The effect of alkaline/hydrogen peroxide pretreatment on hydrogen and methane production from biomasses of different origin: the case of willow sawdust and date palm fibers

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Introduction

One of the major challenges of nowadays is to reduce the world's dependence of fossil fuels. In this context, several approaches have been considered, including the production of gaseous biofuels such as hydrogen and methane. Gaseous biofuels produce lower pollutant emissions while they can be produced from inexhaustible sources such as lignocellulosic biomass. Pretreatment of lignocellulosic biomass is a quite important step before its use as a substrate for anaerobic bioprocesses as it intrudes to its structure leading to enhanced biofuels' yields. The present study focuses on the use of two different agricultural wastes/ lignocellulosic substrates (willow sawdust-**WS** and date palm fibers-**DPF**) as substrates for methane and hydrogen production. Prior to use for biofuels' production, the substrates were pretreated using dilute solutions of sodium hydroxide, hydrogen peroxide or combinations of them.

Materials & Methods

Substrates

Table 1. The main characteristics of the substrates used

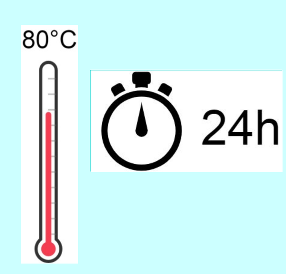
Characteristic (%)	WS	DPF
TS	93.4 ± 0.2	91.2 ± 1.4
VS	94.1 ± 0.2	91.8 ± 0.1
Cellulose	33.4 ± 1.1	36.7 ± 0.2
Hemicellulose	21.5 ± 0.9	21.1 ± 0.2
Lignin	29.1 ± 0.6	22.9 ± 0.8

Pretreatment Methods

Solids load: 5%

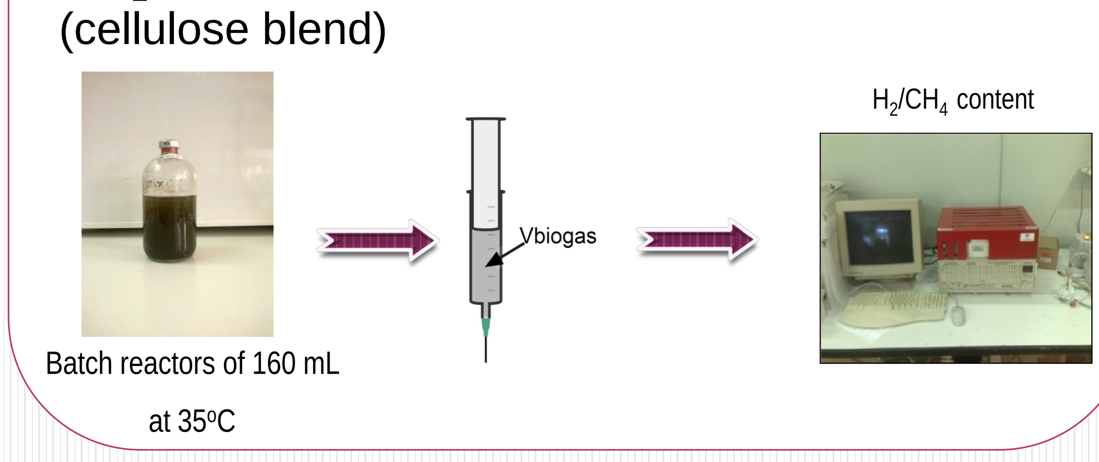
A. NaOH 0.5% (w/v)
B. H_2O_2 0.5% (v/v)
C. H_2O_2 0.5% (v/v) **+** NaOH 0.5% (w/v)
D. NaOH 0.5% (w/v) → H_2O_2 0.5% (v/v)
E. H_2O_2 0.5 % (v/v) → NaOH 0.5 % (w/v)

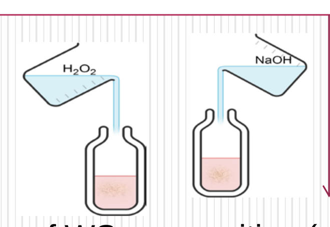
2 step



Biofuels' Production

❖ CH_4 experiments: inoculum was anaerobic sludge from wastewater treatment plant
❖ H_2 experiments: inoculum was anaerobic sludge heat treated at 100°C for 15 min
❖H_2 experiments: addition of commercial enzymes (cellulose blend)





Pretreatment effect

Results & Discussion

Table 2. Changes of WS composition (g/100 g TS initial) after pretreatment

WS			
Pretreatment	Cellulose (%)	Hemicellulose (%)	Lignin (%)
A	31.37 ± 0.20	16.93 ± 0.10	21.69 ± 0.05
B	34.43 ± 0.35	20.38 ± 0.24	29.76 ± 0.06
C	30.85 ± 0.15	17.44 ± 0.23	20.97 ± 0.04
D	28.40 ± 0.20	16.11 ± 0.25	17.94 ± 0.09
E	31.62 ± 0.14	16.89 ± 0.45	20.85 ± 0.09

WS

❖ Hemicellulose was reduced to 21.3%, 18.9%, 25.1% and 21.4% when WS was subjected to pretreatment approaches A,C,D and E respectively

❖ Lignin removal was highest (38.3%) for pretreatment approach D, while approaches A,C and E led to lower lignin reduction (25.5%, 27.9% and 28.4%, respectively)

DPF

❖Approach A for DPF, resulted to a high lignin removal (40.54 ± 1.02%) and to the lowest solubilization of hemicellulose (40.02 ± 0.39%)

❖ Approach D strongly affected lignocellulosic structure. (53.05 ± 0.36% decrease of cellulose, 78.67 ± 0.49% decrease of hemicellulose and 55.61 ± 0.24% decrease of lignin.)

Table 3. Changes of DPF composition (g/100 g TS initial) after pretreatment

DPF			
Pretreatment	Cellulose (%)	Hemicellulose (%)	Lignin (%)
A	22.89 ± 0.14	12.69 ± 0.21	13.59 ± 0.65
B	29.48 ± 0.16	10.12 ± 0.21	19.40 ± 0.01
C	21.25 ± 0.18	7.89 ± 0.23	12.94 ± 0.30
D	17.21 ± 0.17	4.51 ± 0.19	10.14 ± 0.02
E	20.93 ± 0.66	6.87 ± 0.30	13.12 ± 0.05

Biofuels' production
CH_4

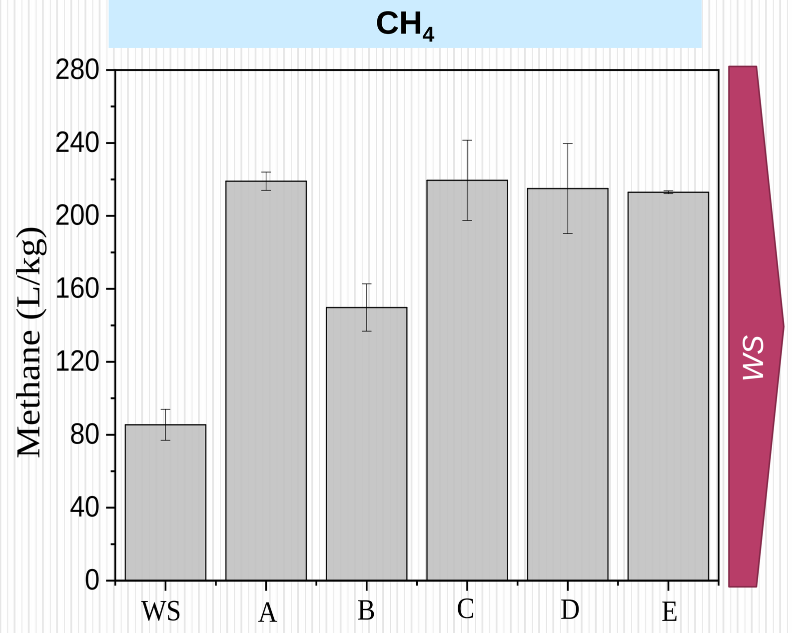


Figure 1. Methane yields of WS for the different pretreatment approaches

❖ The maximum methane yield was equal to 219.03 ± 3.74 L CH_4/kg when WS was pretreated only with the NaOH solution (A).

❖ Also, the yield was equal to 215 LCH_4/kg in the case of two-stage pretreatment approaches (D and E).

❖ Low yield was observed in the case of H_2O_2 (173.22 ± 6.08 L CH_4/kg).

❖ The methane yield of the WS raw was 85.48 ± 8.49 L CH_4/kg

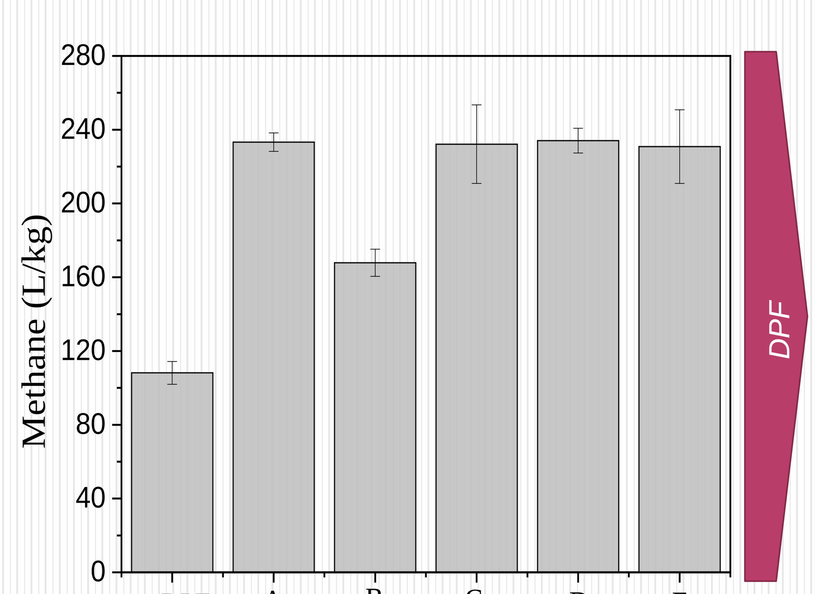


Figure 2. Methane yields of DPF for the different pretreatment approaches

❖ The maximum methane yield was achieved when DPF was subjected to pretreatment D. This yield was equal to 247.04 ± 34.00 L CH_4/kg .

❖ The lowest yield emerged when DPF was treated only with the hydrogen peroxide solution and it was equal to 178.33 ± 8.09 L CH_4/kg (similar with the respective WS yield)

❖High yields were observed when WS was pretreated with NaOH (A) or with the mixture of NaOH/H_2O_2 (C) or with the two-stage pretreatments (D and E) (approximately 114 – 129 LH_2/kg)

❖ Low hydrogen yield was observed in the case of H_2O_2 (22.46 ± 0.90 L/kg), which was similar to the yield of untreated WS at SSF.

❖No hydrogen was produced from untreated WS (without enzymes).

Biofuels' production
H_2

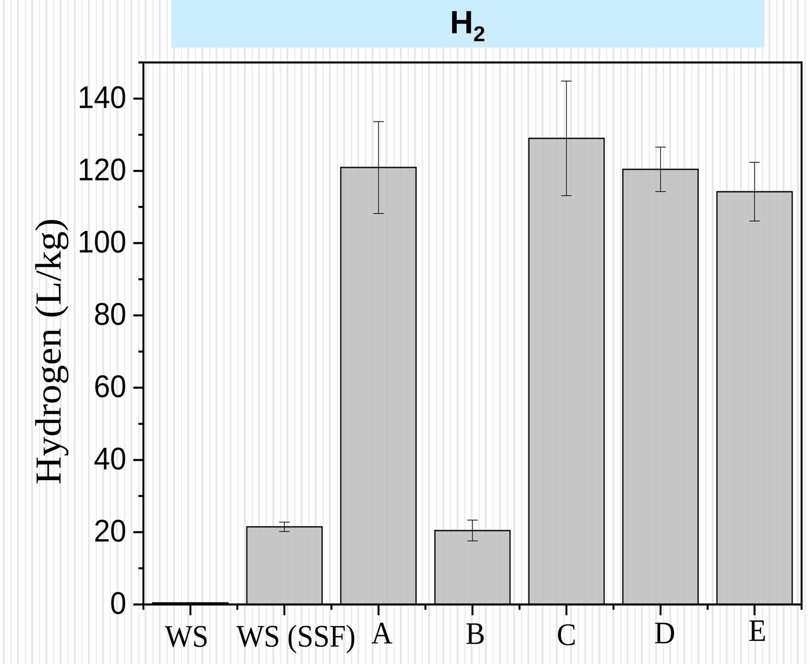


Figure 3. Hydrogen yields of WS for the different pretreatment approaches

❖The maximum hydrogen yield was achieved when DPF was subjected to the two-stage pretreatment E (H_2O_2 first, followed by NaOH) and it was equal to 136.38 ± 9.84 L H_2/kg, which was similar to the pretreatments A, C and D.

❖ Low hydrogen yields were observed when DPF was pretreated with H_2O_2, being the same with the yield of untreated DPF in SSF

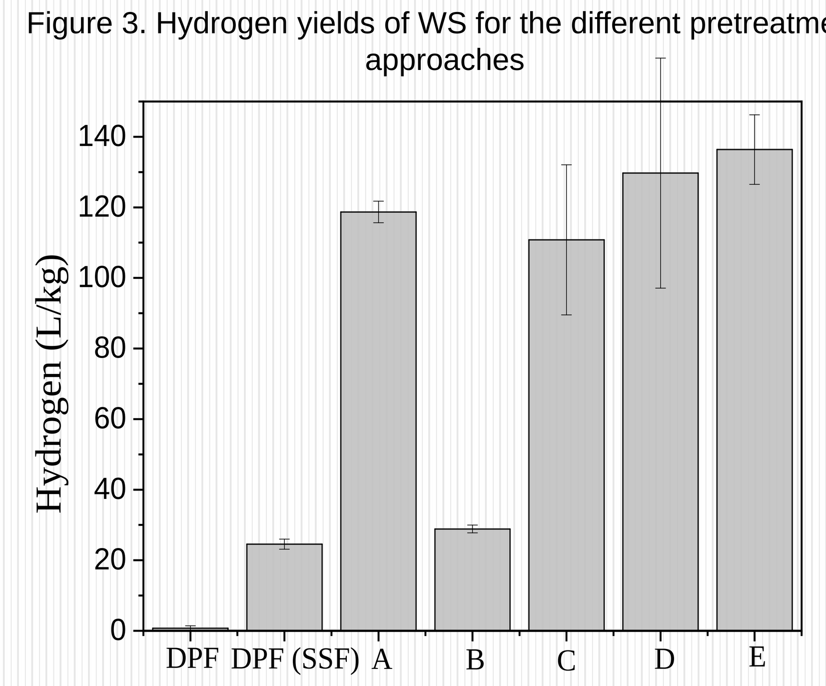


Figure 4. Hydrogen yields of DPF for the different pretreatment approaches

Conclusions

In the present study two different agricultural wastes/lignocellulosic substrates (**WS** and **DPF**) were used as substrates for methane and hydrogen production. Prior to use for biofuels' production, the substrates were pretreated using dilute solutions of sodium hydroxide, hydrogen peroxide or combinations of them. The experimental results showed that almost all pretreatment methods enhanced biofuels production comparing to the raw substrates and that the trends of the resulting yields were similar for the two substrates. Furthermore, it was observed that hydrogen peroxide addition solely did not really increase hydrogen yields .

Acknowledgements *We acknowledge financial support of this work by the project "Research infrastructure for Waste Valorization and Sustainable Management of Resources, INVALOR" (MIS 5002495) which is implemented under the "Action for the Strategic Development on the Research and Technological Sector", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).*