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Corn stover for biogas production: Effect of steam explosion pretreatment on the gas yields and on the biodegradation kinetics of the primary structural compounds

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ABSTRACT

This study evaluated the effect of steam explosion on the chemical composition and biomethane potential of corn stover using temperatures ranging between 140 and 220 °C and pretreatment times ranging between 2 and 15 min. Biodegradation kinetics during the anaerobic digestion of untreated and corn stover, pretreated at two different intensities, 140 °C for 5 min and 180 °C for 5 min, were studied in tandem. Results showed that pretreatment at 160 °C for 2 min improved the methane yield by 22%. Harsher pretreatment conditions led to lower hemicellulose contents and methane yields, as well as higher lignin contents, which may be due to the formation of pseudo-lignin. The biodegradation kinetics trial demonstrated that steam explosion enhances the degradation of structural carbohydrates and acid insoluble lignin.

1. Introduction

Plant-based resources, such as agricultural residues, can help reduce the use of fossil-based raw materials. Lignocellulosic biomass is the most abundant source of unutilized biomass and its use avoids the competition between food, feed and energy production (Lin and Tanaka, 2006). The use of this type of alternative biomass for the production of gaseous and liquid biofuels has met with growing interest in the last decade (Ho et al., 2014).

Agricultural residues can provide large amounts of biomass in a sustainable manner for biogas generation. However, the composition and structure of the lignocellulosic complex limits and often restricts biodegradability during anaerobic digestion (AD), reducing methane production and thus the efficiency of the whole process (Hendriks and Zeeman, 2009; Risberg et al., 2013). In order to weaken and break the links in the lignocellulosic complex and enhance microorganism accessibility to the carbohydrate polymers, a pretreatment step is necessary (Alvira et al., 2010). Steam explosion is currently one of the most attractive and investigated pretreatment methods for both biogas and ethanol production from lignocellulosic biomass. It involves heating up the biomass to a maximum of 240 °C under high pressure (up to 34 bar) for a few minutes. Then, the pressure is released abruptly, causing an explosive decompression of the lignocellulosic biomass. Steam explosion has been proven to be effective for both biogas and ethanol production using different input materials such as wood (Horn et al., 2011a), grasses (Lizasoain et al., 2016), agricultural residues (Bauer et al., 2009), bioethanol by-products (De Paoli et al., 2011) and municipal waste (Li et al., 2007).

The effectiveness of pretreatment on lignocellulosic biomass is generally assessed by measuring the methane yields during its subsequent anaerobic digestion. While it is true that this approach provides important information about the effect of the pretreatment on the final biogas yields, no actual knowledge of the improved biomass degradability can be gained. To learn more about how pretreatment methods improve AD, it is necessary to better understand the biodegradation kinetics of lignocellulosic biomass during the digestion process. Techniques that evaluate the degradation of biomass, such as the rumen derived anaerobic digestion process (RUDAD) and the rumen

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simulation technique (RUSITEC) have been applied in the field of animal husbandry (Bayané and Guiot, 2011; Machmüller et al., 1998). However, techniques to measure the biodegradation kinetics of biomass during AD are very scarce and only few approaches have been documented, such as the studies performed by Stopp et al. (2009) and Theuretzbacher et al. (2015). The latter is considered a suitable model to investigate the degradation of lignocellulosic biomass during AD and will serve as a basis for this study.

The literature on steam exploded corn stover for biogas purposes is very scarce despite corn stover being a widespread source of biomass with an enormous potential for biogas production and steam explosion a technology that is rapidly expanding. Li et al. (2015) studied the effects of steam explosion pretreatment, potassium hydroxide and the sequent pretreatment of potassium hydroxide and steam explosion on the biomethane potential of corn stover. While steam explosion increased the biomethane potential yields by 55% in comparison to the untreated sample, an increase of 80% was obtained after the sequent pretreatment of potassium hydroxide and steam explosion. Siddhu et al. (2016) evaluated the effect of thermal potassium hydroxide, steam explosion and the co-pretreatment of thermal potassium hydroxide and steam explosion on methane yields. They reported maximum improvements in the methane yields in comparison to the untreated biomass of 56%, 40% and 88%, respectively. In addition, Ji et al. (2016) studied the effect of pretreatment with calcium hydroxide, steam explosion and the co-pretreatment of calcium hydroxide and steam explosion in corn stover. The maximum biomethane yields for each type of pretreatment increased 53%, 34% and 62%, respectively over the yields obtained for untreated corn stover. Despite the positive effect of such co-pretreatments on laboratory-scale trials, the utilization of catalysts in full-scale plants has numerous drawbacks as they are generally expensive, corrode the machinery, modify the pH of the reactor content and have negative environmental repercussions. Therefore, optimizing pretreatment systems that only require the use of heat and water, as steam explosion does, is of great interest for the development of sustainable biofuels.

Despite many authors having studied the effects of different pretreatments on the chemical characteristics of biomass or on biomethane yields, there is still a lack of knowledge about the degradation process of biomass during AD. Thus, the aim of this study was to determine the effect of steam explosion on the biomass characterization and methane yields of corn stover without the addition of catalysts and to determine the biodegradation kinetics of the main structural compounds of untreated and pretreated corn stover during the AD process.

2. Material and methods

2.1. Raw material and steam explosion pretreatment

The corn stover used for this study was grown and harvested under standard conditions in Ardud (Romania) in November 2013. The stover was dried on the field, compressed in a round bale and sent to the University of Natural Resources and Life Sciences, Vienna, where it was chopped to a final length of less than 10 cm. The stover was then stored under dry conditions at 4 °C until pretreatment.

The stover was pretreated in March 2014 at the Norwegian University of Life Sciences (NMBU) in Ås (Norway) with a steam explosion unit (Cambi, Asker, Norway), whose performance is described by Horn et al. (2011b). The unit consisted of a 25 KW electric-heated steam boiler (Parat, Flekkefjord, Norway) that could achieve a maximum pressure of 34 bar. An automatic air-actuated valve released the steam into a 20 L pressure vessel that contained the biomass to be pretreated. This valve ensured keeping the pressure in the vessel at the target value. Air was removed from the vessel before every pretreatment was carried out by direct injection of steam until saturation was reached. When each pretreatment was finished, another air-actuated valve was responsible for a rapid pressure reduction in the vessel. This pressure difference transported the pretreated stover to a removable bucket, from which the samples were taken for further tests.

Table 1
Summary of chemical analyses.

Pretreatment	pH	DM	VS	CEL	H-CEL	AIL	XP	WSF
		[% FM]	[% DM]	[% VS]				
Untreated	7.5	86.0	94.3	39.0	26.6	17.3	3.5	12.5
140 °C, 2 min	6.7	45.5	93.3	40.9	27.4	17.9	3.2	15.1
140 °C, 5 min	6.4	42.7	92.2	40.5	27.2	16.8	4.0	19.0
140 °C, 10 min	6.6	33.0	94.6	40.1	27.8	17.9	3.1	17.3
140 °C, 15 min	6.4	18.9	91.8	41.2	28.6	18.6	3.8	19.8
160 °C, 2 min	6.9	51.1	91.6	39.4	26.9	17.6	3.9	18.3
160 °C, 5 min	6.6	43.4	93.4	38.7	27.2	17.8	3.4	23.5
160 °C, 10 min	6.4	32.2	91.5	35.8	22.7	19.5	3.7	22.5
160 °C, 15 min	6.5	29.2	94.2	38.0	24.3	18.8	3.4	25.3
180 °C, 2 min	6.7	51.6	93.5	39.8	27.3	17.9	3.5	24.0
180 °C, 5 min	6.5	45.3	92.4	40.3	28.0	18.4	3.7	27.3
180 °C, 10 min	6.3	31.6	92.6	40.3	25.9	19.8	3.9	27.5
180 °C, 15 min	6.1	22.6	91.5	39.8	24.8	19.3	4.3	32.5
200 °C, 2 min	6.2	49.3	94.0	38.1	25.4	18.3	3.6	27.0
200 °C, 5 min	5.2	35.6	93.6	40.2	22.3	21.5	3.7	36.9
200 °C, 10 min	4.2	28.0	92.8	44.1	12.7	26.6	4.1	36.9
200 °C, 15 min	4.2	20.3	91.8	44.7	7.1	32.7	4.8	41.8
220 °C, 2 min	4.7	37.8	92.1	42.0	19.3	23.5	4.3	38.9
220 °C, 5 min	4.0	34.9	91.2	42.2	3.0	34.5	5.0	n.a.
220 °C, 10 min	3.9	28.7	91.6	36.1	1.2	42.2	5.0	42.0
220 °C, 15 min	4.2	24.2	90.8	30.3	1.0	43.8	5.4	51.6

DM: dry matter; FM: fresh matter; VS: volatile solids; CEL: cellulose; H-CEL: hemicellulose; AIL: acid insoluble lignin; XP: crude protein; WSF: water soluble fraction; n.a.: not analyzed.

The pretreatment step was carried out with temperatures ranging from 140 to 220 °C, using intervals of 20 °C (Table 1). Residence times in the pressure vessel were 2, 5, 10 and 15 min. The amount of sample used in all pretreatments was 500 grams. After every pretreatment, the unit was cleaned by running three steam-only pretreatments and flushing the flash tank and bucket with clean tap water. All steam-exploded samples were subsequently vacuum stored at 4 °C until physicochemical analysis and biogas tests were carried out.

2.2. Substrate characterization

The analysis of structural carbohydrates was carried out to gain a deeper understanding of the effect of steam explosion on the chemical properties of corn stover. The composition of untreated and steam exploded biomass was determined by analyzing the following parameters: pH, dry matter, raw ash, volatile solids, cellulose, hemicellulose, acid insoluble lignin (AIL) and crude protein.

The dry matter content of the corn stover was determined by drying the samples in an oven at 105 °C until constant weight was reached. The volatile solids (VS) were determined after dry oxidation in a muffle furnace as the difference between the dry matter and the raw ash content (Sluiter et al., 2008a).

The cellulose, hemicellulose and acid insoluble lignin (AIL) of native and pretreated samples were analyzed in duplicates using a two-step acid hydrolysis (Sluiter et al., 2008b). The dried biomass was milled until the entire sample passed through a 1 mm sieve. 300 mg ± 10 mg of the samples were weighted into pressure tubes. Then 3 ml of 72% sulfuric acid was added and the mixture was incubated at 30 °C for 60 min. In the second step, 84 ml of deionized water was added to reduce the sulfuric acid to 4% and then the samples were incubated for one hour at 121 °C in an autoclave. In addition to the samples, a set of sugar recovery standards (SRS) was prepared. The structural carbohydrates were analyzed from the hydrolysis liquor. To determine the acid insoluble lignin (AIL), the autoclaved hydrolysis solution was filtered using filtering crucibles and the remaining insoluble residue was washed, dried overnight at 105 °C and weighed. Then, the ash content of