Model based assessment of anaerobic digestion of lignocellulose containing waste materials

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Abstract

Purpose. Hydrolysis of lignocellulosic substrates is impeded by the lignin polymer, acting as a seal around the cellulose and hemicellulose polymer. To facilitate hydrolysis and improve biomethane production, pretreatment of the substrate is required. However harsh pretreatments prior to anaerobic digestion can cause a release of inhibitory phenolic compounds i.e. vanillic acid, p coumaric acid, ferulic acid and hydroxybenzoic acid.

Methods. In this study the developed anaerobic digestion model takes the substrate lignin concentration as well as the concentration of such phenolic compounds into account. The biomethane production and hydrolysis rate of seven different substrates were simulated. The impact of higher concentrations of the phenolic compounds, up to 2000 mg/l, was simulated for two of the substrates namely, hemp straw and miscanthus. As significant inhibition only occurred for the anaerobic digestion of miscanthus, a global sensitivity analysis and parameter estimation (assessing all the processes in the model) was done for this substrate.

Results. A good agreement between simulations and measurements was obtained, as the maximum Theil's inequality coefficient for the different substrates was 0.14. The global sensitivity analysis showed the great importance of the hydrolysis rate and the need to research factors, i.e. inhibitors and substrate types, influencing this hydrolysis step.

Conclusion. In this study a model was designed for substrates in a large range of lignin content, showing that a good prediction of the BMP can be achieved without extensive substrate characterization. Only the lignin content needs to be determined.

Keywords

Anaerobic Digestion, Modeling, Biogas Production, Lignin, Phenolic Compounds

Introduction

Lignocellulose containing waste materials can be found as agricultural waste streams (e.g. corn stover, hemp straw or miscantus). To valorize these low cost waste streams, anaerobic digestion can be applied in order to produce biogas. The hydrolysis is the rate-limiting step during anaerobic digestion, mainly because of the recalcitrant lignin seal in lignocellulosic material [1]. In order to improve anaerobic digestion, hydrolysis of the lignocellulosic matrix should be facilitated by a pretreatment. The lignocellulosic substrate can be pretreated by different methods: mechanical, chemical, physical and physico-chemical. All these pretreatments have advantages and disadvantages. An important disadvantage is the release of unwanted by-products. These by-products include organic acids, furan derivatives and phenolic compounds, which will inhibit further process steps (e.g. hydrolysis) for obtaining biogas [2].
Modelling is an efficient tool to gain knowledge on the potential of the used substrate, the effect of the pre-treatment and the prevailing concentrations of phenolic compounds. In this study a specially developed anaerobic digestion model is used (based on Van Hulle et al.[3]). This model describes the degradation of lignocellulosic solid waste to biogas taking into account the lignin content (and as such the type) of the substrate as well as the impact of phenolic compounds (which are formed during pretreatment). The model is used to assess the biogas production of 7 substrates with different lignin content, while the impact of phenolic compounds is simulated for 2 of these substrates. A global sensitivity analysis is performed to identify the model parameters with the most influence on the predicted biogas concentration. The identifiability of these parameters is also assessed.

Materials and methods

Data collection

The experimental data from anaerobic digestion of seven different lignocellulosic substrates used in this study was obtained in a previous studies[1,4]. Batch tests (with a duration of 30 days) were performed and biogas production, lignin content and phenolic compound concentration was measured. Tests were done in a lab-scale completely stirred tank reactor (CSTR) with an overall volume of 250 ml operated in batch mode [5] at 37 °C with a substrate to inoculum ratio of 0.5 (g VS/g VS). The substrates, corn stover, ensilaged maize, wheat straw, flax straw, hemp straw, miscanthus and willow, were mixed with inoculum which was collected from a co-digestion plant treating cow manure and maize silage. The inoculum was filtered, defermented and stored at 4 °C until 3 days before use, when it was placed at 37 °C. The biogas production was measured daily via a water displacement system and samples were taken 3 times during the anaerobic digestion to determine the methane (±70%) and carbon dioxide content by gas chromatography (GC).
The inhibition of the anaerobic digestion was examined while adding 0, 100, 500, 1000 and 2000 mg/l of the individual phenolic compounds, vanillic acid (VA), p-coumaric acid (PCA), 4-hydroxybenzoic acid (HBA) and ferulic acid (FA) to the inoculum with hemp straw or miscanthus[1]. The applied concentration range mimics the production of phenolic compounds during (harsh) pre-treatment.

Modelling

The model used was an adaptation from the model proposed by Van Hulle et al.[3]. The model was extended with the inhibition effect of phenolic compounds on hydrolysis and the effect of lignin content on biogas production (Table 1). The model assumes the insoluble organic matter or volatile suspended solids (VSS) is hydrolysed to volatile dissolved solids (VDS). Acetogenic bacteria transform the VDS to volatile fatty acids (VFA), which were transformed by methanogenic bacteria to (bio)methane.

Table 1. Gujer Matrix of the anaerobic digestion model used in this work

Process	VSS	VDS	VFA	CH_4	X_1	X_2	Process rate
Hydrolysis	*-1*	*1*					$k_1[VSS]\frac{K_L}{K_L+C_L}\frac{SP*C_P+K_I}{C_P+K_I}$
VFA formation		*-1*	*1-Y_1*		*Y_1*		$k_2\ \frac{[VDS]}{k_3+[VDS]}\ [X_1]$
CH_4 formation			*-1*	*1-Y_2*		*Y_2*	$k_4\ \frac{[VFA]}{k_5+[VFA]}\ [X_2]$
Decay acetogenic bacteria					*-1*		$b_1\ [X_1]$
Decay methanogenic bacteria						*-1*	$b_2\ [X_2]$

To determine the initial value of the VSS, data from previous research was taken [1,4]. Most parameter values presented in Table 3 were derived from Van Hulle et al.[3], while the affinity constants K_I and K_L were selected based on the performed experiments. Lignin concentration (C_L) was substrate dependent, taken from Schroyen et al.[4] and ranged from 0.8 to 17 g/100 gDM. Also the concentration of phenolic compounds (C_P) varied in every experiment from 17 to 74 mg/g, as the increase in concentration of total phenolic compounds was used from Schroyen et al.[4]. It was assumed that the phenolic compounds present originated from the applied (harsh, enzymatic or other) pretreatment only and were not (or very limitedly) formed during anaerobic digestion.
The parameter S_P was chosen as 1 for hemp straw as no inhibition by the phenolic compounds was noted, while for miscanthus it ranged between 0.4 and 0.8 as an increased inhibitory effect was seen with an increased concentration of phenolic compounds. The anaerobic digestions of hemp straw and miscanthus with the addition of the various phenolic compounds were performed with sludge obtained later, resulting in different BMP values if no phenolic compounds were added [1]. Hence different initial VSS values were used in the simulations.
The model was simulated by using R, while the Flexible Modeling Environment (FME) package allowed sensitivity analysis and parameter estimations [6].

Results and discussion

Effect of substrate

Seven different substrates were anaerobically digested and the experimental biomethane production was measured. With the model described above, the biomethane production was also simulated. For these simulations the effect of the phenolic compounds was not taken in to account as the concentrations of phenolic compounds were too low to have a significant inhibitory effect. In Figure 1, the resulting experimental and simulation data is given for the seven substrates. Overall the predictive power of the model is good as a good fit is obtained.

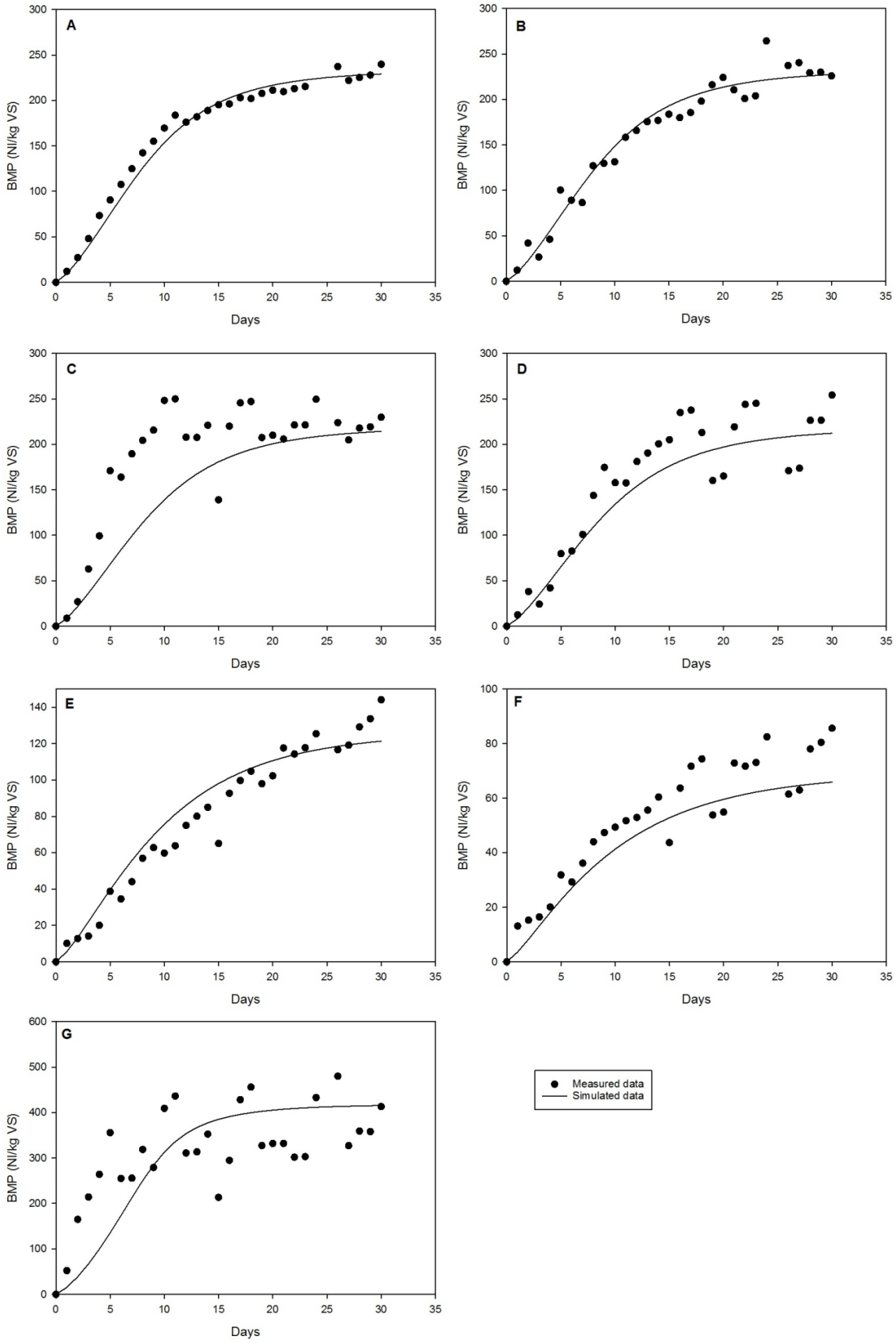

Figure 1. Measured and simulated biomethane curves of the various substrates, corn stover (A), wheat straw (B), flax straw (C), hemp straw (D), miscanthus (E), willow (F) and ensilaged maize (G) (n=3)

Effect of phenolic compound concentration

The lignin concentration of the various substrates plays an important role in the total biogas production. Degrading the lignin through harsh pretreatments could resolve this, however lignin degradation will also lead to the release of phenolic compounds in higher concentrations. These phenolic compounds have a negative impact on the hydrolysis of a substrate, depending on the lignin content of the substrate. For miscanthus (as an example of a substrate with a high lignin content) digested at different concentrations of p-coumaric acid the hydrolysis rate (indicated by the initial slope of a biogas production curve, Figure 2a) decreases with increasing phenolic compound concentration).

This inhibition is taken into account in the developed model (Table 1). The addition of 2000 mg/l ferulic acid (FA) and 4-hydroxybenzoic acid (4-HBA) to miscanthus caused an average inhibition of the hydrolysis rate of 22 %. Vanillic acid (VA) and p-coumaric acid (p-CA) inhibited the hydrolysis rate up to 50 % at a concentration of 2000 mg/l. The difference in inhibition resulted in two different S_P-values for the individual phenolic compounds: S_P = 0.4 was used for VA and p-CA, while SP = 0.8 was used for FA and 4-HBA. As such, the effect of phenolic compounds on the hydrolysis rate (slope of the biogas production profile for the first 7 days of the experiment) could be well described as depicted in Figure 2b.

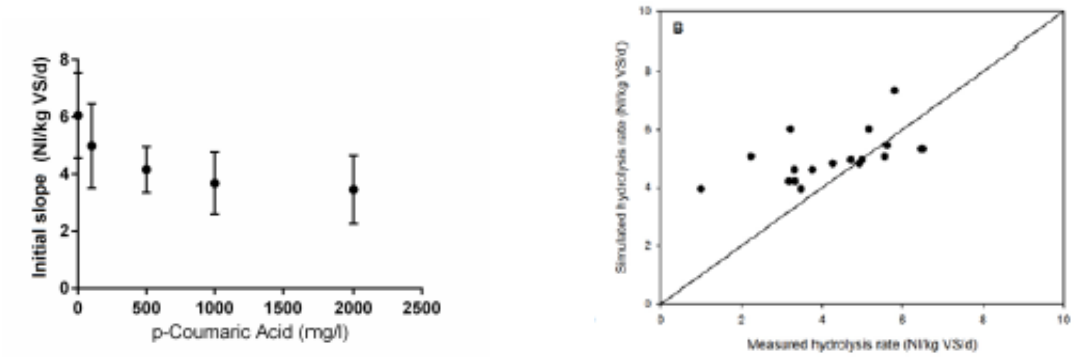

Figure 2. (left): Effect of p-coumaric acid on the hydrolysis rate of miscanthus as determined experimentally (A) and experimental (n=15) and simulated hydrolysis rate of the anaerobic digestion of miscanthus with the addition of phenolic compounds, represented together with the bisector (B)

Global sensitivity analysis

A global sensitivity analysis was done with the starting values of miscanthus with 0 and 500 mg/l of VA or PCA added. A Monte Carlo run with 1500 simulations was performed for the different experiments. Figure 3A shows the tornado plots summarizing the sensitivities of all model parameters with respect to biomethane production after 7 days of digestion without the addition of a phenolic compound. Figure 3B shows the results for the experiment with 500 mg/l VA or p-CA (S_P=0.4).

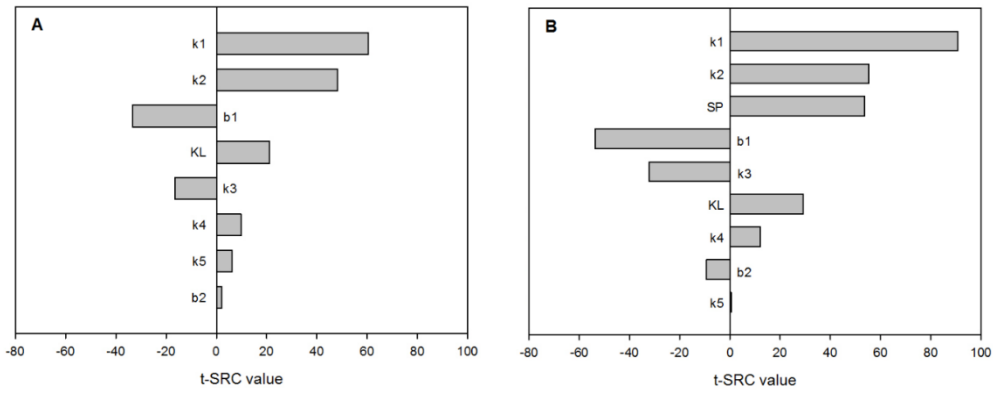

Figure 3. Tornado plot of a Monte Carlo run (n=1500), showing the sensitivity of the biomethane production during anaerobic digestion without the addition of phenolic compounds (A) and with the addition of 500 mg/l vanillic acid or p-coumaric acid (B)

In figure 3A and 3B it can be seen that k_1 and k_2 are the most sensitive parameters, indicating the importance of the hydrolysis step during anaerobic digestion. The maximum hydrolysis rate was noted as the most sensitive parameter by Myint et al.[7], which is in agreement with previous reports of hydrolysis being the rate limiting step in the digestion[8]. From figure 3B it can be deduced that the parameter S_P, specifying the level of inhibition at larger concentrations of the phenolic compounds have a sensitive impact on the biogas production. The positive values of the sensitivities for k_1, k_2 and S_P indicate that increasing the parameter will cause a higher biogas production. On the other hand, the negative value of the sensitivity for b_1 signifies that the decay of the acidogenic bacteria has a decreasing effect on the biogas production.

Conclusion

In this study a model was designed for substrates in a large range of lignin content, showing that a good prediction of the BMP can be achieved without extensive substrate characterization. An implementation of inhibiting phenolic compounds in the model enables the prediction of the impact of a release of phenolic compounds during harsh pretreatments.

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