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Bio-Methane Potential (BMP) of Cassava Pulp Waste and Effect of Alkaline Pre-Treatment

Tiềm năng mê tan sinh hoá của bã thải sắn và ảnh hưởng của tiền xử lý bằng kiềm

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Abstract

Cassava starch processing industry produces cassava pulp as a by-product or waste. In the well-known Duong Lieu village, this waste is released in surrounding environment without treatment causing serious environmental problems. The study aimed to (1) determine the Biomethane Potential (BMP) of the waste and to (2) find out if alkaline pre-treatment would improve it. Different cassava pulp samples were going through BMP test: untreated sample; pre-treated samples at different NaOH doses of 2, 6, 8 wt.% (dry weight-based) and pre-treated samples at different $NaHCO_3$ doses of 2, 4, 6, 8 wt.% (dry weight based). BMP assays were conducted in 590 mL bottles at 37 °C for 40 days. As the result, BMP of the untreated waste was 281 $NmLCH_4/gVS$ and alkaline pretreatment increased BMP of the waste up to 479 $mLCH_4/gVS$ by treatment with NaOH 6 wt.% and 450 $mLCH_4/gVS$ by treatment with $NaHCO_3$ 6 wt.%. In addition, there was a significant reduction of lignin content of the substrate after alkaline pre-treatment. The results show that cassava pulp waste has moderate potential for biogas recovery. In addition, alkaline pre-treatment by either NaOH or $NaHCO_3$ would significantly improve its BMP, possibly thanks to the reduction of lignin content.

Keywords: Biomethane potential (BMP), cassava pulp waste, alkaline pre-treatment.

Tóm tắt

Bã thải sắn là sản phẩm phụ và là chất thải của quá trình chế biến tinh bột sắn. Tại làng nghề chế biến công sản Dương Liễu nổi tiếng, bã thải sắn được thải ra môi trường xung quanh mà không được xử lý gây ra vấn đề môi trường nghiêm trọng. Nghiên cứu có mục đích (1) xác định tiềm năng Mê-tan sinh hoá (BMP) của bã thải sắn và (2) ảnh hưởng của tiền xử lý bằng kiềm đến thông số này. Các mẫu bã thải sắn khác nhau đã được xác định BMP gồm: mẫu chưa được tiền xử lý; các mẫu được tiền xử lý ở các liều lượng NaOH khác nhau là 2, 6, 8% wt.% (theo khối lượng khô) và các mẫu được xử lý trước ở các liều $NaHCO_3$ khác nhau là 2, 4, 6, 8 wt.% (theo khối lượng khô). Thí nghiệm xác định BMP đã được tiến hành trong chai 590mL ở 37°C trong 40 ngày. Kết quả cho thấy BMP của chất thải chưa được xử lý là 281 $NmLCH_4$ / gVS và tiền xử lý kiềm đã làm tăng BMP chất thải lên tới 479 $mLCH_4$ / gVS đối với NaOH 6 wt.% và 450 $mLCH_4$ / gVS đối với $NaHCO_3$ 6 wt. %. Hàm lượng lignin của các mẫu chất thải sau tiền xử lý cũng đã được giảm đi đáng kể. Như vậy, chất thải bột sắn không qua tiền xử lý có tiềm năng khá tốt để thu hồi khí sinh học. Thêm vào đó, tiền xử lý bằng kiềm bằng NaOH hoặc $NaHCO_3$ có tác dụng tăng tiềm năng sinh khí sinh học đáng kể, rất có thể đã nhờ vào việc xử lý được đáng kể hàm lượng lignin.

Từ khóa: Tiềm năng mê-tan sinh hóa (BMP), bã thải sắn, tiền xử lý bằng kiềm.

1. Introduction

The cassava starch processing industry is developed in Vietnam with over 100 large-scale cassava starch processing plants and over 4,000 small and medium-sized processing facilities. However, the processing of cassava starch creates a huge amount of cassava pulp residue with an average of 5 tons cassava pulp/ton of starch product [1]. Cassava pulp is a waste of lignocellulose form containing a part of the starch and should be reused or recycled in different ways. In Duong Lieu village, a very small part of cassava pulp is reused as animal feed but it is over the demand. Some big factories started investing in the system of pressing and drying pulp residues for selling, but it is quite expensive, very low profit that might not suitable for small-scale facilities in the village. International recent research on recycling of this biomass includes: enhancing bioconversion for ethanol production, sugar production, or composting [1-5]. Biogas recovery from this material was not much-paid attention. A study in Thailand reported a significant methane potential of the waste collected with 0.37 L CH_4/ gVS [6] while data on the Bio-Methane Potential (BMP) of the cassava pulp in Vietnam was not found.

Biochemical methane potential or Bio-methane potential (BMP, CH_4/gVS) is an important parameter for determining the ability to convert a material into biogas. By definition, it is a measure of anaerobic

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biodegradability of an organic matter, determined by measuring the amount of methane produced from a sample which is incubated at favorable anaerobic conditions and at a certain temperature.

Cassava pulp waste is a type of lignocellulosic substrate and its methane production depends on their complex structure, which might limit their biodegradability. The structure of lignocellulosic materials is mainly composed of cellulose, hemicellulose, and lignin, strongly linked to each others. Cellulose and hemicelluloses are quite easily degradable by anaerobic microorganisms and can be converted to methane. However, lignin limits their accessibility to hydrolytic enzymes, reducing their degradation [7,8]. Various pretreatment methods could make changes in the physical and chemical composition of lignocellulose materials by breaking down the linkage between polysaccharides and lignin. Pre-treatments include mechanical, chemical (alkaline or acidic), thermal, and biological processes or a combination of them. In many cases, alkaline pre-treatment exhibits as the cost-effective, easily applicable method in comparison with acidic or thermal pre-treatment [7,8]. The effect of alkaline pretreatment of cassava pulp waste on its methane potential is still unknown.

The objectives of the study were (1) to determine the Biomethane Potential (BMP) of the cassava pulp waste sample collected in Duong Lieu village and (2) the effect of alkaline pre-treatment by sodium hydroxide and sodium bicarbonate on composition and anaerobic biodegradability of the waste.

2. Materials and Method

2.1. Substrate Collection, Analysis and Pre-Treatment

A composite sample of cassava pulp waste was collected in Duong Lieu village, Hanoi, Vietnam. The sample was sorted manually for eliminating visible inert materials, ground and mixed using a blender, then were analysed in terms of dry matter content (DM), volatile solids (VS) (according to APHA 2006), organic carbon content, and nitrogen content (according to TCVN 6498: 1999, TCVN 6644: 2000). Lignin content, cellulose content, and hemicellulose content of the samples were analysed according to TAPPI T222, TAPPI T17, and TAPPI T204. The samples were stored for about 2 days in 5 °C refrigerator before alkaline pre-treatment and BMP test.

A part of a sample, then, went through alkaline pre-treatment using Sodium Hydroxide (NaOH) or Sodium bicarbonate ($NaHCO_3$). The pretreatment was performed in 590 mL Duran bottles in batch mode and a total solid content of 50 gTS/L. In each bottle, the sample was soaked in the NaOH or $NaHCO_3$ solution at the dose of 2, 4, 6, 8% gNaOH or $NaHCO_3$/gDM (wt.%). The bottles then were closed and kept at 37 °C in an incubator for 120 hours, with daily manual stirring. After pre-treatments, samples were dried at 80 °C for 48h for analysis of the above parameters.

2.2. Biochemical Methane Potential (BMP) Experiment

BMP experiment: The BMP was determined in anaerobic batch reactor of 590 mL DURAN bottles (BMP reactor) with hermetically sealed stopper and controlled gas opening valves. For each reactor, 5g VS of substrate and 1mL nutrient solution - which is prepared according to literature [9] was added. The effective volume was maintained at 490 mL by adding inoculums (obtained from a lab reactor; TS of 8%WW and VS of 67%TS) leaving 100 mL headspace for gas phase. The headspace was flushed with a gas mixture of 80% N_2 and 20% CO_2. The reactor, then, was kept at a temperature-controlled mechanical shaker operating at 37 °C and 100 rpm mixing. Biogas is withdrawn every 2 to 5 days. Methane volume measurement was conducted by liquid displacement method after the biogas passing through 5% NaOH solution in order to absorb CO_2 [9].

In addition to reactors for substrates, a blank reactor was set up with deionized water instead of substrates, and a reactor for pure cellulose was set up as a control reactor. Cumulative methane volume for each reactor was recorded and the net methane volume of a substrate was obtained by subtracting the methane volume of the substrate reactor from that of the blank reactor. Finally, the net methane production will be converted to a value at standard temperature and pressure per gram volatile solid of the substrate (NmL/gVS).

Estimation of ultimate methane production (uBMP) and kinetic constant (k): Degradation of each substrate can be assumed to follow a first-order rate of decay [9]: $BMP = uBMP\,[1 - \exp(-k^* t)]$, where: *BMP* (NmL of CH_4/gVS) is the cumulative methane volume at time t (day); *uBMP* (NmL of CH_4/gVS) is the ultimate methane production and; *k* (day^{-1}) is the first-order kinetic constant. *uBMP* and *k* were estimated using sigmaplot software.

3. Results and Discussion

3.1. Characterization of Untreated and Alkaline Pre-Treated Cassava Pulp Waste

The result of proximate analysis of untreated samples showed that the waste has dry matter content of 8.4%WW, and VS of 98.5% DM which is quite similar to a cassava pulp sample collected in Thailand [6]. High moisture content and VS content of the waste should be favorable for biological treatment. The ultimate analysis resulted in C/N ratio of 124 which is very high compared to optimum value for anaerobic digestion, but this ratio will be adjusted by nutrient addition in BMP experiment.

Table 1. Characteristics of cassava pulp samples (* data from [6])

Sample	DM (%WW)	VS (%WW)	Cellulose (% DM)	Lignin (%DM)	Hemicellulose (% DM)	TOC (mgC/gDM)	TKN, (mgN/gDM)
Cassava pulp sample in this study	8.4	98.5	12.6	7.6	65.2	367	3.0
Cassava pulp sample in a study in Thailand*	8.7	98.1	12.5	1.9	-	447	2.8

Table 2. The main composition of original cassava pulp and $NaOH/NaHCO_3$ pretreated samples

	Lignin	**Hemicellulose**	**Cellulose**		**Lignin**	**Hemicellulose**	**Cellulose**
Sample	**% DM**	**% DM**	**% DM**	Sample	**% DM**	**% DM**	**% DM**
Without pre-treatment	7.4	65.2	12.6		7.4	65.2	12.6
NaOH 2 wt%	5.6	57.2	15.2	$NaHCO_3$ 2wt%	6.6	54.0	18.7
NaOH 4 wt%	5.0	51.8	17.4	$NaHCO_3$ 4 wt%	5.5	52.9	17.6
NaOH 6 wt%	3.2	50.9	16.1	$NaHCO_3$ 6wt%	4.0	51.2	16.7
NaOH 8 wt%	0.8	43.9	12.4	$NaHCO_3$ 8 wt%	3.0	50.5	13.9

The untreated sample consisted of cellulose: 12.6% DM, hemicellulose: 65.2% DM, lignin: 7.6% DM, confirming the lignocellulose characteristic of the material. Normally, for fresh waste samples, the contents of some of the above components could be lower. However, in this case, there is a possibility that the collected sample had been in the environment for some days before the collection date which resulted in the decomposition of starch content. In the case that the starch content has reduced, the contents of the other components that are harder to decompose (lignin, hemicellulose, etc) could increase correspondingly. High lignin content is considered to be one of the important barriers to biological conversion. It is in the range found in literature for other cassava pulp samples which was reported at 1.9%; 2.4% or 16.3% [6,10,11]. In another hand, this lignin level is comparable with other lignocellulose materials that were often objects for pre-treatment study such as rice straw: 7.4%; corn straw: 7.5%; wheat straw: 6.5% [12,13,14].

The purpose of alkaline pretreatment is to remove or dissolve lignin and/or reduce the crystallinity of the biomass which is finally expected to result in enhancing enzymatic hydrolysis rate and yield. Table 2 shows lignin, hemicellulose, and cellulose content while Fig. 2 shows lignin/hemicellulose removal rate and cellulose increasing rate (% of untreated sample's values) of pretreated samples. We can see the gradually decreasing trend of both lignin and hemicellulose as $NaOH/NaHCO_3$ dose increased while cellulose content tends to increase then reduce according to the increase of chemical doses. Maximum lignin removal rate of 89% could be obtained for NaOH 8 wt% (lignin content reduces from 7.4% DM to 0.8%DM). Maximum hemicellulose removal rate of 33% could be obtained at the same treatment (hemicellulose content reduces from 65.2% DM to 43.9%). However, highest cellulose content was not observed at highest NaOH dose nor highest $NaHCO_3$ dose but at $NaOH_4$ wt% and $NaHCO_3$ 2%.

Changes of the main composition by alkaline pre-treatment are quite similar to that for rice straw, corn straw reported in literatures [12,13,15]. Literature reported a maximum lignin removal rate of 46.7% at NaOH 10% for rice straw [15] or 43.2% at NaOH 10% for corn straw [12]. Therefore, the effect of NaOH pre-treatment on lignin reduction for cassava pulp in this study is relatively good. It is possible that NaOH effectively attacks the linkage between lignin and hemicellulose in lignin-carbohydrates complexes, in particular, it cleaves the ether and ester bond in the complex structure. During the NaOH pre-treatment reaction, sodium hydroxide is dissociated into OH- and Na^+ and, as OH^- concentration increases, the rate of hydrolysis reaction increases accordingly [8].

3.2. BMP of Untreated and NaOH/NaHCO3 Pretreated Samples

Cumulative methane production curves obtained from BMP test are graphed in Fig. 1 (NaOH 4 wt.% pretreated sample is missing due to a technical failure during the experiment). For all curves, net methane production tends to stop increasing at the end of the experiment. The first order kinetic model describes rather well the anaerobic degradation of all substrates with R^2 always above 0.97. Then, *uBMP* and reaction rate constant *k* are shown in Table 3. The cellulose control sample has *uBMP* of 419 NmL/gVS which is quite close to values reported in the literature [16,17]. The result of cellulose sample demonstrates the good response of inoculums used in the test.

Table 3. Methane production at the end of BMP essays and estimated uBMP of all samples

		BMP at the end of experiment (Nml CH_4/gVS)	Estimated *uBMP* (Nml CH_4/gVS)	*K* (day $^{-1}$)	R^2
Cellulose control		408.4	419	0.120	0.972
Without pre-treatment		281.6	281	0.183	0.999
NaOH pre-treatment	NaOH 2wt%	324.8	321	0.238	0.997
	NaOH 6wt%	485.7	479	0.140	0.990
	NaOH 8wt%	452.7	446	0.160	0.991
$NaHCO_3$ pre-treatment	$NaHCO_3$ 2wt%	303.3	307	0.189	0.993
	$NaHCO_3$ 4wt%	340.5	344	0.184	0.994
	$NaHCO_3$ 6wt%	449.0	450	0.192	0.996
	$NaHCO_3$ 8wt%	354.0	359	0.195	0.990

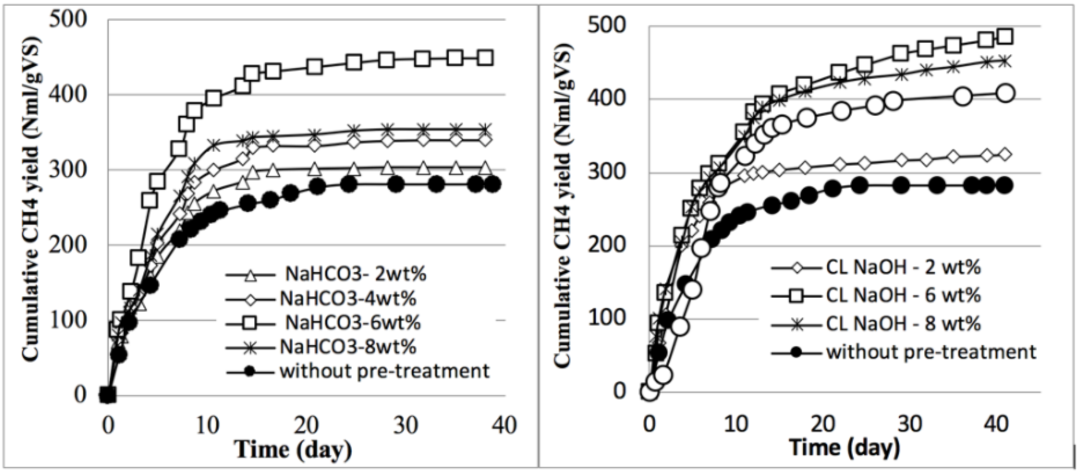

Fig. 1. BMP curve of cellulose control, original cassava pulp and NaOH/$NaHCO_3$ pretreated samples

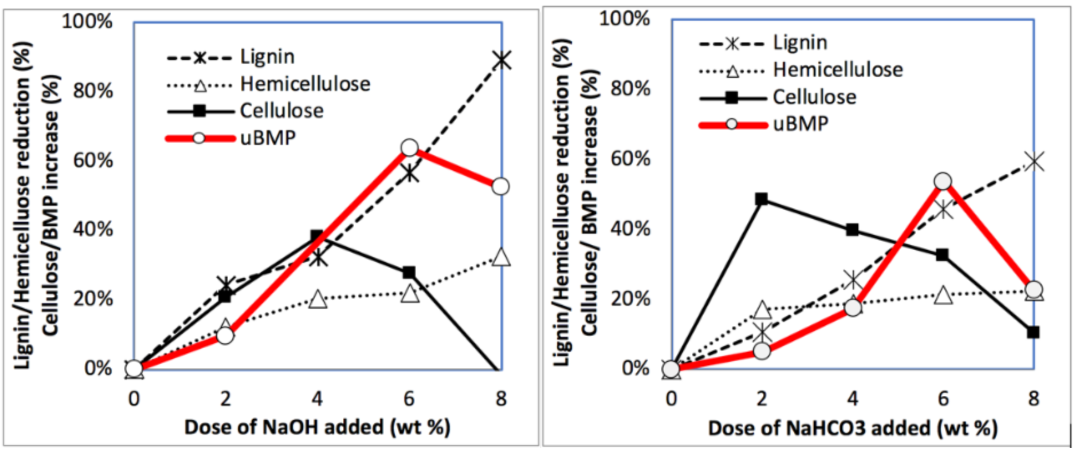

Fig. 2. Changes in main composition and uBMP of NaOH/$NaHCO_3$ pretreated samples
(Reduction rate /Increase rate are in percentage of untreated samples values)

For untreated cassava pulp, *uBMP* was 281 (NmLCH_4/gVS), indicating that bio-methane potential of the waste is relatively good, especially in comparison with other lignocellulose materials. It was reported in literature *BMP* (NmLCH_4/gVS) of yard wastes at 123-209, corn straw at 100, rice straw at 430 [13,16,18]. Research in Thailand reported *BMP* value at 370 NmL/gVS [6], which is rather higher than the value reported in this study. Notably, lignin content of that sample (1.9% *DM*) was much lower than that of sample in this study (7.4% *DM)*. Higher lignin content could contribute largely to the low *BMP* of this study.

Alkaline pre-treatment by either NaOH or $NaHCO_3$ increased *uBMP* of the waste in all studied cases as shown in Table 3 and Fig. 2, with the increase rate of 14% - 71% for NaOH pretreatment, and 9% - 60% for $NaHCO_3$ pretreatment. It is possibly thanks to the reduction of lignin and hemicellulose. It was suggested that the removal of lignin, to some extent, increases the accessibility of the microorganism to cellulose and hemicellulose. Similarly, the removal of hemicellulose has a positive effect on the degradation of cellulose because it serves a connection between the lignin and the cellulose fibers and gives the whole cellulose-hemicellulose-lignin network more rigidity [7]. In another hand, there were possibly positive effects that could not be seen from the changing of composition such as saponification of the uronic bonds between hemicelluloses and lignin, swell fibers, and increase pore size, facilitating the diffusion of the hydrolytic enzymes [7] which might play important roles in the pretreatment.

However, picked *uBMPs* were not obtained at the highest NaOH/$NaHCO_3$ doses although higher chemicals doses made higher lignin/hemicellulose reduction. The highest *BMP* of 479 NmL/gVS, corresponding to an increase of 71%, was observed at NaOH 6 wt% pre-treated sample, following by $NaHCO_3$ 6 wt% pre-treated sample. At the highest NaOH/NaHCO3 dose, the loss of hemicellulose was highest and the increase of cellulose drop further from the top. Higher loss of cellulose and hemicellulose could be a reason BMP reduction. The other reason that could contribute to this is inhibition caused by more soluble lignin content [12,13] and toxicity caused by the leftover NaOH/$NaHCO_3$ [19], etc.

4. Conclusion

The ultimate *BMP* of untreated cassava pulp waste 281 $NmLCH_4$/gVS showing that the waste has a moderate biodegradability. Pre-treatment by NaOH (from 2 to 8 wt.%) resulted in 14% - 71% more methane yields and the highest yield of 479 $NmLCH_4$/gVS was achieved at NaOH dose of 6%. Pre-treatment by $NaHCO_3$ (from 2 to 8 wt.%) resulted in 9% - 54% more methane yields and the highest yield of 450 $NmLCH_4$/gVS was achieved at Na HCO_3 dose of 6%. Thus, it is a possible pre-treatment method for enhancing anaerobic digestion of this waste. Nevertheless, as the untreated waste has a moderate biomethane potential, anaerobic digestion with or without pre-treatment seems to be a possible method for the treatment of arrowroot waste while obtaining energy recovery.

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