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Published in:
Waste Management

Link to article, DOI:
10.1016/j.wasman.2022.10.040

Publication date:
2023

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Lymperatou, A., Engelsen, T. K., Skiadas, I. V., & Gavala, H. N. (2023). Prediction of methane yield and pretreatment efficiency of lignocellulosic biomass based on composition. *Waste Management*, *155*, 302-310. https://doi.org/10.1016/j.wasman.2022.10.040

Waste Management 155 (2023) 302–310

Contents lists available at ScienceDirect

Waste Management

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

Prediction of methane yield and pretreatment efficiency of lignocellulosic biomass based on composition

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ARTICLE INFO

Keywords:
Biogas
Ammonia
Anaerobic digestion
Modeling
Pretreatment
Regression

ABSTRACT

Lignocellulosic biomass is considered a key resource for the future expansion of biogas production through anaerobic digestion (AD), and research on the development of pretreatment technologies for improving biomass conversion is an intensive and fast-growing field. Consequently, there is a need for creating tools able to predict the efficiency of a certain pretreatment on different biomass types, fast and accurately, and to assist in selecting a pretreatment technology for a specific biomass. In this study, seven different types of raw lignocellulosic biomass of industrial relevance were systematically analyzed regarding their composition (carbohydrates, lignin, lipids, ash, extractives, etc.) and subjected to a common pretreatment. The aim of the study was to identify the most important characteristics that make a biomass good receptor of the specific pretreatment prior to AD. A simple ammonia pretreatment was chosen as a case study and partial least squares regression (PLS-R) was used for modeling initially the ultimate methane yield of raw and pretreated biomass. In the sequel, PLS-R was used for modeling the efficiency of the pretreatment on increasing the ultimate methane yield and hydrolysis rate as a function of the biomass composition. The fit of the models was satisfactory, ranging from $R^2 = 0.89$ to $R^2 = 0.97$. The results showed that the most decisive characteristics for predicting the efficiency of the pretreatment were the lipid ($r = -0.88$), ash ($r = +0.79$), protein ($r = -0.61$), and hemicellulose/lignin ($r = -0.53$) content of raw biomass. Finally, the approach followed in this study facilitated an improved understanding of the mechanism of the pretreatment and presented a methodology to be followed for developing tools for the prediction of pretreatment efficiency in the field of lignocellulosic biomass valorization.

1. Introduction

Lignocellulosic biomass has been in the spotlight of research during the last few decades due to its recognized potential for contributing to the production of sustainable and renewable energy, fuels and chemicals. In Europe (EU-28), agricultural and residual lignocellulosic biomass is considered to be a key resource for the significant expansion of the biogas and biomethane production sector in the near future, which is expected to double at least until 2030 as compared to year 2015 (Meyer et al., 2018). The use of residual lignocellulosic biomass for biogas production through anaerobic digestion (AD) presents certain additional advantages. Besides avoiding the environmental pollution due to its otherwise uncontrolled degradation in the fields and storage containers, residual biomass generation does not require arable land in contrast to energy crops. While a significant effort is needed in determining the most appropriate ways for biomass collection and handling, an important limitation for its integration in AD processes is its low conversion rate and extent, which results in significantly lower methane production compared to the theoretical potential.

Lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin, which are interconnected to form a complex and recalcitrant to biodegradation matrix. Extensive research has been carried out on identifying the most limiting factors to biodegradation, ultimately pointing out the crystallinity of the cellulose fibers and more importantly the lignin barrier for conversion to methane (Carrère et al., 2016). In an effort to improve the ultimate methane yield and production rate of lignocellulosic biomass, numerous pretreatment methods have been developed in the past few decades, i.e. mechanical, chemical, thermal, biological and combinatorial methods (Olatunji et al., 2021).

The theoretical methane potential, which can be calculated for a biomass of known elemental composition (Symons and Buswell, 1933), is a poor indicator of the ultimate methane yield under real conditions. This is due to the variable degree of matrix complexity among different types of biomass, or even among biomass of the same type depending on

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https://doi.org/10.1016/j.wasman.2022.10.040
Received 10 June 2022; Received in revised form 28 September 2022; Accepted 30 October 2022
Available online 18 November 2022

its source and state. In order to obtain a more reliable estimation of the ultimate methane yield, both raw and pretreated biomass is traditionally subjected to biochemical methane potential (BMP) assays. These assays consist of batch AD trials of biomass seeded with anaerobic inoculum and monitoring of the methane production under laboratory conditions. However, BMP tests are time-consuming and can be costly when it comes to fast decision-making e.g., as to whether a certain biomass should be included in industrial AD processes. Thus, the prediction of the ultimate methane yield of different types of biomass and eventually the choice of pretreatment by faster methods would undoubtedly be a valuable tool for the AD industry.

Earlier studies have focused on predicting the ultimate methane yield of AD substrates based on biomass compositional characteristics by using linear and multiple regression models (Raposo et al., 2020). Since the biodegradability of lignocellulosic biomass is a multifactor problem, models constructed with single regressors (e.g. lignin, carbohydrates, chemical oxygen demand (COD), etc.) were insufficient for modeling the ultimate methane yield (usual R^2 less than 0.65), (Gunaseelan, 2007). On the other hand, the use of multiple regressors has resulted in models with an improved prediction potential, for example for food and vegetable waste (Gunaseelan, 2007), grassland biomass (Dandikas et al., 2015) and a variety of lignocellulosic biomass types (Monlau et al., 2012; Triolo et al., 2011). Nonetheless, models developed for predicting the ultimate methane yield of raw biomass may fail to predict satisfactorily the yield of biomass that has undergone a pretreatment step. This is due to the alterations caused in the matrix that were not considered during model calibration. The rise of pretreatment technology development, along with a significant effort for developing technologies that can be implemented at industrial scale, calls for the development of models able to identify which types of biomass are good receptors of a certain pretreatment in a fast and accurate way. This, besides shedding more light on the mechanism of a specific pretreatment, would ease the pretreatment technology selection and application for industrial plants.

In this study, seven different types of lignocellulosic biomass considered of industrial relevance (two types of animal manure, four types of agricultural straw and grass) have been collected and systematically subjected to compositional analysis according to the two-step sulfuric acid hydrolysis (SAH) procedure of NREL (Sluiter et al., 2011). In the sequel, all biomass types were subjected to BMP tests. This permitted the determination of the ultimate methane yield and hydrolysis rate of each biomass, without any pretreatment (raw biomass) and after pretreatment. The aim of the study was to identify different regressors for predicting the ultimate methane yield before and after pretreatment, as well as to identify which compositional characteristics make different matrices good candidates for a specific pretreatment. For this purpose, a simple ammonia pretreatment at room temperature was selected as a case study and partial least square (PLS) regression was used for model generation. This pretreatment has so far been tested on some types of biomass with a variable efficiency (Antonopoulou et al., 2015; Jurado et al., 2013b, 2013a; Mirtsou-Xanthopoulou et al., 2014), and has recently been reported to be promising for industrial application given the mild conditions and possibility for ammonia recovery (Lymperatou et al., 2021). The developed models are valuable tools for estimating the ultimate methane yield of lignocellulosic biomass and for evaluating the suitability of the ammonia pretreatment based on the initial composition of the biomass. The present study develops a methodology that can be established as an evaluation tool of the application potential of newly designed pretreatment technologies and for enhancing the comparability among studies.

2. Materials and methods

2.1. Biomass and inoculum source

Seven different types of biomass were selected for evaluating the effect of ammonia pretreatment on the increase of the CH_4 yield and hydrolysis rate, namely, wheat straw, barley straw, rye straw, rape straw, grass, chicken manure and horse manure. The wheat and barley straw were collected from the experimental field of the University of Copenhagen (Taastrup, Denmark), and the rye and rape straw from Vestforsyning (Holstebro, Denmark) during the month of September. The grass was harvested from the gardens of the Technical University of Denmark (Kgs. Lyngby, Denmark) during the month of September. The manure samples were provided from Madsen bioenergi (Spøttrup, Denmark), which receives livestock manure from neighboring farms on a weekly basis, and were stored at −20 °C until used. Prior to BMP tests, all biomass samples were cut to a 4 mm length with a cutting mill (Retsch SM 2000, Germany); The grass, horse manure and chicken manure were previously dried in a conventional oven at 45 °C to reach a total solids (TS) content higher than 90%. The inoculum used for the BMP tests was a mixture of 50% inoculum collected from a manure-based lab-scale digester and 50% inoculum collected from the Solrød biogas plant (Solrød, Denmark). TS, volatile solids (VS), soluble COD, NH_4^+-N concentration and pH of the inoculum were 2.3% wet mass, 1.4% wet mass, 2.8 g O_2/L, 3.7 g NH_4^+-N/L and 8.2 respectively.

2.2. Ammonia pretreatment

Each biomass was subjected to ammonia pretreatment in a 2-L blue-cap bottle sealed with Parafilm tape (Fig.S1) at the following conditions: 50 g TS biomass/L reagent, 4 days duration, 20 °C temperature, and 15% w/w NH_3 in water. During the pretreatment, all bottles were kept in a fume hood. The conditions applied were chosen based on previous knowledge from the statistical optimization of the pretreatment of swine manure fibers and wheat straw for maximizing their CH_4 yield (Lymperatou et al., 2020, 2017). The pretreatment was considered finalized after the removal of NH_3 by means of vacuum evaporation as described in Lymperatou et al. (2020). The final NH_3 concentration of all pretreated biomass was less than 1.0 g/L.

2.3. BMP tests

The effect of the ammonia pretreatment on the ultimate CH_4 yield and hydrolysis rate of the substrates was assessed through BMP tests. Three replicates of each ammonia-treated biomass, three replicates of each raw biomass and three control experiments (only inoculum) were set up in 320 mL vials at a substrate to inoculum ratio of 1:2 on a VS basis (Fig.S2). All vials were flushed with a mixture of 20% CO_2 and 80% N_2 and sealed with rubber stoppers and aluminum crimps for ensuring anaerobic conditions. The vials were incubated under mesophilic conditions (37 °C) and headspace sampling was carried out three times per week for determination of CH_4 production through Gas Chromatography (GC). All gas volumes reported correspond to STP conditions (1 atm, 0 °C). All vials were manually stirred after gas sampling and placed back in the incubator. The ultimate CH_4 yield of each biomass was calculated as the average cumulative CH_4 yield of triplicates during the last measurements when CH_4 production from each test ceased.

2.4. Analytical methods

Determination of TS, VS and ash content was carried out according to APHA standard methods (APHA, 2005). All raw biomass was milled down to 1 mm prior to compositional and elemental analysis and determination of NH_4^+-N concentration. Soluble (non-structural) sugar quantification and NH_4^+-N determination was performed in raw milled biomass (after suspension in Millipore-grade water for 3 h) and in pretreated biomass liquors after a centrifugation at 10000 rpm for 10 min and filtration through 0.45 μm. The NH_4^+-N concentration of the biomass was determined by HACH Lange kits 305 (HACH Lange, Germany). Soluble sugars (oligosaccharides and free sugars) were quantified in both raw biomass and in biomass after ammonia pretreatment, following a mild sulfuric acid hydrolysis procedure as described in

Table 1
Elemental composition of raw biomass samples.

Element (% TS)	Wheat straw	Barley straw	Rye straw	Rape straw	Grass	Chicken manure	Horse manure
C	44.96 ± 0.00	46.84 ± 0.26	48.47 ± 0.69	44.96 ± 1.30	40.87 ± 0.23	42.87 ± 0.23	42.30 ± 0.13
O	43.31 ± 0.53	44.70 ± 0.37	41.74 ± 0.67	42.07 ± 1.29	37.96 ± 0.16	36.11 ± 0.34	33.66 ± 0.30
H	5.15 ± 0.13	5.32 ± 0.13	5.58 ± 0.04	4.91 ± 0.04	4.48 ± 0.01	5.42 ± 0.06	4.68 ± 0.13
N	0.04 ± 0.01	0.14 ± 0.02	0.13 ± 0.06	0.12 ± 0.05	2.16 ± 0.04	4.27 ± 0.06	1.15 ± 0.04

Bjerre et al. (1996). All raw substrates were subjected to compositional analysis for the determination of extractives and volatiles (Sluiter et al., 2008), structural carbohydrates and lignin (Sluiter et al., 2011) and to elemental analysis. Elemental analysis was performed with an EA3000 elemental analyzer (EuroVector, Italy) on all raw biomass using He as carrier gas and sulphanilamide as standard. Sugar detection and quantification (glucose, xylose, arabinose) was carried out by means of high performance liquid chromatography (HPLC, Shimadzu, USA) equipped with a refractive index detector (Lymperatou et al., 2017). The CH_4 content in biogas samples was determined by means of a gas chromatograph (GC82–22, Mikrolab Aarhus, Denmark) equipped with a thermal conductivity detector (Lymperatou et al., 2022).

2.5. Calculations and assumptions

The theoretical CH_4 yield of biomass was calculated based on the elemental composition of each substrate and by using the Buswell formula (Symons and Buswell, 1933):

$$C_nH_aO_b + \left(n-\frac{a}{4}-\frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2}-\frac{a}{8}+\frac{b}{4}\right)CO_2 + \left(\frac{n}{2}+\frac{a}{8}-\frac{b}{4}\right)CH_4 \quad (1)$$

The increase of ultimate CH_4 yield and hydrolysis rate of the biomass after the ammonia pretreatment were calculated as:

$$x_i(\%) = \frac{\left(x_{i,pretreated} - x_{i,raw}\right)}{x_{i,raw}}100 \quad (2)$$

where x_i, is the ultimate CH_4 yield in mL/g TS or the hydrolysis rate in d^{-1} of each i biomass. The hydrolysis rate was calculated by fitting a 1st order kinetic model on the BMP curves of each biomass and by following the assumption that the hydrolysis is the limiting step in the AD of lignocellulosic biomass:

$$B = B_0\left(1-e^{-k_ht}\right) \quad (3)$$

where: B and B_0 is the CH_4 yield after t (d) digestion time and at the end of digestion respectively, and k_h, is the hydrolysis rate in d^{-1}.

The protein content of biomass was calculated based on the elemental N content, subtracted by the NH_4^+-N content, and multiplied by the factor 6.25 (Galí et al., 2009). The content of lipids in biomass was assumed to correspond to the ethanol extractives quantified gravimetrically according to the protocol of NREL (Sluiter et al., 2008).

2.6. PLS regression analyses

PLS regression analyses were performed using the statistical software The Unscrambler® Version 11 (CAMO A/S, Norway). A data matrix was formed with the main compositional characteristics of the seven substrates used as x variables (regressors), and the y variables (one at a time) being: the ultimate CH_4 yield of raw biomass, the ultimate CH_4 yield of ammonia pretreated biomass, the % increase of the ultimate CH_4 yield after ammonia pretreatment, and the % increase of k_h of the biomass after the pretreatment. All variables and responses were centered and weighted. The validation of the models was performed by full cross validation; based on this approach, a model is generated by keeping out of the calibration set one sample (biomass) at a time, which is used for model validation. This is done sequentially until all samples have been used for validation once. The final model is selected based on the highest coefficient of regression R^2 and the lowest root mean square error of the calibration (*RMSEC*).

3. Results and discussion

3.1. Composition of raw biomass and effect of ammonia pretreatment

The substrates used in this study (agricultural straw, animal manure and grass) were chosen based on their high potential for contributing to a significant expansion of the AD industry (Meyer et al., 2018). Agricultural straw refers to the parts of a crop plant remaining after the harvest of the seed that is usually left to decompose in the fields or stored in bales for other uses. Straw is characterized by a high C and a low N content that can be variable, depending, among others, on the extent of degradation prior to collection. On the other hand, livestock manure contains the recalcitrant part of lignocellulose that has not been digested during animal digestion, together with bedding material, impurities from the collection and handling process and urine. As a result, manure is characterized by a significantly higher N content than straw. Grass is also characterized by a high N content due to its increased need for N for the formation of chlorophyll compared to crop plants. The results obtained from the biomass elemental analysis (Table 1) are in agreement to these trends. The C content was higher in agricultural straw ranging from 45 to 49% of TS, while the highest N content corresponded to the chicken manure and grass (2–4% TS). From a C/N ratio point of view, the only biomass that presented a value close to the optimal range for AD

Table 2
Main composition of lignocellulosic biomass used in the study.

Component	Wheat straw	Barley straw	Rye straw	Rape straw	Grass	Chicken manure	Horse manure
Total solids (% wet mass)	92.2 ± 0.6	92.8 ± 0.3	87.6 ± 1.1	85.9 ± 0.3	87.0 ± 0.2*	85.6 ± 0.1*	93.3 ± 0.3*
Total structural carbohydrates (% TS)	63.1 ± 0.3	62.2 ± 3.0	74.6 ± 0.6	51.2 ± 0.7	34.7 ± 0.4	39.7 ± 0.2	49.5 ± 1.1
Cellulose (Glucan) (% TS)	38.5 ± 0.2	37.9 ± 2.6	45.7 ± 0.5	33.0 ± 0.6	20.2 ± 0.3	20.7 ± 0.1	33.1 ± 0.1
Xylan (% TS)	22.0 ± 0.2	21.7 ± 1.4	26.0 ± 0.3	16.8 ± 0.3	11.2 ± 0.2	12.8 ± 0.1	14.2 ± 0.4
Arabinan (% TS)	2.6 ± 0.0	2.7 ± 0.2	2.8 ± 0.0	1.4 ± 0.0	3.0 ± 0.0	6.1 ± 0.2	2.2 ± 0.0
Hemicellulose (% TS)	24.6 ± 0.2	24.3 ± 1.4	28.8 ± 0.3	18.1 ± 0.3	14.5 ± 0.4	18.9 ± 1.0	16.4 ± 0.4
Total extractives and volatiles (% TS)	12.0 ± 0.5	9.3 ± 0.2	16.2 ± 2.6	17.4 ± 0.1	23.9 ± 0.2	31.3 ± 1.9	15.22 ± 0.3
Water extractives (% TS)	9.2 ± 2.3	7.1**	11.1 ± 0.2	14.2 ± 0.9	13.5 ± 1.1	16.1 ± 3.2	9.9 ± 0.8
Lipids (% TS)	2.0 ± 0.6	3.4 ± 0.5	3.5 ± 0.3	4.0 ± 0.3	11.9 ± 0.5	16.9 ± 0.1	5.3**
Proteins (% TS)	0.2 ± 0.1	0.7 ± 0.1	0.8 ± 0.5	0.7 ± 0.4	12.2 ± 0.4	21.6 ± 0.5	7.0 ± 0.4
Lignin (% TS)	17.6 ± 0.5	16.8 ± 0.3	16.5 ± 0.3	15.4 ± 0.4	17.2 ± 0.5	12.3 ± 0.5	22.9 ± 0.5
Ash (% TS)	5.3 ± 0.1	3.3 ± 0.2	4.2 ± 0.3	7.8 ± 0.1	17.3 ± 0.5	13.2 ± 0.2	17.9 ± 0.2

*after drying, **replicates lost during handling.

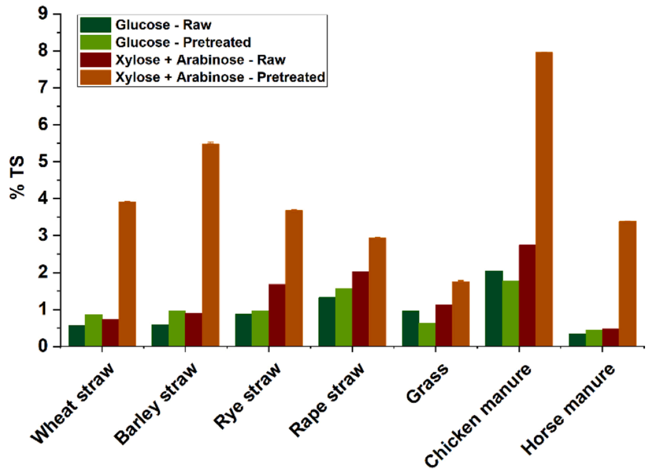

Fig. 1. Soluble sugar content of biomass samples before and after ammonia pretreatment. Vertical bars represent standard deviation.

(25–30:1) (Wang et al., 2012) was horse manure. As expected, the C/N ratio of the agricultural straw was excessively high (>100:1) and the ratios of the chicken manure and grass were very low (≤19:1). These characteristics make chicken manure and grass prone to induce NH_3 inhibition events in AD, while agricultural straw is considered a suitable substrate for balancing the C/N ratio in co-digestion practices (Neshat et al., 2017).

All substrates were further analyzed for their composition in structural carbohydrates, total extractives and volatiles, lipids, proteins, lignin and ash content (Table 2). The compositional analysis showed a large variation in total structural carbohydrates (cellulose and hemicellulose) in different types of straw, with the rye straw presenting the highest content (75%TS) and rape straw the lowest (51%). On the contrary, the N-rich biomass presented significantly lower structural carbohydrates (35–40%) but a higher lipid, protein and total extractives content (Table 2). The horse manure presented middle values in all components except for lignin, which was the highest compared to the rest of substrates. Overall, the total structural carbohydrate content ranged from 35 to 75% TS, the lipids content from 2 to 17% TS, the proteins content from 0.2 to 22.0% TS and the lignin content from 12 to 23% TS. The variation of the biomass composition was considered to be satisfactory to support the regression analyses.

In the sequel, all biomass samples were subjected to ammonia pretreatment and liquid fractions were collected for quantification of the soluble sugars content. As it may be observed in Fig. 1, all biomass samples presented an increase of soluble sugars after the pretreatment, which is more evident for C-5 sugars (xylose and arabinose) that were derived from the hemicellulose fraction. On the other hand, the glucose content was increased in all biomass samples after the pretreatment except in grass and chicken manure, where a slight reduction was observed. Previous applications of ammonia pretreatment at room temperature have shown that most substrates exhibited a significantly reduced hemicellulose fraction (quantified as structural C-5 sugars) while the cellulose content remained invariable (Lymperatou et al., 2020, 2017), or deviated slightly from the initial content (Antonopoulou et al., 2015; Jurado et al., 2013a, 2013b; Mirtsou-Xanthopoulou et al., 2014). The slightly reduced glucose content in the soluble fraction of chicken manure and grass indicated that the pretreatment may have resulted to a partial glucose degradation in these biomass samples. This could be a result of a higher fraction of glucose being degraded than solubilized by ammonia, or due to already soluble glucose being degraded by ammonia. Previous studies on the effects of ammonia on lignocellulosic cell walls have identified a series of nitrogenous compounds formed during pretreatment (Balan et al., 2012; Chundawat et al., 2010). While most of these reactions take place at harsher ammonia pretreatment conditions, e.g. at high temperature, earlier studies have shown that ammonia reacts with free sugars even at low temperature when applied at prolonged durations (Kort, 1970).

3.2. Methane potentials and hydrolysis rates of biomass

The theoretical CH_4 yields of the different substrates ranged from 373 to 461 mL/gTS, with the highest corresponding to rye straw and the lowest to grass. The ultimate CH_4 yields obtained experimentally highlighted the importance of taking the matrix complexity into account, as the substrates reached a biodegradation extent (ultimate CH_4 yield expressed as % of the theoretical) between 47 and 82% (Table 3). For instance, substrates with a similar theoretical CH_4 yield (407–409 mL/g TS) such as wheat straw, rape straw and horse manure, resulted to a much wider range of experimentally obtained yields (192–337 mL/g TS). The pretreatment resulted in an increase of the ultimate CH_4 yield in most substrates but also in a decrease in three of them (Table 3). Interestingly, two of the substrates exhibiting a negative effect on the ultimate CH_4 yield after the ammonia pretreatment, grass and chicken manure, also presented a reduced soluble glucose fraction (section 3.1). Furthermore, these substrates presented a high share of extractives, lipids and proteins in contrast to other substrates. It could be hypothesized that the ammonia pretreatment affected negatively the ultimate CH_4 yield of these substrates due to the destruction of readily available organic matter already present in the extractives fraction (section 3.1), since the presence of common inhibitory by-products has been found to be very limited even in harsher conditions of this pretreatment compared to the ones applied in this study (Antonopoulou et al., 2015). This hypothesis is supported by the relatively high biodegradability of the respective raw substrates prior to pretreatment (74% and 73% for grass and chicken manure respectively). Overall, the increase of the ultimate CH_4 yield of the substrates that responded positively to the pretreatment ranged from 4 to 17%.

Ammonia pretreatment at room temperature has been applied in the

Table 3
Methane yields and hydrolysis rates of raw and ammonia-treated biomass.

	Wheat straw	Barley straw	Rye straw	Rape straw	Grass	Chicken manure	Horse manure
Theoretical methane yield (mL/g TS)*	409 ± 5	428 ± 10	461 ± 14	408 ± 25	373 ± 4	424 ± 7	407 ± 8
Ultimate methane yield raw (mL CH_4/ g TS)*	337 ± 15	340 ± 15	374 ± 15	280 ± 17	277 ± 5	309 ± 8	192 ± 7
Ultimate methane yield raw (% theoretical)	82.4	79.4	81.1	68.6	74.3	72.9	47.2
Ultimate methane yield pretreated (mL CH_4/ g TS)*	393 ± 12	353 ± 15	352 ± 15	326 ± 21	232 ± 6	295 ± 9	210 ± 7
Ultimate methane yield pretreated (% theoretical)	96.1	82.5	76.4	79.9	62.2	69.6	51.6
% increase Ultimate methane yield	+16.7	+4.0	−5.7	+16.3	−16.5	−4.7	+9.1
k_h raw (d^{-1}) (R^2)	0.0987 (0.99)	0.0995 (0.99)	0.1080 (0.98)	0.0919 (0.99)	0.1333 (0.98)	0.1786 (0.99)	0.1045 (0.99)
k_h pretreated (d^{-1}) (R^2)	0.1198 (0.99)	0.1053 (0.98)	0.1488 (0.99)	0.1244 (0.99)	0.2355 (0.99)	0.2262 (0.99)	0.1776 (0.98)
% increase k_h	21.4	5.8	37.8	35.4	76.7	26.7	70.0

*Values reported correspond to average ± standard deviation of triplicates.

past in various biomass types with a variable efficiency. Jurado et al. (2013b) reported an increase of the CH_4 yield of 30–80% after ammonia application on raw swine manure fibers and 178% on digested manure fibers. Antonopoulou et al. (2015), tested the effect of ammonia pretreatment on sunflower straw, poplar and grass and reported an increase of 38%, 149% and 26% of CH_4 yield respectively. However, these results correspond to ammonia application at a much higher concentration (32% w/w) than the one applied in this study (15% w/w). Later experiments have shown that 18% and 7% NH_3 w/w corresponded to the optimal concentrations for maximizing the CH_4 yield of wheat straw and swine manure fibers respectively (Lymperatou et al., 2020, 2017). It is expected that the optimal pretreatment conditions vary depending on the biomass in question. However, in an industrial set up it is more likely to aim at conditions that will ensure pretreatment efficiency on most substrates. For this reason, middle range conditions of ammonia pretreatment were chosen in this study.

As discussed earlier, the limitation of using lignocellulosic biomass in AD processes may result not only due to the limited biodegradation extent, but also due to the slow hydrolysis rate. The ammonia pretreatment resulted in an increase of the hydrolysis rate of all substrates tested in this study, including the ones that did not present an increased ultimate CH_4 yield (Table 3). As a matter of fact, the highest increase of the hydrolysis rate (77%) was observed in grass, which had a −16% ultimate CH_4 yield after the pretreatment compared to that of the raw biomass. Thus, depending on the hydraulic retention time (HRT) of the AD process applied, the ammonia pretreatment can be efficient also on substrates that do not exhibit an improved ultimate CH_4 yield, (the CH_4 production will be higher when the AD duration is shorter).

3.3. PLS regression models

After the termination of the BMP experiments and the biomass compositional analyses, data were collected for modeling the ultimate CH_4 yield of raw and pretreated biomass, as well as the efficiency of the ammonia pretreatment (expressed as % increase of the ultimate CH_4 yield and as % increase of the hydrolysis rate). Initially, all measured compositional characteristics (including cellulose, hemicellulose, xylan, arabinan, total structural carbohydrates, lignin, ash, total extractives, water extractives, lipids, proteins, hemicellulose/lignin ratio, and xylan/arabinan ratio) were used as regressors aiming at identifying the most important factors showing a strong correlation to the response. In continuation, models were constructed by using as regressors the most strongly correlated x-variables to the respective response. Previous attempts included modeling of the biogas or CH_4 yield of biomass by using only one regressor (monocausal regression models), usually the lignin content, since its role in impeding biodegradation is well known and documented (Dandikas et al., 2014; Triolo et al., 2011). While the estimation of the response based on only one biomass compositional characteristic could be faster or easier, in this study, the focus was on identifying all compositional characteristics that play an important role for maximizing the prediction accuracy of the constructed models. This approach may also permit a better understanding of the mechanism of a pretreatment when evaluating as a response the pretreatment efficiency.

3.3.1. Prediction of ultimate CH_4 yield of raw and pretreated biomass based on the initial composition

The regression analyses showed that only a few biomass characteristics affected significantly the ultimate CH_4 yield for both raw and pretreated biomass. Two factors were sufficient for explaining the variation of 95% and 94% of the x variables and 89% and 90% of the response for modeling the ultimate CH_4 yield of raw and pretreated biomass respectively. The strongest correlations to the ultimate CH_4 yield of raw biomass (model 1) corresponded to hemicellulose ($r = +0.42$), lignin ($r = -0.43$) and ash ($r = -0.34$), (Fig. 2a). Similar correlations were observed for model 2 constructed for the prediction of the CH_4 yield after ammonia pretreatment, with the addition of a negative correlation to the total extractives content of the raw biomass (Fig. 2b).

It is well known that the conversion of lignin to CH_4 is very limited under anaerobic conditions, presenting also a physical barrier to biodegradation as it impedes microbial access to structural carbohydrates. Thus, a negative correlation to the CH_4 yield was expected, as also reported in multiple studies (Dandikas et al., 2014; Monlau et al., 2012; Triolo et al., 2011; Tsapekos et al., 2018). Similarly, a positive correlation of CH_4 to hemicellulose was anticipated as, due to its amorphous structure, it is more easily hydrolyzed than cellulose. On the other hand, cellulose fibers are composed by glucose units in both amorphous and highly crystalline zones (Carrère et al., 2016). Cellulose has been found to be both positively and negatively correlated to the ultimate CH_4 yield of various biomass types (Raposo et al., 2020), possibly due to the variable degree of crystallinity as also reported by (Monlau et al., 2012). However, in agreement also to the results of the present study, the cellulose content is a weak regressor for predicting the ultimate CH_4 yield of lignocellulosic biomass and, as a result, it is usually excluded from regression models (Dahunsi, 2019; Dandikas et al., 2014; Tsapekos et al., 2018). Finally, the strong correlation of the ultimate CH_4 yield to the ash content is an interesting finding. Some researchers have

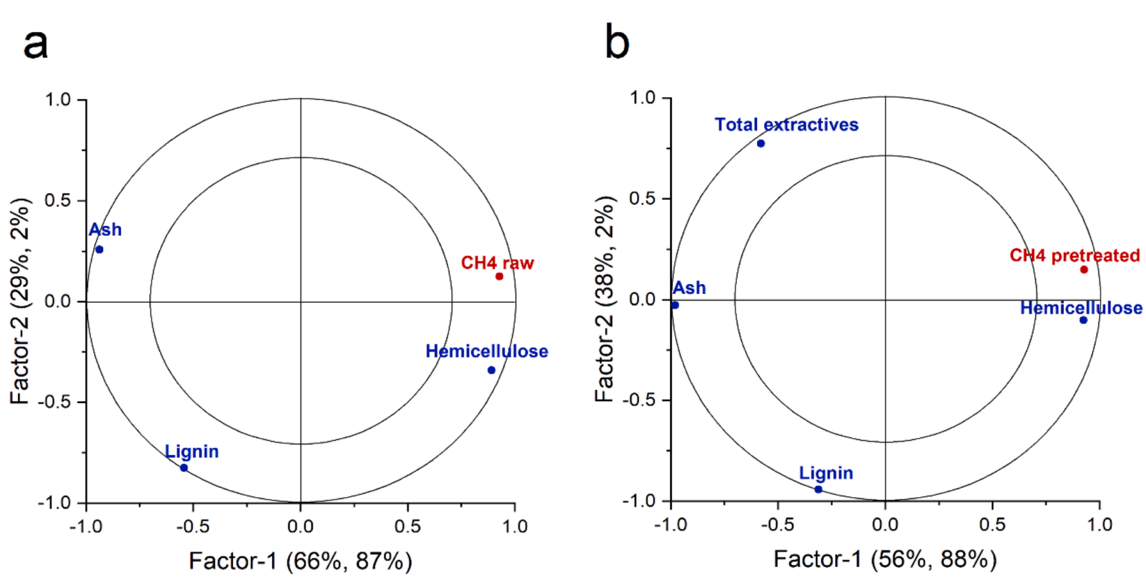

Fig. 2. Correlation loadings of PLS models (a) 1 (eq.4) and (b) 2 (eq.5) for the prediction of the ultimate CH_4 yield of raw and pretreated biomass respectively.

excluded the ash content as a regressor for modeling the CH_4 yield of biomass and chose to express the response in mL per g VS instead of g TS. However, a preliminary attempt to model the CH_4 yield per g VS in this study resulted to models of lower quality ($R^2 = 0.70$, $R^2 = 0.85$ for CH_4 yield of raw and pretreated biomass respectively), indicating the importance of including the inert material as a factor in the regression analysis and expressing the yield per g TS.

Model 2 presented some differentiation regarding the degree of correlation of the regressors to the response in comparison to model 1. Both regressors of hemicellulose and lignin became weaker for describing the CH_4 yield of the pretreated biomass ($r = +0.34$, $r = -0.30$ for hemicellulose and lignin respectively). This indicates, that while these were still important factors for CH_4 yield prediction, their influence on the response after ammonia pretreatment was weaker in contrast to the ash content that became more important ($r = -0.45$). The most evident difference between the two models though lies on the negative correlation of the CH_4 yield of pretreated biomass to the total extractives and volatiles content of the raw biomass ($r = -0.15$). Extractives, depending on the type of biomass, may consist of fats, waxes, soluble proteins, soluble sugars, starch, resins, salts and other volatile or non-volatile soluble organic material along with soluble ash (Karimi and Taherzadeh, 2016). Their correlation to the ultimate CH_4 yield of raw biomass can be considered limited, due to their low share of total organics converted to CH_4 as related to the total biodegradable material of the biomass. This is also demonstrated in low correlations found between the CH_4 yield of substrates and their soluble COD, which serves as an indirect measurement of soluble organics, as reported previously (Lymperatou et al., 2017; Tsapekos et al., 2015),. The negative correlation between the extractives content of raw biomass and the ultimate CH_4 yield of ammonia-treated biomass observed in this study may be explained by the destruction of soluble organics by the chemical reagent, confirming also our previous hypothesis (section 3.2).

Overall, the fit of the data and the calibration errors were satisfactory for both model 1 ($R^2 = 0.89$, RMSEC = 18 mL/g TS) and model 2 ($R^2 = 0.90$, RMSEC = 20 mL/g TS). Fig. 3a and 3b show the fit of the models to the data, where the predicted responses are plotted versus the actual values of the substrates in this study as well as versus data retrieved from literature (Monlau et al., 2012) when this was possible (Table S1). The availability of literature data for validating model 2 was limited, as in previous ammonia applications on biomass, more often than not, the total extractives content has not been determined or reported, and the conditions of the pretreatment differed significantly. As it may be observed in Fig. 3a, the model presented a fair fit to the literature data with a few exceptions. However, it is important to point out that not all compositional characteristics retrieved from literature were within the calibration range. For instance, maize cobs were characterized by a 34.6% TS hemicellulose and Jerusalem artichoke leaves a 57.9% TS ash content, when the ranges of these regressors were 15–29 % TS and 3–18% TS respectively in the calibration data. The final models for the calculation of the ultimate CH_4 yield of raw and pretreated biomass respectively are:

$$CH_4yield_{raw} = 371.0233 - 8.1289 \bullet Lig - 3.2705 \bullet Ash + 4.8242 \bullet hemi \quad (4)$$

$$CH_4yield_{pretreated} = 394.5840 - 6.3368 \bullet Lig - 4.8595 \bullet Ash - 1.3054 \bullet tot.extr. + 4.4641 \bullet hemi \quad (5)$$

where, CH_4yield_i is the ultimate CH_4 yield of the raw or ammonia pretreated biomass, *Lig*, *Ash*, *hemi* and *tot.extr.* , are the lignin, ash, hemicellulose (sum of xylan and arabinan) and total extractives and volatiles contents of the raw biomass in % TS, respectively.

3.3.2. Prediction of efficiency of pretreatment based on raw biomass composition

Two responses were considered for modeling the efficiency of the pretreatment based on the composition of the raw biomass; the increase

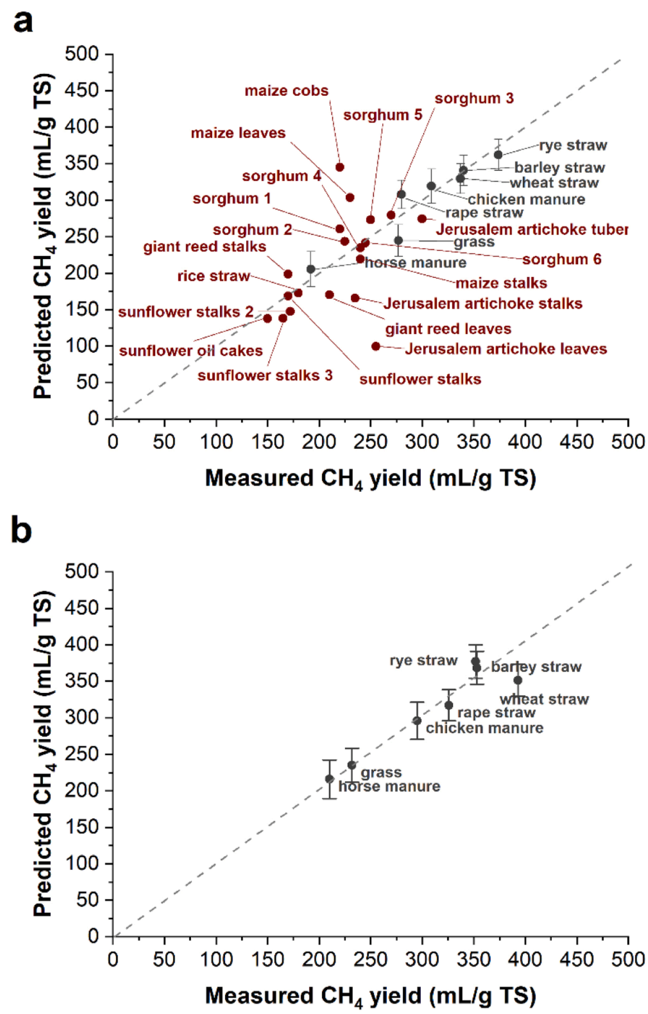

Fig. 3. Experimental versus predicted values of ultimate CH_4 yield of lignocellulosic biomass (a) without pretreatment (model 1, eq.4), and (b) after ammonia pretreatment (by model 2, eq.5). Grey dots correspond to the data used for calibration and dark red dots to data extracted from literature (Table S1). Vertical bars correspond to standard error of predicted values. Dashed line represents a perfect fit of the models to the experimental data (x = y).

of the ultimate CH_4 yield (model 3), and the increase of the hydrolysis rate, k_h, after the pretreatment (model 4), in order to express the effect of the pretreatment on the biodegradation extent and rate respectively. The models generated by including the biomass characteristics with the strongest correlations as regressors explained 98% and 94% of the variation of the x variables and 97% and 94% of the variation of the response when modeling the increase of the ultimate CH_4 yield and hydrolysis rate, respectively.

The increase of the ultimate CH_4 yield due to the ammonia pretreatment was found to be strongly and negatively correlated with the lipids ($r = -0.88$) and the proteins content ($r = -0.61$), (Fig. 4a). Following the observations discussed in section 3.3.1, this result was of no surprise as lipids and proteins are associated to the total extractives content of biomass, which were found to affect negatively the ultimate CH_4 yield of pretreated biomass. Lipids are composed by long chain fatty acids (LCFAs) and glycerol, and are generally characterized by a high CH_4 potential. Nevertheless, the accessibility of LCFAs by microbes during AD may be limited due to their low solubility and tendency to float on the surface (Carrère et al., 2016). Application of alkaline reagents results to saponification, improving thus the solubility of fatty substances. As a matter of fact, saponification has been considered as a

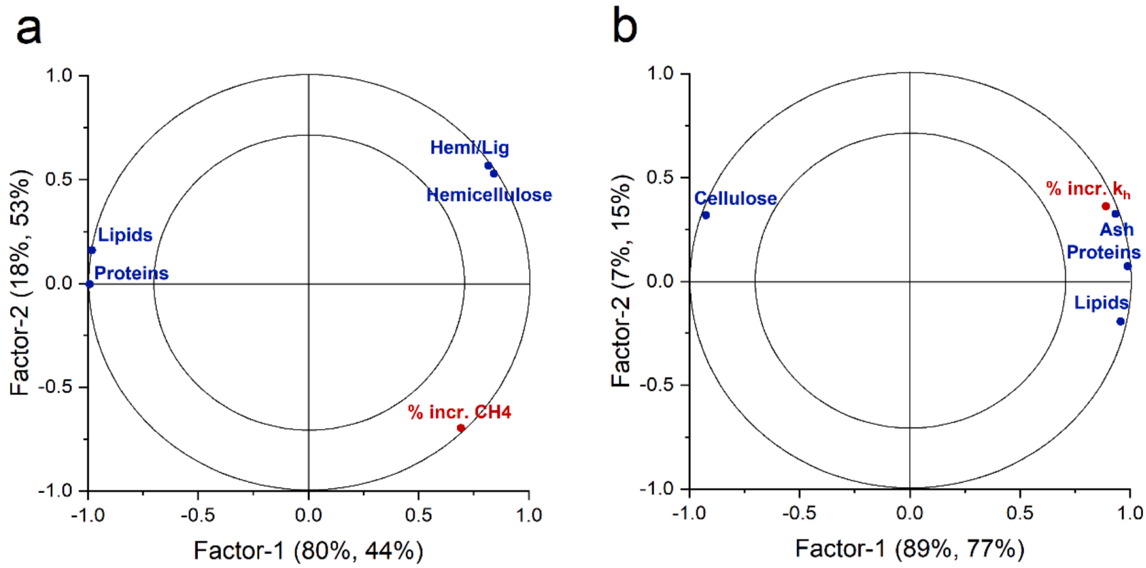

Fig. 4. Correlation loadings of PLS regression models for the prediction of (a) the increase of the ultimate CH_4 yield after ammonia pretreatment (eq.6), and (b) the increase of the hydrolysis rate after ammonia pretreatment (eq.7).

promising pretreatment for improving the anaerobic biodegradability of high-fat residues (e.g. slaughterhouse waste) in previous studies (Harris et al., 2017; Mouneimne et al., 2003). Moreover, an improved reduction of lipids during AD of ammonia-treated manure fibers has been reported recently in continuous AD (Lymperatou et al., 2021). However, the strong negative correlation found between the biodegradation extent after the ammonia pretreatment and the lipid content indicates that the pretreatment may be harsh on biomass with a high lipids share, resulting to a loss of fatty material easily convertible to CH_4. Both grass and chicken manure shared this characteristic (Table 2) and presented a reduction of their ultimate CH_4 yield after pretreatment (Table 3). Interestingly, the biodegradation extent was also negatively correlated to the hemicellulose content ($r = -0.47$) and to the hemicellulose/lignin ratio of the raw biomass ($r = -0.53$). Ammonia is known to attack the ester and ether bonds of lignin-carbohydrate complexes, which is assumed to facilitate microbial and enzymatic access to structural sugars (Kim et al., 2016). Thus, a low ratio of hemicellulose to lignin limits the efficiency and importance of the pretreatment, as the biomass is probably more easily hydrolyzed. The same assumption may explain the negative correlation to the hemicellulose fraction, i.e. a high hemicellulose content may not require an ammonia pretreatment as this may result to destruction of easily hydrolyzed sugars.

The increase of the hydrolysis rate presented correlations with some similar compositional characteristics as the increase of the CH_4 yield, however, in an opposite way. The model suggests that raw biomass with a high lipid ($r = +0.0865$) and protein ($r = +0.1032$) content result to a higher increase of its hydrolysis rate after pretreatment. More importantly though, strong positive correlations to the response were found with the ash ($r = +0.79$) and cellulose content ($r = +0.32$) of raw biomass. Regarding the influence of the pretreatment on the cellulose content of the raw biomass, it has been reported that ammonia can affect significantly the crystallinity of cellulose due to the formation of cellulose-ammonia complexes, improving this way microbial access for enzymatic attack, as explained by Bellesia et al. (2011). However, this effect has been confirmed in ammonia applications that involve high temperatures. Thus, the effect of ammonia application at low temperatures on the cellulose crystallinity of biomass needs to be further investigated. Similarly, the positive correlation of the increase of the hydrolysis rate to the ash content is an interesting finding that has not been reported previously and deserves further investigation.

The fit of the data and the calibration error of models 3 and 4 were $R^2 = 0.97$, RMSEC = 2% and $R^2 = 0.92$, RMSEC = 7% respectively. The models were capable of predicting the respective responses satisfactorily for most substrates as it may be observed also in Fig. 5. However, the chicken manure was detected as an outlier in both models for the prediction of the efficiency of the pretreatment. The AD of chicken manure is a topic that has attracted a lot of research due to its high N content and tendency to cause NH_3 inhibition (Bayrakdar et al., 2017). Our findings (negative ultimate CH_4 yield increase and limited hydrolysis rate increase) imply that this biomass would not benefit from an ammonia pretreatment process, however the AD may be improved if the biomass undergoes only the NH_3 recovery step that would be associated to ammonia pretreatment application in an industrial setup (Lymperatou et al., 2021).

The final expressions for modeling the increase of the CH_4 yield and the increase of the hydrolysis rate after the ammonia pretreatment, are respectively:

$$CH_4 yield\ increase = 69.6236 - 3.2328{*}Lip - 1.6263{*}Pro - 1.0995{*}hemi - 16.5006{*}hemi/lig \tag{6}$$

$$k_h increase = -36.2244 + 1.0376{*}Cell + 3.2870{*}Ash + 0.6725{*}Lip + 2.0579{*}Pro \tag{7}$$

where *CH_4yield increase*, is the % increase of the ultimate CH_4 yield of the biomass after the ammonia pretreatment as compared to the ultimate CH_4 yield of the raw biomass, *$k_h$increase* is the % increase of the hydrolysis rate of the biomass after the ammonia pretreatment as compared to the hydrolysis rate of the raw biomass, *Lip*, *Pro*, *hemi*, *Cell*, *Ash* and *hemi/lig* is the lipid, protein, hemicellulose, cellulose, ash content and hemicellulose/lignin ratio of the raw biomass before pretreatment.

4. Conclusions

This study showed that the compositional characteristics of raw lignocellulosic biomass that are decisive to an improved biodegradation efficiency after ammonia pretreatment, differ from those that result to an increased hydrolysis rate. Substrates that are more recalcitrant to biodegradation with a relatively low content in lipids ($r = -0.88$), proteins ($r = -0.61$) and hemicellulose/lignin ($r = -0.53$), are the best candidates for ammonia pretreatment when aiming at improving their ultimate CH_4 yield. On the contrary, an increased hydrolysis rate after

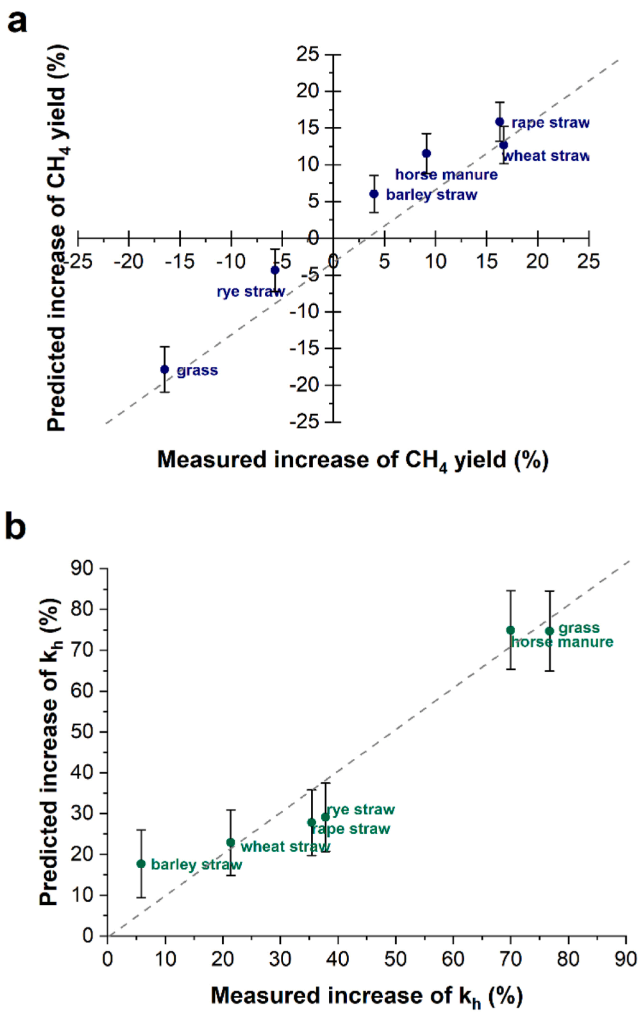

Fig. 5. Experimental versus predicted values of increase of (a) the ultimate CH_4 yield (model 3, eq. (6)) and (b) hydrolysis rate (model 4, eq.7) of raw biomass after ammonia pretreatment. Vertical bars correspond to standard error of predicted values. Dashed line represents a perfect fit of the models to the experimental data (x = y).

ammonia pretreatment can be expected from substrates with a high ash ($r = +0.79$) and cellulose ($r = +0.32$), content. Alkaline reagents are considered to be appropriate for lignocellulosic biomass pretreatment as they are known to be selective on lignin-carbohydrate complex cleavage and often a significant lignin removal is reported. Interestingly, in this study, no strong direct correlation was found between the efficiency of the ammonia pretreatment and the lignin content of lignocellulosic biomass. This is more likely due to the lack of heat application, resulting to milder effects of the pretreatment. Finally, the generated models ($R^2 = 0.92–0.97$) may be used for identifying trends of efficiency of the ammonia pretreatment on different biomass types based on their main compositional characteristics, thus eliminating the need of actually applying the pretreatment and the subsequent BMP test in order to estimate the efficiency of this pretreatment. The approach followed for the development of models for the prediction of ammonia pretreatment efficiency on improving the AD of lignocellulosic biomass may be used as a methodology for evaluating other promising pretreatments for lignocellulosic biomass.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This research was funded by EUDP Energistyrelsen, grant number 64018-0070, in the frame of the DEMONIAGAS project.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2022.10.040.

References

Antonopoulou, G., Gavala, H.N., Skiadas, I.V., Lyberatos, G., 2015. The effect of aqueous ammonia soaking pretreatment on methane generation using different lignocellulosic biomasses. Waste Biomass Valorization 6, 281–291. https://doi.org/10.1007/s12649-015-9352-9.

Apha, 2005. Standard Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association/American Water Works Association/Water Pollution Control Federation, Washington DC.

Balan, V., da Costa Sousa, L., Chundawat, S.P.S., Humpula, J., Dale, B.E., 2012. Overview to Ammonia Pretreatments for Lignocellulosic Biorefineries. Dyn. Biochem. Process Biotechnol. Mol. Biol. 6, 1–11.

Bayrakdar, A., Sürmeli, R.Ö., Çalli, B., 2017. Dry anaerobic digestion of chicken manure coupled with membrane separation of ammonia. Bioresour. Technol. 244, 816–823. https://doi.org/10.1016/j.biortech.2017.08.047.

Bellesia, G., Chundawat, S.P.S., Langan, P., Dale, B.E., Gnanakaran, S., 2011. Probing the Early Events Associated with Liquid Ammonia Pretreatment of Native Crystalline Cellulose. J. Phys. Chem. B 115, 9782–9788. https://doi.org/10.1021/jp2048844.

Bjerre, A. B., Plöger, A., Simonsen, T., Woidemann, A., & Schmidt, A.S., 1996. Quantification of solubilized hemicellulose from pretreated lignocellulose by acid hydrolysis and high-performance liquid chromatography. Forskningscenter Risoe. Risoe-R; No. 855(EN), Roskilde, Denmark.

Carrère, H., Antonopoulou, G., Affes, R., Passos, F., Battimelli, A., Lyberatos, G., Ferrer, I., 2016. Review of feedstock pretreatment strategies for improved anaerobic digestion: From lab-scale research to full-scale application. Bioresour. Technol. 199, 386–397. https://doi.org/10.1016/j.biortech.2015.09.007.

Chundawat, S.P.S., Vismeh, R., Sharma, L.N., Humpula, J.F., da Costa Sousa, L., Chambliss, C.K., Jones, A.D., Balan, V., Dale, B.E., 2010. Multifaceted characterization of cell wall decomposition products formed during ammonia fiber expansion (AFEX) and dilute acid based pretreatments. Bioresour. Technol. 101, 8429–8438. https://doi.org/10.1016/j.biortech.2010.06.027.

Dahunsi, S.O., 2019. Mechanical pretreatment of lignocelluloses for enhanced biogas production: Methane yield prediction from biomass structural components. Bioresour. Technol. 280, 18–26. https://doi.org/10.1016/j.biortech.2019.02.006.

Dandikas, V., Heuwinkel, H., Lichti, F., Drewes, J.E., Koch, K., 2015. Correlation between Biogas Yield and Chemical Composition of Grassland Plant Species. Energy Fuels 29, 7221–7229. https://doi.org/10.1021/acs.energyfuels.5b01257.

Dandikas, V., Heuwinkel, H., Lichti, F., Drewes, J.E., Koch, K., 2014. Correlation between biogas yield and chemical composition of energy crops. Bioresour. Technol. 174, 316–320. https://doi.org/10.1016/j.biortech.2014.10.019.

Galí, A., Benabdallah, T., Astals, S., Mata-Alvarez, J., 2009. Modified version of ADM1 model for agro-waste application. Bioresour. Technol. 100, 2783–2790. https://doi.org/10.1016/j.biortech.2008.12.052.

Gunaseelan, V.N., 2007. Regression models of ultimate methane yields of fruits and vegetable solid wastes, sorghum and napiergrass on chemical composition. Bioresour. Technol. 98, 1270–1277. https://doi.org/10.1016/j.biortech.2006.05.014.

Harris, P.W., Schmidt, T., McCabe, B.K., 2017. Evaluation of chemical, thermobaric and thermochemical pre-treatment on anaerobic digestion of high-fat cattle slaughterhouse waste. Bioresour. Technol. 244, 605–610. https://doi.org/10.1016/j.biortech.2017.07.179.

Jurado, E., Gavala, H.N., Skiadas, I.V., 2013a. Enhancement of methane yield from wheat straw, miscanthus and willow using aqueous ammonia soaking. Environ. Technol. 34, 2069–2075. https://doi.org/10.1080/09593330.2013.826701.

Jurado, E., Skiadas, I.V., Gavala, H.N., 2013b. Enhanced methane productivity from manure fibers by aqueous ammonia soaking pretreatment. Appl. Energy 109, 104–111. https://doi.org/10.1016/j.apenergy.2013.03.075.

Karimi, K., Taherzadeh, M.J., 2016. A critical review of analytical methods in pretreatment of lignocelluloses: Composition, imaging, and crystallinity. Bioresour. Technol. 200, 1008–1018. https://doi.org/10.1016/j.biortech.2015.11.022.

Kim, J.S., Lee, Y.Y., Kim, T.H., 2016. A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass. Bioresour. Technol. 199, 42–48. https://doi.org/10.1016/j.biortech.2015.08.085.

Kort, M.J., 1970. Reactions of Free Sugars with Aqueous Ammonia. In: Tipson, R.S., Horton, D. (Eds.), Advances in Carbohydrate Chemistry and Biochemistry. Academic Press Inc, New York, pp. 311–349.
Lymperatou, A., Engelsen, T.K., Skiadas, I.V., Gavala, H.N., 2022. Different pretreatments of beach-cast seaweed for biogas production. J. Clean. Prod. 362, 132277 https://doi.org/10.1016/j.jclepro.2022.132277.
Lymperatou, A., Gavala, H.N., Skiadas, I.V., 2020. Aqueous Ammonia Soaking of Wheat Straw at Ambient Temperature for Enhancing the Methane Yield: Process Optimization by Response Surface Methodology. Waste Biomass Valorization 11, 4821–4835. https://doi.org/10.1007/s12649-019-00806-7.
Lymperatou, A., Gavala, H.N., Skiadas, I.V., 2017. Optimization of Aqueous Ammonia Soaking of manure fibers by Response Surface Methodology for unlocking the methane potential of swine manure. Bioresour. Technol. 244, 509–516. https://doi.org/10.1016/j.biortech.2017.07.147.
Lymperatou, A., Rasmussen, N.B., Gavala, H.N., Skiadas, I.V., 2021. Improving the Anaerobic Digestion of Swine Manure through an Optimized Ammonia Treatment: Process Performance. Digestate and Techno-Economic Aspects. Energies 14, 787. https://doi.org/10.3390/en14030787.
Meyer, A.K.P., Ehimen, E.A., Holm-Nielsen, J.B., 2018. Future European biogas: Animal manure, straw and grass potentials for a sustainable European biogas production. Biomass Bioenergy 111, 154–164. https://doi.org/10.1016/j.biombioe.2017.05.013.
Mirtsou-Xanthopoulou, C., Jurado, E., Skiadas, I.V., Gavala, H.N., 2014. Effect of aqueous ammonia soaking on the methane yield and composition of digested manure fibers applying different ammonia concentrations and treatment durations. Energies 7, 4157–4168. https://doi.org/10.3390/en7074157.
Monlau, F., Sambusiti, C., Barakat, A., Guo, X.M., Latrille, E., Trably, E., Steyer, J.-P., Carrere, H., 2012. Predictive models of biohydrogen and biomethane production based on the compositional and structural features of lignocellulosic materials. Environ. Sci. Technol. 46, 12217–12225. https://doi.org/10.1021/es303132t.
Mouneimne, A.H., Carrere, H., Bernet, N., Delgenes, J.P., 2003. Effect of saponification on the anaerobic digestion of solid fatty residues. Bioresour. Technol. 90, 89–94. https://doi.org/10.1016/S0960-8524(03)00091-9.
Neshat, S.A., Mohammadi, M., Najafpour, G.D., Lahijani, P., 2017. Anaerobic co-digestion of animal manures and lignocellulosic residues as a potent approach for sustainable biogas production. Renew. Sustain. Energy Rev. 79, 308–322. https://doi.org/10.1016/j.rser.2017.05.137.
Olatunji, K.O., Ahmed, N.A., Ogunkunle, O., 2021. Optimization of biogas yield from lignocellulosic materials with different pretreatment methods: a review. Biotechnol. Biofuels 14, 159. https://doi.org/10.1186/s13068-021-02012-x.
Raposo, F., Borja, R., Ibelli-Bianco, C., 2020. Predictive regression models for biochemical methane potential tests of biomass samples: Pitfalls and challenges of laboratory measurements. Renew. Sustain. Energy Rev. 127, 109890 https://doi.org/10.1016/j.rser.2020.109890.
Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Crocker, D., 2011. Determination of Structural Carbohydrates and Lignin in Biomass NREL/TP-510-42618.
Sluiter, A., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., 2008. Determination of Extractives in Biomass NREL/TP-510-42619. Colorado, USA.
Symons, G.E., Buswell, A.M., 1933. The methane fermentation of carbohydrates. J. Am. Chem. Soc. 55, 2028–2036. https://doi.org/10.1021/ja01332a039.
Triolo, J.M., Sommer, S.G., Møller, H.B., Weisbjerg, M.R., Jiang, X.Y., 2011. A new algorithm to characterize biodegradability of biomass during anaerobic digestion: Influence of lignin concentration on methane production potential. Bioresour. Technol. 102, 9395–9402. https://doi.org/10.1016/j.biortech.2011.07.026.
Tsapekos, P., Kougias, P.G., Angelidaki, I., 2018. Mechanical pretreatment for increased biogas production from lignocellulosic biomass; predicting the methane yield from structural plant components. Waste Manag. 78, 903–910. https://doi.org/10.1016/j.wasman.2018.07.017.
Tsapekos, P., Kougias, P.G., Angelidaki, I., 2015. Biogas production from ensiled meadow grass; effect of mechanical pretreatments and rapid determination of substrate biodegradability via physicochemical methods. Bioresour. Technol. 182, 329–335. https://doi.org/10.1016/j.biortech.2015.02.025.
Wang, X., Yang, G., Feng, Y., Ren, G., Han, X., 2012. Optimizing feeding composition and carbon–nitrogen ratios for improved methane yield during anaerobic co-digestion of dairy, chicken manure and wheat straw. Bioresour. Technol. 120, 78–83. https://doi.org/10.1016/j.biortech.2012.06.058.