Contemporary Engineering Sciences, Vol. 11, 2018, no. 9, 415 - 423
HIKARI Ltd, www.m-hikari.com
https://doi.org/10.12988/ces.2018.8232

Biogas Production from Pretreated Maize Wastes

Elely Castro-Cogollo, Karina Ojeda-Delgado and Yuly Ramirez-Ramos

Chemical Engineering Program
Process Design and Biomass Utilization Research Group
University of Cartagena, Campus Piedra Bolivar
Street 30 # 48-152. Cartagena, Colombia

Abstract

The use of fossil fuels affects the environment due to the increase of pollutants such as sulfur and carbon dioxide. New resources have been proposed increase the energy production. Thus, agricultural waste can be used as raw material to obtain biogas which represents an alternative form of energy in rural communities where there is no direct access to electric power as a conventional energy source.
In this paper, the production of biogas from corn residues using ruminal liquid and pig manure as inoculum, by applying mechanical pretreatments, using urea and NaOH, and catalyzed with nanoparticles, was evaluated.

Keywords: Biogas, maize, ISR, pretreatment, urea, nanoparticles

1. Introduction

Biomass has become a renewable energy source that can contribute significantly in supplying the rapidly increasing energy demand in a sustainable way [19]. Clear benefits are that biomass fuels increase agricultural productivity and they have relatively a clean combustion when compared with the fossil fuels; although some greenhouses are produced, these are far less than those produced by fossil fuels [7]. Biogas production is constituted as a renewable energy source; this process is environmentally friendly because it uses the increasing amounts of organic waste produced worldwide [11]. Biogas has been widely promoted for its economic and environmental benefits; its capacity to utilize wide range and different mixes of biomass flows and its ease of implementation in smaller units [22]. It leads to a lesser dependency on the non-renewable fossil fuels, it is carbon dioxide neutral, also it provides cheaper fertilizers, and it creates an integrated waste management system which reduces the water pollution [17].

Anaerobic digestion (AD) is a suitable technology for organic materials management, and it has potential to provide clean and reliable energy. Around the world, several studies have been carried out using biomass as mono-substrates; however the AD process could turn difficult because of the nutritional imbalance, lack of diversified microorganisms and the effect operational factors [6]. The co-digestion process is recommended to overcome this difficulty, since it improves the process stabilizations, increasing the load of biodegradable organic matter inside the bioreactor. However, lignocellulosic biomass has complex structure which is the main obstacle for degradation process.

Therefore, the main objective of this study was to evaluate the effect of three chemical pretreatments to the substrate over the biogas production from maize agricultural wastes (leaves and stalks), co-digested with ruminal fluid (RF) and pig manure (PM), in order to improve the biogas productivity.

2. Materials and Methods

Lignocellulosic maize wastes being constituted by 50 % (w/w) leaves and 50 % (w/w) stalks were chosen as the raw material for biogas production. Hemicellulose, cellulose, and lignin were determined to characterize the residual maize biomass. RF and PM were used as inoculums. Some of their characteristics are mentioned below:

- ✓ PM has been extensively used for the production of biogas since the assurance that animal manures are wealthy with various kinds of microorganisms [5]. PM is composed of biodegradable material and is considered a good base for anaerobic digestion process, since it contains buffer capacity and a wide variety of nutrients [20]. It has high contents of chemical oxygen, suspended solids, nitrogen, and phosphorus compounds [28].

- ✓ RF possesses high cellulosic-degrading properties and enhances the digestion of lignocellulosic biomass by hydrolyzing the bonds between cellulose, hemicellulose, and lignin [24]. Rumen microorganisms are able to decompose the rigid lignin molecular structure and its fermentation is associated with the formation of biogas rich in methane. This inoculum possesses a high hydrolytic and acidogenic activity when using lignocellulosic biomass as substrates [27].

2.1 Experimental methodology

The experiments were conducted over a period of 15 days, and the biogas production was quantified based on the liquid displacement method [2, 18]. For the experiments, anaerobic digesters of 500 mL, with a working volume of 350 mL were used. The biodigesters were manually stirred and the methane production through the mentioned method was recorded every 24 hours. Each reactor was flushed with nitrogen to assure anaerobic conditions [25, 26].

Three chemical pretreatment to the substrate were applied, using a substrate particle size of 0.5mm and inoculum/substrate ratio (ISR) of 1:1; pretreatment is mainly applied to improve the digestibility of cellulose by increasing enzyme accessibility [3]. The specific operating conditions regarding to the three different pretreatment are described below:

Urea pretreatment: This treatment was performed with a urea solution of 10% w/w, in a solid liquid ratio of 1:15 at 80 °C for 20 hours in a shaker.

Urea Pretreatment combined with nanoparticles Fe_3O_4-ZnO: In this treatment was added 1 g of nanoparticles per each 10 g of substrate to be pretreated, with a urea solution of 10% w/w in a solid liquid ratio of 1:15 at 80 °C for 20 hours.

Synthesis of zinc oxide nanoparticle was done through green chemistry method, using extracts of mango tree leaves (*Mangifera indic*a). Zinc chloride was used as the precursor agent.

Alkaline pretreatment with NaOH: This treatment was performed in an autoclave for 30 minutes at a temperature of 121°C, using NaOH 1% w/v. The solid liquid ratio was 1:15.

3. Results and Discussion

Table 1 shows the content of hemicellulose, cellulose and lignin for maize wastes, compared with other types of biomass that were analyzed in other studies.

Table 1. Hemicellulose, cellulose, and lignin content

Parameter (%w/w)	Method	This research	[21]	[14]
		Maize Stalk and leaves	**Coffee wastes**	**Sisal fiber wastes**
Cellulose	Gravimetric	47.39	33.5	63.0
Hemicellulose	analysis -HPLC	40.43	24.97	18.0
Lignin	(NREL/ASE)	26.37	17.80	8.6

According to the information shown in Table 1, the main component of the lignocellulosic maize wastes is cellulose; this represents a large potential in biogas production, in spite of its degrading difficulty [6]. The smallest component is lignin; this is the most recalcitrant component of the plant cell wall, and the higher the proportion of lignin, the higher the resistance to chemical and enzymatic degradation [13]. Hemicellulose, on its behalf, is constituted as a barrier that surrounds the cellulose fibers, and it protects the cellulose from the cellulose enzyme attack. In lignocellulosic materials, cellulose is tightly linked to hemicellulose and lignin, and these bonds hinder their biodegradability [15]. In this regard, a proper pretreatment is necessary to remove the lignin, degrade the hemicellulose and change the crystalline structure of cellulose in order to release the cellulose, improving at the same time the enzymatic hydrolysis [3].

Pretreatment is an important process to transform lignocellulosic biomass to high value chemicals [3]. Pretreatment clears away the physical and chemical barriers that make native biomass recalcitrant and makes cellulose amenable to enzymatic hydrolysis [9,10].
Three chemical pretreatment were applied to the substrate using urea, NaOH, and urea combined with nanoparticles Fe_3O_4-ZnO. It should be noted that these pretreatments are considered chemical-mechanical since there was a previous size reduction to 0.5 mm particle size. After the pretreatment of the substrate, this was washed and neutralized to a pH between 6 and 7. Since the substrate was chemically treated, the volatile solids (VS) contents were determined to know the amount of substrate to be added in each biodigester. Table 2 shows the VS values for pretreated biomass.

Table 2. Volatile solids of biomass after a chemical-mechanical pretreatment

Parameter	Pretreatment	Leaves (% w/w)	Stalks (% w/w)
VS	Urea	90.94	98.51
	Urea combined with nanoparticles Fe_3O_4-ZnO	92.76	97.02
	NaOH	98.77	99.58

Figure 1 shows the comparison between the daily methane productions from the mechanically and chemically pretreated and the pretreated biomass just mechanically.

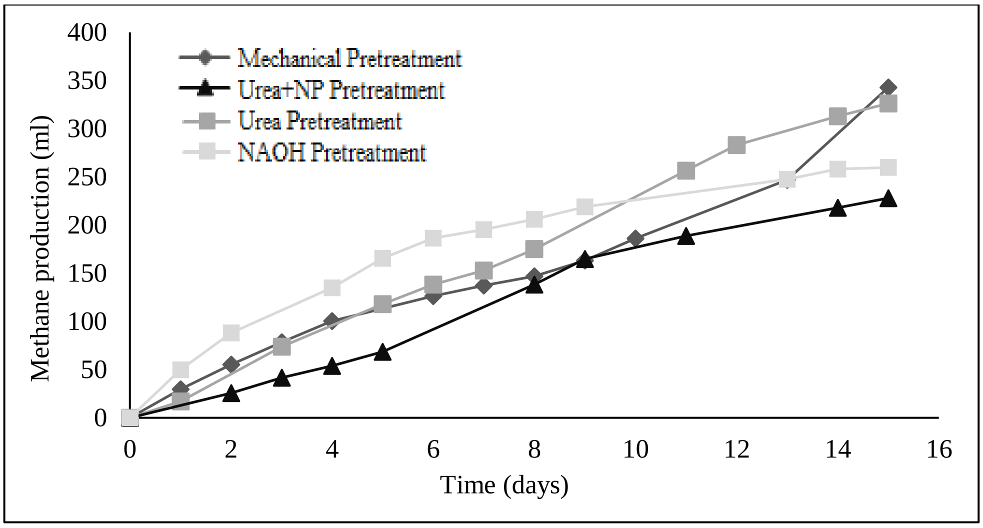

Figure 1. Daily biogas productions of pre-treated biomass.

According to Figure 1, the biogas production from pretreated biomass with urea and NaOH had a higher production of methane until day 14 and 13, respectively, when these treatments were compared with the mechanical pretreated system; but at day 15, the pretreated biomass only mechanically, obtained the highest production, surpassing it by 4.91%. This behavior was possibly due to:

- *Lignin content.* The efficiency of NaOH pretreatment depended on the lignin content of the material to be treated. The biomass used in this research contained 26% lignin, a little high compared to 7.06% of the cassava leaves evaluated by [16] and 12.7% for rice straw evaluated by [4], where the degradability of biomass and reduction of lignin were higher. Biomass with these low amounts of lignin and pretreated with NaOH improved methane production [23] and methane yield [8].

- *High concentration of heavy metals*. Methane production from pretreated biomass using urea and Fe_3O_4-ZnO nanoparticles was low when compared to the other systems, since high concentrations of elements like Fe and Zn can inhibit the biological degradation process in anaerobic reactors [1].

- *Nitrogen supplementation.* The application of the chemical pretreatment with urea contributed a considerable amount of nitrogen from an organic source (urea) for the biodegradation of the substrates; this promoted the production of biogas during much of the process [12].

Although the production of the mechanical pretreated system increased considerably during the last day, increasing its accumulated methane production, the combination of these two types of pre-treatment (chemical-mechanical) improved biodigestability and increased biogas production during most of the process and significantly improved the efficiency of enzymatic hydrolysis [3,12].

4. Conclusions

The application of a chemical pretreatment using urea and NaOH to the substrate generates stability in the biodigesters throughout the AD process. The contribution of the pretreatment with urea allows to an accelerate decomposition of the substrate during initial stages of the process, promoting the biogas production. However, implementing mechanical pre-treatment presents better results when compared with the application of chemical-mechanical pre-treatment using urea combined with Fe_3O_4-ZnO nanoparticles.

Acknowledgments. Authors want to thank to the University of Cartagena, for the financial support to the Research Project 012-2015.

References

[1] E. Abdelsalam, M. Samer, Y. Attia, M.A. Abdel-Hadi, H.E. Hassan, Y. Badr, Comparison of nanoparticles effects on biogas and methane production from anaerobic digestion of cattle dung slurry, *Renewable Energy*, **87** (2016), 592 -598. https://doi.org/10.1016/j.renene.2015.10.053

[2] B. Budiyono, I. N.Widiasa, S. Johari, S Sunarso, Increasing Biogas Production Rate from Cattle Manure Using Rumen Fluid as Inoculums, *International Journal of Science and Engineering*, **6** (2014), no. 1, 31-38. https://doi.org/10.12777/ijse.6.1.31-38

[3] H. Chen, J. Liu, X. Chang, D. Chen Y. Xue, P. Liu, H. Lin and S. Han, A review on the pretreatment of lignocellulose for high-value chemicals, *Fuel Processing Technology*, **160** (2017), 196–206. https://doi.org/10.1016/j.fuproc.2016.12.007

[4] Y. Dai, M. Si, Y. Chen, N. Zhang, M. Zhou, Qi Liao, D. Shi, Y. Liu, Combination of biological pretreatment with NaOH/Urea pretreatment at cold temperature to enhance enzymatic hydrolysis of rice Straw, *Bioresource Technology*, **198** (2015), 725–731. https://doi.org/10.1016/j.biortech.2015.09.091

[5] D. Divya, L.R. Gopinath, P. Merlin Christy, A review on current aspects and diverse prospects for enhancing biogas production in sustainable means, *Renewable and Sustainable Energy Reviews*, **42** (2015), 690–699. https://doi.org/10.1016/j.rser.2014.10.055

[6] K. Hagos, J. Zong, D. Li, C. Liu and X. Lu, Anaerobic co-digestion process for biogas production: Progress, challenges and perspectives, Renewable and Sustainable Energy Reviews, **76** (2017), 1485–1496. https://doi.org/10.1016/j.rser.2016.11.184

[7] G.M., Herbert, A. Krishnan, Quantifying environmental performance of biomass energy, *Renewable and Sustainable Energy Reviews*, **59** (2016), 292–308. https://doi.org/10.1016/j.rser.2015.12.254

[8] L. Janke, A. Leite, K. Batista, S. Weinrich, H. Sträuber, M. Nelles and W. Stinner, Optimization of hydrolysis and volatile fatty acids production from sugarcane filter cake: Effects of urea supplementation and sodium hydroxide pretreatment, *Bioresource Techno*logy, **199** (2016) 235–244. https://doi.org/10.1016/j.biortech.2015.07.117

[9] L. Janke, S. Weinrich, A. Leite, F. Terzariol, M. Nikolausz, M. Nelles, W. Stinner, Improving anaerobic digestion of sugarcane straw for methane produ-

ction: Combined benefits of mechanical and sodium hydroxide pretreatment for process designing, *Energy Conversion and Management*, **141** (2017), 378–389. https://doi.org/10.1016/j.enconman.2016.09.083

[10] L. Jonsson and C. Martín, Pretreatment of lignocellulose: Formation of inhibitory by-products and strategies for minimizing their effects, *Bioresource Technology*, **199** (2016), 103–112. https://doi.org/10.1016/j.biortech.2015.10.009

[11] R. Kumar, K. Karimi, M. Tabatabaei, Ilona Horváth, Recent updates on biogas production - a review, *Biofuel Research Journal*, **3** (2016), 394-402. https://doi.org/10.18331/brj2016.3.2.4

[12] C. Martínez Hernández, Y. García, Utilización de pre-tratamientos básicos y específicos para la producción de biogás. Revisión y análisis, *Revista Ciencias Técnicas Agropecuarias*, **25** (2016), no. 3, 81-92.

[13] T. Mohammad, K. Keikhosro, Pretreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production: A Review, *International Journal of Molecular Sciences*, **9** (2008), 1621-1651. https://doi.org/10.3390/ijms9091621

[14] A. Mshandete, L. Björnsson, A. Kivaisi, M.S.T. Rubindamayugi, Bo Mattiasson, Effect of particle size on biogas yield from sisal fibre waste, *Renewable Energy*, **31** (2006), 2385–2392. https://doi.org/10.1016/j.renene.2005.10.015

[15] S. Neshat, M. Mohammadia, G. Najafpoura, P. Lahijani, Anaerobic co-digestion of animal manures and lignocellulosic residues as a potent approach for sustainable biogas production, *Renewable and Sustainable Energy Reviews*, **79** (2017), 308–322. https://doi.org/10.1016/j.rser.2017.05.137

[16] L. Niño, A. Acosta, R. Gelves, Evaluation of chemical pretreatments for enzymatic hydrolysis of lignocellulosic residues cassava (Manihot esculenta Crantz), *Revista Facultad de Ingeniería de la Universidad de Antioquia*, **69** (2013), 317 – 326.

[17] J. Ogbulie, C. Ngumah, J. Orji, E. Amadi, Biogas potential of organic waste in Nigeria, *Journal of Urban and Environmental Engineering*, **7** (2013), 110-116. https://doi.org/10.4090/juee.2013.v7n1.110116

[18] N. Partha, P. Elaiyaraju, Biogas production from co-digestion of orange peel waste and jatropha de-oiled cake in an anaerobic batch reactor, *African Journal of Biotechnology*, **11** (2012), no. 14, 3339-3345. https://doi.org/10.5897/ajb11.2622

[19] D. Patowary, H. West, M. Clarke, D.C. Baruah, Biogas Production from Surplus Plant Biomass Feedstock: Some Highlights of Indo-UK R&D Initiative, *Procedia Environmental Sciences*, **35** (2016), 785 – 794. https://doi.org/10.1016/j.proenv.2016.07.094

[20] T. Pérez, I. Pereda, D. Oliva, M. Zaiat, Anaerobic digestion technologies for the treatment of pig wastes, *Cuban Journal of Agricultural Science*, **50** (2016), no. 3, 343-354.

[21] C. Triana, *Producción De Etanol a Partir De Residuos Provenientes Del Cultivo Del Café*, PhD Tesis, Universidad Nacional de Colombia Sede Manizales, 2010.

[22] O. Tunrayo, K. Helming, A. Voinov, H. Wiggering, Integrating agronomic factors into energy efficiency assessment of agro-bioenergy production – A case study of ethanol and biogas production from maize feedstock, *Applied Energy*, **198** (2017), 426–439. https://doi.org/10.1016/j.apenergy.2017.02.017

[23] S. Vigueras, G. Zafra, M. García, M. Martínez and J. Pérez, Efecto del pretratamiento sobre la biodegradabilidad anaerobia y calidad microbiológica de lodos residuales secundarios, *Revista Mexicana de Ingeniería Química*, **12** (2013), 293-301.

[24] D.M. Wall, B. Straccialini, E. Allen, P. Nolan, C. Hermann, P. O'Kiely and J.D. Murphy, Investigation of effect of particle size and rumen fluid addition on specific methane yields of high lignocellulose grass silage, *Bioresource Technology*, **192** (2015), 266–271. https://doi.org/10.1016/j.biortech.2015.05.078

[25] X. Wang, X., Lu. F. Li and G. Yang, Effects of Temperature and Carbon-Nitrogen (C/N) Ratio on the Performance of Anaerobic Co-Digestion of Dairy Manure, Chicken Manure and Rice Straw: Focusing on Ammonia Inhibition, *PLOS One*, **9** (2014), no. 5, e97265. https://doi.org/10.1371/journal.pone.0097265

[26] E. Yildirim, O. Ince, S. Aydin, B. Ince, Improvement of biogas potential of anaerobic digesters using rumen fungi, *Renewable Energy*, **109** (2017), 346 – 353. https://doi.org/10.1016/j.renene.2017.03.021

[27] Z. Yue, W. Li, H. Yu, Application of rumen microorganisms for anaerobic bioconversion of lignocellulosic biomass, *Bioresource Technology*, **128** (2013), 738–744. https://doi.org/10.1016/j.biortech.2012.11.073

[28] J. Zhou, R. Zhang, F. Liu, X. Yong, X. Wu, T. Zheng, M. Jiang, H. Jia, Biogas production and microbial community shift through neutral pH control during the anaerobic digestion of pig manure, *Bioresource Technology*, **217** (2016), 44-49. https://doi.org/10.1016/j.biortech.2016.02.077

Received: February 20, 2018; Published: March 14, 2018