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Effect of combined chemical and thermal pretreatments on biogas production from lignocellulosic biomasses

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ABSTRACT

Anaerobic digestion of lignocellulosic biomass like crop residues have gained attention due to their surplus availability in rural areas. However, anaerobic digestion of such biomass feedstock require pretreatment to increase their digestibility. A combination of chemical (banana peel ash and calcium hydroxide) and thermal treatments (60–90 °C for time intervals of 2, 6 and 10 h) is investigated to understand the degradation behavior of two agro-residue biomasses *viz.* rice straw and corn stalk. Various analytical methods like FTIR, SEM and degradation of fiber (lignin, cellulose and hemicellulose) were employed to assess the efficacy of the pretreatment technique. Post pretreatment, biogas production is also investigated from the pretreated biomass along with the degradation of volatile solids during anaerobic digestion. Longer duration and higher temperature improved biodegradability as compared to short duration and low temperature treatments with differentiated results on both samples. Lignin of corn stalk (~47%) degrades better than rice straw (~39%) under identical pretreatments. The biogas production in cubic meter per unit kilogram of volatile solids of rice straw and corn stalk pretreated at 90 °C for 6 h was enhanced by 62% and 66%, respectively as compared to untreated rice straw and corn stalk. The know-how generated form the study will be useful to explore the potential benefits of banana peel ash as a pretreatment source for energy recovery via anaerobic digestion from surplus biomasses in rural India.

1. Introduction

Biogas resulting from the anaerobic digestion of solid wastes like cattle excreta, kitchen waste, wastewater sludge, lignocellulosic biomass has been one of the most favorable bioenergy sources (Neshat et al., 2017; Cheng et al., 2011). Moreover, its popularity over conventional non-renewable resources has paved way to its widespread domestic applications (specially as cooking fuel in developing countries) and also large scale plants for power generation (Sawatdeenarunat et al., 2015). In addition, it has its added benefits of lowering greenhouse gas emissions, waste reduction, supplementing conventional energy systems used in cooking and heating applications (Neshat et al., 2017).

Out of a variety of feedstocks, anaerobic digestion of lignocellulose biomass has gained importance in recent years (Neshat et al., 2017; Abudi et al., 2016). In fact, lignocellulosic biomass like crop residues and energy crops have been under the radar as potential feedstock for biogas production (Sawatdeenarunat et al., 2015). One reason for their acceptance is their high biogas yield and fertilizer production with low energy inputs making them potential biomass for anaerobic digestion (McKendry, 2002).

Rice straw and corn stalk are such lignocellulosic biomass found abundantly in rural areas of India. Rice is the major crop in India with an annual production of 104.32 Mt in 2016–17 whereas, Maize is the third most important cereal crop in India after rice and wheat with an annual production of 21.8 Mt in 2016–17 (Annual Report 2016-17, Ministry of Agriculture and Farmers Welfare). Maize production in India has been estimated to be 9% of the total food grain production in the country by Singh (2014). In addition, it has also been estimated that there is an enormous availability of surplus rice straw (43.5 MT) and corn straw/stalk (9 MT) in India (Hiloidhari et al., 2014) which can be potential feedstocks for anaerobic digestion (Patowary et al., 2016; Abudi et al., 2016; Qingming et al., 2005; Zheng et al., 2009). However, there are certain technical issues which needs attention to make these lignocellulosic biomass resources a versatile feedstock for biogas production.

Lignocellulosic biomass like rice straw and corn stalk are composed of lignin, cellulose and hemicellulose fragments. Out of this, Lignin is

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composed of an interconnected network of polymeric compounds which is fairly hard to break down when subjected to anaerobic digestion (Hatfield and Fukushima, 2005). The presence of lignin is a hindrance to the enzymatic hydrolysis of cellulose during the anaerobic digestion process (Gallert and Winter, 2005). Consequently, the hydrolysis of lignocellulose often becomes the rate-limiting step during traditional anaerobic digestion (Khanal, 2008). There have been studies relating to the enhancement of biodegradability of lignocellulosic biomass via physical, chemical, biological and in some cases hybrid pretreatment for bioenergy production (FitzPatrick et al., 2010; Zhang et al., 2016). Pretreatment processes like mechanical grinding of biomass, treating with alkali, washing by hot water, explosion by steam, etc., have found applications in improving the biodegradability of lignocellulosic biomass (Monlau et al., 2013; Agbor et al., 2011). Chemical pretreatment is one of the most commonly used pretreatment process used for treatment of lignocellulose biomass for biogas production. But, due to the high cost of chemicals, it has become an uneconomical mode of pretreatment process (Pavlostathis and Gossett, 1985). Further, a majority of the pretreatment processes mentioned are disparaging both environmentally as well as economically (Monlau et al., 2013; Agbor et al., 2011).

Among the pretreatments, from practical point of view, alkali pretreatment has an upper hand over other pretreatment for anaerobic digestion (Pavlostathis and Gossett, 1985). However, owing to the need of huge quantities of chemical solution, facility requirement to store chemicals and their management after use may not only result to be a costly process but also a concern on environment pollution (Pavlostathis and Gossett, 1985; Wu et al., 2006). In addition, high temperature processes, besides requiring high energy inputs also produce inhibitory compounds or products that are recalcitrant for the anaerobic digestion process (Wilson and Novak, 2009; Appels et al., 2010). In thermal processes ranging above 100 °C, the effect of temperature is more pronounced than duration of treatment (Valo et al., 2004). However, during pretreatment at moderate temperatures, treatment time plays a more dominant role than the treatment temperature (Appels et al., 2010; Rani et al., 2012; Pang et al., 2008). Overall, pretreatment at moderate or low temperature also prevents the formation of inhibitory or toxic substances harmful for biogas production. Therefore, a low temperature pretreatment could be potential for anaerobic digestion of lignocellulosic biomass. Moreover, combination of low temperature and alkali is expected to provide a favorable outcome in improving the degradation of such biomass.

Significant amount of potassium (K), calcium (Ca) and sodium (Na) are available in different fruits and vegetable species such as banana, potato, beets etc. (Baciocchi et al., 2013). With a production volume of 29.8 million metric tons per annum, India stands out to be the largest producer of banana in the world. Considering such a huge production of banana, its stems (whole plant excluding leaves and fruits) which are available in large quantities are generally rejected as a postharvest measure to make space for new cultivation (Gogoi et al., 2014). To prevent any possible adverse effect on soil and water, proper management of banana stems is needed for its safe disposal. Previous studies reported the presence potassium and calcium in different parts of banana plants ranging from 9.4 to 33.4% of K and 7.5–32.3% of Ca (Cordeiro et al., 2004; Mohapatra et al., 2010) indicating it to be potential renewable source of alkali. Banana peel ash (locally known in Assam, (India) as *kalakhar*) is obtained when banana peels are burnt. This product is highly alkaline in nature and is used as an alternative for salt in preparation of some Asssamese delicacies, a northeastern Indian cuisine (Baruah et al., 2017). No literature was found indicating the uses of such potential agro-wastes and their derived products for pretreatment applications of lignocellulosic biomass.

Calcium hydroxide ($Ca(OH)_2$), also known as lime, has also been reported as potential pretreatment chemical agent in biodegradation of lignocellulose by structural deformation of lignin (Mosier et al., 2005). Further, it is reported that calcium hydroxide treatment can be performed at low temperatures with better effect (Kim and Holtzapple, 2005). Therefore, investigation on the potential use of banana peel ash and lime as pretreatment agents in combination with moderate thermal environment for achieving enhanced production of biogas from lignocellulosic biomass is required.

The objective of this study is to investigate the effects of chemical pretreatment method on rice straw and corn stalk under some pre-set thermal conditions. The chemical used for the pretreatment are derived from locally available biomass. The efficacy of the applied pretreatment method is being tested by the characterization of the pretreated biomass in terms of FTIR and SEM analyses and estimating the degradations of lignin, cellulose and hemicellulose. Anaerobic digestion is also performed to investigate the biogas production of the pretreated biomass.

2. Materials and methods

2.1. Materials

The rice straw and corn stalk used in the study were collected from Jhawani village, Bihaguri Development block, Sonitpur District, Assam (India). The collected samples were chopped (15–20 mm in length) and then grinded in a mixer grinder (Brand: Philips, 750 W). The ground particles were passed through a 2 mm sieve. For anaerobic digestion (AD) of rice straw and corn stalk, inoculum was collected from a cow dung fed biogas plant in Amolapam village, near Tezpur University (India). The inoculum contained 9 g/L total solids (TS), 40.57 g/L volatile solids (VS), and 27.31 g/L ash (non- volatile solids).

2.2. Description of chemical and thermal pretreatments

Both the feedstock samples, viz., rice straw and corn stalk were separately pretreated using a mixture of banana peel ash and lime and then undergone a thermal treatment to understand the degradation behavior to make them favorable for anaerobic digestion. A total of 20 different pretreatments of rice straw and corn stalk were considered in the present investigation. The detailed description of the treatments is presented in Table 1.

Table 1
Description of different treatments considered to investigate degradation behavior of lignocellulosic biomass.

Treatment description			Nomenclature
Treatment	Type	Biomass	
Banana peel ash + Lime	Kept at room temperature for seven days (Chemical pretreatment only)	Rice straw	BCRS
		Corn stalk	BCCS
	Chemically treated biomass heated at 60 °C for 2 h	Rice straw	6BCRS2
		Corn stalk	6BCCS2
	Chemically treated biomass heated at 60 °C for 6 h	Rice straw	6BCRS6
		Corn stalk	6BCCS6
	Chemically treated biomass heated at 60 °C for 10 h	Rice straw	6BCRS10
		Corn stalk	6BCCS10
	Chemically treated biomass heated at 75 °C for 2 h	Rice straw	7BCRS2
		Corn stalk	7BCCS2
	Chemically treated biomass heated at 75 °C for 6 h	Rice straw	7BCRS6
		Corn stalk	7BCCS6
	Chemically treated biomass heated at 75 °C for 10 h	Rice straw	7BCRS10
		Corn stalk	7BCCS10
	Chemically treated biomass heated at 90 °C for 2 h	Rice straw	9BCRS2
		Corn stalk	9BCCS2
	Chemically treated biomass heated at 90 °C for 6 h	Rice straw	9BCRS6
		Corn stalk	9BCCS6
	Chemically treated biomass heated at 90 °C for 10 h	Rice straw	9BCRS10
		Corn stalk	9BCCS10