Dilute acid hydrolysis of softwood chips for the production of hemicellulose sugars

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Introduction

Lignocellulosic materials like wood, straw, and by-products from agriculture and food industry contain between 20 and 40% hemicellulose. Hemicellulose is a heteropolysaccharide consisting mainly of pentoses and hexoses. These sugars can be obtained as monomers by acid hydrolysis. Conventional hydrolysis methods concentrate on the hydrolysis of cellulose to glucose and use high temperatures or high acid concentrations. Such severe conditions lead to the degradation of the hemicellulose sugars to furfural or 5-hydroxymethylfurfural. The hydrolysis of hemicellulose takes place at less severe conditions, typically at temperatures below 180°C and acid concentrations below 1% [1, 2]. The hydrolysates can be used as a substrate for fermentation in order to produce ethanol or organic acids [3], while the remaining solids are a source for cellulose and lignin or can be burned as a fuel.

Materials and Methods

Hydrolysis experiments were carried out with spruce chips (particle size: 1mm) in a 20 l batch hydrolysis reactor. The effect of acid concentration, temperature, and reaction time on the yield of monosaccharides, sugar degradation products and organic acids was investigated using a central composite statistical experiment design. Acid concentration was varied between 0.2 and 0.6% H_2SO_4, temperature between 160 and 180°C, and reaction time between 8 and 20 min. The concentration of dry solids in the reaction mixture was kept constant at 15%.
Complete hydrolysis of the raw material and the solid remainings was carried out according to standard methods [4]. Sugars and sugar degradation products were analyzed by HPLC using a Macherey-Nagel ET 300/7.8 Nucleogel SUGAR Pb Column and water as solvent, while a Merck Polyspher OA KC RT 300-700 Column with 0.01 N H_2SO_4 as solvent was used for sugars and organic acids.

Table 1: Yields of Monosaccharides and Degradation of Sugars in g/100 Dry Softwood

Acid [mol/l]	Temperature [°C]	Reaction Time [min]	Recovered Monosaccharides [g/100 g]	Degraded Sugars [g/100 g]
0.02	160	8	6.04	0.03
0.02	160	20	10.76	0.20
0.02	180	8	14.12	0.42
0.02	180	20	7.51	0.73
0.06	160	8	14.71	0.33
0.06	160	20	15.32	1.27
0.06	180	8	14.37	3.06
0.06	180	20	8.56	6.57
0.04	170	8	13.20	0.31
0.04	170	20	12.20	1.07
0.02	170	14	13.03	0.36
0.06	170	14	12.31	1.60
0.04	160	14	13.56	0.28
0.04	180	14	14.56	3.05
0.04	170	14	16.42	1.21

Results and Discussion

The results of the experiments are summarized in Table 1. The highest yield obtained in the current experiments was 16.5 g/100 g dry wood and was observed at 170°C, 14 min, and 0.04 mol/l sulfuric acid. This is about 75% of the expected maximum level. Acid concentration shows the highest effect on sugar yields. There is also a strong negative interaction between temperature and time, which is resulting in lower yields at high temperatures and long reaction times. An analysis of a response surface model based on these results indicates that higher yields could be reached at low temperatures (160°C) and acid concentrations between 0.05 and 0.06 mol/l. Since temperature has the strongest impact on the formation of sugar degradation products these conditions will also provide hydrolysates with low concentrations of furfural and 5-hydroxymethylfurfural. This is favorable because these substances are known to act inhibiting on fermentations [5].

Mannose is the dominant sugar in softwood hemicellulose. Xylose and glucose can also be found at higher concentrations. Glucose in the hydrolysate is derived from hemicellulose as well as from cellulose. At conditions combining high acid concentrations with high temperatures degradation of glucose from hemicellulose occurs while new glucose is formed from cellulose hydrolysis. Therefore the glucose concentration stays constant or is even rising when hemicellulose sugar yields are reduced due to degradation at the same time.

Conclusion

The described method is useful for producing fermentable hydrolysates containing hemicellulose sugars. In order to limit the formation of sugar degradation products the temperature should be kept below 170°C. In the current experiments up to 75% of the hemicellulose could be converted into monosaccharides.

References

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