Thermo-alkaline pre-treatment to solubilise and improve biodegradability of press mud

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Abstract
Thermo-chemical pre-treatment improves the solubilization of the lignocellulosic biomass. Therefore, it could improve biogas production from press mud, the solid residue from sugar cane juice filtration which contains up to 85 % insoluble organic matter. The impact of thermo-alkaline pretreatment conditions (100 ^oC, $Ca(OH)_2$) on press mud was investigated for different times and concentrations, thus different pretreatment severities. The biochemical methane potential (BMP) was determined in batch assays under mesophilic conditions (37 ± 1 ^oC). The best treatment resulted in 72 % of methane yield in surplus, adding 10 g $Ca(OH)_2$ 100 g^{-1} TS^{-1} for 1 h. Pretreatment also increased the solubilization of the chemical oxygen demand (COD), but the optimal severity for COD solubilization did not ensure the highest methane production. Inhibitory effects on anaerobic digestion were noticed when severity was increased. These results show the importance of thermo-alkaline pretreatment severity both in terms of concentration and reaction time to obtain optimal anaerobic biodegradability of lignocellulosic biomass.

Keywords
Anaerobic digestion; thermo-chemical pre-treatment; press mud; pre-treatment severity.

INTRODUCTION

Press mud is one of the main residues from the sugarcane juice separation processes. Merely in Cuba, around 43.5 x 10^3 tons of press mud are generated yearly from the sugarcane industry, becoming an important high strength stream. As press mud contains up to 85 % of insoluble organic matter with high fiber (lignocellulose) content, its biodegradability is expected to enhance as a result of applying different pre-treatments. It has been shown that pre-treatment of lignocellulosic biomass can accelerate the hydrolysis process and improves the biogas production (Pavlostathis and Giraldo-Gómez, 1991).

The objective of the present paper was to verify the potentiality of a thermo-alkaline pre-treatment at 100 ^oC in order to enhance the anaerobic digestion of press mud in terms of methane yield augmentation. The effects of the lime loading and pre-treatment time on Chemical Oxygen Demand (COD) solubilization and Volatile Fatty Acids (VFAs) production were determined for different experimental conditions.

MATERIALS AND METHODS

The press mud (15 g) was presoaked at 30 ^oC in a $Ca(OH)_2$ solution using an orbital shaker for 15 min at 150 rpm. Different conditions of lime loading (LL) and pre-treatment time (t) (Table 1) were used according to a Central Composite Design (CCD) setup. Afterwards the samples were put in an oven at 100 ^oC and manually shaken every 30 min. A constant water loading value of 10 g water g-1 TS^{-1} press mud was used for all experiments (Chang et al., 1998). Schott bottles of 500 mL were used as reactors. After the fixed pre-treatment time, the reactors were placed in ice water for 5 min to stop the reaction. The best trials in terms of improved sCOD percentage were anaerobically digested. Response surface modeling was used to determine the best pre-treatments conditions as well as to explore COD solubilization behavior for critical values of LL and t.

The methane potential was determined in batch assays under mesophilic conditions (37 ± 1 ^oC) according to VDI 4630, (2006). 500 mL capacity Schott bottles were used as reactors, containing 350 mL of inoculum with proper amounts of substrate to keep a substrate to inoculum ratio of 0.5 (g VS/ g VS). The reactors were manually shaken every day. The cumulative methane production was measured by liquid displacement (1.5 % NaOH solution) and reported at normal temperature and pressure (273 K and 101.29 kPa).

Total COD (tCOD), soluble COD (sCOD), total solids (TS), volatile solids (VS) and pH were determined according to standard methods (APHA et al., 1995). VFAs (acetic acid, propionic acid, butyric acid, valeric acid and iso-valeric acid) were determined by gas chromatography (GC). Elemental analysis (C, H and N) were quantified using a Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer. Elemental oxygen content was calculated by difference.

RESULTS AND DISCUSSION

In all cases COD solubilization values were significantly higher than the untreated press mud under studied experimental conditions (Table 1). The values ranged between 28 and 38 %, in comparison with 21.1 % for untreated press mud. In general, better results were obtained when increasing LL at the same pre-treatment time. However, no significant difference was obtained between 7 and 11.24 g $Ca(OH)_2$ 100 g^{-1} TS^{-1} of LL for 2 h of pre-treatment time. Lowest solubilizations were found with A23, A14 and A07 reactors. The values were 28.10, 27.96 and 29.01 %, respectively.

Table 1. Effect of thermo-chemical pretreatment on VFAs, COD solubilization and pH.

	t (h)	LL*	Log (M_o)	sCOD (%)	Acetic acid (mg L^{-1})	pH
Untreated				21.5 ± 1.72^f	N.D.	6.19
A07	0.59	7	1.29	29.0 ± 0.22^e	1600.90 ± 22.19^d	10.63
A14	1	4	1.08	27.9 ± 0.95^e	1347.72 ± 21.37^e	8.48
A110	1	10	1.80	33.9 ± 1.60^c	1850.60 ± 7.71^b	11.44
A23	2	2.76	1.09	28.1 ± 1.01^e	997.41 ± 177.07^f	7.73
A27	2	7	1.82	36.0 ± 0.69^b	1707.11 ± 97.48^{cd}	9.69
A211	2	11.24	2.19	36.2 ± 0.53^b	1870.87 ± 54.89^b	11.87
A34	3	4	1.56	32.3 ± 0.44^d	1802.88 ± 108.86^{bc}	7.69
A310	3	10	2.28	38.0 ± 1.39^a	1811.49 ± 104.68^{bc}	11.13
A37	3.41	7	2.05	33.7 ± 1.19^c	2024.03 ± 10.032^a	7.87

*g Ca(OH)2 100 g^{-1} TS^{-1}
N.D. Not detected.
$^{a–f}$ means groups with different superscripts differ (P < 0.05)

COD solubilisation behavior was related to the severity factor (Log (Mo)) as defined by Silverstein et al., (2007). When severity was increased to 1.56 or more, higher values of sCOD were obtained (Table 1). According to statistical analyses significant different between those results were attained.

Acetic acid was the only identified volatile fatty acid (Table 1). It was found that even with a mild pre-treatment severity, its concentration increased rapidly (Table 1). Both higher lime loading and pre-treatment time increased acetic acid formation, except when using 10 g $Ca(OH)_2$ 100 g^{-1} TS^{-1}. It is possible that all acetyl groups were removed after 1h of pre-treatment time. Panagiotopoulos et al., (2011) found 1 g L^{-1} acetic acid with a minimum pre-treatment severity of –1.6, confirming its rapid rate of formation.

The pre-treatment of press mud with $Ca(OH)_2$ at 100 °C increased the methane yield for all experimental conditions tested (Fig. 1). Methane yield increased in 72 and 85 % as compared to untreated press mud for pre-treatments A110 and A211, respectively.

There is a significant difference between the results obtained by the best pre-treatments -A110 and A211- compared to the control reactor. As there is no significant difference in between, the best pre-treatment is therefore A110, because less reagents as well as less pre-treatment time is required.

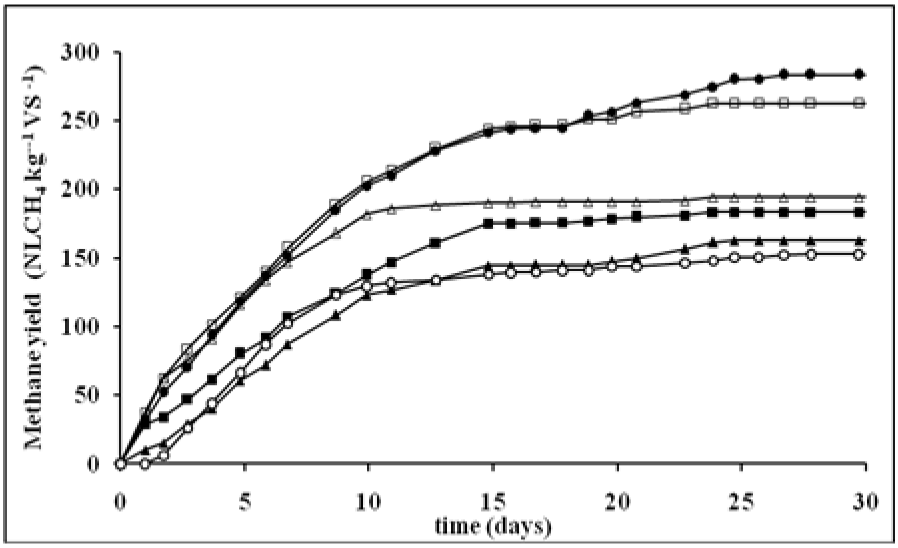

Figure 1. Cumulative methane production (STP) for untreated and pretreated pressmud. Untreated pressmud (○), 10 g $Ca(OH)_2$ 100 g^{-1} TS^{-1} and1 h (□), 10 g $Ca(OH)_2$ 100 g^{-1} TS^{-1} and 3 h (■), 7 g $Ca(OH)_2$ 100 g^{-1} TS^{-1} and 3.41h (▲), 7 g $Ca(OH)_2$ 100 g^{-1} TS^{-1} and 2 h (△), 11.24 g $Ca(OH)_2$ 100 g^{-1} TS^{-1} and 2h (●).

Based on the analyzed press mud composition ($C_{3.74}H_6O_{2.96}N_{0.12}$) determined, the theoretical methane yield was 410.98 mL CH_4 g^{-1} VS^{-1}. Only 39.07 % of this potential was achieved for untreated press mud, which is in the range (30 – 60 %) for high particulate organic matter. For the pretreated press mud with the best pre-treatment (A110), 66.11 % of this potential was obtained, clearly demonstrating the increase in potential by pre-treatment. Methane production by the remainder other pre-treatments was superior to the control, but no significant differences were observed when compared with each other (Table 2).

For pre-treatment times less than 3 hours, methane yield was increased with lime loading, but when it was prolonged to 3 h and 3.41 h (A310 and A37) it decreased drastically. In comparison with the untreated press mud, the methane yield of these pre-treatments increased only in 7 % and 20 % for A37 and A310, respectively. Moreover, it can be seen that the highest methane yield (A211) was not attained for the best solubilization COD (A310). The formation of toxic compounds and/or complex recalcitrant substances in the substrate matrix might explain these findings.

Table 2. Maximum methane yield, first order rate constant (k) and efficiency for anaerobic digestion both untreated pressmud and under different pretreatment conditions.

	y_{max}(mL CH_4 g^{-1} VS^{-1} added)	η (%)*	k (d^{-1})	R^2
Untreated	160.55±26.18^b	39.07	0.138±0.055$^{a, b}$	0.96
A110	271.69±6.15.^{a}	66.11	0.135±0.001$^{a, b}$	0.99
A310	195.24±12.66^b	47.51	0.126±0.036$^{a, b}$	0.99
A37	174.86±15.42^b	42.55	0.102±0.007^a	0.99
A27	196.84±18.41^b	47.90	0.204±0.021^b	0.99
A211	300.79±34.74^a	73.19	0.112±0.039^a	0.99

$^{a–b}$ means groups with different superscripts differ (P < 0.05)

* calculated as $Y_{Methane}^{max} \cdot 100 / Y_{Methane}^{theo}$ (%)

To our knowledge, press mud thermo-alkaline pre-treatment has not yet been reported. Thermo-alkaline pre-treatment has however been applied to others substrates with positive results (Fernandes et al., 2009; Xie et al., 2011). Xie et al., (2011) reported that the methane production improves up to 38.9 % after alkaline pre-treatment (5 % (w/w) NaOH, on VS basis) in dried grass silage at 100 ^oC for similar reaction times as applied in this study

Regarding first-order kinetic model, the values for k ranged from 0.1086 to 0.2022 d^{-1} (Table 2). The highest value of k found was for A27, apparently for upper lime concentrations more acclimation was needed.

Conclusions

Combinations of different lime loading and pre-treatment times were applied to enhance the anaerobic biodegradability of press mud. Pre-treatment increases the solubilization of COD. A methane yield surplus of 72% was obtained when using 10 g $Ca(OH)_2$ 100 g^{-1} TS^{-1} for 1 h when comparing with untreated press mud.

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