Bioresource Technology 143 (2013) 251–257

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Influence of thermal pretreatment on the biochemical methane potential of wheat straw

L.C. Ferreira [a], A. Donoso-Bravo [b], P.J. Nilsen [c], F. Fdz-Polanco [a], S.I. Pérez-Elvira [a,*]

[a] Department of Chemical Engineering and Environmental Technology, University of Valladolid, C/Dr. Mergelina, s/n, 47011 Valladolid, Spain
[b] Escuela de Ingeniería Bioquímica, Pontificia Universidad Católica de Valparaíso, General Cruz 34, Valparaíso, Chile
[c] Camni AS, Skysstasjon 11A, 1383 Asker, Norway

HIGHLIGHTS

- Influence of thermal pretreatment on the anaerobic biodegradation of wheat straw.
- Evaluation through BMP tests and modeling.
- Optimum severity factor at 220 °C and 1 min (3.5 severity factor).
- First order model confirmed that the hydrolysis is the limiting step.
- Surface response evaluation indicated negligible interaction temperature–time.

ARTICLE INFO

Article history:
Received 25 February 2013
Received in revised form 15 May 2013
Accepted 17 May 2013
Available online 23 May 2013

Keywords:
Biochemical methane potential
Thermal hydrolysis
Pre-treatment
Mathematical modeling
Wheat straw

ABSTRACT

The biochemical methane potential of steam exploded wheat straw was evaluated in a pilot plant under different temperature–time combinations. The optimum was obtained for 1 min and 220 °C thermal pretreatment (3.5 severity factor), resulting in a 20% increase in methane production respect non-treated straw. For more severe treatments the biodegradability decreased due to a possible formation of inhibitory compounds. The results of the tests were modeled with a first order equation to estimate the hydrolysis constant and biodegradability extent, and the influence of temperature and time on the kinetic parameters was obtained with a response surface study. The data processing confirmed the accuracy of the model and the optimum operation conditions, and demonstrated that the biomethanization of raw and pretreated wheat straw is limited by the hydrolysis, being the individual influence of temperature and time much more important than the interaction between them.

1. Introduction

In many countries, lignocellulosic materials are an abundant agricultural residue which can be used either for animal feeding or for energetic valorization in power plants. In Europe, wheat straw represents the largest agricultural waste, being in Spain an important part of the crop wastes which could be used as biomass for renewable energy production. The use of renewable energy sources is becoming increasingly necessary in order to cope with the impacts of global warming. The conversion of biomass into energy can be achieved in a number of ways, being anaerobic digestion a very sustainable alternative.

Anaerobic digestion is a well-known process for the treatment of wastewater of organic wastes. This process presents advantages over some conventional aerobic technologies, such as the better handling of wet waste, the production of biogas as a renewable source of energy and the attenuation of odor problems (Palmowski and Muller, 2000; Pérez-Elvira et al., 2011, 2010). Furthermore, anaerobic digestion is the most cost-effective treatment, due to high energy recovery and low environmental impact (Mata-Alvarez et al., 2000). However, the application of anaerobic digestion with lignocellulosic biomass has not been a subject of enough research.

Lignocellulosic material is mainly composed of three different types of polymers: cellulose, hemicellulose and lignin. While cellulose has a rigid and crystalline form, hemicellulose has a lower molecular weight and short lateral chains, which corresponds to an easy hydrolysable polymer. The third compound, lignin, is one of the most abundant polymers in nature. It is a complex and amorphous heteropolymer consisting of three different phenylpropane units, and is also non-water soluble (Hendriks and Zeeman, 2009). Wheat straw consists mainly of cellulose (30–40%), hemicellulose (20–30%) and lignin (10–20%). The cellulose and hemicellulose

* Corresponding author. Tel.: +34 983184934; fax: +34 983423013.
E-mail address: sarape@iq.uva.es (S.I. Pérez-Elvira).

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http://dx.doi.org/10.1016/j.biortech.2013.05.065

fractions can be enzymatically hydrolyzed to monomeric sugars after a pre-treatment aiming to hydrolyze its partially crystalline structure (Puls and Schuseil, 1993).

The hydrolysis of this type of biomass is limited by several factors, such as the lignin content. In cellulose the molecules are linear, and therefore they can form hydrogen bonds between the chains that limit their solubility in water, and reduce the available surface area, making cellulose difficult to degrade. A number of pretreatments for ligmocellulosic biomass are currently available, such as mechanical, milling into smaller pieces (Mshandete et al., 2006; Palmowski and Muller, 2000), physico-chemical such as dilute alkaline pretreatment (McIntosh and Vancov, 2011) or dilute acid pretreatment (Schell et al., 2003), wet oxidation, thermal treatment (Sapci, 2013), or a combination of them (Linde et al., 2008; Nkemka and Murto, 2013). From the point of view of its applicability, the total energy balance of the global process (considering both pre-treatment and digestion) must be taken into consideration. Compared to other pretreatment methods, the thermal hydrolysis can be cost effective if a proper steam-explosion and energy recovery is performed. The warranty that the process is energetically self-sufficient is described in Pérez-Elvira and Fdz-Polanco (2012). Furthermore, hydrothermal treatment can be performed without addition of chemicals or oxygen, representing a potential solution for the pretreatment of large quantities of lignocellulosic biomass including woods material (Horn et al., 2011a; Sipos et al., 2010) and agricultural by-products (Horn et al., 2011b; Ohgren et al., 2006).

Thermal pretreatment is a method where the substrates are subjected to heating under a specific pressure during a certain period of time. At the end of the heating, a steam explosion occurs, where the biomass is rapidly discharged into normal pressure causing an explosion of the macromolecules. At temperatures in the range 150–180 °C, parts of lignocellulosic materials will start to solubilize (Garrote et al., 1999). Some studies have shown that the effect of the thermal treatment depends on several factors, such as: residence time, operating temperature, chip size, and moisture content (Bauer et al., 2009; Han et al., 2010; Zhang et al., 2008). A too harsh treatment of lignocellulosic biomass may result in a lower methane yield and longer retention time. The reason is that when lignin is broken, there is a risk of formation phenolic and hererocyclic compounds from hemicellulose and cellulose degradation, like furfural and hydroxymethylfurfural (HMF), which are known to inhibit many fermented microorganisms, including those involved in the biogas generation (Hendriks and Zeeman, 2009). According to Raj (2009) the concentration of furfural that inhibits methanogens ranges from 2400 to 3000 mg/L.

The aim of this research is to study the impact of thermal hydrolysis on the biodegradability of wheat straw under mesophilic anaerobic conditions, by using an experimental approach and mathematical modeling of the results. The final applicable objective is to define the pretreatment parameters that optimize the methane productivity.

2. Methods

2.1. Raw material

Wheat straw was grown in Valladolid (Spain) and harvested in 2011. For all the experiments, the straw was cut into pieces of 10 cm long. The average values obtained in wheat straw characterization are: 922 ± 2 g TS/kg (92%VS/TS), 1078 ± 8 g TCOD/kg, 4.72 g N-TKN/kg, and a ratio C/N around 92.

2.2. Thermal pre-treatment pilot plant and operation conditions

The Cambi® thermal treatment plant, steam explosion unit, consists of a 30 L reactor and a flash tank with a removable bucket to collect the pretreated material (Fig. 1). The steam is generated by a 25 kW electric steam boiler (200 L capacity) which can supply steam up to a maximum pressure of 34 bar (240 °C). Wheat straw is loaded into de reactor using a motorized (M) ball valve (V4) at the top of the reactor. Steam is added to the reactor from the bottom, through an air-actuated valve (V1), heating the waste during the time established. The desired operation pressure (corresponding to a certain temperature) is set on the control panel unit, controlled automatically by the air-actuated valve (V1). For security reasons also a manual valve (V2) has to be opened to add steam to the pressure reactor. An air-actuated ball valve at the bottom of the vessel (V3) is responsible for the rapid pressure drop (explosion) and release of the pretreated biomass to the flash tank. The pretreated biomass is collected in a removable bucket at the bottom of the flash tank. The steam that is leaving the flash tank is condensed and led to a water tank (WT). Any steam that is not condensed leaves the unit via a carbon filter (CF) to remove smell.

Different pre-treatment conditions were tested varying both temperature (ranging 150–220 °C) and time (ranging 1–15 min). In all the experiments, one kilogram of wheat straw was used. The reactor was preheated for about 15 min at the same temperature selected for the pre-treatment before starting the experiments.

Temperature and time determine the severity factor of the treatment. This parameter ($\log R_0$, Eq. (1)) is most widely accepted for steam pre-treatments (Hendriks and Zeeman, 2009) to express the severity of the pre-treatment:

$$\log R_0 = \log\left(t \cdot \exp\left(\frac{T-100}{14.75}\right)\right) \tag{1}$$

where t is the time (min), T the temperature (°C), 100 is the base temperature (100 °C), and 14.75 is the activation energy based on the assumption that the reaction is hydrolytic and the overall conversion is first order (Xu et al., 2011). This expression only takes into account time and temperature, and does not consider the effect of the flash. The study of this effect is not assessed in this paper.

Theoretically, the more severe a treatment is, the more cellulose is made available for digestion. However, very severe pre-treatments can lead to formation of inhibitory compounds from the macromolecules, driving to an indirect relationship between the severity factor and the biodegradability. Therefore there should be an optimum value for the severity factor.

2.3. Anaerobic biodegradability

Batch anaerobic digestion tests (BMP) were carried out in triplicate to assess the wheat straw biodegradability after the different pre-treatment conditions applied. A control test without substrate and a control with cellulose were included in order to check the methanogenic activity of the inoculum. All the experiments were carried out at mesophilic conditions in a thermostatic room (35.1 ± 0.3 °C), with constant mixing in a rotary desk.

The anaerobic inoculum used for the batch test was taken from a pilot-scale mesophilic anaerobic digester treating mixed sludge from a municipal wastewater treatment plant, with a volatile solids (VS) concentration of 12 gVS/kg. The inoculum was pre-incubated for four days (35.1 ± 0.3 °C) in order to minimize its residual biodegradable organic material content.

Bottles of 2 L volume were used, made of borosilicate glass (260 mm height, 160 mm diameter and a 40 mm bottleneck), placed horizontally in a rotary table to achieve a good mixing.

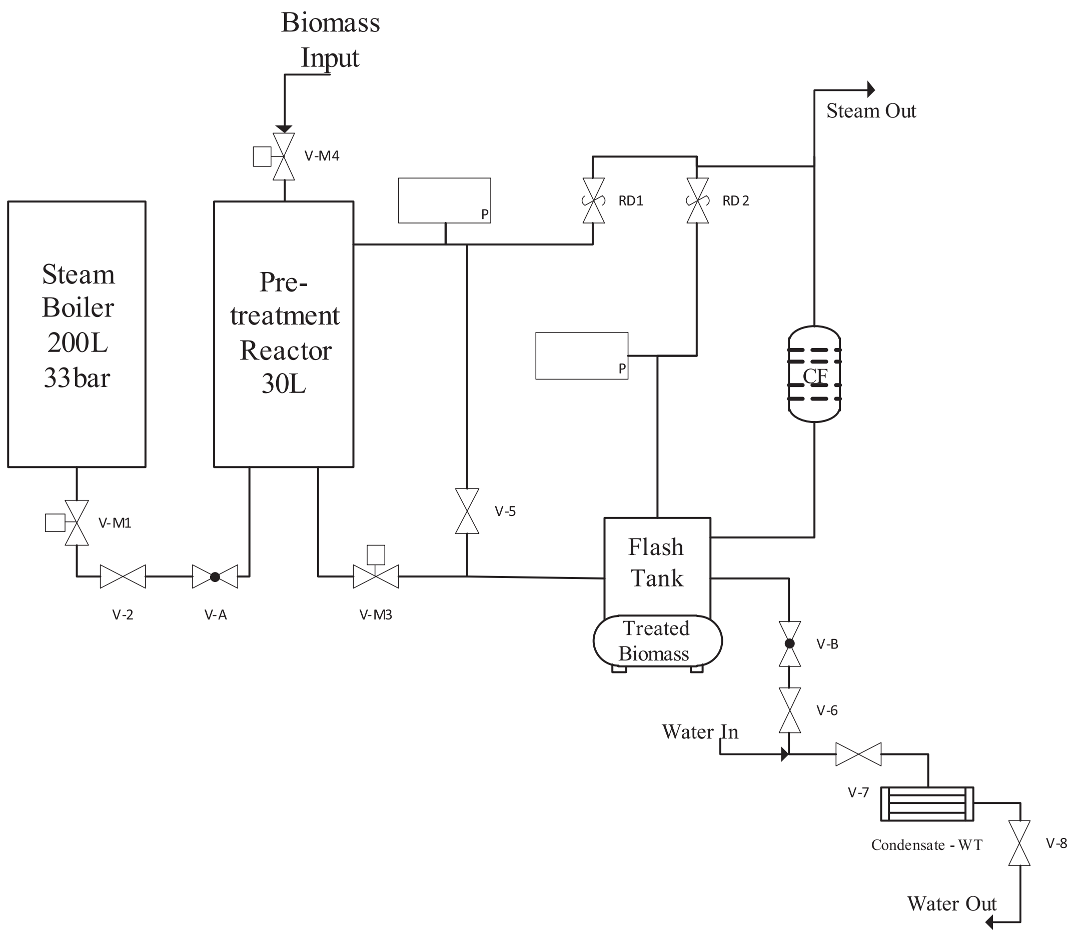

Fig. 1. Cambi® steam explosion unit. V – valves; VM – motorized valves; VA,B – one way valves; P – manometers to measure pressure; RD – safety valves; CF – carbon filter; TB-T – treated biomass tank; WT – water tank.

The liquid volume was 400 mL in order to have enough headspace, and the substrate/inoculum (S/I) ratio selected was 0.5 gVS/gVS as suggested by Neves et al., 2004 and Angelidaki et al., 2009.

Biogas production was measured manually by a pressure transmitter (ifm, PN5007, range 1 bar) in the head space of each reactor and the biogas composition was measured by gas chromatography (Varian CP-3800 CG TCD). The biogas production was followed for about 40 days. All values of specific methane yield (mL CH_4/gVS_{fed}) are presented under standard temperature and pressure conditions (STP – 0 °C, 1 atm) defined by IUPAC (International Union of Pure Applied Chemistry), and divided by the mass of volatile solids of substrate fed into the assay.

Theoretical methane yield (Nm^3 CH_4/kg VS) was calculated from the characterization performed to the wheat straw as follows:350 mL CH_4/g $TCOD_{removed}$ × 1.27 g TCOD/g VS = 444 mL CH_4/g $VS_{removed}$.

This value is in agreement with the one calculated by Kaparaju et al. (2009) considering the stoichiometric conversion of the organic matter (426 mL CH_4/g $VS_{removed}$).

2.4. Analytical method

Substrates, inoculum and digestates were characterized in all the experiments. Total and volatile solids (TS and VS) and total Kjeldahl nitrogen (TKN) were measured following the procedures given in Standard Methods for Examination of Water and Wastewater (APHA et al., 2005). Total chemical oxygen demand (TCOD) was determined according to standard UNE 77004:2002 based in dichromate method. A combustion infrared method, with SHIMADZU TOC-SM5000A equipment, was used to determine the total organic carbon (TOC). The biogas composition (CO_2, H_2S, O_2, N_2, CH_4) was measured by gas chromatography in a Varian equipment CP-3800 CG TCD, being helium the carrier gas.

Table 1
Conditions applied for the different experiments performed.

Experiments	Ref.	P (bar)	*T* (°C)	Time (min)	log R_0	mLCH_4/g VS_{fed}	FN
Untreated	0	–	–	–	–	226 ± 11	–
TH-1	1	5	150	15	2.65	185 ± 28	0.82
TH-2	2	8	170	5	2.76	159 ± 16	0.70
TH-3	3	8	170	15	3.24	250 ± 19	1.10
TH-4	4	16	200	2	3.25	211 ± 22	0.93
TH-5	5	16	200	5	3.64	238 ± 18	1.05
TH-6	6	16	200	15	4.12	202 ± 2	0.89
TH-7	7	23	220	1	3.53	273 ± 3	1.21
TH-8	8	23	220	5	4.23	214 ± 28	0.95

2.5. Parameters determination and evaluation methodology

2.5.1. Parameters determination from BMP test

When the hydrolysis reaction is the rate-limiting step of the global process, as happens in the anaerobic degradation of lignocellulosic substrates, the first order model (Eq. (2)) is commonly used to estimate the reaction extent B_0 (related to the substrate

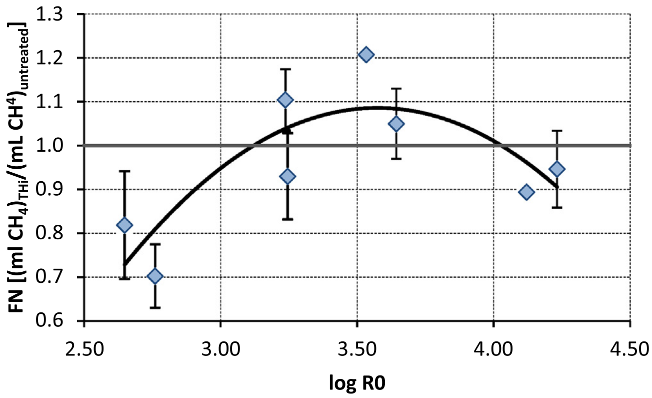

Fig. 2. Normalized methane productivity (FN [(mL CH_4)$_{THi}$/(mL CH_4)$_{untreated}$]) with respect to the severity factor (log R_0).

biodegradability) and the hydrolysis constant k_h, which both could be used in a global model of the anaerobic digestion process (such as ADM1) to predict the performance of the anaerobic digester (Batstone et al., 2009; Donoso-Bravo et al., 2010; Ge et al., 2011).

$$B = B_0 \cdot (1 - \exp(-K_h \cdot t)) \tag{2}$$

where B is the biogas production (ml/gVS$_{fed}$)

2.5.2. Model accuracy determination

Apart from obtaining the best combination of parameters, it is even more important to know the accuracy of the estimated values. The Fisher matrix (FIM) summarizes the quantity and quality of the information obtained in the experiment and, assuming proper model selection with no data autocorrelation and uncorrelated error, the inverse of the FIM (Eq. (3)) corresponds to the parameter estimation covariance matrix (C_j).

$$C_J = (F(\theta))^{-1} \quad \text{where} \quad F(\theta) = \sum_{i=1}^{N} \left[\frac{\partial y_i(t,\theta)}{\partial \theta}\right]^{\mathrm{T}} Q_i^{-1} \left[\frac{\partial y_i(t,\theta)}{\partial \theta}\right] \tag{3}$$

Finally, once the covariance matrix is available, an approximation of the standard deviation of the parameters can be estimated through Eq. (4).

$$\sigma(\theta_i) = \sqrt{C_J} \tag{4}$$

2.5.3. Response surface methodology (RSM)

This methodology allows evaluating the combined effect of several variables (temperature and time in this case) and the interaction between them on a specific response (in this case, those parameters obtained in Section 2.5.2). The polynomial shown in Eq. (5) considers the effect of both variables as well as the combined influence of them. The coefficients of the equation were obtained by minimizing the least square function, and determination coefficient was calculated to know the fraction of the variability of the data that is explained by the model. The analysis was carried out in Matlab®.

$$Y = p_1 + p_2 x_1 + p_3 x_2 + p_4 x_1 x_2 \tag{5}$$

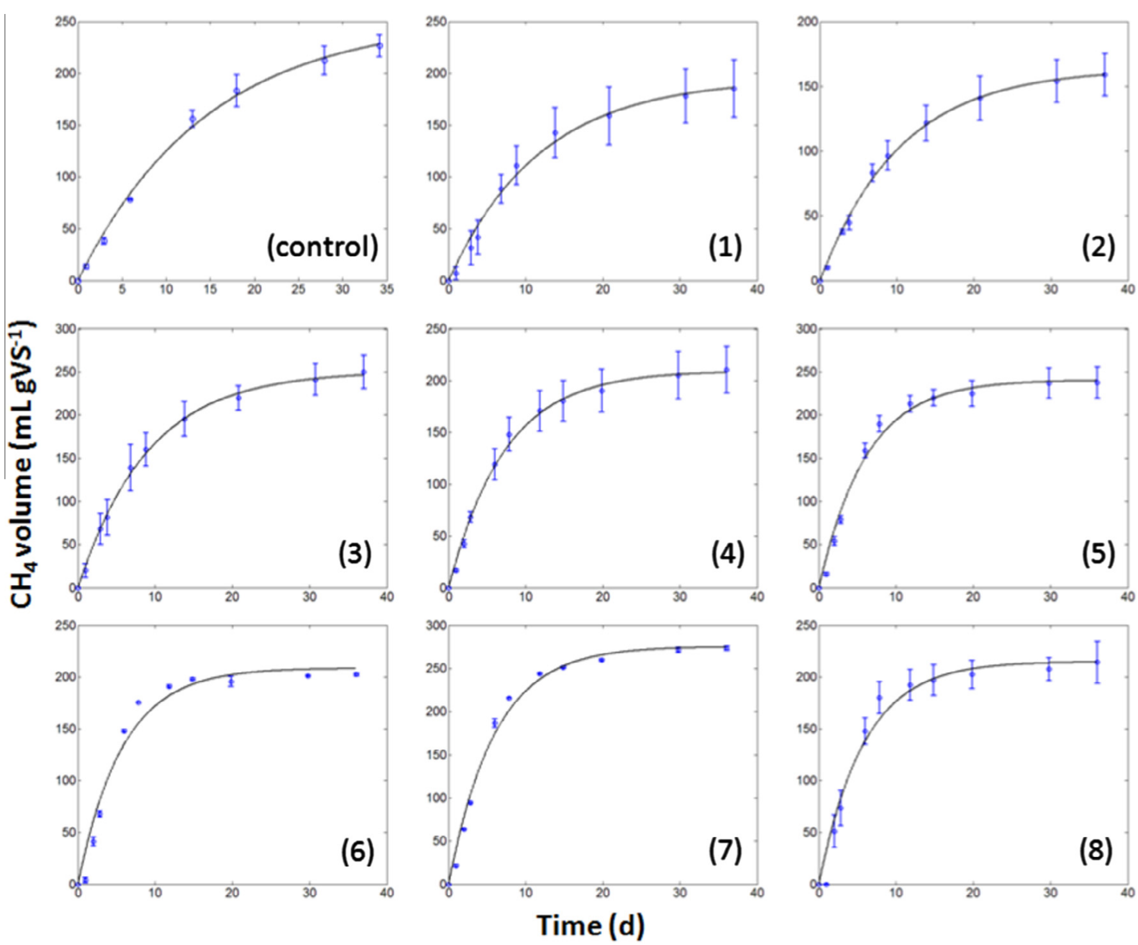

Fig. 3. First order model fit. Experimental information (blue points), model profile (black solid line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Results of the parameters determination.

Exp.	T (°C)	t (min)	First order model				
			B_0		k_h		R^2
			mean	SD[a]	mean	SD[a]	
0	0	0	252.1	9.2	0.069	0.006	0.997
1	150	15	194.6	8.2	0.085	0.009	0.989
2	170	5	163.4	3.0	0.097	0.005	0.997
3	170	15	250.6	3.6	0.110	0.004	0.998
4	200	2	209.2	4.0	0.138	0.008	0.995
5	200	5	240.7	6.8	0.164	0.015	0.987
6	200	15	208.6	9.3	0.175	0.025	0.968
7	220	1	275.5	6.9	0.168	0.014	0.989
8	220	5	214.9	8.7	0.173	0.023	0.973

[a] SD: standard deviation.

where Y is the variable response, x_1 is the pretreatment time, x_2 is the pretreatment temperature, and p_1...p_4 are the regression coefficients of the model.

3. Results and discussion

3.1. Pre-treatment experimental study

The temperature–time combinations selected for the study are presented in Table 1. For each experiment the severity factor ($\log R_0$) was calculated according to Eq. (1). The last column in Table 1 presents the results for the normalized production on methane (FN) defined as the ratio between the production of methane for the treated and untreated wheat straw: (mL CH_4)$_{THi}$/(mL CH_4)$_{untreated}$.

Compared to the theoretical methane productivity (444 mL CH_4/g $VS_{removed}$), the experimental value obtained in the BMP test of the untreated wheat straw indicates that only 51% of the volatile solids were converted into methane. For the best thermal hydrolysis conditions (TH-7) the anaerobic biodegradability increased until a value of 61%.

Fig. 2 shows the relation between the severity factor and the normalized production of methane. The influence of the severity factor is quite clear: when increasing the severity factor, the production of methane increases until reaching a maximum. Over this optimum, the efficiency of the pretreatment decreases and therefore the methane production does, probably due to the formation of inhibitory compounds. For example, Thomsen et al. (2009) obtained an increase in the furfural concentration from 50 mg/L to 1200 mg/L when increasing the pretreatment temperature from 190 °C to 205 °C (6 min treatment).

In the present study, the highest improvement with respect to the untreated sample corresponds to the severity factor in the range 3.25–3.5.

Further analysis of the results is necessary in order to determine the best way of coupling temperature and time to get a desired severity factor (that is: short pre-treatment at high temperature,

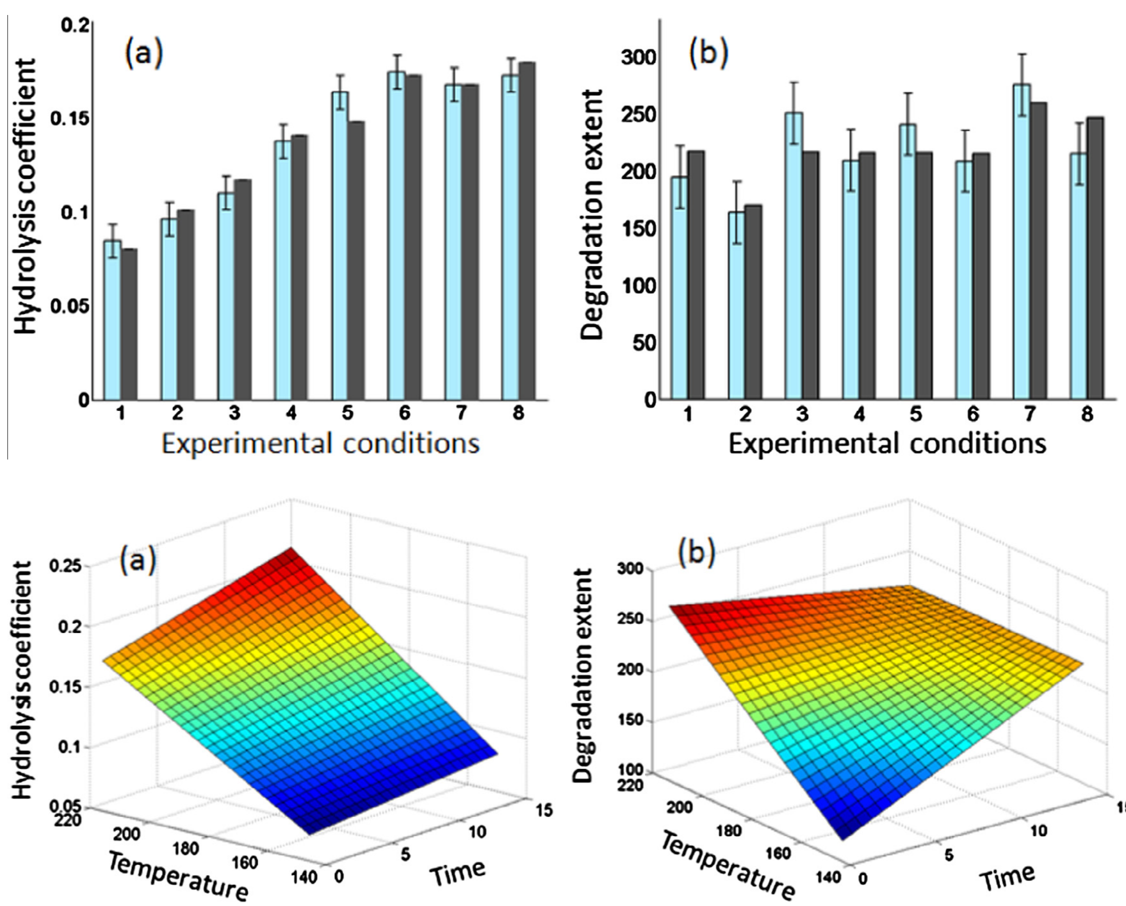

Fig. 4. Comparison between model prediction and the experimental data by using the optimal set of parameter values. (a) Hydrolytic coefficient (b) degradation extent. Light blue bars: real values, grey bars: predicted by the polynomial. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

or the contrary). Therefore, subsequent modeling and RSM evaluation was performed.

3.2. Modeling of the results and parameters determination

Fig. 3 presents the fitting process between the experimental methane production and the first order model curve. It can be observed that the model is able to reproduce the methane production profiles in a proper way since in most of the cases the model curve lies inside the corridor given by the standard deviation (SD). Moreover, the determination coefficients (R^2) are mostly above 0.98, which indicates that this model is able to explain around 98% of the experimental data variability. Table 2 shows the values obtained in the parameters estimation where it can be observed that the standard deviation of the estimated parameters was not significant with respect to the mean values, hardly over 10% compared to the optimized values, which is also an indicator of the model fitting procedure success.

With respect to the values of the parameters, the first order model fit shows that the thermal pretreatment had a positive influence on the hydrolysis rate (Fig. 3): this means that the higher the severity factor, the higher the hydrolysis constant. These results show that the solubilisation of particulate organic matter is a consequence of both temperature and time effects. Although the solubilized biomass is expected to be more available for the anaerobic biomass, the results show that in some cases the pretreatment lead to a decrease in biodegradability, especially for the highest severity factors. This can be explained due to the appearance of some recalcitrant compounds after the pretreatment, as aforementioned.

3.3. Response surface methodology (RSM) results

The parameters of the first order model were fitted to a polynomial equation to evaluate the influence of the two independent variables (temperature and time). The obtained equations are shown next:

$$K_H = 0.152 - 0.003 \cdot T + 0.0014 \cdot t + 0.000027 \cdot T \cdot t \quad (6)$$

$$B_0 = -249.48 + 31.58 \cdot T + 2.33 \cdot t - 0.1582 \cdot T \cdot t \quad (7)$$

In the operation range evaluated, the influence of the interactions between both parameters is low compared to the independent influence of each one. In the case of k_H, the determination coefficient (R^2) was 0.958, which means that the model correlates around 96% of the variability in the parameter. Therefore, this empirical model can be used to predict the hydrolysis constant using the data of temperature and pretreatment time within the studied design range. For B_0, the determination coefficient was not as good as expected (0.569), which may indicate that this type of polynomial model may not be the best option to predict this parameter. The results of the agreement between the k_H and B_0 values obtained from the BMP test and the predicted ones with the polynomial are presented in Fig. 4. Globally, there is a good agreement between the predicted and the actual values of the parameter, especially in the case of the hydrolysis constant.

By applying these polynomial equations, two surface responses were built in order to observe optimum region of the parameters in terms of temperature and time (Fig. 4). In the case of k_H, the optimum zone (red zone) can be observed toward the higher values of both temperature and time, which must entail that the soluble fraction of the organic matter increases when increasing these variables. By contrast for B_0, the best values were obtained at higher temperatures and short times. Therefore, the conclusion about the best way of coupling temperature and time to get the optimum severity factor around 3.5 is: high temperature (220 °C) and short time (1 min), instead of the contrary (lower temperature but higher time).

4. Conclusions

The influence of thermal pretreatment parameters (temperature and time) on the anaerobic biodegradation of wheat straw was evaluated. In terms of "severity factor", the optimum was obtained at 3.5, corresponding to 220 °C and 1 min treatment. A first order model fitted accurately the experimental results on biodegradability, confirming that the hydrolysis is the limiting step. A surface response methodology was applied to assess the combined effect of the temperature and the time on the kinetic parameters, which indicated that influence of the interactions between these variables is low in comparison with the separated influence of each one.

Acknowledgements

This work was financially supported by the company Cambi®, project "Thermal hydrolysis of solid wastes". The group of Valladolid University is Grupo de Excelencia GR 76 de la Junta de Castilla y León and member of the Consolider-Novedar framework (Programa Ingenio 2010). A. Donoso-Bravo is supported by the "Dirección de Investigación (DII)" of the Pontificia Universidad Católica de Valparaíso.

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