

# Enhancement of anaerobic digestion of sludge from Kraft pulp mill wastewater treatment using thermal hydrolysis

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**Abstract:** In the present work, the biodegradation improvement after thermal hydrolysis of the sludge generated in the aerobic wastewater treatment of a cellulose industry was evaluated. Response surfaces are presented for the different variables tested -Biomethane Potential (BMP), methane production rate and Dissolved Organic Nitrogen (DON). The variation of kinetic parameters was also determined. Increases between 100 % and 228 % were obtained for the BMPs of thermally hydrolyzed biosludge compared to untreated biosludge. In addition, increases of up to 112 % for the methane production rate of thermally hydrolyzed substrate were obtained.

**Keywords:** Anaerobic digestion; BMP; Thermal hydrolysis

## Introduction

According to the circular economy approach, anaerobic digestion (AD) of biosludge is a promising alternative for energy recovery and by-product obtention. Due to limitations in the hydrolysis step of organic matter degradation, thermal pretreatment is a widely spread technology to improve biogas production in anaerobic digesters of biosludge from aerobic sewage treatment. Nevertheless, it has not been applied for the case of pulp mills, which generate wastewater with a composition very different from that of sewage. On the other hand, undesired caramelization and/or Maillard reactions may occur at high temperatures. These compounds generate non-biodegradable recalcitrant matter based on carbohydrates and amino groups. (Barber, 2016; Wilson et al. 2009).

Our goals were to find the optimum biogas generation and its production rate and minimum generation of recalcitrant compounds when performing thermal hydrolysis (TH) as a pretreatment of AD. Also, the nitrogen content of the liquid fraction was evaluated.

## Material and Methods

Sludge from the activated sludge system of a Kraft pulp mill was used as substrate and biomass from a UASB reactor of a malting plant was used as inoculum. The substrate was thermally pre-treated in a 2 L sealed batch reactor. The temperature and time conditions tested were defined by an experimental plan (Table 1.1).

The AMPTS® II (Automatic Methane Potential Test System) was used to determine the BMP of each TH condition, following the suggestions of Angelidaki et al. (2009). Volatile suspended solids (VSS), biodegradability ( $B_{vs}$ ), chemical oxygen demand (COD), ammonia nitrogen and total soluble nitrogen were determined for each vial in the supernatant obtained from a centrifugation for 15 minutes at 6500 rpm, as described in Rice et al. (2012). DON was calculated as the difference between total soluble nitrogen and ammonia nitrogen.

A first order model (Pavlostathis and Giraldo-Gomez, 1991) (equation 1) was used to represent the methane production over time. The kinetic parameter  $k$  and the maximum methane production parameter ( $P_0$ ) are expressed in units of  $d^{-1}$  and  $mLCH_4gVS^{-1}$  respectively.

The calculations and the necessary adjustments were performed with *octave 5.2.0 software*. For the generation of the response surfaces, *RStudio 4.0.2 software* was used. Triplicates of each test (BMP,  $k$ , DON) were performed for every TH.

$$P(t) = P_0 [1 - e^{-k t}] \quad [1]$$

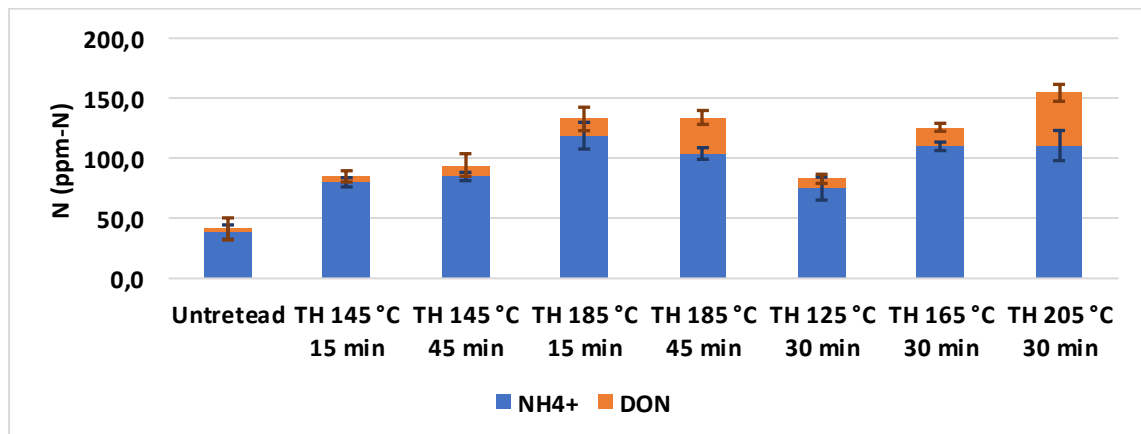
## Results and Conclusions

Table 1 shows the results obtained. The experimental results show a significant improvement when comparing the biosludge treated with TH against the same substrate without any treatment. A larger increase in BMP,  $B_{VS}$  and  $k$  is seen with increasing TH temperature compared to a change in reaction time. Biogas composition does not show significant differences when the variables are modified.

**Table 1** TH conditions, BMP results and kinetic adjustment

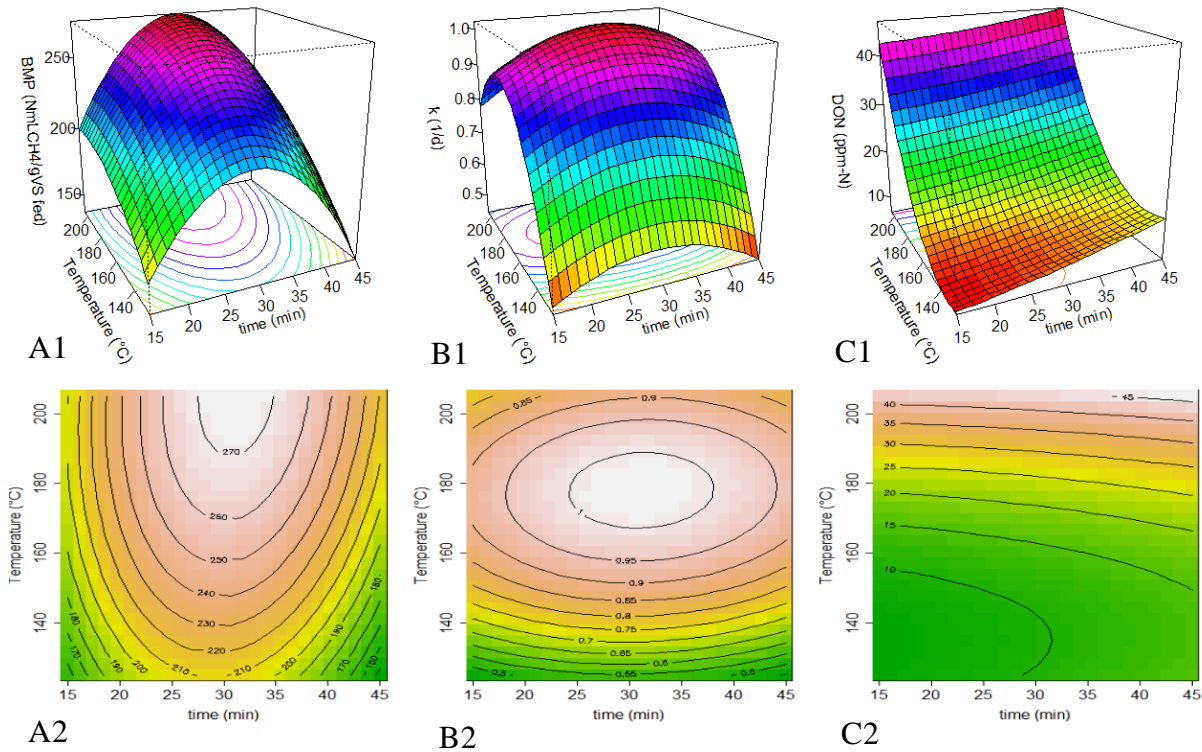
Experimental Thermal Hydrolysis Factors		Anaerobic Digestion Results			Kinetics Results		
T (°C)	t (min)	BMP ± σ (NmLCH <sub>4</sub> /gVS)	B <sub>VS</sub> ± σ (%)	Methane in biogas CH <sub>4</sub> ± σ (%)	k ± σ (d <sup>-1</sup> )	P <sub>0</sub> ± σ (NmLCH <sub>4</sub> /gVS)	r <sup>2</sup>
Untreated	Untreated	84 ± 18	17 ± 5	74.2 ± 0.9	0.468 ± 0.036	77 ± 6	0.984
145	15	181 ± 9	42 ± 2	78.7 ± 1.4	0.755 ± 0.006	181 ± 2	0.993
145	45	171 ± 2	39 ± 1	78.3 ± 0.9	0.755 ± 0.053	170 ± 2	0.990
185	15	197 ± 4	42 ± 14	79.5 ± 0.3	0.890 ± 0.012	198 ± 4	0.990
185	45	207 ± 5	46 ± 4	78.5 ± 0.3	0.911 ± 0.028	208 ± 5	0.990
125	30	208 ± 9	32 ± 8	78.1 ± 1.4	0.535 ± 0.030	207 ± 12	0.988
165	30	257 ± 3	48 ± 4	78.7 ± 0.2	0.992 ± 0.029	257 ± 3	0.999
205	30	276 ± 2	66 ± 10	79.9 ± 0.5	0.906 ± 0.007	276 ± 2	0.990

Temperature has a greater impact on DON than hydrolysis time (Figure 1). The DON concentration represents all the nitrogen that was not degraded to ammonia during AD; therefore, it can be related to recalcitrant for AD organic matter.



**Figure 1** Ammonia nitrogen and DON concentration at the end of each anaerobic digestion, with its corresponding deviation.

Figure 2 presents the two-dimensional contour plots and response surfaces for the fits made to the BMP (A), kinetic constant  $k$  (B) and DON (C). Table 1.2 contains the mathematical models and parameters and  $p$ -values.  $T$  and  $t$  are temperature in  $^{\circ}\text{C}$  and time in min, respectively. Analysis of variance in Table 2 showed that the models are statistically good ( $p < 0.05$ ). For BMP and  $k$  all parameters were statistically significant ( $p$ -value  $< 0.05$ ), except for the interaction parameter between  $t$  and  $T$ . The optimum of BMP is estimated for a temperature of  $208^{\circ}\text{C}$  and 31 min and the optimum of  $k$ , a value of  $178^{\circ}\text{C}$  and 31 min. At higher TH time or temperature, there was a decrease in the rate of methane, possibly influenced by the generation of recalcitrant compounds. It seems to be related with the DON response that can be observed in Figure 2, where temperature and its square have the greatest influence being the parameters with statistical significance ( $p$ -value  $< 0.05$ ).



**Figure 2** Response surfaces (upper graphs) and the two-dimensional contour plots (lower graphs) for BMP (A1 and A2),  $k$  (B1 and B2) and DON (C1 and C2) responses.

**Table 2** Models determined and adjustments for each evaluated response

Responses	Results for the models	Adjusts Results		
		$P$ - value	$r_{Adjust}^2$	$r^2$
$BMP \left( \frac{Nml CH_4}{gVS} \right)$	$-302.87 + 14.394 t + 3.337 T$ $+0.016 t T - 0.285 t^2 - 0.009 T^2$	$<0.05$	0.985	0.990
$k(d^{-1})$	$-4.59180 + 0.02062 t + 0.05947 T$ $+0.00003 t T - 0.00041 t^2 - 0.00017 T^2$	$<0.05$	0.962	0.975
$DON (ppm)$	$126.353 + 0.286 t - 1.846 T$ $-0.001 t T + 0.003 t^2 + 0.007 T^2$	$<0.05$	0.850	0.900

The thermal pretreatments applied achieved increases of more than 100 % in all cases in biodegradability, BMP,  $k$  and ammonia nitrogen compared to the untreated samples. The increase in the value of  $k$  accounts for the overcoming of the limitations in the hydrolysis step compared to the untreated biosludge. There is a different optimum for BMP and  $k$ , which creates an opportunity to optimize pretreatment according to different objectives. The higher levels of ammonia nitrogen that would be obtained on an industrial scale could allow potential uses as a fertilizer or as a nutrient. Since in this case the non-pretreated sludge has remarkably low BMP values compared to sewage sludge, the effect of HT is more noticeable and with better economic prospects.

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