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## Combined Microwave - Acid Pretreatment of the Biomass

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### 1. Introduction

Bioethanol represents an important alternative for the fossil fuels. The limited fossil fuel stock, the growth of the energy necessary all over the world and the environmental safety lead to an increasing interest in alternative fuels [Balat et al., 2008]. One of the most important renewable energy sources is the lignocellulosic biomass, including wood and crop residues, and that may have applications in the energetic field (both thermal energy and biofuels). There are four main steps in the conversion process of lignocellulosic biomass to ethanol: pretreatment, enzymatic hydrolysis, fermentation and separation [Petersen et al., 2009]. One of the key factors that influence the obtaining of bioethanol is the pretreatment stage. Biomass composition consists in 70-85% cellulosic materials (cellulose and hemicelluloses) and 15-30% lignins. For a corresponding capitalization of biomass, the removal of the lignin content and the transformation of cellulose and its derivatives in sugars are required.

Pretreatment of the lignocellulosic biomass is an important preliminary step that is performed in order to improve the yield of the hydrolysis reaction of cellulosic derivatives in fermentable sugars. The goal of the pretreatment stage consists in changes that are made in the lignocellulosic materials structure, in order to facilitate the access of enzymes in the hydrolysis reaction (Soccol, 2010). A corresponding pretreatment stage must fulfill the following conditions (Balat et al., 2008; Del Campo, 2006; Balat, 2010):

- to improve the sugar formation or the capacity to subsequently obtain sugars by hydrolysis
- to prevent degradation or the loss of carbohydrates
- to prevent the obtaining of possible inhibitory by-products in the hydrolysis and fermentation stages
- costs efficiency
- to avoid the destroy of cellulose and hemicelluloses
- the use of a minimum amount of chemical products

The above-mentioned characteristics represent the basis for the comparisons among various pretreatment methods that are used in the bioethanol industry. A number of different methodologies have been developed in order to accomplish the first stage of the lignocellulosic biomass to ethanol, namely the pretreatment of the biomass.

## 2. Pretreatment methods of the lignocellulosic biomass

### 2.1 Acid pretreatment

The main objective of the acid pretreatment is the solubilization of the hemicellulosic fraction of the biomass, in order to increase the accessibility of the enzymes in the enzymatic hydrolysis reaction (Alvira et al., 2010). Inorganic acids like  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{H}_3\text{PO}_4$  have been used for the pretreatment of the lignocellulosic biomass, in order to improve the enzymatic hydrolysis. There may be used both concentrated and diluted inorganic acids. Pretreatment of the biomass with concentrated acids, at ambient temperature, will lead to higher yields of fermentable sugars and to the hydrolysis of both cellulose and hemicelluloses. There are frequently used acids like  $\text{H}_2\text{SO}_4$  72%,  $\text{HCl}$  41% and trifluoroacetic acid 100%. In this case, a necessary step is the recovery of the acid, in order to lower the economic costs of the process (Girio et al., 2010). The method has the advantage not to use enzymes for saccharification in the further stage, but there are also a number of drawbacks: energy consumption, the use of equipment that is resistant to corrosion, a longer reaction time and the necessary operation of acid recovery (Talebnia et al., 2010).

Pretreatment with diluted acids presents many advantages for an industrial use and it may be applied to different types of biomass. The pretreatment stage may occur at higher temperatures (180°C) for a shorter time, or at lower temperatures (120°C) and a longer residence time. Pretreatment with dilute acid shows the advantage of hemicellulose solubilization, but also of the conversion of the solubilized hemicellulose in fermentable sugars. Pretreatment with diluted acids leads to the obtaining of a fewer degradation products than the pretreatment with concentrated acids (Alvira et al., 2010). The highest yields of the hydrolysis reaction have been recorded after treating the lignocellulosic material with dilute sulfuric acid. Usually, sulfuric acid concentrations are in the range 0.5-1.5%, and the working temperatures are 120-160°C (Alvira et al., 2010).

Organic acids (fumaric acid, maleic acid) appear as alternatives for the improving of the hydrolysis yield of the lignocellulosic biomass. Maleic acid is proven to be more efficient than the fumaric acid, and has the advantage to lead to the obtaining of lower amounts of furfural (compared to the dilute sulfuric acid) (Kootstra et al., 2009). Another pretreatment method with dilute acids uses  $\text{H}_2\text{CO}_3$  (obtained through the absorption of  $\text{CO}_2$  in aqueous solutions) (van Walsum and Shi, 2004).

### 2.2 Alkaline pretreatment

Pretreatment with alkaline solutions increases the digestibility of cellulose and favors the solubilization of lignins (Alvira, 2010). It may occur at room temperature and reaction time may vary from seconds to days. It leads to a smaller degradation of sugars than in the case of acid pretreatment, but is proven to be more efficient for crop residues than for lignocellulosic biomass (Kumar and Wyman, 2009). For the optimization of the pretreatment conditions, the possibility of losing the fermentable sugars and the formation of some inhibitory compounds must be taken into account.

Reagents that are frequently used for the alkaline pretreatment are  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca}(\text{OH})_2$ ,  $(\text{NH}_4)_2\text{OH}$ . Among them, most widely used is  $\text{NaOH}$ . For example, pretreatment with  $\text{NaOH}$  solutions leads to swelling and the increasing of internal surface of cellulose (Alvira et al., 2010). The same authors mentioned that pretreatment with  $\text{NaOH}$  of hardwood increases the digestibility by the decreasing to 20% of the lignin content.

Although alkaline pretreatments show great efficiency as regards the lignin solubilization, they are less efficient concerning the solubilization of cellulose and hemicelluloses (Girio, 2010).

A widely spread alkaline pretreatment method of the biomass is represented by the ARP (Ammonia Recycle Percolation) procedure (Wu and Lee, 1997). It consists in the use of aqueous ammonia at temperatures around 170°C (Kim and Lee, 2005). The solubilization of hemicelluloses in an oligomeric form occurs within 40-60% range (Girio et al., 2010). The cellulosic fraction is hardly degraded, but in the following steps of the hydrolysis the yields are closed to the theoretic ones (Kim and Lee 2005, Kim et al. 2008). The mechanism of the reaction with aqueous ammonia is very similar to the pretreatment with  $\text{Ca}(\text{OH})_2$  and  $\text{NaOH}$ , especially as regarding the swelling of biomass and the breakdown of the ester and ether bonds of the carbohydrates that exist in lignin (Girio et al, 2010). The advantages of the use of  $\text{NH}_3$  are: swelling of the lignocellulosic material, a selective reaction for the removal of lignin, low interaction with carbohydrates, high volatility. One of the known reactions of aqueous  $\text{NH}_3$  with lignin is represented by the breakdown of the C-O-C bonds from lignin, as well as of the etheric and esteric bonds from the complex lignin-carbohydrates (Stavrinides et al., 2010). As a result of ARP pretreatment, 60-85% from the entire lignin content is removed (Kim et al., 2008).

Another procedure that uses ammonia for the pretreatment of biomass is the AFEX (Ammonia Fiber Explosion) process. It consists in the contact of biomass with liquid ammonia at elevated temperatures and under pressure for a certain time, followed by a fast decompression (Zheng et al., 2009). The method proved to be less efficient in the case of hardwood and softwood residues (Zheng et al., 2009)

### 2.3 Organosolv pretreatment

In the Organosolv process, there are used a number of organic or aqueous solvents (methanol, ethanol, acetone, ethylene glycol) in order to solubilize the lignin and to obtain a corresponding treated cellulose for the hydrolysis process (Chum et al., 1988). The advantage of the Organosolv procedure consists in the recovery of lignin as secondary product. The maximum working temperature is 205°C, regarding the used solvent. The economicity of the process depends on the recovery of the organic solvent (Zhao et al., 2009).

The main advantages of the Organosolv pretreatment are: organic solvents can be easily removed by distillation and they can be reused; lignin may be isolated as solid materials (solids) and the carbohydrates are isolated as syrup (Zhao et al., 2009; Kim et al., 2008).

Disadvantages: the pretreated solids need to be initially washed with organic solvents in order to prevent reprecipitation of the dissolved lignin. Also, the process must be strictly controlled, due to the volatility of the organic solvents (Zhao et al., 2009).

Regarding the economy of the process, recovery of the solvents is necessary, even though high amounts of energy are needed. Due to these considerations, Organosolv pretreatment has no applications at industrial level.

The Organosolv pretreatment undergoes both in the presence or absence of a catalyst, at temperatures in the range 185-210°C. The yields of delignification process are improved if mineral acids like  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$  or organic acids like formic, oxalic or acetylsalicylic acid (Sun and Cheng, 2002) are used. After pretreatment with Organosolv, three fractions are obtained: dry lignin, an aqueous hemicellulosic phase and a cellulosic fraction (Duff and Murray, 1996).

The most frequently used is the Organosolv pretreatment with aliphatic alcohols (especially methanol and ethanol), mostly due to their low price. Among the alcohols with higher

boiling points, mostly used are polyhydroxylic alcohols like ethylene glycol and glycerol. The main advantage is the fact that the process could occur at atmospheric pressure. Pretreatment with aqueous glycerol leads to the removal of the lignin, but also to a significant loss of cellulose (Kucuk, 2005).

## 2.4 Pretreatment with solid superacids

The solid acid catalysts appeared as a consequence of the developing of a new, eco-friendly process for the obtaining of bioethanol. Particles of solid acid can be separated by the liquid products through decantation or filtration, and the catalyst may be reused without further processing stages to be necessary.

Solid superacids are made from a solid medium treated with Lewis or Bronsted acids (Zhao et al., 2009). They have the great advantage of being non-toxic, non-corrosive and safe for the environment. They are better donors than pure sulfuric acid and show a higher selectivity in the hydrolysis reaction and require low temperatures and atmospheric pressure (Zhao et al., 2009; Yamaguchi and Hara). Some of the superacids used in the process of the obtaining of bioethanol are: niobic acid ( $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ), zeolite, Amberlyst-15, amorphous C that contains  $\text{SO}_3\text{H}$ ,  $\text{COOH}$  and  $\text{OH}$  groups (Zhao et al., 2009).

Another superacid used for the selective conversion of cellulose to glucose is the heteropoly acid  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (Tian et al., 2010). The selectivity of the pretreatment method is very high (around 90%) and requires mild reaction conditions (160-180°C). Another advantage of this method is the possibility to reuse the catalyst, which can be recycled by extraction with diethyl ether (Tian et al., 2010).

## 2.5 Ionic liquids

The main advantage of using ionic liquids for the bioethanol production is represented by the possibility of a complete solubilization of the lignocellulosic biomass. Swatloski et al. suggested that solubilization is due to the breakdown of the H bonds of the polysaccharides by the anion of the ionic liquids. In the present, the process cannot be applied at industrial level due to the high costs of the ionic liquids (Swatloski et al., 2002).

A variant of the pretreatment with ionic liquids is represented by the microwave-assisted pretreatment of lignocellulosics in ionic liquids (Zhang and Zhao, 2009; Zhu et al., 2006). The method is characterized by shorter reaction time (due to the microwave irradiation) and a better solubilization of the biomass. According to Zhu et al., the raw lignocellulosic material is directly solubilized in the ionic liquid in the presence of microwaves and cellulose is precipitated by adding water. The other organic compounds (like lignins) remain in solution. Experimental results (Zhu et al., 2006) showed that the yields in ethanol are very similar to the ones obtained through steam explosion or chemical pretreatment.

## 2.6 Hydrothermal methods of pretreatment

The hydrothermal reactions for the pretreatment of biomass are new, eco-friendly pretreatment methods. They consist in the contact of the lignocellulosic materials with water at elevated temperature and pressure. During the process, hemicelluloses are hydrolyzed to sugars. The reaction time is very short (seconds) in order to avoid degradation of the sugars (<http://www.ecn.nl/units/bkm/biomass-and-coal/transportation-fuels-and-chemicals/transportation-fuels/biomass-pre-treatment-fractionation/>).



A variant of the hydrothermal pretreatment consists in the use of catalytic hydrothermal reaction that uses a solid catalyst (for example, amorphous carbon that contains  $-\text{SO}_3\text{H}$  groups) and results in higher amounts of fermentable sugars (Onda et al., 2009).

## **2.7 Ozonolysis**

Pretreatment with ozone occurs in mild conditions (room temperature, atmospheric pressure) and results in a strong delignification of the biomass (Sun and Cheng, 2002). The major drawback of the process is represented by the high costs, due to the large quantity of ozone that is needed during the pretreatment (Sun and Cheng, 2002).

## **2.8 Combined methods of pretreatment**

### **2.8.1 Pretreatment with alkaline peroxides, followed by steam explosion**

The procedure combines the advantages of alkaline pretreatment and steam explosion. It will lead to an efficient delignification and to the chemical swelling of the lignocellulosics fibers (Zhao et al., 2009). Use of a combined process (steam explosion and NaOH 10%) led to a significant increase of the free sugars concentration towards the pretreatment with  $\text{H}_2\text{O}_2$  1% and NaOH 1% (Chen and Qiu, 2010).

### **2.8.2 Pretreatment with ionic liquids coupled with steam explosion**

Pretreatment of the lignocellulosics biomass with ionic liquids coupled with steam explosion led to the degradation of hemicelluloses in fermentable sugars (Chen and Qiu, 2010). Lignin with high molecular mass is insoluble in ionic liquids, so it can be separated from cellulose.

### **2.8.3 Biological pretreatment**

For the biological pretreatment of the lignocellulosic biomass there are used both microorganisms (fungi and bacteria) and enzymes (Mtui, 2009; Balat, 2011). There are used white, brown and soft-rot fungi for the solubilization of hemicelluloses and also for the lignin degradation (Mtui, 2009; Balat, 2011). For the enzymatic pretreatment of the biomass, different cellulases (endoglucanases, exoglucanases and  $\beta$ -glucosidases) are used (Sun and Cheng, 2002).

## **3. Studies regarding the determination of the optimum parameters of the microwave-assisted dilute acid pretreatment of lignocellulosic biomass**

Lignocellulosics biomass has three main components: cellulose (40-50%), hemicelluloses (25-35%), lignin (15-20%) and also small amounts of proteins, lipids, acids, mineral salts. As it was mentioned before, the aim of the pretreatment stage is the removal of hemicelluloses and lignin. Also, the cellulose structure is altered in order to facilitate the enzymatic attack.

From all the pretreatment methods presented in the former chapter, pretreatment with dilute mineral acids (especially  $\text{H}_2\text{SO}_4$ ) combined with microwave irradiation has been chosen. The advantages of this process are the reaction conditions (that does not involve corrosion problems, or volatility or very high temperatures issues) and the low economic costs. Also, the use of microwave irradiation leads to shorter reaction time and also provides a uniform heating of the reaction mixture.

**Experimental part:** three types of sawdust (hardwood (oak) and softwood (fir) essences and herbs (hemp)) were treated with dilute sulfuric acid (for different concentrations: 0.55, 0.82, 1.23 and 1.64%) and heated (in the presence of microwaves) at three different temperatures: 120, 140 and 160°C, for 15 and 30 minutes, in order to perform an extensive study on the pretreatment in acid medium. The concentration in sugars (expressed as free glucose) of the solutions obtained after the hydrolysis reactions was considered in order to establish the best pretreatment method.

After cooling, the suspension was neutralized with CaCO<sub>3</sub> until a pH value of 5.5-6, for the removal of sulfates. Pretreated sawdust were filtered and washed with water, in order to remove the entire amount of sugars.

Determination of the total amount of carbon hydrates after performing dilute acid pretreatment on different types of sawdust was made by the colorimetric method with 3,5-dinitrosalicylic acid. 5 milliliters from the solution obtained after pretreatment were treated with DNS 1%, boiled for 15 minutes on a water bath and then cooled. Extinction was measured (against blank) at 575 nm.

Results of the pretreatment method with dilute sulfuric acid (H<sub>2</sub>SO<sub>4</sub> 0.55%) at 120°C, for 15 and 30 minutes, are presented in the table below:

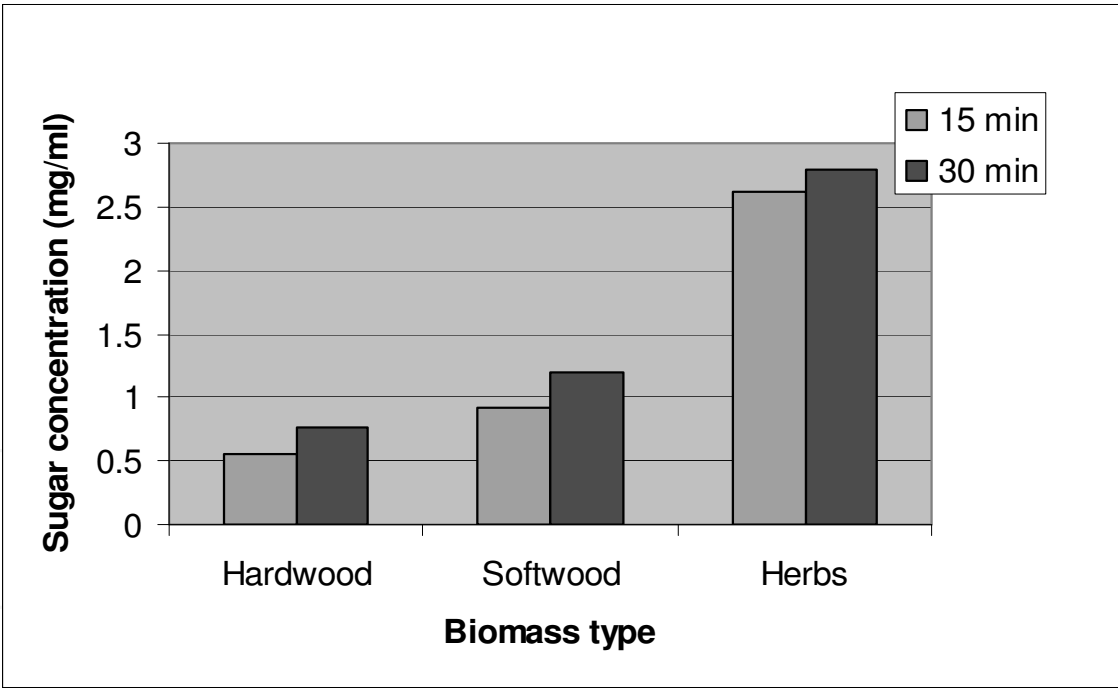


Fig. 1. Pretreatment of the biomass with H<sub>2</sub>SO<sub>4</sub> 0.55% at 120°C

As it may be seen, best results are obtained for the sawdust from herbaceous plants (in our case, hemp). The amount of sugars (expressed as free glucose) obtained after pretreatment is almost three times higher in the case of hemp sawdust than in the case of hardwood sawdust.

Pretreatment with the same acid solution (H<sub>2</sub>SO<sub>4</sub> 0.55%) at 140 and 160°C, respectively, led to the following results:

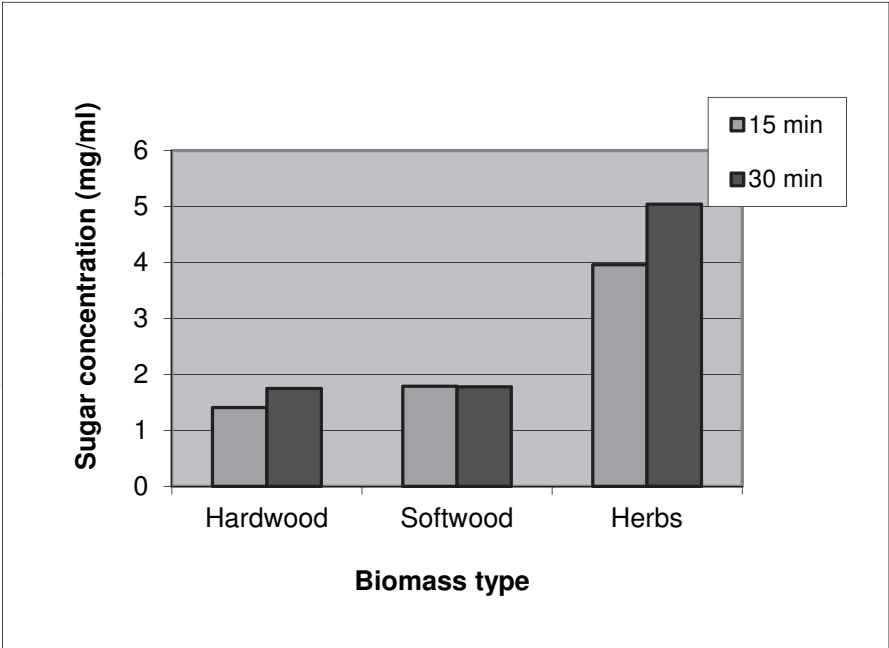


Fig. 2. Pretreatment of the biomass with H<sub>2</sub>SO<sub>4</sub> 0.55% at 140°C

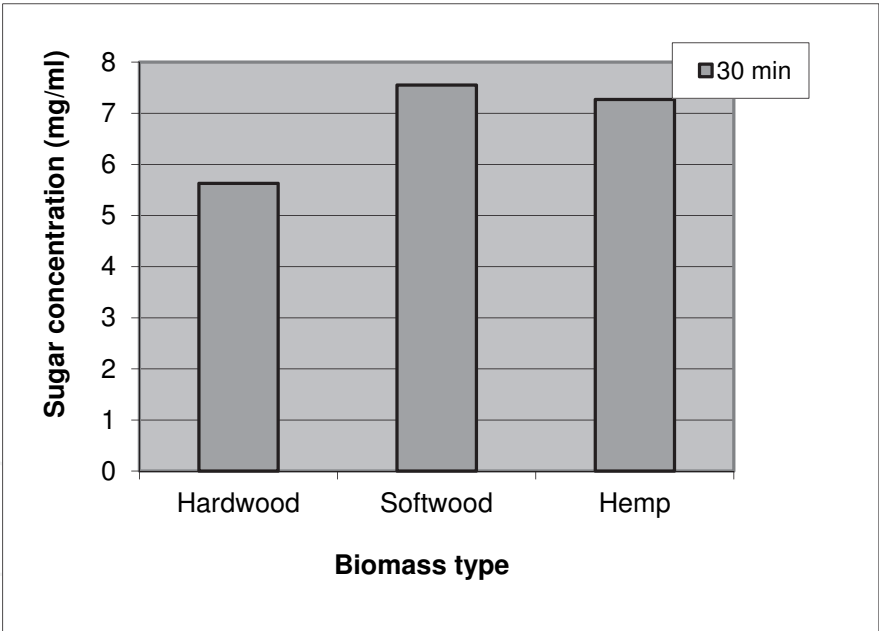


Fig. 3. Pretreatment of the biomass with H<sub>2</sub>SO<sub>4</sub> 0.55% at 160°C

In the case of the pretreatment with H<sub>2</sub>SO<sub>4</sub> 0.55% at 140°C, an increase of the reaction (pretreatment) time has significant consequences only in the case of hemp sawdust, when higher concentration of free sugars are obtained when the pretreatment time is 30 minutes instead of 15 minutes. For the hardwood (oak) and softwood (fir) sawdust, an increase of the pretreatment time does not lead to a significant improvement of the free sugars yield. In the case of pretreatment with dilute acid at 160°C, our previous studies showed that there is no difference between the results of the pretreatment process at 15 or 30 min. Taking into



account that in the other pretreatment methods best results have been obtained when the pretreatment lasted 30 minutes, the same period was chosen for the hydrolysis with  $\text{H}_2\text{SO}_4$  0.55% at 160°C.

All the presented results show that, best results are obtained when pretreatment at 160°C is performed. The highest yields in free sugars are obtained for softwood and herbaceous sawdust, respectively, so it may be said that the softwood and herbaceous sawdust structure is more easily attacked than the hardwood sawdust structure during the acid hydrolysis.

The same pretreatment method with dilute sulfuric acid (0.82%) combined with microwave irradiation was used for the same types of sawdust (hardwood-oak, softwood-fir, herbaceous-hemp) at three different temperatures. The experiments were carried out in the same conditions as mentioned before, the only change being the different concentration of the acid. The aim of the study was to establish if an increase of the acid concentration leads to an increase of the amount of obtained sugars in the same temperatures conditions or, as a result, much of the already formed sugars will be degraded. The results are presented in the figures below:

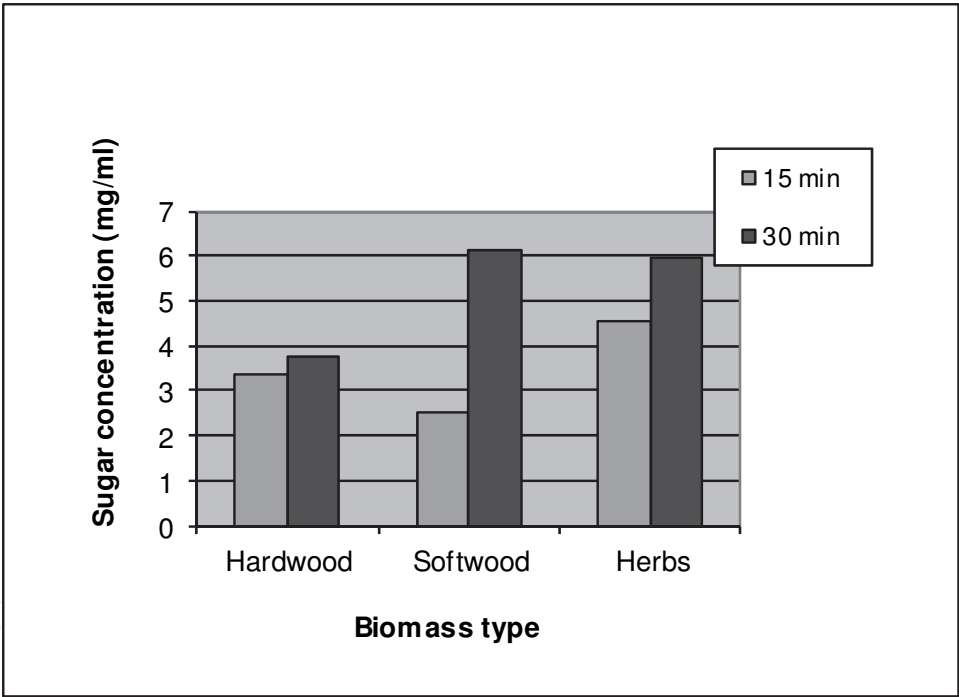


Fig. 4. Pretreatment of the biomass with  $\text{H}_2\text{SO}_4$  0.82% at 120°C

According to these results, a slight concentrated solution of sulfuric acid has better results regarding the concentration in fermentable sugars of the solutions obtained after pretreatment. Good results are obtained especially for the fir sawdust, the level of sugars is almost 5 times higher when treated with  $\text{H}_2\text{SO}_4$  0.82% at 120°C for 30 minutes than with  $\text{H}_2\text{SO}_4$  0.55% for an identical time and temperature. Also the results of hardwood sawdust pretreatment are improved, the concentration of final solutions after pretreatment in free sugars is almost three times higher than in the case when  $\text{H}_2\text{SO}_4$  0.55% was used. The results of the pretreatment are much poorer for the oak (hardwood) sawdust than for the fir (softwood) and herbaceous (hemp) sawdust.

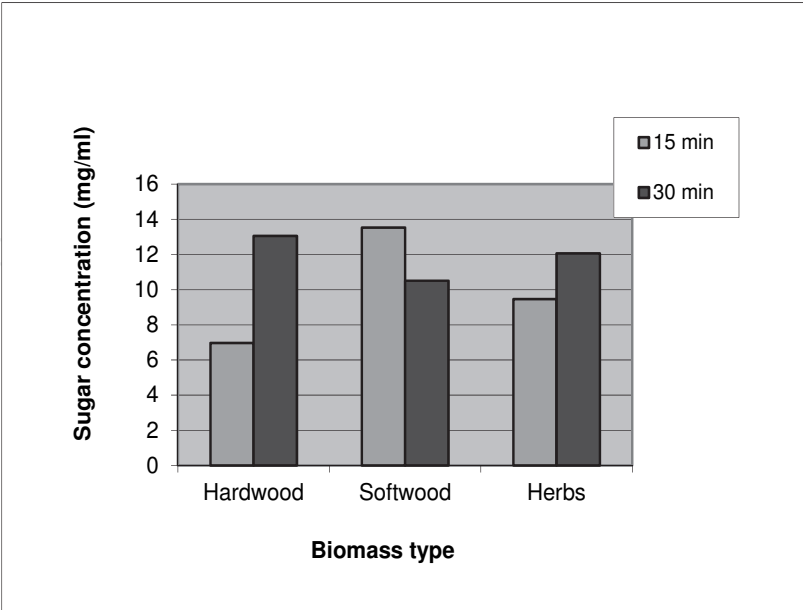


Fig. 5. Pretreatment of the biomass with H<sub>2</sub>SO<sub>4</sub> 0.82% at 140°C

Pretreatment with sulfuric acid 0.82% at 140°C led to the obtaining of very similar results for all the sawdust types used in the study. Except the softwood sawdust, when best results were obtained for a shorter reaction time (15 minutes), pretreatment with H<sub>2</sub>SO<sub>4</sub> 0.82% at 140°C for 30 minutes is more efficient than the similar one with H<sub>2</sub>SO<sub>4</sub> 0.55%.

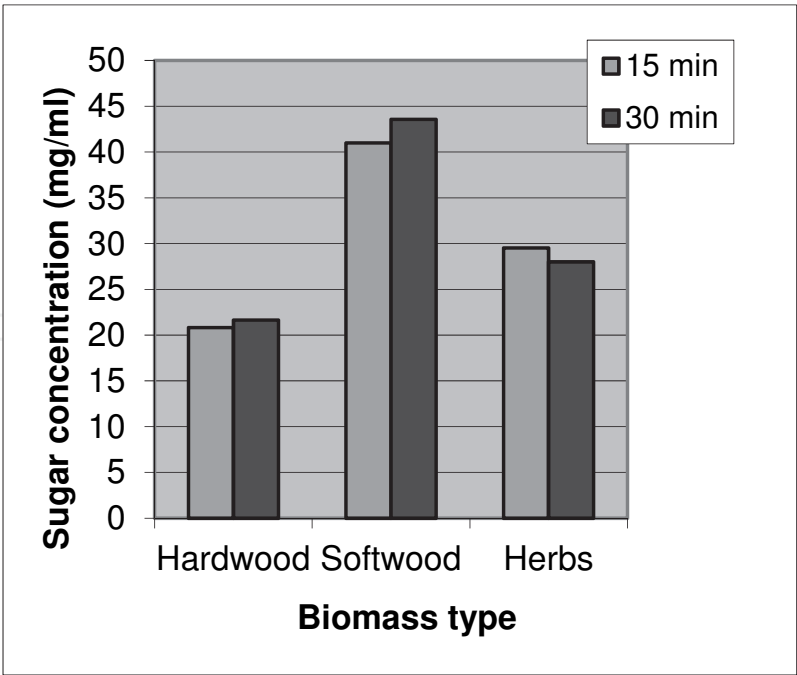


Fig. 6. Pretreatment of the biomass with H<sub>2</sub>SO<sub>4</sub> 0.82% at 160°C

When temperature is increased to 160°C, much higher concentrations of fermentable sugars are obtained. It may be observed that, at this temperature, there are almost no differences

between the results of the 15 minutes and 30 minutes pretreatment. The pretreatment method shows its efficiency especially as regards the fir sawdust, followed by the hemp sawdust. As happened in all of the previous cases, poorer concentrations in fermentable sugars are obtained for the oak sawdust. Same pretreatment method was used for the three types of sawdust, but in this case a solution of  $H_2SO_4$  1.23% was used. The results are presented below in a graphic form:

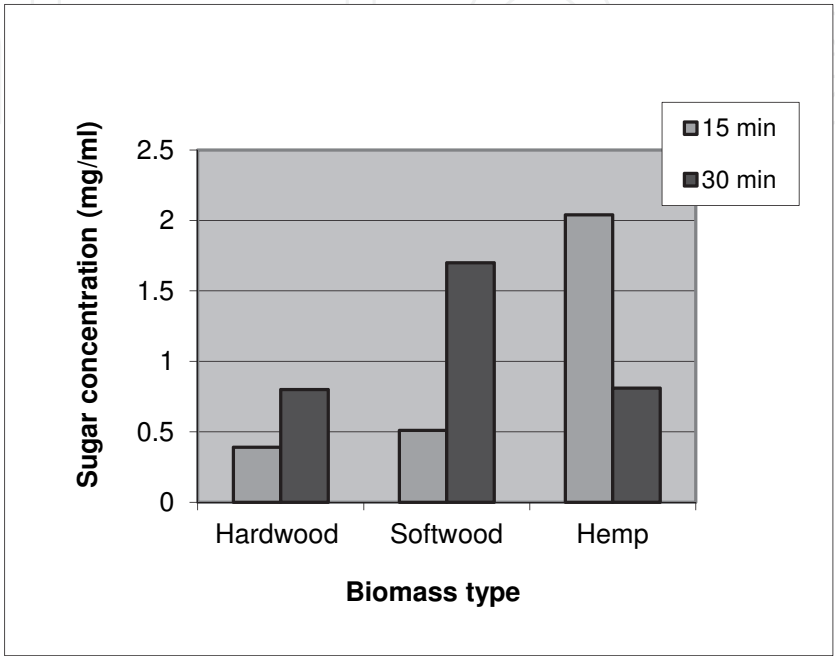


Fig. 7. Pretreatment of the biomass with  $H_2SO_4$  1.23% at 120°C

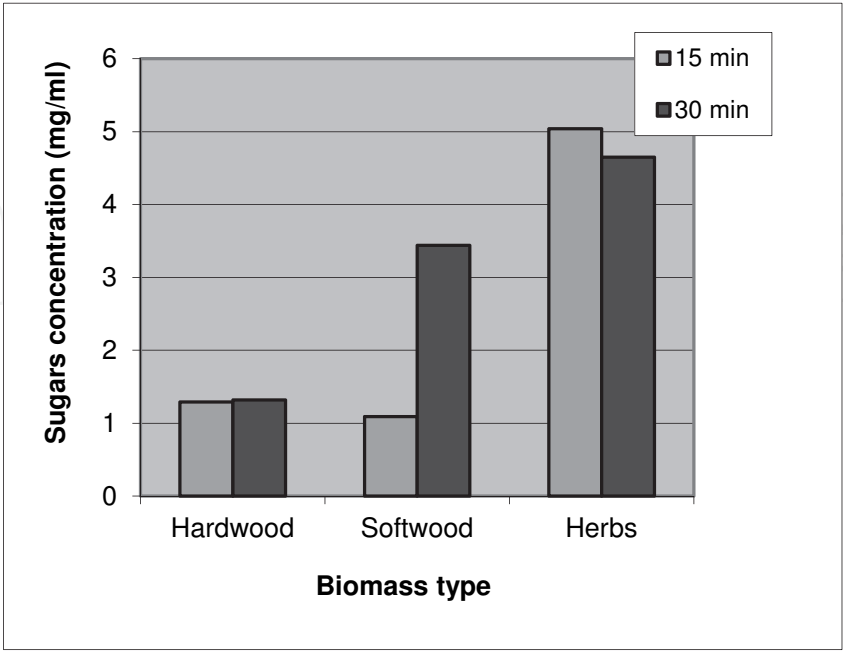


Fig. 8. Pretreatment of the biomass with  $H_2SO_4$  1.23% at 140°C

It may be seen that the results of the pretreatment with a solution of sulfuric acid 1.23% in the same conditions of temperature and residence time result in much poorer results than in the above-mentioned case, when sulfuric acid 0.82% was used. A possible explanation consists in the fact that, at higher concentrations of acidic solution, the already formed sugars to be destroyed and degraded.

Taking into account the similarity of the results of the pretreatment with  $\text{H}_2\text{SO}_4$  0.82% at 160°C for 15 and 30 minutes respectively, reaction of the sawdust with  $\text{H}_2\text{SO}_4$  1.23% at 160°C was carried out only for 30 minutes. The results are presented below:

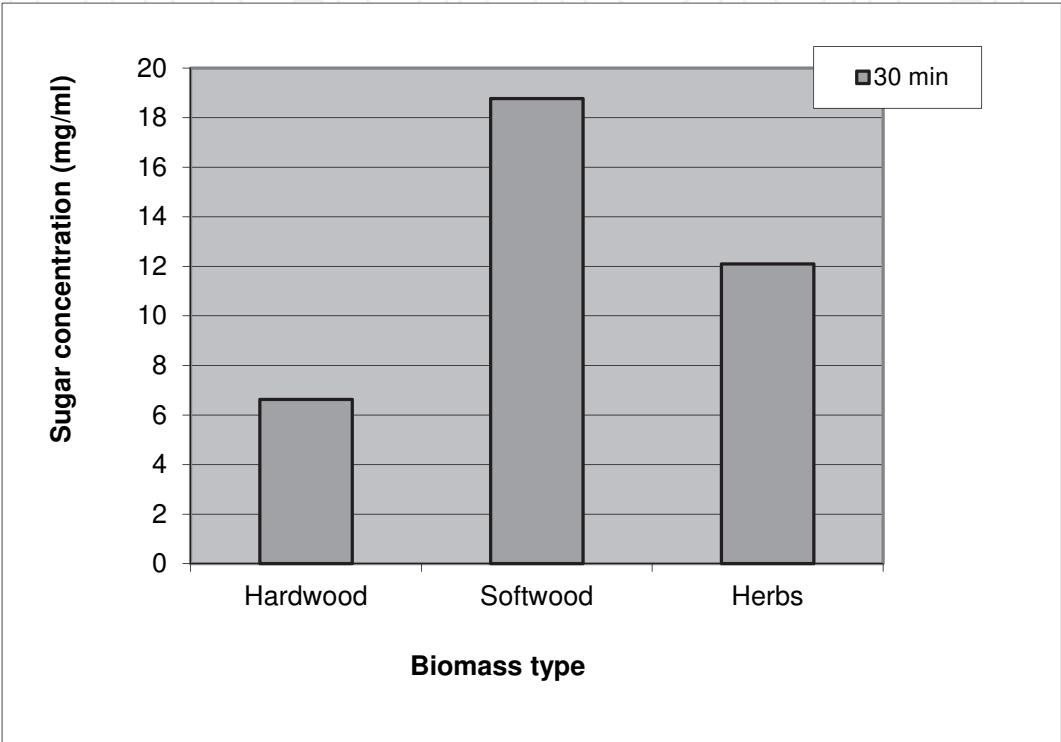


Fig. 9. Pretreatment of the biomass with  $\text{H}_2\text{SO}_4$  1.23% at 160°C

Unlike the pretreatment with  $\text{H}_2\text{SO}_4$  0.55%, it may be observed that in the case of herbaceous sawdust (hemp), an increased reaction time leads to smaller amounts of fermentable sugars. A stronger acid and a longer pretreatment time have better results only for the softwood (fir) sawdust, while as regarding the herbaceous sawdust it appears that a shorter reaction time leads to an increase yield in fermentable sugars. Data presented in Figures... show that the best results are obtained for the fir sawdust, and, as in the previous case ( $\text{H}_2\text{SO}_4$  0.55%), the pretreatment method gives the poorer results for the hardwood sawdust. It appears that a prolonged acid pretreatment, with a slight acidic solution (than the concentrations of  $\text{H}_2\text{SO}_4$  used before, namely 0.55% and 0.82%) is not benefic for the herbaceous sawdust, being possible that a great part of the already formed fermentable sugars to be simultaneously degraded during the pretreatment time.

In order to see if a more concentrated acid has a positive influence on the acid hydrolysis of the lignocellulosic materials, a solution of  $\text{H}_2\text{SO}_4$  1.64% was employed for the pretreatment of the three types of sawdust, at the same temperatures (120, 140 and 160°C) and 15 and 30 minutes reaction time, respectively. The results are the following:

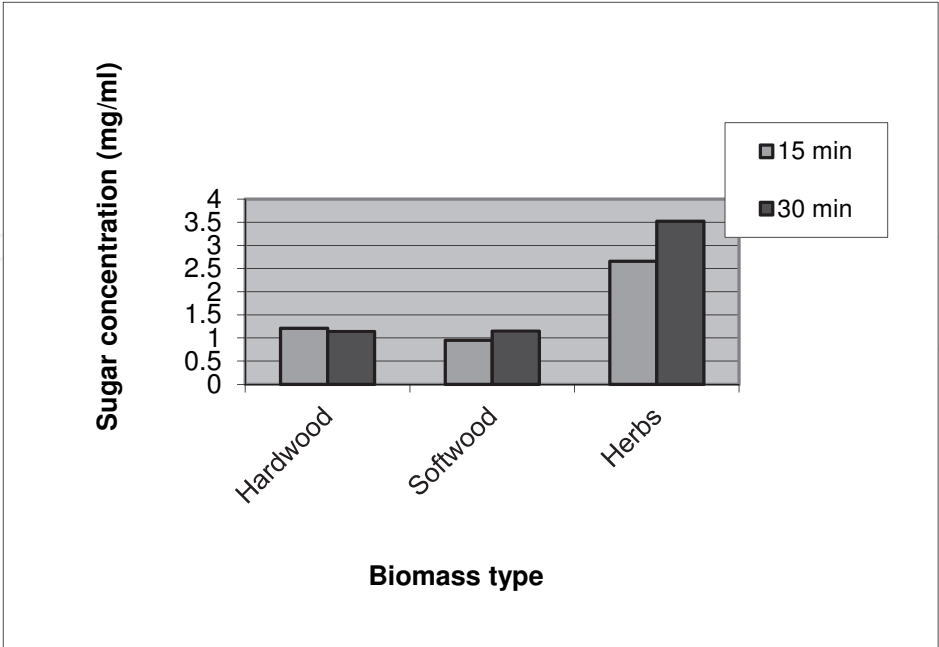


Fig. 10. Pretreatment of the biomass with H<sub>2</sub>SO<sub>4</sub> 1.64% at 120°C

The results show that hemp sawdust is favored by this pretreatment method, but the concentrations in fermentable sugars are lower than the ones obtained in the same conditions, but when H<sub>2</sub>SO<sub>4</sub> 0.82% was used.

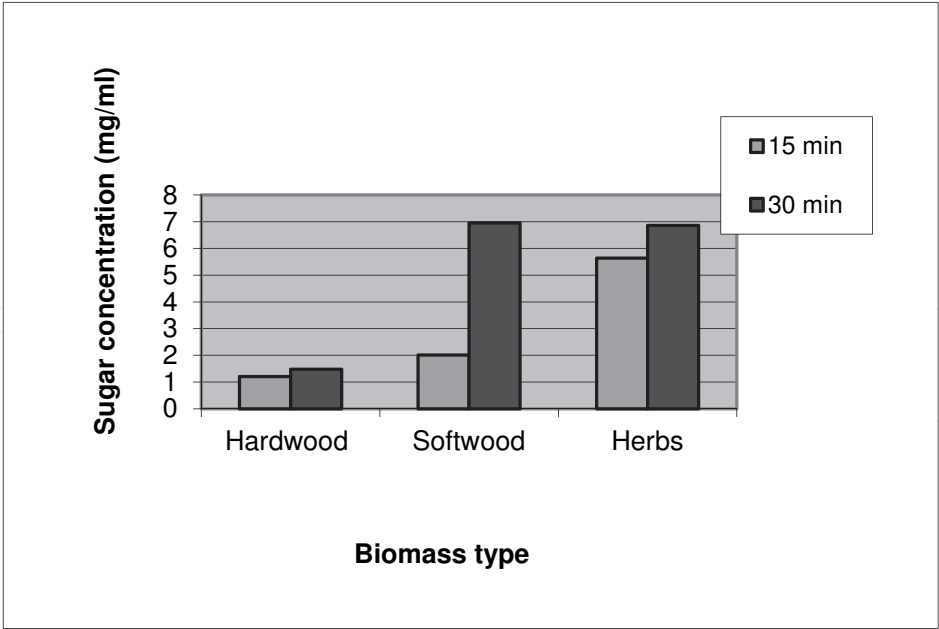


Fig. 11. Pretreatment of the biomass with H<sub>2</sub>SO<sub>4</sub> 1.64% at 140°C

An increase of the temperature leads to a higher concentrations in free sugars, but only for fir and hemp sawdust, respectively. Elevated residence time led to considerably improved results, especially as regarding the hemp sawdust.

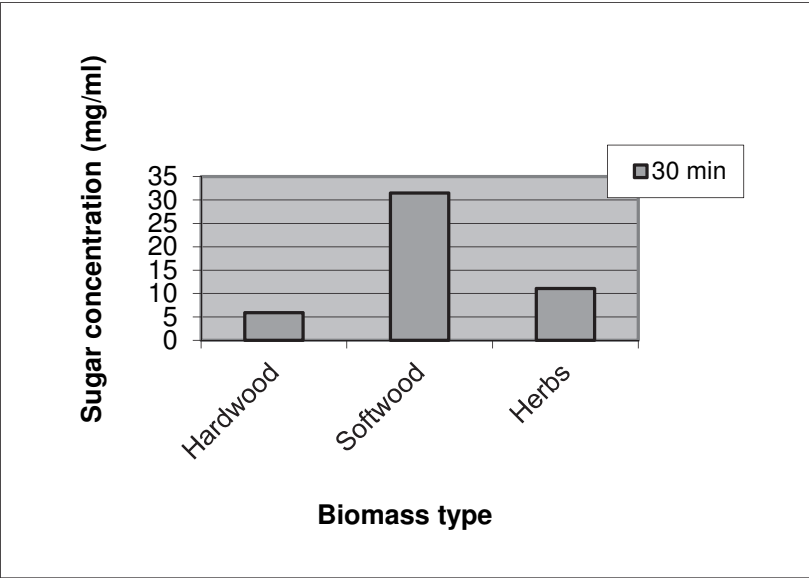


Fig. 12. Pretreatment of the biomass with H<sub>2</sub>SO<sub>4</sub> 1.64% at 160°C

The profile of the results is, somewhat, similar to the pretreatment with H<sub>2</sub>SO<sub>4</sub> 0.82% in the same conditions. It may be observed that, quantitatively, pretreatment at higher temperatures and longer time leads to better results. The amount of fermentable sugars increases with the acid concentration and with the residence time. Best results are obtained for the fir sawdust, when pretreated with H<sub>2</sub>SO<sub>4</sub> 1.64% at 160°C. Poorer results are obtained for the herbaceous sawdust (hemp) and hardwood sawdust, respectively. It appears that harsh conditions are required for a corresponding pretreatment in the case of fir sawdust (30 minutes residence time and 140 or 160°C).

Best results are obtained for the fir sawdust, when pretreated with H<sub>2</sub>SO<sub>4</sub> 0.82% at 160°C, with no significant difference due to the residence time (15 or 30 minutes).

As regarding the hemp sawdust, the best results are obtained when pretreatment with H<sub>2</sub>SO<sub>4</sub> 0.82% at 160°C for 15 minutes is employed. It can be said that a corresponding hydrolysis of the lignocellulosics from herbaceous sawdust requires less harsh conditions than the acid hydrolysis of softwood sawdust.

Concerning the hardwood sawdust, it may be said that pretreatment with dilute acids at temperatures in the range 120-160°C is not suitable. In all of the cases, only small amounts of free, fermentable sugars are obtained after the pretreatment. From all the pretreatment variant presented, it appears that the most suitable is the method that uses H<sub>2</sub>SO<sub>4</sub> 0.82% at 160°C for 15 minutes (the differences are very small between results of the 15 minutes and 30 minutes pretreatment, respectively).

It may be said that a corresponding microwave-assisted pretreatment of oak, fir and hemp sawdust is achieved by means of dilute sulfuric acid (0.82%) at 160°C, for 15 minutes.

In order to determine the pretreatment severity, the combined severity factor (CSF) that includes acid concentration, temperature and pretreatment time was used (Hsu et al., 2010).

$$CSF = \log\{t \cdot \exp[(T_H - T_R)14.75]\} - pH$$

Where: t - time (minutes), TH - temperature of the process, TR - reference temperature (100°C), pH - pH of the dilute sulfuric acid.



Pretreatment conditions	Acid concentration (%)	CSF
120°C, 15'	0.55	0.65
	0.82	0.80
	1.23	0.95
	1.64	1.10
120°C, 30'	0.55	0.95
	0.82	1.10
	1.23	1.25
	1.64	1.40
140°C, 15'	0.55	1.25
	0.82	1.40
	1.23	1.55
	1.64	1.65
140°C, 30'	0.55	1.55
	0.82	1.70
	1.23	1.85
	1.64	1.95
160°C, 30'	0.55	2.10
	0.82	2.30
	1.23	2.45
	1.64	2.55

Table 1. The combined severity factor (CSF) of the different variants of the microwave-assisted dilute acid hydrolysis process

4. A study concerning the possibility of using lyophilization as an efficient pretreatment method of the lignocellulosic residues

Experimental part: a suspension of sawdust and NaOH 1% and H<sub>2</sub>SO<sub>4</sub> 1% solution (1:10 w/v) was lyophilized at -52°C for 24 hours. The pretreated suspensions were filtered, washed with ultrapure water and the filtrate was neutralized with a solution of H<sub>2</sub>SO<sub>4</sub> 0.82% (the alkaline ones) and with CaCO<sub>3</sub> (the acid ones). The concentration in free, fermentable sugars was determined using the colorimetric method with 3,5-dinitrosalicylic acid.

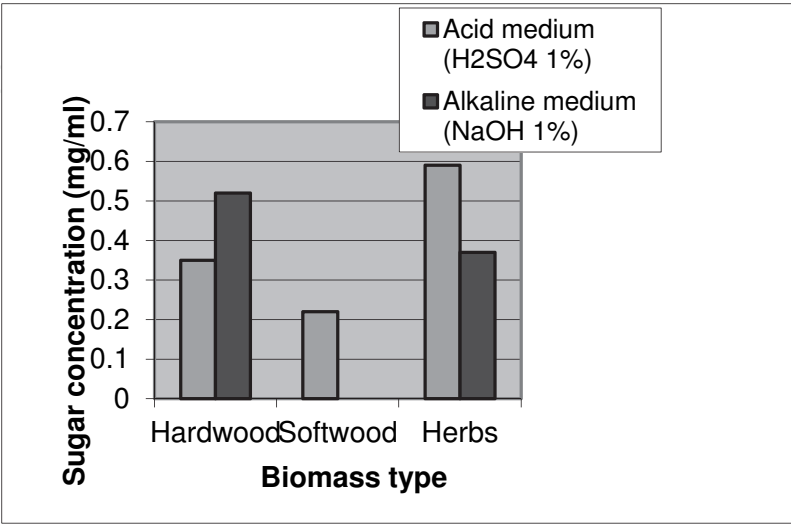


Fig. 13. Results of the alkaline and acid lyophilization pretreatment

The concentrations of free sugars are much poorer compared to the ones obtained after the combined pretreatment of microwave irradiation and dilute acid hydrolysis. No detectable concentrations of fermentable sugars were obtained for fir sawdust, when treated with an alkaline solution. A comparison between the two proposed methods is clearly in the favor of the microwave-assisted acid hydrolysis, which requires much less time and lower economic costs.

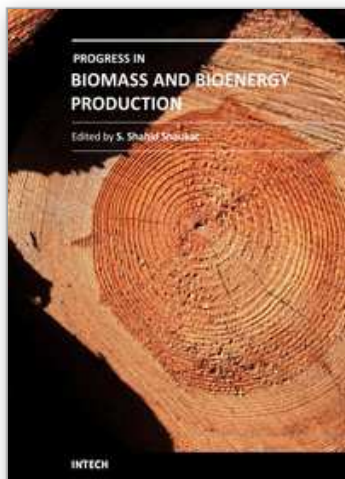
## 5. Conclusions

The results of the microwave-assisted acid pretreatment of the lignocellulosic biomass show that for good results in free sugars concentration there are not necessary elevated temperatures and high acid concentration. As results from the performed study, very efficient seems to be the pretreatment with sulfuric acid 0.82% at a temperature of 140°C, conditions that are characterized by a combined severity factor of 1.7. As regarding the possibility of using lyophilization in acid or alkaline medium, the obtained results are very poor and do not stand for the use of lyophilization as a viable pretreatment method.

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## **Progress in Biomass and Bioenergy Production**

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Alternative energy sources have become a hot topic in recent years. The supply of fossil fuel, which provides about 95 percent of total energy demand today, will eventually run out in a few decades. By contrast, biomass and biofuel have the potential to become one of the major global primary energy source along with other alternate energy sources in the years to come. A wide variety of biomass conversion options with different performance characteristics exists. The goal of this book is to provide the readers with current state of art about biomass and bioenergy production and some other environmental technologies such as Wastewater treatment, Biosorption and Bio-economics. Organized around providing recent methodology, current state of modelling and techniques of parameter estimation in gasification process are presented at length. As such, this volume can be used by undergraduate and graduate students as a reference book and by the researchers and environmental engineers for reviewing the current state of knowledge on biomass and bioenergy production, biosorption and wastewater treatment.

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