impact of pretreatment on sugars (defined as reducing sugars) occurring in the hydrolyzate was studied. Hydrolyzate was accrued after hydrolysis from raw materials as the main product for bioethanol production.

Raw material

Lignocellulosic phytomass – wheat straw, variety Bardotka, was used as a raw material. The straw was grown, harvested and stored in hay after a drying period in Slovakia (village: Dolné Zelenice) during the summer 2010. The straw was cut into 40 – 100 mm pieces and stored in plastic bags at room temperature until use for pretreatment. The chemical composition of the untreated wheat straw can be seen in Table no. 1.

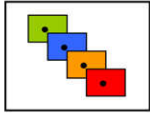


Table no. 1 Chemical composition of untreated wheat straw used in the experiment

Total solids	Cellulose	Lignin (insoluble)	Lignin (soluble)	Ash
96.16 %	44.38 %	22.07 %	2.56 %	5.1 %

Pretreatment

The first type of pretreatment was breaking and grinding of straw. The straw was pretreatment into pieces from ≤ 1 to 30 mm. Pre-treated straw was divided according to the sieve analysis (size: ≤ 1 mm, 1 – 12 mm, 15 – 30 mm). After this pretreatment, the suspension was prepared according to hydrolysis conditions. Suspension was hydrolyzed with acid at a pressure of (1) 101.325 kPa, (2) 120 kPa \pm 10 kPa - hereinafter 120 kPa, (3) 150 kPa \pm 10 kPa - hereinafter 150 kPa.

The second type of pretreatment of straw was hydrothermal pretreatment. Straw with particle size ≤ 1 mm, 1 – 12 mm, 15 – 30 mm we used for analysis. Suspension was prepared in a ratio of 1 part straw and 8 parts distilled water. Thus prepared suspension was placed in a boiling flask and placed in a water bath for 15 minutes at 80 °C. After the suspension was placed into an autoclave and heated for 12 minutes at a pressure of (1) 120 kPa, (2) 150 kPa. After this pretreatment, the suspension was hydrolyzed with acid at a pressure of 101.325 kPa.

The hydrolysis was realized with sulphuric acid. Acid hydrolysis was conducted under the following conditions:

- hydrolysis duration – 60 minutes,
- 10 % (w/w) straw, sulphuric acid 20 % v/v aqueous solution in an amount of 30 % for landfills phytomass,
- pressure: (1) 101.325 kPa, (2) 120 kPa, (3) 150 kPa.

Autoclave we used for hydrothermal pretreatment and for hydrolysis under elevated pressure (120 kPa, 150 kPa). After time the autoclave was shut out of the cooker. This is to ensure of decreasing pressure in autoclave to value 101.325 kPa, when we can open autoclave. All process increasing and decreasing pressure in autoclave lasted 60 – 63 minutes. Suspension was not homogenously mixed. Scheme of experiment is show to Figure no. 1.

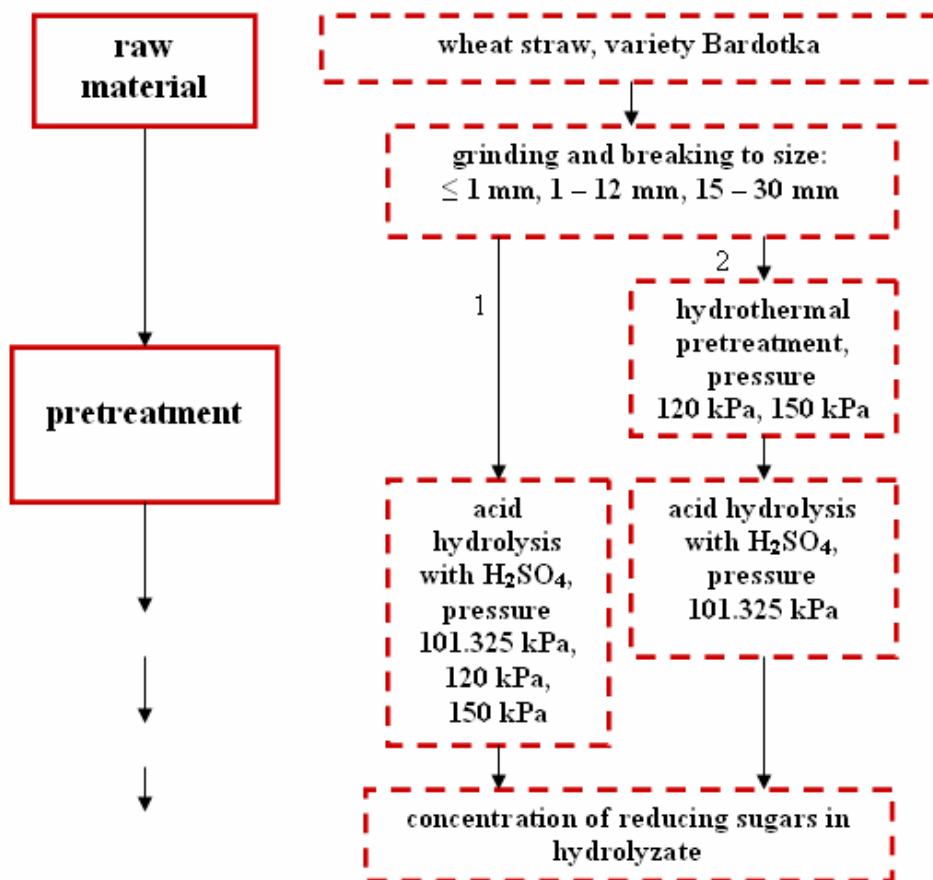
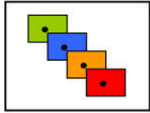


Figure no. 1 Scheme of experiment



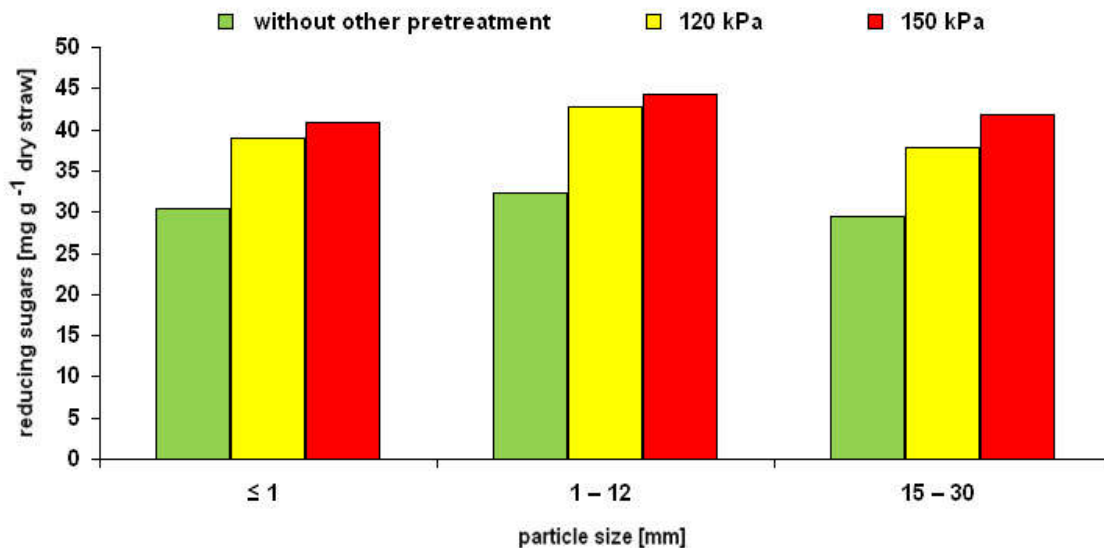
Analytical methods

The total solids content in the solid fraction was determined by drying of app. 1 g of the sample overnight at 105 °C. The ash content of the solid fraction was determined by incineration of app. 1 g of dried sample at 575 °C for 7 hour. The cellulose content of the solid fraction was determined by oxidative hydrolysis. Acid insoluble lignin and acid soluble lignin in the raw material were estimated following NREL laboratory analytical procedures Lap 003 and 004. The reducing sugars in the hydrolyzate were determined by Miller (1959) with 3.5-Dinitrosalicylic acid.

RESULTS

The impact of pretreatments on sugars (defined as reducing sugars) occurring in the hydrolyzate was analyzed. Results are averages of four measurements.

In the next Graph no. 1 there can be seen the concentration of reducing sugars in hydrolyzate for samples which were pretreated by (1) breaking, grinding (without other pretreatment) and (2) breaking, grinding and hydrothermal pretreatment (120 kPa, 150 kPa). Samples (1, 2) were hydrolysed at a pressure of 101.325 kPa.



Graph no. 1 Concentration of reducing sugars in hydrolyzate (hydrothermal pretreatment)

Pretreatment by breaking, grinding (without other pretreatment)

In the Graph no. 1 there can be seen that the most of reducing sugars are in sample with size 1 – 12 mm, about 32.3 mg g⁻¹ dry straws. At least of reducing sugars are in sample with size 15 – 30 mm, about 29.5 mg g⁻¹ dry straws.

Breaking, grinding and hydrothermal pretreatment (pressure 120 kPa)

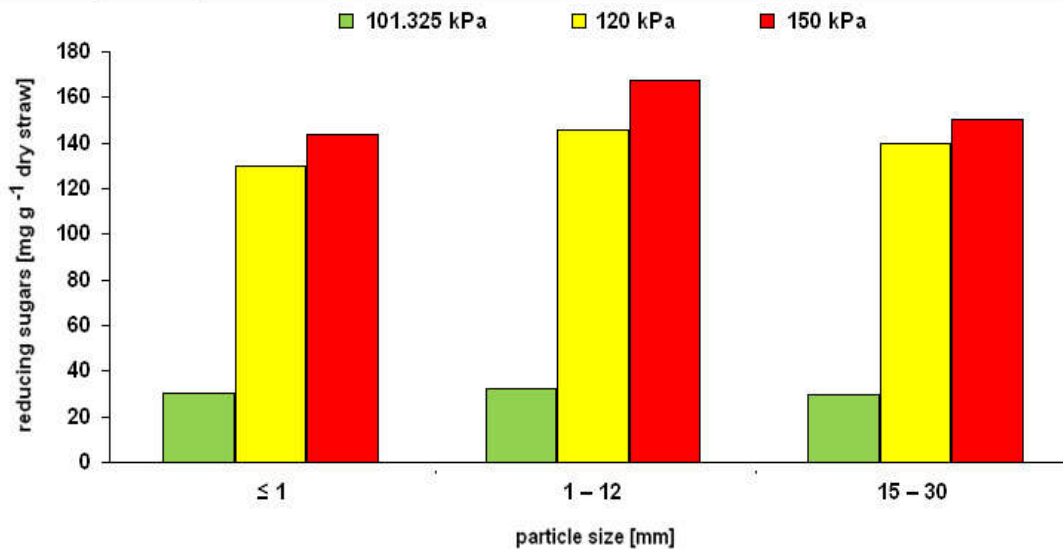
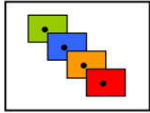
In the Graph no. 1 can be seen that the most reducing sugars are in sample with size 1 – 12 mm, about 42.7 mg g⁻¹ dry straws. At least of reducing sugars are in sample with size 15 – 30 mm, about 37.8 mg g⁻¹ dry straws.

Breaking, grinding and hydrothermal pretreatment (pressure 150 kPa)

In the Graph no. 1 there can be seen also that the most of reducing sugars are in sample with size 1 – 12 mm, about 44.3 mg g⁻¹ dry straws. At least of reducing sugars are in sample with size ≤ 1 mm, about 40.9 mg g⁻¹ dry straws.

In the next Graph no. 2 there can be seen the concentration of reducing sugars in hydrolyzate for samples which were pretreated by breaking, grinding and were hydrolysed at a pressure of 120 kPa and 150 kPa.

As we can see in the next graph concentration of reducing sugars depends on pressure which we used at hydrolysis. Concentration of reducing sugars increases with increasing pressure used in hydrolysis. We obtained the highest concentration of reducing sugars in sample with size 1 – 12 mm and pressure 150 kPa, about 44.3 mg g⁻¹ dry straws. At least of reducing sugars are in sample with size 15 – 30 mm and pressure 101.325 kPa, about 29.5 mg g⁻¹ dry straws.



Graph no. 2 Concentration of reducing sugars in hydrolyzate (acid hydrolysis at a pressure of 101.325 kPa, 120 kPa, 150 kPa)

CONCLUSION

The aim of this contribution was assess the impact pretreatment and pretreatment conditions to concentration of reducing sugars in hydrolyzate. Concentration of reducing sugars depends on particle size of straw and depends on type of pretreatment which we used.

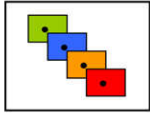
For the pretreatment of wheat straw, breaking and grinding pretreatment was the best for size particle 1 – 12 mm, then size particle ≤ 1 mm and size particle 15 – 30 mm was the worst regarding of concentration of reducing sugars. For the pretreatment of wheat straw, hydrothermal pretreatment (150 kPa) of wheat straw with size particle 1 – 12 mm was the best method regarding of concentration of reducing sugars, followed by the hydrothermal pretreatment (120 kPa) of wheat straw with size particle 1 – 12 mm. This result can be compared with hydrothermal pretreatment, 150 kPa, of wheat straw with size particle 15 – 30 mm. It is necessary to evaluate the pros and cons, because of finance. For the pretreatment of wheat straw, using higher pressure at hydrolysis affected the increasing of reducing sugars concentration in hydrolyzate. We obtained the higher quantity of reducing sugars in samples with size 1 – 12 mm for all values of pressure. The highest concentration of reducing sugars we obtained when we used pressure 150 kPa. Concentration of reducing sugars ranged from 129.72 to 167.24 mg g⁻¹ dry straw for hydrolysis at elevated pressure. For hydrolysis at elevated pressure to release four to five times more reducing sugars than the hydrolysis at atmospheric pressure (101.325 kPa). On achievements we can state that acid hydrolysis at elevated pressure is very good method for obtaining higher of concentration of reducing sugars.

Acknowledgements

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