Pre-treatments effect on the enhance of the biogas production from rice straw anaerobic digestion

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Abstract

Colombia as the third largest producer of paddy rice in Latin America, requires increasing profitability and improve its environmental performance. Focusing on the rice straw as main residue, the prevention and mitigation of environmental impacts, derived from the management and inadequate disposal of these, can be done by the valorisation through bioconversion processes. Therefore, the present research evaluates different pre-treatment alternatives to enhance the anaerobic digestion performance of rice straw, improving the biogas production in lignocellulosic materials. Alkaline and thermal hydrolysis were evaluated as pre-treatmentspre-treatments by the variation of the organic load (10 and 20 g VS, an inoculum substrate ratio of 3) in biomethane potential experiments. This was carried out in batch reactors under mesophilic conditions, each pre-treatment was evaluated per triplicate, including a control trial. The results obtained show that the alkaline hydrolysis for an organic load of 20 g VS present the highest biogas production (125.565 ml of CH_4 g⁻¹ VS fed), increasing the BMP 44.1% compared to the experiments without pre-treatment. In comparison, the thermal hydrolysis tests in 10gSV as organic load, showed an increase of 11.9% in the production of biogas with respect to the untreated substrate.

Introduction

Residues from agro-industrial activities are abundantly available and susceptible to be used in the bioconversion process, to prevent the current environmental impact of un-proper management and disposal. It is the case of rice straw, a lignocellulosic residual biomass highly available around the world. Colombia is the third producer of rice in Latin America, with approximately 2 million tonnes, with CH₄ emissions about 0.24 tonnes of CH₄ ha⁻¹ [1]. The production of rice generates 2% of the gross domestic product and is the economic support of up to 500.000 families of 21.800 rice farms [2]. Nevertheless, the paddy rice production has competitive issues due to the use of traditional farming, reducing the competitiveness of the product in the market. As a result of current practices, the disposal of the crop residues is predominantly managed either through open-burning or left in the fields uncollected for open decomposition, which leads to health and environmental impacts [3].

The anaerobic digestion is being used as a conversion technology to generate biofuels and other value added products. The anaerobic digestion comprises the conversion of organic carbon to usable products such as alcohols, volatile fatty acids and gases, through redox reactions, in which microorganisms interact in the absence of oxygen [4]. This biochemical process has different stages: 1) hydrolysis, organic matter composed of carbohydrates, proteins and lipids are transformed into soluble molecules through extracellular enzymes; 2) acidogenesis, monomers are converted into volatile fatty acids (VFAs) and CO₂ as a residue; 3) acetogenesis, in which the VFAs that were not transformed in previous stages process are oxidized to acetates by acetogens organism, leaving hydrogen molecules as the result; and 4) methanogenesis, hydrogen and CO₂ are transformed into CH₄ by hydrogen trophic methanogenesis, and acetate is converted into CH₄ and CO₂ by acetoclastic methanogenesis [5].

Accordingly, previous studies have evaluated the anaerobic digestion of rice straw, in the frame of the search for environmentally friendly and cost-efficient alternatives to minimize the impacts and generate value-added products [6, 7]. However, anaerobic digestion efficiency implies the follow up of control variables such as: temperature, pH, inoculum, organic load and C/N ratio; also, the use of physical, chemical and biological pre-treatmentspre-treatments to enhance the degradation potential, especially with lignocellulosic biomass. Therefore, the present research evaluates different pre-treatment methods to improve the biomethane potential (BMP) of rice straw available in the department of Tolima, Colombia.

Materials and methods

Substrate and inoculum

As a first stage, the rice straw was supplied by Biocultivos S.A coming from different farms located in Tolima, Colombia; and a physicochemical characterization was conducted, see Table 1. The rice straw was dried at 60°C for 24h, and a particle size reduction was applied to guarantee its conservancy before the pre-treatmentspre-treatments and the biochemical methane potential assays. The inoculum used was provided by Alpina S.A, from a stabilized anaerobic reactor.

Two (2) different pre-treatments were evaluated: 1) Alkaline hydrolysis by 10 g l⁻¹ NaOH in a relation 10:1 liquid:solid. it was autoclaved for 60 minutes at 102 °C, then it is washed with tap water until reaching an approximate pH of 9, and put in contact with a 3 % H_2O_2 solution [8]. 2) Thermal hydrolysis, the rice straw is hydrated with distilled water in an 8:1 liquid:solid ratio, and autoclaved for 30 min at 102°C. The evaluation of the pre-treatments was based on the initial characterization of the substrate; the organic load varied between 10 and 20 grams of volatile solids (VS), and an inoculum to substrate ratio of 3 was used.

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	Total solids (%)	Volatile solids (%)	Total Kjeldahl nitrogen (%)	C/N ratio
Rice strawa ^a	92.35±0.02	72.93±0.03	1.06±0.15	43.21
Inoculum ^b	4.79±0.00	4.31±0.02		

^{*a*} Sample on dry basis.

^b Sample on wet basis.

Experimental procedure

The evaluation of the BMP of the pretreated rice straw was based on changes in the initial organic load, evaluating loads of 10 and 20 g VS, with a substrate to inoculum ratio (S/X) of 3 [9]. Each pre-treatment was evaluated per triplicate, along with a test of the rice straw with only a particle reduction process. The anaerobic digestion process was conducted in 250 ml amber bottles (further called reactors), which were filled once with a quantity of the pre-treated substrate, inoculum, and distilled water to complete 200 ml of working volume; and sealed with silicone to guarantee anaerobic conditions. The reactors were placed in a thermostatically controlled bath under mesophilic conditions ($35 \pm 1 \circ C$) for 21 consecutive days, and the volume of biogas was measured by the displacement of a 0.5M NaOH solution (pH > 9) used as a CO2 trap [10], biogas composition was measured using BIOGAS 5000[®] Landtec and samples were collected for the further quantification of the volatile solids (VS) removal (g/L), see Figure 1.



Figure 1. Experimental configuration, for anaerobic assessment; 1. reactors, 2. 0.5M NaOH solution, 3. silicone tubing, 4. compiler bottles.

Analytical methods

The physicochemical characterization of rice straw and digested samples were carried out according to international standards; using as methods: 2540B APHA - SM for total solids (TS), ASTM D3174 for volatile solids (VS), ASTM D1426 for Total Kjeldhal Nitrogen (TKN) and ASTM D1252 for Chemical Oxygen Demand (COD). For TS, 1 g of solid sample was taken for the substrate and 25 ml of liquid sample for the inoculum, which were taken to an oven for 24 hours at 105°C, dried and weighted. The VS were determined from the TS, where the samples were placed in an oven for 1 hour at 550°C, dried and weighted. The TKN was found from samples of 1 g of substrate, 5 g of Kjeldahl catalyst and 15 ml of H₂SO₄, which were placed in the "Bloc-Digest" digestion unit, later it was taken to a "Pro-Nitro M" distiller where the extract of the digested sample is deposited in a 4% H₃BO₃ solution with an indicator, then resultant was titrated with HCl to determine the percentage of TKN. COD was measured with commercial vials HI 93752, with range of 0 to 150 mg l⁻¹.

Results and discussion

Substrate characteristics

According to the characterization presented in Table 1, the rice straw shows a VS/TS ratio of 78.96% which is low compared to other lignocellulosic materials such as wheat straw, corn stalk and leaves, seeds and stalk; which denotes complexity of this substrate in digestive processes, high VS/ST ratios are more appropriate for optimal methane production [11]. However, it is important to highlight that the pre-treatments carried out to the substrate do not mean a change in said VS/TS ratio, as could be observed in previous studies where rice staw without pretreatment was compared with physical and chemical pre-treatments, obtaining similar ratios of this relationship for each of the characterizations [12]. In the same way, the C/N ratio (43.21) is considered high compared to other types of non-lignocellulosic residues [11]; where a proper C/N ratio (20-30) reflects an adequate supply of nutrients to microorganisms by these materials during the process [13], and suggests low concentrations of ammonia that can inhibit microbial growth [14].

Biomethane potential

The anaerobic digestion of the initial pre-treatments showed that the thermal hydrolysis had the best performance for the assays that managed an organic load of 10gVS (132.63 ml CH₄ g^{-1} VS fed), while for the combinations with 20gVS, the best performance was from the alkaline hydrolysis (125.56 ml CH₄ g^{-1} VS fed). In comparison with the rice straw with no pretreatment, the biogas yield was increased by 44.1% with alkaline hydrolysis for 20 g VS, and 11.9% with thermal hydrolysis for 10 g VS. This results are similar to previous researches, such as Chandra, Takeuchi and Hasegawa [15], and He et al. [16].

The rice straw pretreated appeared to enhance the enzymatic hydrolysis in the anaerobic digestion process, by the efficient degradation of lignin, cellulose and hemicellulose content in the substrate [12, 17]. The alkaline hydrolysis allowed the efficient degradation of complex molecules enhancing the anaerobic digestion process [12, 18]. Although, previous researches have pointed out that thermal hydrolysis as a physical pretreatment has limitations due to the high-energy and high-pressure requirements that increase costs it is necessary to carry out a complete assessment for the region which generates the biomass. It is important to remark that alkaline treatment has registered increases the methane yields for rice straw by up to 67.55% (28.83% was achieved), besides, chemical treatments can be hazardous to environment if released untreated [3].



Figure 2. BMP for the raw rice straw, thermal and alkaline hydrolysis pre-treatments.

In addition, previous researches have pointed that large amounts of organic load results in microbial activity inhibitions during the initial phases of the anaerobic digestion [19]. In accordance with these, Zealand, Roskilly, and Graham [20], conducted an experiment to test the effect of feeding frequency and organic loading rates, finding suitable organic loading rates of 1 g VS l⁻¹ with an infrequent loading 1/21d. Therefore, there is a scope for the increase of the organic load when including pre-treatments at the beginning of the process.

According with literature, anaerobic digestion of lignocellulosic biomass is not feasible without pre-treatment process, the yields of the rice straw evaluated showed a BMP yield around 70-60 ml CH₄ g⁻¹ VS [3, 6, 7]. Additionally, Figure 3 shows that, for alkaline hydrolysis, the biogas production is increased with the organic load, which suggests that there is an benefit on substrate degradability by allowing a greater enzymatic accessibility for microorganisms to the carbohydrates of the substrate as a consequence of the removal of lignin and hemicellulose [19]. Even though, it is important to highlight that the concentration of NaOH used in the alkaline pre-treatment affects biogas production, thus different authors have pointed an optimal concentration of 6%, for mesophilic batch anaerobic digestion [21, 22].



Figure 3. Biogas production performance for a retention time of 21 days; a) 10 g VS and b) 20 g VS.

In the same way, the process can be enhancing by the inclusion of other substrates that compensate the improper nutrient structure of lignocellulosic biomass itself. The inclusion of other anaerobic residues available in the country may increase the biogas yield, enhance the process stabilization, diluting inhibitory effects, generating positive synergism in digester and increasing nutrient balance; along with generating positive a economic impact in a real-scale process [19, 23, 24].

Characterization of digestate

Table 2. shows the characterization of the effluent at the end of the 21 days experiment. The effective removal of organic matter calculated for the assays with 20 g VS was of 42.04%, while for the assays with 10 g VS was of 74.51%, this data is presented as and average for all the assays assessed. Moreover, the characterization of VS and TS showed the biodegradability process, where the highest VS removals are shown for the alkaline hydrolysis pre-treatment in both organic loads, indicating a greater amount of organic matter transformed into biogas [25], and an acceleration of the digestion process with the evaluation of each pre-treatment, selectively.

	10 g VS			20 g VS		
	Alkaline hydrolysis	Thermal hydrolysis	No pre- treatment	Alkaline hydrolysis	Thermal hydrolysis	No pre- treatment
TS (g ml ⁻¹)	1.48	3.83	3.62	1.597	4.834	5.113
VS (g ml ⁻¹)	0.349	0.684	0.68	0.412	0.887	1.008
COD (g l ⁻¹)	6.6	5.65	6.35	7	7.1	7.05

Table 3. Physicochemical characterization of digestate.

Conclusions

The initial evaluated pre-treatments seem to be suitable in the improvement of the biodegradability of rice straw, generating a significant increase in the biogas yields. The thermal hydrolysis treatment with an organic load of 10 g VS increased the biogas production by 11.9%, 39.64 ml CH_4 g⁻¹ VS higher than the untreated one, while for alkaline hydrolysis is 11.9 ml CH_4 g⁻¹ VS. The results obtained are interesting to assess possible codigestion processes taking as a starting point the yields of the rice straw pretreated. Although, the evaluation of other pre-treatments is needed to recommend a real-scale process.

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