CELLULOSE CHEMISTRY AND TECHNOLOGY

DILUTE SULPHURIC ACID HYDROLYSIS OF VEGETAL BIOMASS

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In this study, the influence of the temperature in the flow-through dilute sulphuric acid hydrolysis (0.5% w/w of sulphuric acid) of vegetal biomass on the sugar yield of the hydrolysate was investigated. For the hydrolysis of vegetal biomass, a reactor was used at a designed reaction temperature between 150 °C and 180 °C. The study indicated that prehydrolyzed rapeseed stalks presented higher values of sugar yields, which did not exceed 19%, while beech sawdust hydrolysis led a maximum of 5.96%. Therefore, we can conclude that rapeseed stalks have superior hydrolytic potential compared to beech sawdust. By raising the temperature from 150 °C to 180 °C, there is an increase in TRS yield of the hydrolysates, thus the temperature increase favours the TRS.

Keywords: dilute acid hydrolysis, flow through, vegetal biomass

INTRODUCTION

In recent years, because of limited energy resources, the interest in using vegetal materials as potential sources of energy and chemical intermediates has increased, as they are biodegradable, low-cost and can be converted into valuable products with numerous applications in various industries.[1] Also, the plant material used as a source of energy may derive from crops, forest residues, animal manure, the organic fraction of municipal solid waste and agro-industrial processing by-products, such as bagasse, oil-palm residues, sawdust and wood offcuts. Biomass might gradually replace oil to face the increased energy demand, allowing virtually any county to rely on it to satisfy at least a part of the local consumption.[2]

Most methods of flow-through hydrolysis are based on the principles of polysaccharides hydrolysis. Regardless of the method applied, the final goal of hydrolytic treatment is to remove selective hemicelluloses from vegetal materials, with the subsequent separation of sugars for fermentation and for obtaining furfural, of cellolignins to be used in the manufacture of chemical pulps, or to achieve wood saccharification for obtaining glucose (hydrolysis in two steps: of pentoses and hexoses).[3] Also, polysaccharides have received special attention due to the diversity of their sources, their non-toxicity, biodegradability and biocompatibility, but also due to the fact that they are renewable sources capable of chemical modifications.[4]

Most of dilute acid pretreatments are carried out at high temperature from 150 °C to 250 °C and even high pressure from 2 atm to 24 atm.[5] Under such severe conditions, some cellulose will be converted into sugars and then quickly degraded to other compounds.[6]

Some of the most well-known hydrolysis processes include: the percolation hydrolysis at 130-190 °C with dilute sulphuric acid realized in fixed bed reactors of different sizes; the continuous hydrolysis of wood in counter-current with dilute sulphuric acid column reactors constructed from titanium alloy to 380 m^3 to process 8-12 tons of dry wood/hour; the continuous mechano-chemical saccharification of sawdust with 75% sulphuric acid (1:1.5 w/w) – the so-called Riga hydrolysis processes tested in the late 1950s - early 60s.[7]

Acid hydrolysis of wood polysaccharides has been the subject of numerous investigations, which revealed some characteristic aspects of this treatment:[8]

- the glycosidic bond strength depends on the structure of polysaccharides;
- if monomer units included in the polysaccharide structure are found as furanose (araban), only dilute acids and a short time are required for complete hydrolysis;

- the polysaccharides composed of pentose units of the pyranose type are more resistant to hydrolysis than the corresponding furanose, but they are more easily hydrolyzed than the polysaccharides composed of hexose units of the pyranose type;
- the bonds are most resistant to hydrolysis by binding the glucuronopyranoside ring to anhydro-monosaccharide;
- hemicellulosic fractions usually contain a variable percentage of uronic acids, which initially hydrolyze easily, but show particular resistance in the last phase, as a result of the accumulation of aldobiouronic acid (small amounts of aldotriuronic acid);
- acetyl groups and, to a lesser extent, the methoxyl content of the wood are also hydrolyzed by the action of acids.[8]

Ideally, the effective pretreatment of vegetal materials should allow the following: recovering the maximum of carbohydrates and by-products to improve economic feasibility; reducing the generation of inhibitors obtained from carbohydrates degradation during pretreatment, such as furfural, 5-hydroxymethylfurfural and acetic acid, which could significantly inhibit the enzymatic hydrolysis and fermentation of the vegetal material; reducing the need for subsequent processes, such as washing and neutralization; reducing consumption of water and chemical agents; moderately low power consumption and relatively high yields. Understanding the pretreatment fundamentals and the relationship between the structural characteristics and enzymatic hydrolysis of vegetal material, pure delignification should be developed, which would bring the benefits of hexose and pentose sugars co-fermentation, and economic efficiency, low investment cost and low environmental impact.[9]

The objective of this work has been to study the flow-through hydrolysis of vegetal biomass with dilute sulphuric acid and the influence of the hydrolysis temperature of each component during the acid hydrolysis process.

EXPERIMENTAL

Materials

In this study, we used two types of vegetal biomass: rapeseed stalks and beech sawdust from Romania. Liquid hydrolysate samples obtained by prehydrolysis of vegetal biomass with 0.5% H_2SO_4 solution were noted as: P0 – the hydrolysate collected after 15 min, P1 – the hydrolysate collected after 45 min, P2 – the hydrolysate collected after 75 min, P3 – the hydrolysate collected after 105 min, P4 – the hydrolysate collected after 125 min.

Methods

Dilute acid hydrolysis step

The rapeseed stalks and beech sawdust used in this study were pretreated at reaction temperatures ranging from 150 °C to 180 °C with 0.5% H_2SO_4 solution in laboratory designed equipment, consisting of a stainless steel flow-through reactor with dimensions of 150 x 10 mm. The flow-through experiments followed a procedure similar to that described previously by Liu and Wyman.[10,11] The reactor vessel was sealed and heated in a sand bath temperature controller provided with a HPLC pump. Then the reactor was transferred to a sand bath at 150 °C to 180 °C to maintain the target temperature. After completion of the experiment, the reactor was cooled down to room temperature, the solids were separated from the liquid hydrolysate through centrifugation for 5 min. The solids were collected and washed with demineralized water to neutralize and remove possible degradation products.[12]

Methods of analysis for vegetal biomass hydrolysate

Total reducing substances (TRS) of hydrolysates

The concentration of total reducing substances (TRS) in hydrolysates was estimated using DNS (3,5 dinitrosalicylic acid) reagent with a JASCOV-550 spectrophotometer at a wavelength of 540 nm.[13] DNS can determine the concentration of all reducing sugars in the hydrolysis medium, not only glucose. After determining the total reducing substances, a posthydrolysis of the hydrolysates was performed with 4% H_2SO_4 for one hour at the temperature of 121 °C.[14]

Yields of total dissolved solids (TDS) of hydrolysates

The concentration of the total dissolved solids was determined by pipetting 5 mL liquid fraction of samples in a porcelain capsule previously dried and weighed. The capsule was placed in a convection oven and dried to constant weight at 105 ± 2 °C for 24 hours.[15]

RESULTS AND DISCUSSION

Effect of hydrolysis temperature on TRS yields of the rapeseed stalk hydrolysate

In order to improve the yields of reducing substances (related to oven dried material) in the prehydrolysis of rapeseed stalks, hydrolytic treatments were performed with 0.5% H_2SO_4 solution, in the flow-through regime and the temperature range 150 °C-180 °C.

From the mathematical algorithm correlation equations were obtained with reducing substances yield (related to oven dried material) as a dependent variable, and duration and temperature as independent variables. As an example, Figure 1 shows the response surface f (X_1, X_2) and contour plots applied to the content of the yield in the reducing substances. According to Figure 1, at 170 °C pretreatment temperature, the TRS yield in the hydrolysates increased with time, ranging from 1.09% after 20 min to 17.0% after 150 min related to oven dried material.

Figure 2 presents the TRS yields of the rapeseed stalk hydrolysate (related to oven dried material) obtained by flow-through prehydrolysis with 0.5% H_2SO_4 solution, as a function of temperature.

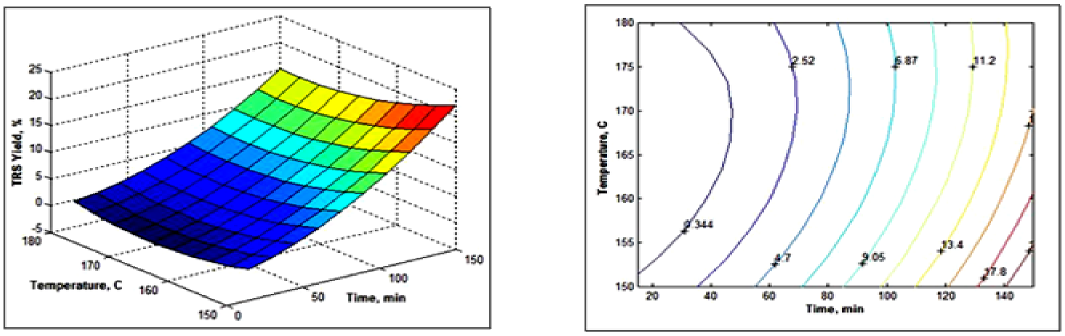


Figure 1: Response surface and contour plots for TRS yields (related to oven dried material) in rapeseed stalk hydrolysates depending on time and temperature

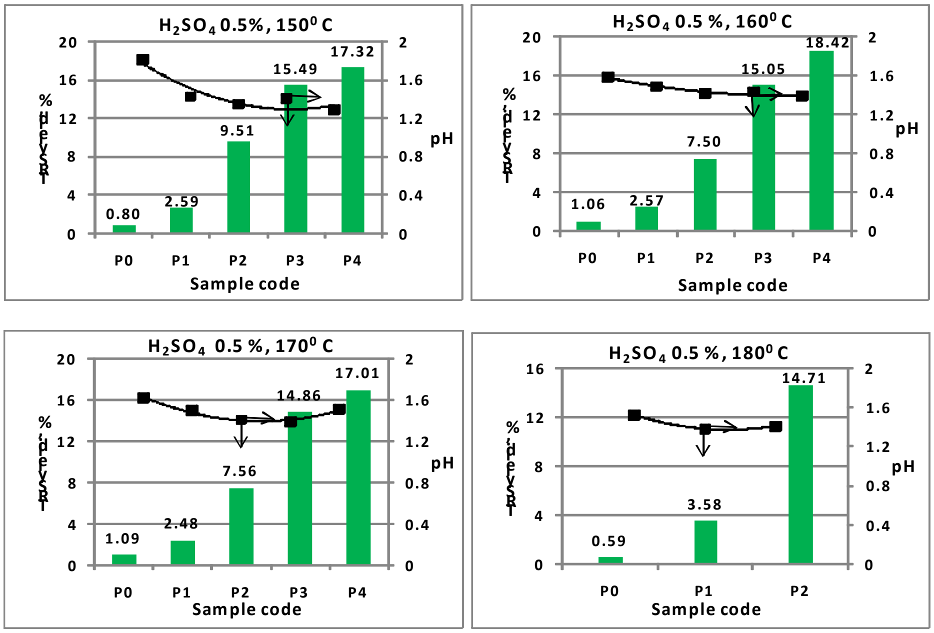


Figure 2: Evolution of TRS yields (related to oven dried material) and pH in rapeseed stalk hydrolysates as a function of temperature

Effect of hydrolysis temperature on TRS yields of the beech sawdust hydrolysate

In order to estimate the hydrolysis potential of rapeseed stalks, a comparative study was carried out on beech sawdust prehydrolysed with 0.5% H_2SO_4 solution, in the same temperature range (150 °C-180 °C). Thus, the conditions under which the best results were achieved for rapeseed stalks were applied also for beech sawdust. The focus was on the sugars yield of beech sawdust after flow-through prehydrolysis. The results obtained were processed mathematically; the response surface and contour plots at constant levels are shown in Figure 3.

Analysing the contour constant at 170 °C, an increase in sugars yields (related to oven dried material) is remarked from 0.42% (30 min) to 5.26% (130 min). From Figure 4, it is noted that with increasing temperature the sugar yields increased from 1.44% (150 °C) to 5.96% (180 °C).

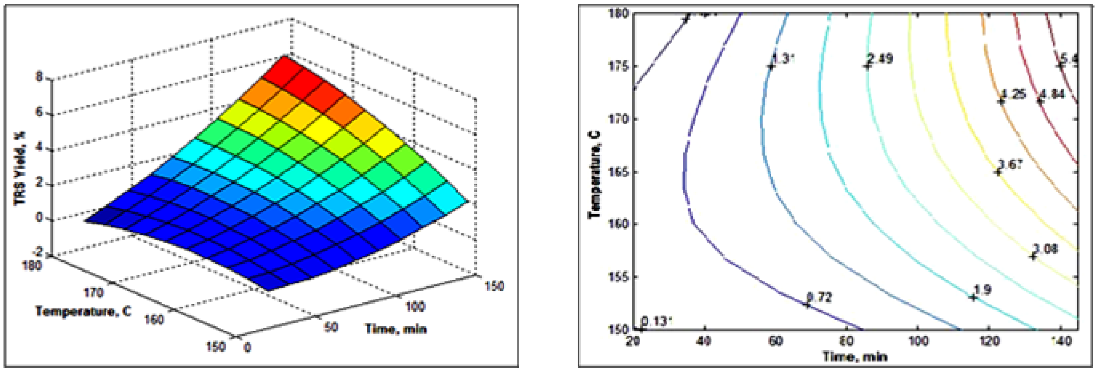


Figure 3: Response surface and contour plots for TRS yields (related to oven dried material) in beech sawdust hydrolysates depending on time and temperature

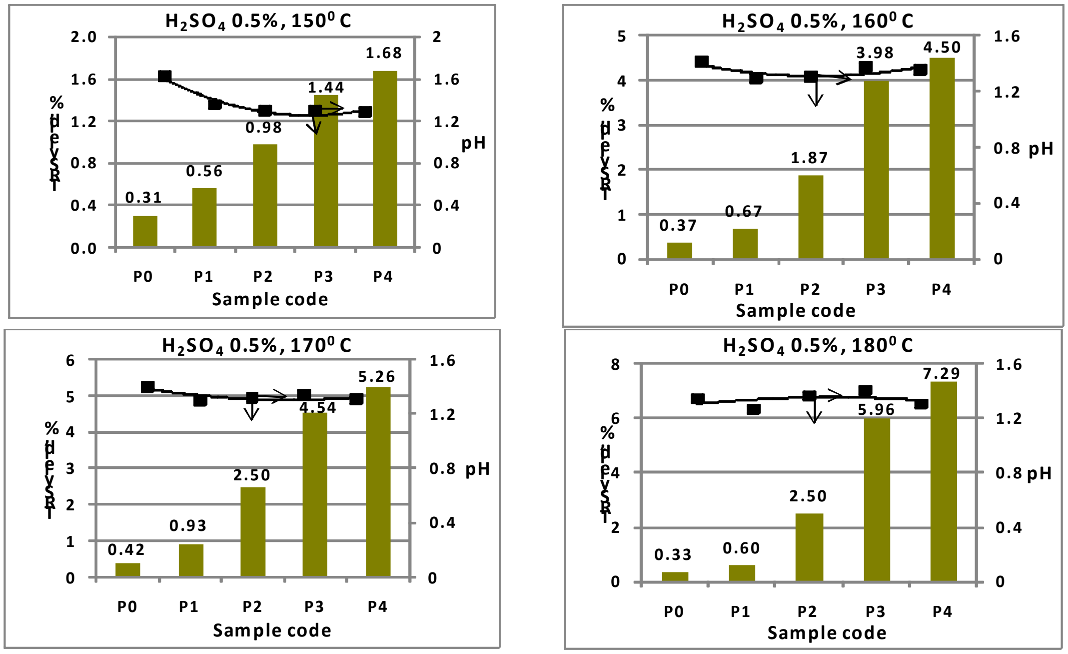


Figure 4: Evolution of TRS yields (related to oven dried material) and of pH in beech sawdust hydrolysates depending on temperature

The study of the rapeseed stalks prehydrolysis reveals that the highest values of sugar yields do not exceed 19%, while for beech sawdust a maximum of 5.96% is achieved, which leads to the conclusion that rapeseed stalks have superior hydrolytic potential to that of beech sawdust.

To assess the depth of prehydrolysis and the intensity of hydrolysis reactions, the severity factor (R_0)[16] and the criterion of hydrolysis (CS)[17,18] were calculated for the hydrolytic treatments studied. The severity factor (R_0) expressed the effects of reaction temperature and duration during the prehydrolysis of rapeseed stalks with 0.5% H_2SO_4 solution and ranged from 445 (150 °C) to 19271 (180 °C). To achieve the maximum duration of hydrolysis, (P_3) CS values ranged from 2.09 (150 °C) to 2.81 (180 °C). This parameter assesses the depth of hydrolysis and can be modified when considering the pH of the reaction medium.

Effect of hydrolysis temperature on dry matter yields in the rapeseed stalk hydrolysate

Further, the dry matter yield was monitored during the hydrolytic treatments, providing information on the amount of organic substance in solution, by the degradation of both polysaccharides and lignin fragments of low molecular weight. The data were processed mathematically and the resulting curves are shown in Figure 5.

Figure 5 exhibits the response surface and contour plots obtained from the mathematical algorithm applied to the solid content yields. The analysis shows that after the flow-through prehydrolysis of rapeseed stalks with 0.5% H_2SO_4 solution at constant temperature (160 °C), the dry matter content reached 14.19% after 105 min, and then decreased with increasing duration (Figure 6). This is explained by the increasing amount of hemicelluloses recorded in solution and the partial hydrolysis of lignin fragments of low molecular weight.

Effect of hydrolysis temperature on dry matter yields in the beech sawdust hydrolysate

Figures 7 and 8 show that, in the flow-through prehydrolysis with 0.5% H_2SO_4 solution at constant temperature (160 °C), the dry matter content (related to oven dried material) decreases with increasing the duration – from 7.19% (75 min) to 4.47% (140 min).

Effect of hydrolysis agent pH

The pH measurements of rapeseed stalk prehydrolysates obtained by prehydrolysis with 0.5% H_2SO_4 solution afforded values between 1.81÷1.20 (150 °C), 1.58÷1.38 (160 °C) and 1.62÷1.51 (170 °C).

The decrease in the pH value with the increase in hydrolysis duration was due to the occurrence of acetic acid of acetyl groups present in the initial structure of hemicelluloses. The increasing acidity is proportional to the duration of the prehydrolysis. It can be concluded that the resistance to degradation of sugars is much lower in a strongly acid (1.4-1.6) medium, and therefore a weakly acid medium (3.5-4.5) is advised.

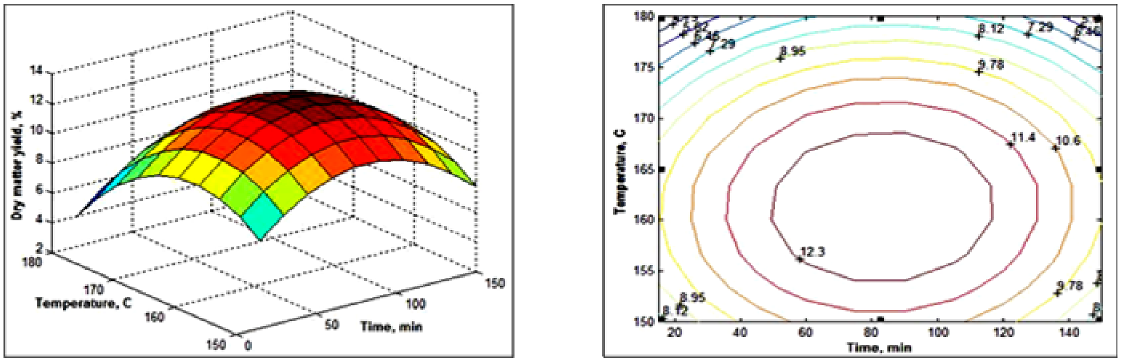
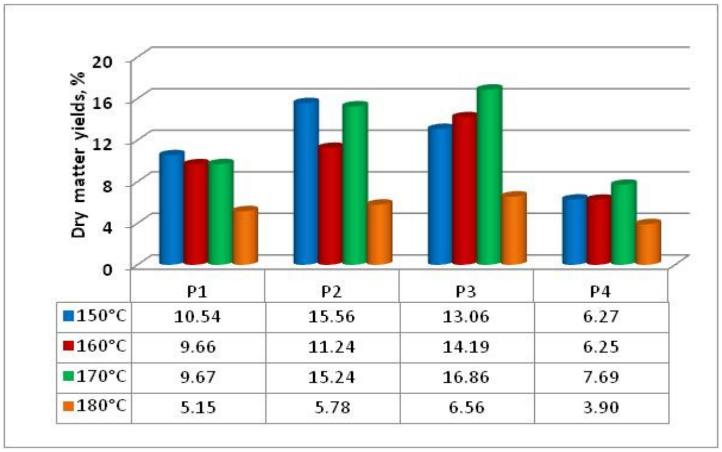


Figure 5: Response surface and contour plots for dry matter yields (related to oven dried material) in rapeseed stalk hydrolysates depending on time and temperature



	P1	P2	P3	P4
🟦150°C	10.54	15.56	13.06	6.27
🟥160°C	9.66	11.24	14.19	6.25
🟩170°C	9.67	15.24	16.86	7.69
🟧180°C	5.15	5.78	6.56	3.90

Figure 6: Dry matter yields (related to oven dried material) obtained after rapeseed stalk prehydrolysis with 0.5% H_2SO_4 solution

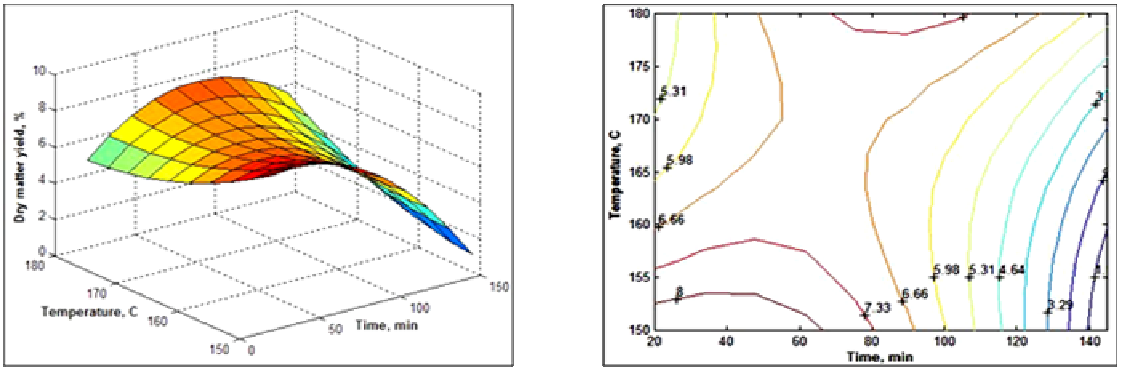
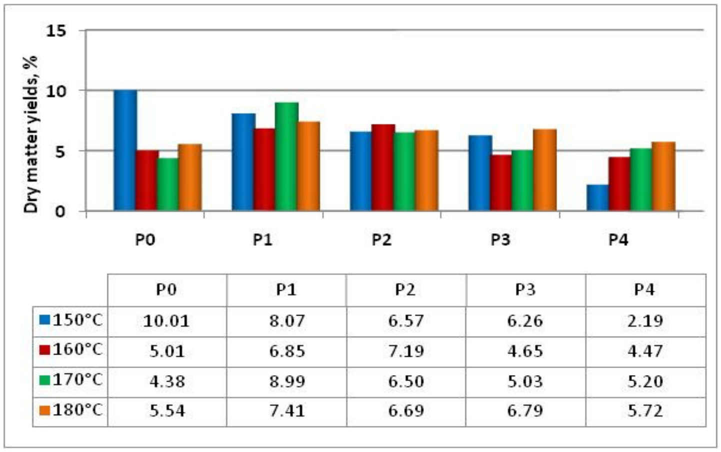


Figure 7: Response surface and contour plots for dry matter yields (related to oven dried material) in beech sawdust hydrolysates depending on time and temperature



	P0	P1	P2	P3	P4
🟦150°C	10.01	8.07	6.57	6.26	2.19
🟥160°C	5.01	6.85	7.19	4.65	4.47
🟩170°C	4.38	8.99	6.50	5.03	5.20
🟧180°C	5.54	7.41	6.69	6.79	5.72

Figure 8: Dry matter yields obtained after beech sawdust prehydrolysis with 0.5% H_2SO_4 solution

CONCLUSION

The behaviour of vegetal materials during the hydrolysis of polysaccharides was studied in a flow-through process at different temperature levels. The results shows that, by raising the temperature from 150 °C to 180 °C, there is an increase in TRS yield, thus the temperature increase favours the TRS. The study of the rapeseed stalks prehydrolysis reveals that the highest values of sugar yields do not exceed 19%, while for beech sawdust a maximum of 5.96% is achieved, which leads to the conclusion that rapeseed stalks have superior hydrolytic potential to that of beech sawdust. The prehydrolysis of rapeseed stalks with 0.5% H_2SO_4 solution afforded the highest values, which increased with increasing temperature due to the decomposition of monosaccharides caused by the conditions in the reactor during hydrolysis.

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