USING HYDROTHERMAL PRETREATMENT TO ENHANCE GASEOUS BIOFUELS FROM FORESTRY RESIDUES

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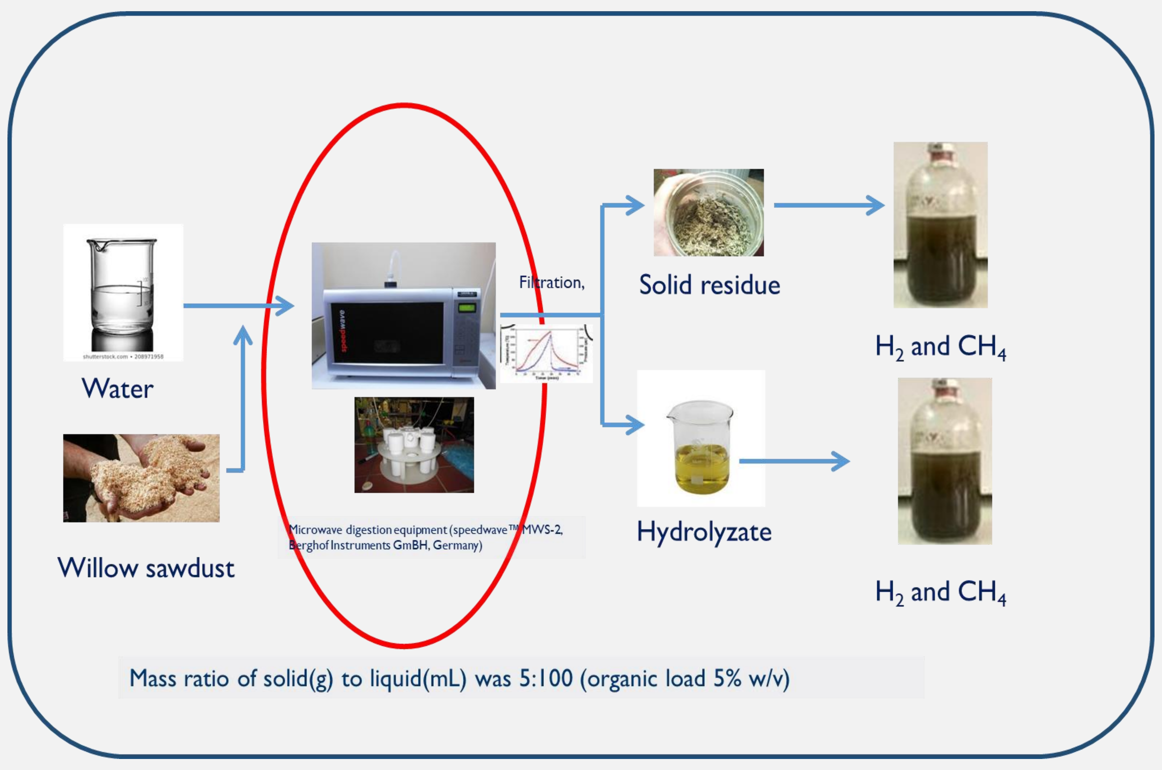
Abstract

Lignocellulosic biomass including forestry residues such as willow sawdust (WS) could be used as feedstock for anaerobic digestion (AD) and fermentative hydrogen production (FHP). Hydrolysis has been shown to be the rate-limiting step in the case of AD and FHP 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 and FHP could improve the hydrolysis and the total methane and hydrogen yield.

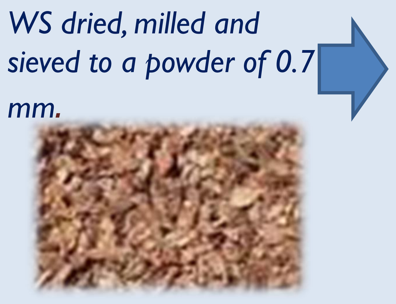


Objective

In the present study, the effect of hydrothermal pretreatment (HP), on the production of hydrogen, through dark fermentation and methane, through AD, from WS, was investigated. Four different temperatures (130, 180, 215 and 230°C) were evaluated for 15 min, during HP, to enhance WS solubilization, as well as hydrogen and methane generation through batch FHP and biochemical methane potential (BMP) tests, respectively.

Characterization

WS dried, milled and sieved to a powder of 0.7 mm.

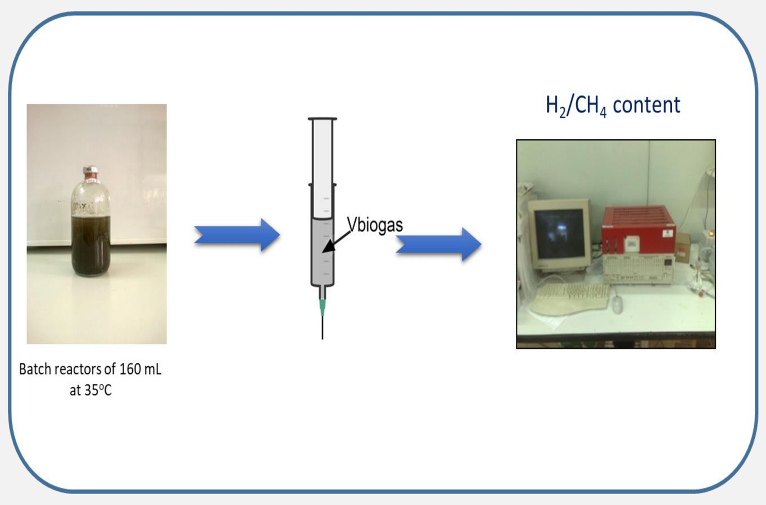


Characteristic	Value
TS ,(%)	93.4 ± 0.1
VS, (%TS)	94.1 ± 1.2
Cellulose, (%TS)	33.4 ± 1.1
Hemicellulose, (%TS)	21.5 ± 0.9
Lignin, (%TS)	29.1 ± 0.6
Extractives ,(%TS)	3.0 ± 0.1
Proteins, (%TS)	0.7 ± 0.1

Methods

BMP tests: *were carried out in both separated fractions (liquid and solid fraction) obtained after HP, based on Antonopoulou et al. (2020).*
Inoculum: *20 % v/v of anaerobic sludge from wastewater treatment plant*
Solid fractions *obtained after HP at a final loading of 2g VS / L*
Liquid fractions *at a final chemical oxygen demand (COD) concentration of 2 g/L.*

FHP tests: *in liquid and solid fraction obtained after HP, based on Antonopoulou (2020).*
Inoculum: *20 % v/v of anaerobic sludge heat treated at 100°C for 15 min*
Solid fractions *obtained after HP at a final loading of 10g TS / L + commercial enzymes (cellulase at a loading of 40 FPU /gTS (Celluclast 1.5L) and glycosidase (Novozyme 188) at a ratio of 3:1 (v/v)*
Liquid fractions *80 % of the hydrolysate, supplemented with the nutrient medium.*



Results

Pretreatment

Pretreatment severity

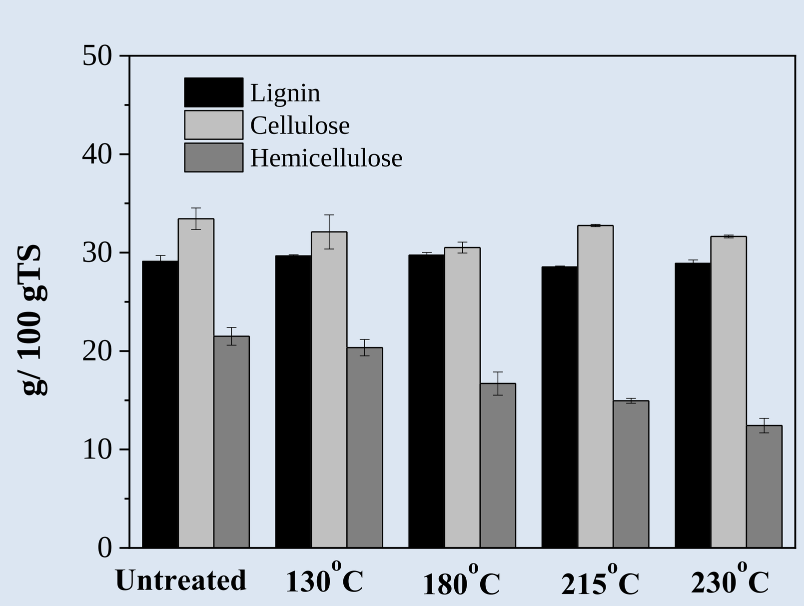
The severity factor (SF):

$$SF = log\left\{t\ exp\left(\frac{T-T_{ref}}{14.75}\right)\right\} \quad (1)$$

t and T is the reaction time (min) and temperature (°C), respectively, T_{ref} is the reference temperature (usually 100°C) and 14.75 is an empirical parameter

Pretreatment	Severity Factor	Material Recovery
130°C	2.1	88.7 ± 1.1
180°C	3.5	86.9 ± 0.1
215°C	4.6	78.8 ± 1.3
230°C	4.9	77.5 ± 4.4

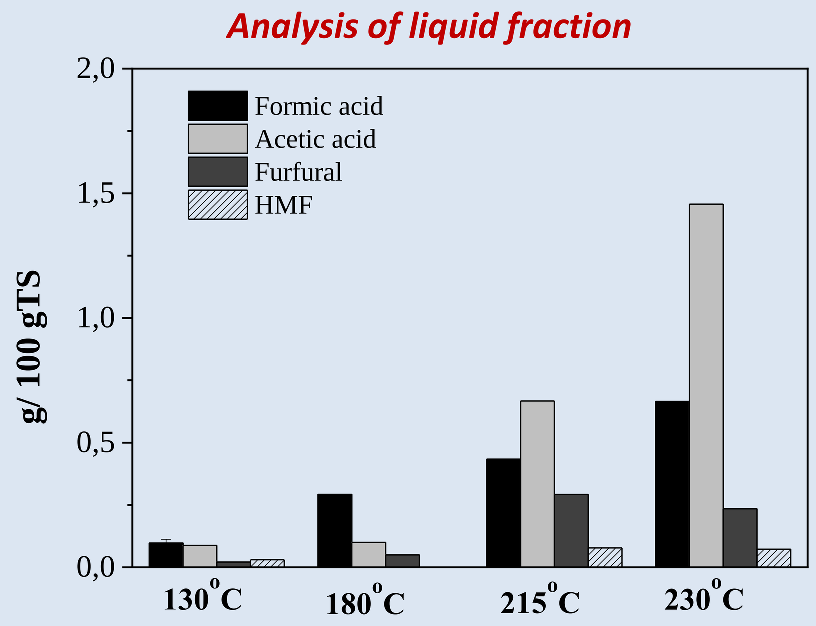
Analysis of lignocellulosic fraction



- *Lignin and cellulose were not influenced by HP as also confirmed by Dimitrellos et al. (2020).*
- *Hemicellulose was reduced by 5.6, 22.3, 30.5 and 42.2 % for HP at 130, 180, 215 and 230°C, respectively.*
- *Higher severity in HP, resulted in relatively higher hemicellulose solubilization, lower material recovery and significant structural changes in cellulose and lignin.*

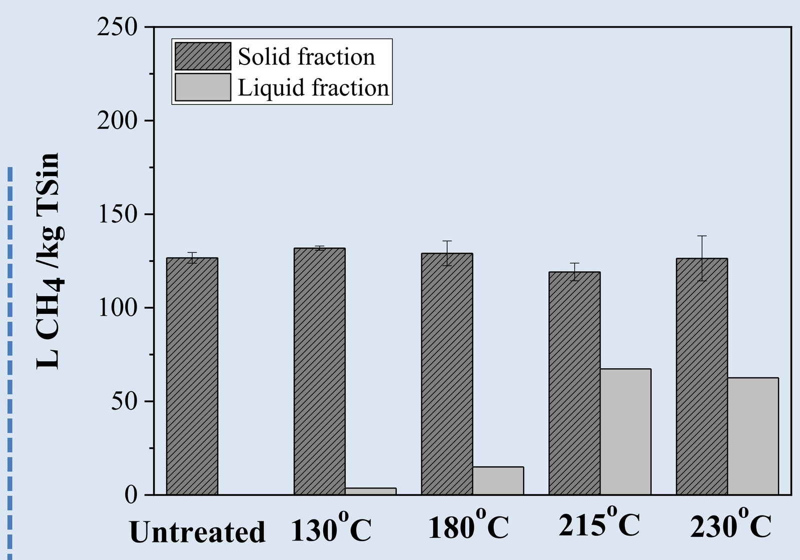
- *In high temperatures, degradations of sugars might lead to the production of furfural and 5-HMF, which are characterized as inhibitors to the microorganisms involved in the next biochemical process steps. Further degradation of 5-HMF at severe HP conditions might result in the formation of formic acid, while acetic acid is another common product released due to hemicellulose bond cleavage.*
- *Formic and acetic acid production was favored by the pretreatment severity, with their concentration being highest at 230°C.*
- *Furfural and 5-HMF were produced at temperatures above 200°C.*

Analysis of liquid fraction



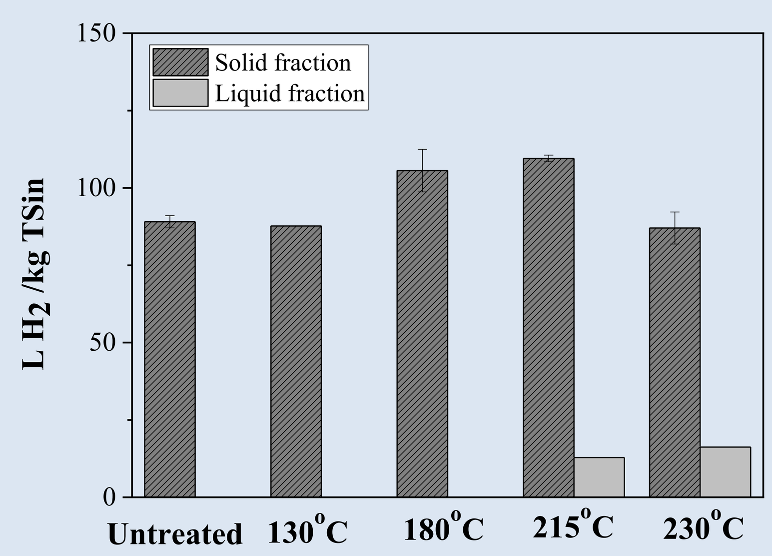
Biofuels production

Biochemical methane potential (BMP)



- *BMP of the solid fraction was not significantly influenced by HP.*
- *BMP of the liquid fraction increased with the pretreatment severity, due to the higher sugar content, coming from hemicellulose solubilization.*
- *The release of compounds (furfural, 5-HMF, acetic and formic acid etc.) seems not to have an inhibitory effect on methanogenic bacteria, even at the most severe conditions.*

Fermentative Hydrogen production tests



- *Regarding the solid fraction, HP at higher temperatures led to higher FHP yields.*
- *FHP yields of the liquid fraction increased, especially at temperatures above 200°C, due to the higher sugar content.*
- *HP at 215 and 230°C led to the production of 118.5 ± 7.2 and 125.7 ± 0.5 L H_2/kg $TS_{initial}$, respectively.*

Energy Recovery

Pretreatment	Energy from BMP (MJ/kg TS)	Energy from FHP (MJ/kg TS)
130°C	5.4 ± 0.0	1.1 ± 0.0
180°C	5.7 ± 0.0	1.1 ± 0.2
215°C	7.4 ± 0.2	1.5 ± 0.0
230°C	7.5 ± 0. 1	1.6 ± 0.1

Conclusions

The experimental results obtained showed that HP of WS led to high BMP and FHP yields, especially at the highest temperature of 230°C (188.9 L CH_4/kg $TS_{initial}$ correlating to 7.5 MJ/kg $TS_{initial}$ and 125.8 L H_2/kg $TS_{initial}$ correlating to 1.6 MJ/kg $TS_{initial}$). The release of compounds (furfural, 5-HMF, acetic and formic acid etc.) seems not to have an inhibitory effect on methanogenic or fermentative bacteria, even at the most severe conditions.

- Antonopoulou, G., Vayenas, D and Lyberatos, G. (2020) Biogas production from physicochemically pretreated grass lawn waste: comparison of different process schemes. Molecules,25, 296.
- Antonopoulou, G. (2020) Designing efficient processes for sustainable bioethanol and bio-hydrogen production from grass lawn waste. Molecules 25, 2889.
- Dimitrellos, G., Lyberatos, G., Antonopoulou, G. (2020) Does acid addition improve liquid hot water pretreatment of lignocellulosic biomass towards biohydrogen and biogas production? Sustainability, 12, 8935