Evaluation of pretreatment methods for the anaerobic digestion of bean straw

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Abstract

Purpose Agriculture residues such as bean straw are worldwide sources of biomass that hold large potential as feedstock for bioenergy production in the form of biogas via anaerobic digestion (AD).

Methods Bean straw was subjected to a biological (fungi *fermentation*), thermal (121°C) and chemical (2.8% HCl, 132.2 °C) pretreatment to determine the hydrolysis of the lignocellulosic compounds (lignin, cellulose and hemicellulose). Then, the hydrolysates from each pretreatment were used as substrate in three UASB lab-scale bioreactors for biogas production. Methane yield, cost of reagents, energy consumption/production associated to each pretreatment were compared.

Results The chemical pretreatment displayed higher lignin and hemicellulose degradation (66.91 and 67.93%, respectively) as well as a higher amount of cellulose release (68.12%). The biological, chemical and thermal hydrolysates contained 7.28, 14.58 and 10.61 g/L of total sugars, respectively, which correspond to a chemical oxygen demand (COD) of 7.91, 18.87 and 12.45 g/L, respectively. Similar biogas production (646-811 mL of biogas and 0.23-0.27 L CH_4/gCOD) as well as total sugars and COD degradation (above 80%) were encountered in the three bioreactors. Biological pretreatment displayed higher energy consumption during the pretreatment in comparison with the thermal and chemical pretreatment, however the chemical pretreatment resulted more expensive due to the costs of reagents.

Conclusions The results demonstrated that the COD biodegradability and total sugars characteristics are similar regardless the pretreatment. The total energy consumption and costs associated to each pretreatment surpass the total energy production on the three pretreatments, thus demonstrating the need for process improvement.

Keywords: anaerobic digestion, bean straw, biogas, hydrolysate, pretreatment.

1. Introduction

Biomass provides approximately 9.2% of the total worldwide energy needs and is an important contributor to the world economy [1]. There are several conversion technologies for the exploitation of energy from biomass, which, include direct combustion, gasification, pyrolysis, and biological conversions [2]. The latest includes conversion to liquid or gaseous fuels such as ethanol, methanol, and biogas, using agricultural residues, animal manure, industrial and food waste, among other sources [3].

Biogas production (CH_4 and CO_2), via anaerobic digestion (AD) is a promising technology for bioenergy production as the biomass that can depend on is considered a “waste” or with little economic value. Bean straw, for instance, is generated in thousands of tons mainly in the state of Zacatecas, Mexico (156,000 tons in

2014) [4]. The disposal of these residues after harvesting/threshing, have been burying, which leads to unbalance the C/N ratio in soils, as well as burning, which gives a very low contribution to mineral wealth of soils, while damaging its humic content and killing surface microflora and microfauna [3]. Biogas production from bean straw could thus be an attractive option and generate an economic value for society by revitalizing rural areas [5]. Nevertheless, the lack of information that has been published regarding AD of bean straw and the slow hydrolysis of these type of residues, hampers its applicability [3]. The latter is related to the complex lignocellulose structure, which limits the accessibility of the sugars contained in cellulose and hemicellulose. This means that a pretreatment is necessary to gain access to these sugars thus facilitating the following AD stages (acidogenesis, acetogenesis and methanogenesis). For this, several pretreatment methods have been explored in residues with lignocellulose structure to facilitate the hydrolysis step and decrease the hydraulic retention time in anaerobic farm digesters [5]. Current leading pretreatment technologies include physical, chemical and biological methods [6].

The chemical pretreatments can be divided into acid and alkaline pretreatments. In the acid pretreatment H_2SO_4, HNO_3 or HCl are used to remove the hemicellulose and expose the cellulose for enzymatic digestion [7]. The results obtained with this type of pretreatment, when applied to different straws, have shown high hydrolysis rates (70 to 90% degradation) [8,9], particularly with the additional application of high temperatures (80-170°C) [10]. Nonetheless, this pretreatment have been considered economically unattractive due to the costs of chemicals [3] and, when heating is also applied, the coupled energy costs. Other drawbacks include the formation of inhibitors (carboxylic acids, furans and phenolic compounds) that prevent microbial growth and thus methanogenesis, corrosion of the equipment and further neutralization requirements prior the AD process [8]. Notwithstanding, the current increase in energy prices and concomitantly increase in energy demand leads to keep interest in chemical pretreatments [9].

The thermal pretreatment consists on heating the lignocellulosic residues in a range between 120 and 150 ºC, where the hemicellulose and followed by the lignin are solubilized [11]. Thermal pretreatments have been applied to improve the anaerobic digestibility of different agriculture substrates such as wheat straw, sorghum forage and sugarcane bagasse for bioethanol and biogas production where the results obtained have shown hydrolysis rates of 70 and 85 % [11,12]. The non-addition of chemicals avoids the corrosion problems, and decreases the formation of toxic compounds. Other advantages include the lower requirement of chemicals for the neutralization of the hydrolysates produced, and the smaller amount of waste produced in comparison to other processes [6]. The disadvantages of this pretreatment, besides the energy costs due to the temperature requirements, are the destruction of sugars as xylans from the hemicellulose, incomplete rupture of the matrix lignin-carbohydrates and generation of inhibitors that affect the fermentation process [13].

The biological pretreatments, apply microorganisms such as fungal strains, which naturally produce enzymes capable of degrading lignocellulosic compounds [14]. It is believed that biological pretreatments generate less negative impacts to the environment in comparison with other types of pretreatments, due to the low generation of waste and low energy requirements as the pretreatment can be carried out at ambient temperatures [6]. Nevertheless, the results obtained in wheat and rice straw have shown that the rate of hydrolysis and level of degradation are low compared with others pretreatments [15,16].

As observed, the above mentioned pretreatment technologies display advantages and drawbacks using different agricultural wastes and based on different evaluation criteria. Main criteria are the effect on the lignin structure upon the straw used, biogas yield, energy consumption, cost of reagents, viability of the process for technology transfer and process sustainability [8]. This work aimed to compare the effectiveness of a biological (fungi fermentation), thermal and chemical (acid/heat addition) pretreatment on the degradation of lignocellulosic compounds from bean straw and subsequently, on the biogas production from the hydrolysates produced during each pretreatment. Agricultural residues, like wheat, rice and oat straw, are already common substrates in anaerobic digesters [5], while bean straw is not yet used as a substrate despite its large potential in crop producer countries like Mexico. Therefore, a further knowledge on the effect of pretreatments as well as on the AD of this substrate is needed. Prior batch experiments demonstrated that biogas production from bean straw with rabbit manure as inoculum is effectively assessed, however, maximum biogas production was not completely met due to volatile fatty acids accumulation and thus acidification in the system occurred [17]. Therefore, continuous experiments, which imply the use of bioreactors, were used in this work for a better control of parameters and performance. Additionally, methane yield, cost of reagents, energy consumption/production associated to each pretreatment were also compared.

2. Materials and methods

2.1 Feedstock

Bean straw and rabbit manure (inoculum) were obtained from local farmers in Zacatecas. The straw corresponds to the variety of bean crop known as "Negro San Luis” that was harvested in October 2013. The straw was ground and sieved, to obtain a range of particle between 250 µm and 1 mm. Prior its used, the bean straw was stored in plastic containers at room temperature. The white-rot fungi *Pleurotus ostreatus*, used for the biological pretreatment, was obtained from the culture collection of the “CIIDIR, Instituto Politécnico Nacional, Durango, Mexico” and stored at 4°C. The inoculum contained (mg/Kg sample): N 1070, P 3239.7 and COD 74.58. P and N content in the inoculum contributed to macronutrient supply to the system [18].

2.2 Pretreatments of bean straw

The pretreatments were applied to the bean straw mixed with water to obtain final total solids of 8% (w/v), being the ideal total solids concentration for optimum methane production [5]. The optimal conditions of the biological and chemical pretreatment were chosen upon previous screening experiments. The biological pretreatment was carried out in flaks containing 1g straw per 30 mg fungi and 100 mL of distilled water to moisten the sample. The flasks, covered with gauze pads to allow the entry of oxygen, were incubated at 30°C and shaken at 100 rpm for a period of 28 d. Chemical pretreatment followed the procedures of Arreola-Vargas *et al.*[19] and consisted on adding HCl at 2.8 % (v/v) and heating to a temperature of 132.2 °C for 2.5 hours in a stove (Mka. binder. Mod. KT115). Thermal pretreatment followed the procedures of Bolado-Rodríguez *et al.* [10] and consisted on heating the sample in an autoclave (Mka. AESA, Mod. CV300) at 121 °C and 20 psi for 1 h. The hydrolysates obtained from each pretreatment were diluted to adjust the chemical oxygen demand (COD) to 2-2.5 g/L and thus the total sugars (TS) to 1.5-2 g/L in the three hydrolysates. Then the pH was adjusted to 7.

2.3 Bioreactors set up and operation

In order to compare biogas production from the hydrolysates produced on each pretreatment, three independent upflow anaerobic sludge blanket (UASB) bioreactors were run for 37 days. Two bioreactors were made of transparent acrylic and one of polyvinyl chloride (PVC) with a working volume of 1.1 L. The temperature of the bioreactor was controlled at 30°C (±3) by using an electric jacket. Table 1 shows the parameters of design and operation used in each bioreactor.

Table 1. Parameters used in the design and operation of bioreactor.

Parameter	Bioreactor 1	Bioreactor 2	Bioreactor 3
Hydrolysate	Biological pretreatment	Chemical pretreatment	Thermal pretreatment
Flow rate (mL/d)	240	230	235
HRT (d)	4.58	4.34	4.68
Initial COD (g/L)	2.34	2.64	2.10

Organic load rate (gCOD/L·d)	0.45	0.57	0.49
Inoculum (gVS/L)	10	10	10
Temperature rate (°C)	28-32	28-31	27-30

2.4 Analysis

COD, VS and total solids were evaluated using standard methods (APHA 5220, APHA 2540-B, APHA 2540-E, respectively) [20]. Total sugars analysis was carried out using the phenol-sulphuric acid method [21]. The quantification in percentage of lignocellulosic compounds before and after the pretreatments was done using TAPPI (T222 om-98 and T212) methods [22]. Volatile fatty acids (VFA) were determined with a gas chromatograph (Agilent Technologies 7890A) with a flame ionization detector and a polar capillary column (DB-FFAP). The biogas production in the bioreactors was calculated every third day using pressure manometers (Keller America Inc.®).

2.5 Calculations.

The volume of biogas produced was calculated with the changes in pressure using Boyle’s law. Methane yield was calculated from the volume of biogas produced, assuming 70% CH_4 and 30% of CO_2, divided by the COD entering the system. The percentages of degradation for lignin and hemicellulose were calculated from the difference between the initial and the final content in percentage after each pretreatment. Total energy consumption in Watts hour (Wh) was calculated from de energy consumed of the equipment used on each pretreatment (incubator, autoclave, stove) based on the maximum capacity (volume) of each equipment.

Total energy production was calculated from the total biogas produced in m^3 during the 37 days of bioreactor operation and assuming a total CH_4 content in the biogas of 70 %. Then, the m^3 of CH_4 were converted to Wh from using the CH_4 lower heating value of 35,800 KJ/m^3. The energy consumption and production was also converted to US dollars (USD) based on the price of kWh in Mexico (0.189 USD) in order to compare them with the costs of reagents. Costs of reagents were calculated based on the amount used during each pretreatment and their price in Science Company® the 15 of April 2016 (HCl $16.57 USD/L and NaOH $4.64 USD/Kg).

3. Results and discussion

3.1 Effect of the biological, acid and thermal pretreatments

Cellulose, hemicellulose and lignin content, volatile solids, total solids, dissolved COD and total sugars of the initial bean straw, as well as after the pretreatments, are shown in table 2. The cellulose, hemicellulose and lignin content of the bean straw before pretreatment (initial) display similarities with the previously reported by González-Rentería *et al.* [23], on straws coming from other varieties of bean crops. Lignin content, is however lower, in comparison with other straws such as rice and wheat straw [24,25]. This could have a positive effect on the AD, since minor percentage of lignin should lead to faster degradation rates and consequently, a higher biogas production [3].

Table 2. Results obtained from the pretreatment of bean straw and from the bioreactors operation with the hydrolysates of each pretreatment.

Parameter	Initial	Biological pretreatment	Chemical pretreatment	Thermal pretreatment
Lignin (%) (% degradation)	9.70± 0.22	7.97± 0.24 (17.83)	3.21±0.78 (66.91)	6.63± 0.59 (31.64)
Hemicellulose (%)	23.92± 0.21	13.33± 0.32 (44.27)	7.67±0.58 (67.93)	9.50± 1.25 (60.28)

(% degradation)				
Cellulose (%)	31.13± 0.26	57.89± 1.19	68.12±0.75	63.91± 3.37
Volatile solids (%)	89.54 ±0.77	NA	NA	NA
Total solids (%)	98 ± 0.23	NA	NA	NA
Dissolved COD (g/L)	2.74 ±1.21	7.91±0.81	18.87±1.87	12.45±2.01
Total sugars (g/L)	NA	7.28±0.62	14.58±0.89	10.61±0.96

The results obtained after the three pretreatments of study showed similar trends, where lignin and hemicellulose content is decreased while cellulose is release and thus a higher content is observed (Table 2). However the chemical pretreatment resulted in a lower lignin and hemicellulose content meaning a higher degradation of these compounds (66.91 and 67.93%, respectively), as well as higher cellulose content (68.12%), as compared with the biological and thermal pretreatments. Such results are close to the ones obtained in other studies using chemical pretreatments on wheat and oat straw, where lignin and hemicellulose values range between 70 – 85% [8,9] and 60 – 85 % [7,10,26], respectively, but move away from other authors in cellulose content (75 – 90%) [10,25,26].

The results of lignin and hemicellulose degradation for the thermal pretreatment are lower from the previously reported by other authors (70 - 85% and 65-85%, respectively) using rice straw, oat straw and cane waste [12,13,27]. This could partly be due to the difference in temperature and water content on each study. Several authors have reported higher values of cellulose content from bagasse (80 -85%) using temperatures above 160 °C, while for wheat and oat straw have reported lower values in cellulose (65 -80%) using temperatures of 130 °C, demonstrating the direct effect of temperature in the lignocellulosic compounds [10,12,18].

In this study, biological pretreatment was the least effective to degrade the lignin compound among the pretreatments studied, nevertheless the results are in accordance to the ones obtained using different species of white and brown rot fungi including *P. ostreatus* for lignin degradation (17-24%) using oat, wheat and soy straw [5,28] and for hemicellulose degradation (40-55%) using wheat and oat straw [15,28]. On the other hand, the results on cellulose differ slightly from other authors (60 – 80%) using rice straw and the same fungal genus [14,29]. As similar trends were encountered with the chemical pretreatment, cellulose results could be related to the characteristics of the bean straw rather than the effectiveness of the pretreatment. Higher lignin values in other types of straws [24,25] could harbor a higher amount of cellulose that is potentially released after pretreatment. Cellulose content is key to the release of sugars [7,26] and therefore, its content correlates with the concomitant difference of COD and total sugars results with respect to other authors under a similar chemical [30] and biological [14] pretreatment. Notwithstanding, aside from the aforementioned studies, to our knowledge, no studies report COD or total sugars after pretreatment, which are pivotal to understand the effectiveness of the pretreatment on biogas production.

3.2 Biogas production in the continuous experiments

The results obtained during the bioreactors operation show similar trends in biogas production, COD and total sugars in the three bioreactors (Figure 1), thus suggesting similar biodegradability of the COD/sugars regardless the pretreatment. Similarly, COD and total sugars displayed the same decreasing trend during the operation of the bioreactors (Figure 1), demonstrating that the vast majority of the COD obtained from each pretreatment, most likely corresponded to sugars. These results could also imply the same type of sugars released after the pretreatments. This study did not determine the type of sugars present in the hydrolysates, however, other authors have shown that the predominant sugars from oat and wheat straw after chemical pretreatment are glucose and xylose [30].

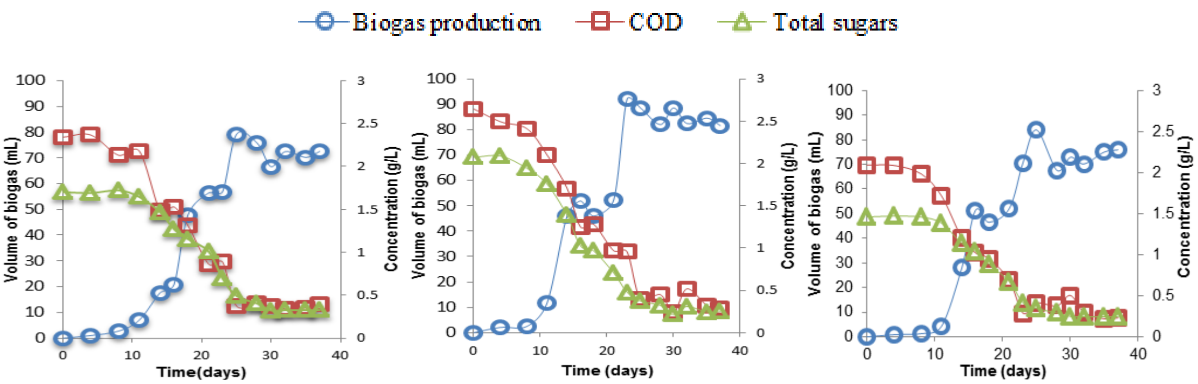

Figure 1. Results of continuous bioreactors at different pretreatments: a) biological, b) chemical and c) thermal.

After 23 days, steady state conditions were reached for the three bioreactors. The maximum total biogas production values for biological, chemical and thermal pretreatment were 646 mL biogas and 0.23 L CH_4/gCOD, 811 mL biogas and 0.25 L CH_4/gCOD, 700 mL biogas and 0.27 L CH_4/gCOD, respectively (Figure 1, Table 3). A similar time was needed by Kaparaju *et al.* [31] to reach methane yield of 0.15 L CH_4/gCOD using hydrolysates of wheat straw in a UASB bioreactor but at an organic loading rate of 2.3 g COD/L·d. Gómez-Tovar *et al.* [30] during the startup obtained 0.34 L CH4/gCOD at an organic loading rate of 1 g COD/L·d after 35 days using hydrolysates of oat straw subjected to similar chemical pretreatment. This is higher as compared to the ones obtained in the present work; however, the aforementioned authors added micronutrients to the influent which is known to increase the biogas production rate [3,6]. This study was carried out without micronutrients aiming to minimize the cost of reagents and to maintain conditions that could be applied in farm digesters.

The differences in biogas production rate for each pretreatment were consistently dependent on the organic loading rate (Table 2) rather than the source of the hydrolysates (Table 3). Thus, despite that the COD was not fully removed in the systems (Table 3), it is hypothesized that an increase in the organic loading rate would increase the biogas production if the bioreactors would have been operated longer time as occurred in other studies [32–34]. This is because microorganisms are increased and better adapted [3,5,34], which also lead to a better balance between acidogens and methanogens, thus reducing the amount of VFA accumulated and thus, the pH variations in the system (Table 3).

3.3 Comparison of methane yield, cost of reagents, energy consumption/production of the three pretreatments.

In order to evaluate the effectiveness of the pretreatment, based not only on the hydrolysis of the lignocellulosic compounds and biogas production; methane yield, energy consumption/production and the cost of reagents associated to each pretreatment were also calculated. As discussed above, the biogas production and methane yield were similar for the three pretreatments during the 37 days of the bioreactors operation. This could derive in a total energy production of 269.81, 338.72 and 292.37 Wh from the total biogas produced in each bioreactor (Table 3). However, the energy demand highly differs on each pretreatment leading to a negative energy balance on the biological and thermal pretreatment. The highest total energy consumption was encountered in the biological pretreatment; this is due to the high energy consumption of the lab scale incubator used. However, the biological pretreatment can be performed at ambient temperatures and without constant stirring [34] with the tradeoff of slowing the process.

When the three pretreatments are compared in terms of costs, it is clear that the chemical pretreatment is more expensive, and even the biogas produced cannot offset the expenses associated to the pretreatment (Table 3). This is due to the cost of reagents used on this pretreatment, particularly the NaOH required to neutralize the pH (around 2) of the hydrolysate before using it for biogas production. Nevertheless, a least expensive option such as lime, commonly available in natural limestone deposits, could be used for the neutralization of the hydrolysate [35].

In terms of viability of the process for technology transfer and process sustainability, biological pretreatments could still be considered advantageous when access to equipment and reagents is difficult as in the case of rural areas where bean crops are grown in Mexico [4]. Furthermore, the residues after biological pretreatment can be directly disposed into soil unlike chemical pretreatment residues [6, 8].

Finally, the total energy/costs associated to consumption surpass the total energy/costs production in the three pretreatments, thus demonstrating the need for further investigation towards process improvement in order to establish biogas production from bean straw as a cost-efficient and environmentally friendly technology. Additionally, research in this field should not be left aside due to the social impact that it represents, as the biogas produced could be beneficial in rural areas, where electricity access is limited and thus energy requirements are met through direct biomass combustion [1].

Table 3. Results from the bioreactors operation with the hydrolysates of each pretreatment

Parameter	Biological pretreatment	Chemical pretreatment	Thermal pretreatment
Total biogas production (mL)	646	811	700
Biogas production rate (mL biogas/gVS·d)	7.28	8.36	7.38
Methane yield (LCH_4/gCOD)	0.23	0.25	0.27
pH (influent-effluent)[a]	6.8 – 6.1	7.4-6.0	6.9– 6
VFA (mg/L)[a]	148.46	141.04	133.33
COD degradation (%)	83.13 ±2.12	89.13 ±1.34	85.18±3.01
Total sugars degradation (%)	80.72±1.21	86.29±1.78	83.28±1.62
Total energy consumption (Wh)	620 (0.132 USD)	200 (0.042 USD)	460 (0.096 USD)
Total energy production (Wh)	269.81 (0.051 USD)	338.72 (0.064 USD)	292.37 (0.055 USD)
Costs of reagents	NA	3.60 USD	NA

[a] Average results of the stationary phase.

4. Conclusion

Bean straw is a promising substrate for bioenergy production. In this work, a comparison of a biological (fungi *fermentation*), thermal and chemical (acid/heat addition) pretreatment to determine the hydrolysis of the lignocellulosic compounds and biogas production in continuous was shown. The results demonstrated that the chemical pretreatment was the most effective method for the degradation and solubilization of lignin compounds. Nevertheless, a similar trend in biogas production, COD and total sugars degradation was observed during the 37 days of the bioreactors operation, showing that the COD biodegradability and total sugars characteristics are alike regardless the pretreatment method.

The biological pretreatment had the highest energy consumption due to the energy demand needed to meet stirring and temperature conditions; however other technological and environmental factors such as the cost of reagents, corrosion, the disposal of the fibrous material after chemical pretreatment, should be considered for technology selection. Despite the low energy and cost surplus of the three pretreatments evaluated, research in this field should not be left aside due to the social impact that it represents.

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