



Improvement of wheat straw anaerobic digestion through alkali pre-treatment: Carbohydrates bioavailability evaluation and economic feasibility



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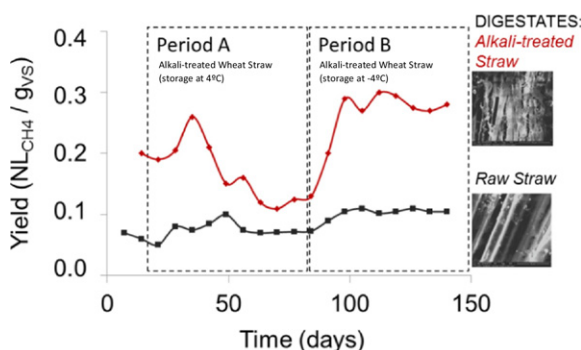
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HIGHLIGHTS

- Alkali pre-treatment increased the biodegradability of wheat straw.
- Alkali pre-treatment increased digester stability and performance.
- Alkali pre-treated wheat straw reaching higher methane yield
- Alkali pre-treatment resulted in a positive energy balance.

GRAPHICAL ABSTRACT



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ABSTRACT

Lignocellulosic biomasses such as wheat straw are widely used as a feedstock for biogas production. However, these biomasses are mainly composed of a compact fibre structure and therefore, it is recommended to treat them prior to its usage for biogas production in order to improve their bioavailability. The aim of this work is to evaluate, in terms of performance stability, methane yield and economic feasibility, two different scenarios: a mesophilic codigestion of wheat straw and animal manure with or without a low-energy demand alkaline pre-treatment (0.08 g_{KOH} g_{TS}⁻¹ of wheat straw, for 24 h and at 25 °C). Besides this, said pre-treatment was also analysed based on the improvement of the bioavailable carbohydrate content in the untreated versus the pre-treated wheat straw. The results pointed out that pre-treated wheat straw prompted a more stable performance (in terms of pH and alkalinity) and an improved methane yield (128% increment) of the mesophilic codigestion process, in comparison to the “untreated” scenario. The pre-treatment increased the content of cellulose, hemicellulose and other compounds (waxes, pectin, oil, etc.) in the liquid fraction, from 5% to 60%, from 11.5% to 39.1% TS and from 57% to 79% of the TS in the liquid fraction for the untreated and pre-treated wheat straws, respectively. Finally, the pre-treated scenario gained an energy surplus of a factor 13.5 and achieved a positive net benefit of 90.4 € t_{VS}⁻¹ d⁻¹, being a favourable case for an eventual scale-up of the combined process.

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1. Introduction

Lignocellulosic biomasses such as wheat straw (WS) are widely used as a feedstock for biogas production (Grontmij et al., 2012; Zhao et al., 2012). The use of lignocellulosic biomasses is favourable due to its availability, low-cost and renewable factors (Vandenbossche et al., 2014). However, lignocellulosic biomass is mainly composed of compact packages of cellulose, hemicelluloses and lignin (Lu et al., 2013), where the main propose of lignin is to give the plant structural support, impermeability and resistance against microbial attacks and oxidative stress (Hendriks and Zeeman, 2009). Therefore it is recommended to treat such biomass prior to its usage for energy production in order to improve its bioavailability. The purpose of this pre-treatment is to breakdown the compact structure of lignocellulose, thus improving the cellulose accessibility for efficient enzymatic hydrolysis (Lu et al., 2013; Saif et al., 2013; Velmurugan and Muthukumar, 2012).

Pre-treatment methods might include physical (temperature, pressure and mechanical-size reduction), chemical (acid or basic), biological (enzymatic) or a combination of some of these procedures (Iskalieva et al., 2012; Saif et al., 2013; Vandenbossche et al., 2014). Among the chemical pre-treatments, alkali pre-treatment has been typically used in lignocellulosic materials with a high lignin content, such as wheat straw and sugarcane bagasse (Rabelo et al., 2011; Taherdanak and Zilouei, 2014), with sodium, potassium, calcium and ammonium hydroxides being the most frequently used reagents (Singh et al., 2015). The main applications of the alkali pre-treatment of lignocellulosic biomasses for biogas production are associated with the solid-state anaerobic digestion (AD) (Table 1). In addition, the alkaline pre-treatment reduces the degree of inhibition in methane fermentation and provides a lower cost of production (Ferreira et al., 2013 and Krishania et al., 2013). For instance, Zhu et al. (2010) reported a +37% increase in biogas yield in the solid-state AD of corn stover using NaOH at 5% w/w. Likewise, Zhang et al. (2013) used NaOH pre-treatment to enhance the solid state anaerobic co-digestion (20% TS) of banana stem and swine

manure: adding NaOH at 6% w/w, the methane yield improved from 0.183 to 0.232 L_{CH₄} kg_{VS}⁻¹, which is equivalent to an increment of +21%. However, Zheng et al. (2009) reported a higher methane yield improvement of +37% after the corn stover wet-state (12% TS) pre-treatment using NaOH at 2% w/w, concluding that NaOH pre-treatment was more efficient on the wet-state than the solid-state, since the wet-state needed a pre-treatment shorter time by +86% (≤24 h) and +67% lower NaOH dose in comparison to the solid-state. Chandra et al. (2012) also confirmed that a WS wet-state (10% TS) pre-treatment using NaOH at 4% w/w led to an increase in methane yield, from 0.078 to 0.166 L_{CH₄} kg_{VS}⁻¹.

Though NaOH is the most commonly reported chemical for treating lignocelluloses, sodium discharges might be environmentally harmful as they can lead to negative impacts such as soil salinization (Zheng et al., 2014). An alternative solution is to replace NaOH with KOH. Moreover, the outflows derived from KOH treatment might have a potential soil amendment value since potassium is a nutrient required for plants growth. Liu et al. (2015) studied WS pre-treatments with a wide KOH dosage range (2–50% w/w), obtaining an increment in methane yield between +16.7% and +77.5%, when compared to untreated WS. Although these reported good yields and its advantages when it comes to digestate management (avoiding soil salinity increase), the implementation of KOH as pre-treatment is still constrained due to its steep price (three times higher than NaOH).

The aim of this study was to assess the process performance improvement (reactor stability and biogas production) through the usage of KOH alkali reagents as pre-treatment in biogas plants, well as so asses its economic feasibility. In order to compare results with a well-known scenario, WS and pig manure (PM) co-digestion was selected, being a common feature in European agricultural AD plants (Mata-Alvarez et al., 2014). In this regard, two mesophilic stirred reactors were operated to co-digest WS and PM with and without the KOH pre-treatment. Process stability, methane production, carbohydrate mass balance and fibre scanning electron microscopy (SEM) analysis were conducted to achieve the objectives set.

Table 1
State-of-art on alkali pre-treatment of lignocellulosic biomass and anaerobic digestion. Notes: "nd" means not determined.

Biomasses	Pre-treatment			Anaerobic digestion conditions				Yield (m ³ _{CH₄} kg _{VS} ⁻¹)				
	Alkali	Ratio (%) ^a	Moisture (%)	Temp (°C)	Time (h)	Inoculum	Reactor	Temp. (°C)	Control	Sample	^b	Reference
Wheat straw	KOH	10	90	20	24	Sludge	Batch	55	0.167	0.210	(VS)	(Liu et al., 2015)
		30								0.224		
Wheat straw	NaOH	4	90	37	120	nd	Batch	37	0.0784	0.166	(VS)	(Chandra et al., 2012)
Corn stover	NaOH	5	50	20	24	Liquid from full scale AD plant	Solid-state AD	37	0.26	0.375	(VS) ^c	(Zhu et al., 2010)
		7.5								0.03 (Fail)		
Sugarcane press mud	Ca(OH) ₂	10	nd	100	1	Full scale codigestion AD plant	Batch	37	0.161	0.272	(VS)	(López González et al., 2013)
		7		100	2					0.197		
		11.24		100	2					0.301		
Banana stem	NaOH	2	nd	55	54	Digestate from beer waste plant	Batch (PM1:1) ^a	35	0.195	0.2	(VS)	(Zhang et al., 2013)
		6		55	54					0.24		
		10		55	54					0.07		
Rice Straw	Ca(OH) ₂	2 ^d	50	20	120	nd	Leaching bed reactor	35	nd	0.177	(VS)	(Liang et al., 2014)
Corn stover	NaOH	4	80	20	72	Full scale sludge digestate	Batch (35) ^e	35	0.16	0.22	(VS)	(Zheng et al., 2009)
		4					(50) ^e		0.15	0.2		
		2					(65) ^e		0.13	0.22		
		2					(80) ^e		0.12	0.18		
Fallen leaves	NaOH	3.5	4.1 ^f	Coupled to anaerobic digestion		Liquid from food processing waste digester	Solid-state AD	37	0.068	0.083	(VS)	(Liew et al., 2011)
		3.5	6.2 ^f						0.004	0.074		
		5	8.2 ^f						0.002	0.038		
	NaOH	10	84	40	24	Granular sludge - sugar factory waste AD	Stirred tank (1–1.8) ^g	35	0.237	0.297	(VS)	(Sambusiti et al., 2013)

^a Dry basis.

^b Methane production on organic basis units in brackets.

^c Expressed in biogas production.

^d Wet basis.

^e Loading rate (g L⁻¹).

^f Expressed in solid to liquid ratio.

^g Organic loading rate (kg_{VS} m⁻³ d⁻¹).

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