Hydrothermal Pretreatment Optimization for Enhanced Anaerobic Digestion of Willow Sawdust

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Abstract

In this study, hydrothermal pretreatment in combination with HCl, at a chemical loading of 2 g /100 g TS was carried out as a pretreatment method to enhance anaerobic digestion of willow sawdust. Regarding hydrothermal pretreatment, various temperatures (130.5-230^{o}C) and process times (15.5 -60 min) were studied, using a Central Composite Design so as to optimize pretreatment conditions and the methane potential.

Keywords: willow sawdust, methane production, hydrotherrmal pretreatment

1. Introduction

Lignocellulosic biomass including forestry residues such as willow sawdust (WS) could be used as feedstock for anaerobic digestion (AD). Hydrolysis has been shown to be the rate-limiting step in the case of AD of such substrates. Although being abundant, since the annual world production of biomass residues exceed 220 billion tons, the main obstacles of their use are the low yields attained, due to the recalcitrant nature of their lignocellulosic content. The application of a pretreatment process prior to AD could improve the hydrolysis and the total methane yield.

In this study hydrothermal pretreatment (HP) with HCl, at different temperature (T) and time combinations was performed in order to optimize pretreatment conditions. Thus, Central Composite Design was used as a guide to select the number of experiments. The pretreated WS samples were then characterized and used for methane production in biochemical methane potential (BMP) experiments so as to enhance AD of WS.

2. Materials And Methods

WS was chopped, milled, sieved to a powder and air-dried at ambient temperature. For all pretreatment methods used, the mass/volume ratio of solid (g TS) to liquid (mL) was 5:100. In Table 1, the pretreatment conditions used in this study are presented. The biomass slurry that resulted from the pretreatment, was separated into solid and liquid fractions, for further characterization and then used for BMP experiments. Characterization of the pretreated samples and BMP experiments were carried out according to Antonopoulou et al. (2015;2013), respectively.

Table 1. Pretreatment conditions used in this study

Run	Temperature	Time (min)
1	145	22
2	145	22
3	215	22
4	215	22
5	145	53
6	145	53
7	215	53
8	215	53
9	130,5	37.5
10	130,5	37.5
11	230	37.5
12	230	37.5
13	180	15.5
14	180	15.5
15	180	60
16	180	60
17	180	37.5
18	180	37.5
19	180	37.5
20	180	37.5
21	180	37.5

3. Results And Discussion

3.1. Characterization of pretreated samples

The composition of the WS used in the present study was: Volatile solids (VS): 94.1 ± 1.2 g/100gTS, cellulose: 35.6 ± 0.6 g/100gTS, hemicellulose: 21.5 ± 0.9 g/100gTS, lignin: 28.7 ± 0.2 g/100gTS, ash: 5.9 ± 1.6 g/100gTS, extractives: 3.0 ± 0.1 % g/gTS. Figure 1 summarizes the effect of pretreatment on the material recovery (1a), on the fractionation of biomass in terms of lignin, cellulose and hemicellulose (1b) and on the production of soluble substances such as phenolics, acetic acid, furfural and hydroxyl-methyl-furfural (HMF), which are referred as possible inhibitors in subsequent bioprocesses.

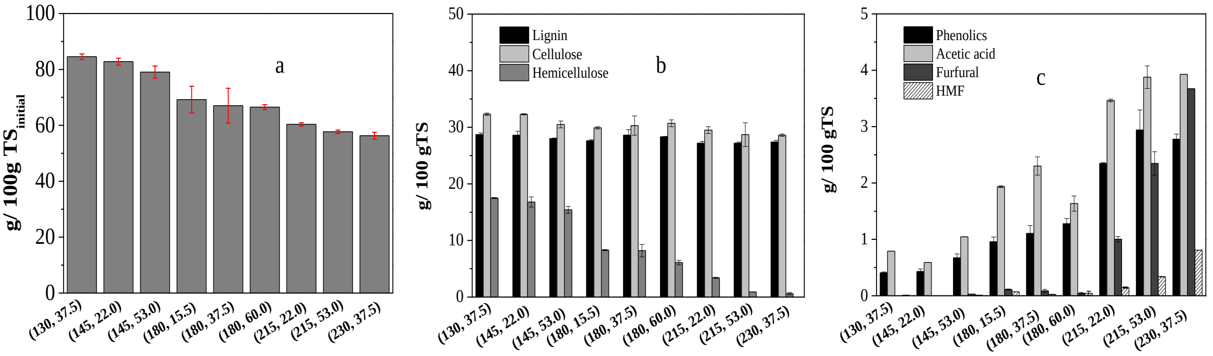

Figure 1. The effect of HP on the material recovery (1a), on the fractionation of biomass (1b) and on the production of soluble toxic compounds (1c)

From the figures it is obvious that material recovery decreases with the pretreatment severity. For example, the percentage material recovery after HP at 130°C for 37.5 min was 84.56 %, while after treatment at 230°C for 37.5 min was 56.28 %. In addition, from figure 1b it is obvious that HP resulted in reduction of the hemicellulose fraction (due to its solubilization) and the removal of hemicellulose increased with the severity factor. As anticipated, the lowest value of reduction, 18.6 % was obtained for the softest pretreatment conditions (lowest severity, 130°C for 37.5 min) while the harshest conditions (higher severity, 230°C for 37.5 min) led to the higher hemicellulose solubilisation of 97.2 %.

Although almost complete hemicellulose degradation was observed, HP was not effective in removing cellulose or lignin. The highest cellulose and lignin removal efficiency, by 19.6% and 4.5 % respectively, was observed at 230°C for 37.5 min.

HP in combination with HCl, led to the production of the compounds presented in Figure 1c. Production of furanic compounds or furaldehydes is a result of sugars such as pentoses and hexoses degradation, while phenolic compounds are predominant products due to the lignin degradation. Finally, acetic acid is also commonly found as a result of hemicellulose bond cleavage. Thus, HP conditions at 215 and 230 °C led to the highest concentrations of all these compounds.

3.2 Production of methane from pretreated samples

The BMP of WS was calculated as 114.6 ± 2.87 mL CH_4/ g TS or 121.74 mL CH_4/ g VS. A theoretical methane potential can be calculated according to the elemental composition of each degradable compound of the substrate $C_aH_bO_cN_dS_e$ (Monlau et al., 2012). Based on the cellulose, hemicellulose and proteins composition of WS, per VS, a methane potential of 256.8 L / kg VS can be theoretically expected. The biodegradability (BD) of WSD before pretreatment which is the ratio of experimental to the theoretical yield, can be determined as 47.5 %.

In Figure 2, the effect of HP combined with acid, on the BMP of the solid and liquid fractions obtained after pretreatment, as well as on the sum of both fractions, is presented. It is obvious that the BMP of the solid fractions decreased with the pretreatment severity, which could be attributed to the hemicellulose solubilization. On the contrary, the BMP of the liquid fractions increased, indicating that xylose or arabinose released due to hemicellulose solubilization converted to methane. In addition it is obvious that under the conditions tested the concentration of compounds depicted in Figure 1c, is not toxic for the implicated methanogenic microorganisms, since no inhibition was observed. Comparing the BMP calculated from the sum of both fractions, it can be concluded that HP above 180°C led to almost the same BMP yields and the HP conditions of 180°C and 15.5 min seems to be the most promising, increasing the BD to 82.5%.

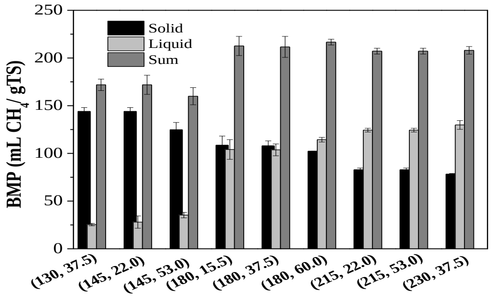

Figure 2. The effect of HP on the BMP of the solid and the liquid fractions obtained after pretreatment, as well as the sum of both.

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