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Modelling and simulation of anaerobic digestion of various lignocellulosic substrates in batch reactors: Influence of lignin content and phenolic compounds II

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ABSTRACT

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 such as vanillic acid, *p*-coumaric acid, ferulic acid and hydroxybenzoic acid. 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 was described and simulated. A good agreement between simulations and measurements was obtained, as the maximum Theil's inequality coefficient for the different substrates was 0.14. 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. 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.

1. Introduction

Fossil fuel reserves keep diminishing, which is one of the reasons why the need for different energy sources is increasing [1]. Bioenergy obtained from biomass is as such a promising alternative. Agricultural waste is an abundant source of lignocellulosic material, which is not in competition for food, nor feed. This low cost material can be used to produce biomethane via anaerobic digestion. Several studies have shown a correlation between lignin concentration of a substrate and its biomethane potential (BMP) [2–4]. Furthermore the hydrolysis process step in the anaerobic digestion is the rate limiting step, this is due to the recalcitrant lignin polymer surrounding the cellulose and hemicellulose chains [5].

There is a great variety of agricultural waste with different concentrations of lignin. Estimation and/or enhancement of the hydrolysis rate is of great importance for assessing the overall digestion performance. To facilitate the hydrolysis, pretreatment of the biomass can be performed as it will degrade the lignin, and thus can improve the BMP [6]. However during harsh pretreatments a release of weak acids, furan derivatives and phenolic compounds occurs [7]. For example, phenolic acids, such as p-coumaric acid and ferulic acid, are common products in pretreatment of annual plants [8]. These compounds (or a combination of them) are known to inhibit the initial rate of biogas production and more importantly the hydrolysis rate, especially when lignin rich substrates are used [9,10]. Harsher pretreatments like alkaline or thermal pretreatments can increase the released concentration of phenolic compounds, i.e. *p*-coumaric acid, ferulic acid, vanillic acid and 4hydroxybenzoic acid, to inhibitory levels. These concentrations (>1000 mg/l) have to be taken into account when performing an anaerobic digestion, and play an important role in estimating the hydrolysis step [11].

Modelling is an efficient tool to gain knowledge on the potential of the used substrate and the prevailing concentrations of phenolic compounds. The Anaerobic Digestion Model 1 (ADM1) is a commonly used anaerobic digestion model, however it focuses only on sewage sludge [12]. The use of different types of substrates has since

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Table 1
Gujer Matrix of the anaerobic digestion model, with inhibition of lignin and phenolic compounds, 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 acidogenic bacteria					−1		$b_1 [X_1]$
Decay methanogenic Archaea						−1	$b_2 [X_2]$

then resulted in modifying the model. A co-digestion of manure and energy crops was studied and modeled by Lübken et al. [13]. Galí et al. [14] proposed a modified version for agrowaste application, emphasizing the need to characterize the substrate. Appropriate modifications allowed a simulation of the anaerobic digestion of microalgae [15]. Bułkowska et al. [16] included fractionation of maize silage and cattle manure mixture in the ADM1.

The main disadvantage of the ADM1 model (and its modifications) is that it requires the calibration of a large number of parameters and the determination of several variables, which is as a consequence difficult for implementation in plant operation. Therefore in this study a simplified anaerobic digestion model is proposed based on the model presented in Van Hulle et al. [17]. This model describes the degradation of solid waste to biogas via a 4 step process. The model assumes the insoluble organic matter or volatile suspended solids (VSS) is hydrolysed to volatile dissolved solids (VDS) respectively through first-order kinetics. Acidogenic bacteria transform the VDS to volatile fatty acids (VFA), which were transformed by methanogenic Archaea to methane according to Monod kinetics. In this study, the model developed by Van Hulle et al. [17] is extended in order to take the lignin content of different types of agricultural waste, which can be used as substrate, into account as well as the impact of phenolic compounds (typically and frequently produced during pre-treatment of the substrate as indicated above). The first order hydrolysis kinetics were adapted to account for the lignin content as well as for the inhibition due to the phenolic compounds. The model is used to assess the biogas production of 7 substrates with different lignin content. These 7 substrates were selected in order to cover a wide range of lignin content (ranging from 0.8 g/100 g to 17 g/100 g, see Table 2). The impact of phenolic compounds is simulated for 2 of these substrates. The most dominant phenolic compounds present after enzymatic pre-treatment as determined by Schroyen et al. [4] were selected. 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.

2. Materials and methods

2.1. Experimental data collection

The experimental data used in this study was obtained in previous studies [4,10]. Seven different lignocellulosic substrates were characterized in Schroyen et al. [4] with a standardized experimental set-up that allows to assess BMP in a uniform and reproducible manner for different substrates [18] in accordance with the test protocol VDI 4630 [19]. Lignin concentration, release of phenolic compounds and BMP over 30 days were determined for untreated and enzymatically pretreated substrate. In this study, the experimental BMP data from the untreated substrates was used. Anaerobic digestion was done in a lab-scale reactors with an overall volume of 250 ml operated in batch mode [20] at 37 °C with a

Table 2
The substrates and BMP values used to calibrate the model based on the different lignin concentrations and initial VSS values.

Substrate	BMP (Nl*/kgVS)	VSS (gCOD/l)	C_L (g/100 g)	C_P (mg/g)
Ensilaged maize	413.9	40.0	0.8	48
Corn stover	242.4	22.8	4.5	35
Wheat straw	247.1	22.8	6.0	47
Flax straw	233.1	21.6	8.6	17
Hemp straw	237.8	21.6	9.2	42
Miscanthus	144.5	13.2	12.0	46
Willow	88.6	8.0	17.0	74

* Nl stands for normal liter.

substrate to inoculum ratio of 0.5 (g VS/g VS). The reactors were shaken daily to ensure proper mixing. Tests were run for at least 30 days. 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, washed, allowed to further react and/or degas for 1 week and stored at 4 °C until 3 days before use, when it was placed at 37 °C to be able to acclimatize to the reactor conditions before the substrates are mixed. 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 BMP analysis was repeated 3 times, however averages of the daily biomethane production were taken of at least 2 (in case of missing data) and maximum 3 repetitions. BMP tests with only inoculum (i.e. without substrate) were also performed in triplicate to account for background biogas production from the inoculum itself (blanks). This background biogas production was subtracted from the measured biogas production. This data (including correction for biogas productions from the blanks) are further used as experimental data for modelling.

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 [10]. The applied concentration range mimics the production of phenolic compounds during (harsh) pre-treatment.

2.2. Reaction and reactor model

The simplified model following Monod kinetics proposed by Van Hulle et al. [17] was extended with an inhibition term for phenolic compounds and a term for the lignin content (Table 1). Thus the effect of lignin content and the concentration of phenolic compounds on hydrolysis were taken into account. The VSS are transformed to VDS according a first-order kinetics (in terms of VSS) as proposed by e.g. Van Hulle et al. [17] and Borja et al. [21]. This hydrolysis is influenced by the lignin and total phenolic content (as indicated by the (adapted) Monod kinetics). An increased content