Chemical Engineering Journal 211–212 (2012) 488–492

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Influence of alkaline pre-treatment conditions on structural features and methane production from ensiled sorghum forage

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HIGHLIGHTS

- ▶ NaOH pre-treatment reduced the content of lignin and hemicelluloses of sorghum.
- ▶ NaOH pre-treatment enhanced TOC and proteins solubilisation of sorghum.
- ▶ The methane yield was not affected by NaOH dosage, temperature and contact time.
- ▶ Digestion kinetics increased with NaOH dosage, temperature and contact time.

ARTICLE INFO

Article history:
Received 12 July 2012
Received in revised form 25 September 2012
Accepted 26 September 2012
Available online 4 October 2012

Keywords:
Anaerobic digestion
Ensiled sorghum forage
Lignocellulosic biomass
Sodium hydroxide pre-treatment
Structural features

ABSTRACT

Alkaline pre-treatment has been widely applied to lignocellulosic biomass but the tested conditions are quite variable in literature. Results are also quite scattered even when similar substrates are compared. Therefore the aim of this study was to test different alkaline dosages (4% and 10% gNaOH/gTS), temperatures (40 °C and 55 °C), and contact times (12 h and 24 h) in order to investigate the influence of the pre-treatment conditions on the structural features and methane production from ensiled sorghum forage. This study confirms the positive effect of NaOH pre-treatment on fibre reduction, total organic carbon and proteins solubilisation, and thereafter the anaerobic degradability of ensiled sorghum forage. An increase in methane yield, with respect to untreated sample (from 8% to 19%), was observed at all pre-treatment conditions tested. Nevertheless, no significant differences on methane yield were observed by varying NaOH dosage, temperature, and contact time. The increase of sodium hydroxide dosage led to an increase of the soluble total organic carbon (TOC) (from 12% to 29%) and proteins (from 56% to 72%), at each temperature and contact time tested. By increasing the NaOH dosage, a reduction of hemicelluloses (from 37% to 70%) and lignin contents (from 26% to 70%), and an increase of the anaerobic digestion kinetics (with a maximum increase of 43% for samples treated at 55 °C for 24 h), were also observed. Finally, the anaerobic digestion kinetics were improved with the increase of contact time (up to 13%) and temperature (up to 20%).

1. Introduction

Nowadays some 80% of the world's overall energy supply is derived from fossil fuels [1]. The Renewable Energy Directive adopted in 2009 focuses on achieving a 20% share of renewable energies in the EU's energy mix by 2020. Among the renewable energy resources, biomass contributes by some 3–13% to the total world energy supplies of the industrialised countries. In developing countries this proportion is much higher [1].

Biomasses, both residual (such as agro-industrial wastes and crop residues) and specifically grown energy crops offer a huge potential for the production of renewable energy, as heat and electricity. Their use could be beneficial to reduce pollution and greenhouse gas emissions and to reduce the dependence on oil and gas.

Anaerobic digestion is considered to be a sustainable way to combine renewable energy generation with sustainable waste

Abbreviations: ADF, acid detergent fibre; ADL, acid detergent lignin; BMP, Biochemical Methane Potential; COD, chemical oxygen demand; NDF, neutral detergent fibre; SMA, specific methane activity; TKN, total kjeldahl nitrogen; TOC, total organic carbon; TS, total solids; VS, volatile solids.

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http://dx.doi.org/10.1016/j.cej.2012.09.103

treatment. The evaluation of biogas and methane production through anaerobic digestion from energy crops or agricultural wastes is not new and is being prompted in recent years, when the number of anaerobic digesters in the EU has increased dramatically. In early 2010, about 5900 biogas plants with an installed electrical capacity of 2300 MWel were operational. Within the next five years, more than 3000 biogas plants with an electrical capacity of more than 1700 MWel will be constructed [2].

Among energy crops, sorghum, with a world cultivated land of 40 million ha in 2009 [3] and with a hectare yield as high as 25 *t* (dry weight) per year, represents an interesting substrate for methane production. Sorghum is a genus with many species and subspecies, including grain sorghums, grass sorghums, and sweet sorghums. Among them, Sudan grass (*Sorghum sudanense*) is one of the most commonly used energy crop for biogas production plants [4,5].

The main challenge in using lignocellulosic crops, such as sorghum, for biogas production, is their structure and composition. Crop biomasses mainly consist of cellulose, hemicelluloses and lignin. It is well known that cellulose and hemicelluloses (holocelluloses) are degradable by anaerobic microorganisms; nevertheless, their association with lignin, which acts as a physical barrier, prevents their degradation [6]. Moreover, the crystalline structure of cellulose prevents penetration by micro-organisms or extracellular enzymes [7]. However, physical structure and composition of lignocellulosic materials can be altered through various methods of pre-treatment. An ideal pre-treatment prior to anaerobic digestion would increase surface area, reduce lignin content and the crystallinity of cellulose, making them more accessible to anaerobic micro-organisms and therefore more easily biodegradable [7,8].

Various methods of pre-treatment have been quite intensively investigated for facilitating the enzymatic hydrolysis and consequent ethanol production from lignocellulosic substrates [9], but there is less information available on the effects of pre-treating crop biomass for methane production [10]. Pre-treatments include physical, chemical, thermal, biological processes or combination of them. Physical pre-treatment such as chopping, grinding, and milling, leads to a reduction in the particle size of the biomass, thus reducing the degree of cristallinity of cellulose and the degree of polymerisation of cellulose and hemicelluloses, increasing the surface area of cellulose. Nevertheless, energy requirement remains a limiting factor of this type of treatment, especially when biomass has high moisture content [11]. Biological pre-treatment (fungi, enzymes) is an energy saving and environmental friendly method of pre-treatment but relative low efficiency, potential loss of carbohydrates and long residence time are the three major disadvantages for fungal pre-treatment. Thermal pre-treatments (steam explosion, ammonia fibre explosion (AFEX), wet oxidation, hydrothermal) are also efficient in solubilising crops but they are energy intensive.

Finally, among chemical pre-treatments (acid, alkali, organic solvents and oxidant agents), alkaline pre-treatments (NaOH, KOH, lime, ammonia, and urea) are efficient in altering the structure of lignin, solubilising hemicelluloses fraction and increasing efficiently the accessibility of cellulose by a swelling and a partial decrystallization of cellulose [12–14]. Sodium hydroxide pre-treatment has been studied for many years and it has been shown to disrupt the lignin structure of the biomass, thus increasing the enzymatic accessibility to cellulose and hemicelluloses. NaOH pre-treatment was also found efficient in the release of soluble organic carbon and proteins. Xie and co-workers [15] found an increase of soluble COD up to almost 30%, by soaking grass silage in a NaOH solution (7.5% gNaOH/gVS) for 12–24 h at 60 °C. Sun et al. [16] found a protein solubilisation of about 38%, by soaking 2.5 g of wheat straw in 100 mL of NaOH solution (1.5%NaOH) at 20 °C for 6 h.

In general, the applied NaOH pre-treatment conditions are quite variable in literature, however the tested temperature varied between 10 °C and 200 °C, the NaOH dosages varied between 0.1% and 10%, and contact times included between few minutes to 5 days and generally decreased at increasing pre-treatment temperature. Results are also quite scattered even when similar substrates are compared, and this fact suggests that no definite consensus on the effectiveness of alkaline pre-treatments for the improvement of the anaerobic biodegradability of agro-waste and energy crops has yet been attained, as also suggested by Us and Perendeci [16] and Fdez Guelfo et al. [17]. Common substrates used for alkaline tests are straws, grasses, bagasses corn stovers, and sunflower stalks. Sun and co-workers [18] studied the effects of different alkaline pre-treatments on wheat straw. They found that best results for delignification and solubilisation of hemicelluloses were obtained by soaking 2.5 g of straw in 100 mL of NaOH solution (1.5%NaOH) for 144 h at 20 °C, which resulted in 60% release of lignin and 80% release of hemicelluloses. Recently, Zhu and co-workers [19] showed the effectiveness of sodium hydroxide pre-treatment to increase biogas production from corn stover by 37%. Zhao and co-workers [20] showed the effectiveness of sodium hydroxide pre-treatment for hardwoods, wheat straw, switch grass, and softwoods with less than 26% lignin content. Finally, Monlau and co-workers [21] studied the effects of NaOH pre-treatments on sunflower stalks at fixed concentration (4 gNaOH/100gTS) and time (24 h). The pre-treatment temperature ranged between 30 °C, 55 °C, and 80 °C. The highest methane production (259 ± 6 $mLCH_4$/gVS) was reached at 55 °C.

The aim of this study was to test different alkaline dosages (4% and 10% gNaOH/gTS), temperatures (40 °C and 55 °C), and contact times (12 h and 24 h) in order to investigate the influence of the pre-treatment conditions on the structural features and methane potential from ensiled sorghum forage. The pre-treatment temperatures, dosages and contact times were chosen, according to the best pre-treatment results of our previous studies [22], obtained on ensiled sorghum forage and according to some literature suggestions on agricultural substrates [19,21].

2. Materials and methods

2.1. Sorghum

Ensiled sorghum forage (*Sorghum sudanense hybrid*) used for animal feed, was collected from a farm near Cremona (Lombardy region, Italy). Sorghum was harvested and then it was left in field for about 4–5 days before ensilage. After collection, it was dried at 60 °C for two days to a moisture content of less than 10%, and ground to 1 mm particles by a cutting mill (Retsch) and finally stored at ambient temperature prior to use. The main characteristics of sorghum, after drying and milling, are given in Table 1.

Table 1
Composition of ensiled sorghum forage after drying and milling. Values correspond to mean ± standard deviation of measurement performed in duplicate.

Characteristics	Mean ± SD
TS (% wet weight)	93.5 ± 0.4
VS (%TS)	77.6 ± 1.2
Cellulose (%TS)	47.5 ± 1.0
Hemicelluloses (%TS)	27.4 ± 1.0
Lignin (ADL) (%TS)	7.0 ± 0.0
N-TKN (%TS)	1.42 ± 0.01
Protein (%TS)	8.9 ± 0.1
TOC (%TS)	41.6 ± 1.0
C/N	29