Effects of sequential pretreatment of rice straw and coconut shell for improved biomethane production

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Abstract. This study aims to determine the effects of sequential pretreatment of selected agricultural biomass wastes in terms of biomass properties as well as its biomethane yield on the anaerobic co-digestion of wastes co-digested with various biomass feedstocks for power generation applications. This was carried out by determining the effects on the biomethane production using the two pre-treatments, that is 3% and 4% w/v of sodium hydroxide subject to ultrasonication and liquid hot water hydrolysis pretreatment for the rice straw and coconut shell feedstocks. As it will be used as substrates for the anaerobic co-digestion experiments; using digested manures as an inoculant. Results show that biomethane production increased by 140% and 290% from the pre-treatment of rice straw and coconut shells, respectively. With these, the pre-treated coconut shell subjected to Ultrasonication with 3% sodium hydroxide and liquid hot water shows the best effect among the pre-treatment of biomass feedstocks of rice straw and coconut shell at various sodium concentrations. The results of this experiment would give a viable estimate of the possible biomethane production from these agricultural wastes.

1. Introduction
At present, feed stocks from the municipal solid waste, industry, food processing plants and wastewater treatment plant, are limited; thus, new renewable sources are sought after. With the abundant availability of agricultural biomass in the Philippines makes it a highly interesting source of feedstock, from a variety of crops like palay, corn, sugarcane, cassava, and coconut, and from livestock manure of carabao, cattle, hog, goat and dairy, that can be utilized for biogas production. These sources can serve as fuel for power generation or as feedstock for advanced biofuels production. Given these abundant supplies of biomass in the country, it would be advantageous for the Philippines to exploit these resources to address the country’s energy dependence, mitigate climate change and eventually achieve economic growth and prosperity.

Biogas is a renewable, high-quality fuel which can be produced from various organic raw materials and used for various energy services. Biogas technology has been developed and widely used over the world because it has several advantages – reduction of the dependence on non-renewable resources, high energy-efficiency, environmental benefits, available and cheap resources to feedstock, relatively easy and cheap technology for production, and extra values of digestate as a fertilizer [1]. However, the current status of biogas production and utilization varies largely among countries. To overcome the issues related to the utilization of lignocellulosic materials like rice straw and coconut shell for biogas
production, new pretreatment strategies have been evaluated and developed. One of these strategies is the combination of sodium hydroxide hydrolysis, ultrasonication, and liquid hot water pretreatment.

Typically, the ultrasonication and liquid hot water pretreatment were used to modify the lignin and cellulose structure of the biomass to generate ethanol [2] but for this case, said pretreatments were done to improve biogas yield. In a study by sodium hydroxide hydrolysis was found to substantially increase the biogas yield of rice straw. Currently, there are many researches on the pretreatment of biomass wastes similar to paddy straw using sodium hydroxide-microwave pretreatment [3], it was reported that 4% NaOH-30 minutes of microwave was found to be the best pretreatment which resulted in 65.0% decrease in lignin content and 88.7% reduction in silica content that resulted in 54.7% increase in biogas production [3]. Moreover, a mechanical disruption of algae using ultrasound homogenizer and thermo-alkaline pretreatment enzymatic hydrolysis demonstrated the best biogas yield than other pre-treatment which reached 626.5 mL/g COD with 62.65% of biodegradability [4]. Furthermore, liquid hot water pretreatment of giant reed in a Parr reactor and alkaline pretreatment was studied using the various NaOH concentrations which improve glucose yield that is significantly increased the cumulative methane yield by 63% than of the untreated biomass [5]. In addition, the ultrasonication of Cotton Gin Trash (CGT) followed by a liquid hot water pretreatment and lignolytic enzymes pretreatment combination generated high amounts of sugar that increased delignification and modified the cellulose structure of the CGT as confirmed by the FT-IR Spectrum [2].

However, a combination of these pretreatments (ultra-sonication, liquid hot water, and NaOH hydrolysis), has not been tested in rice straw (RS) and coconut shell (CS) biomass wastes. Thus, the synergic effect of these technologies may raise de-lignification, cellulose conversion, and biogas yield from RS & CS. The effect of these pretreatments over the RS & CS structure can be determined using the Fourier transform infrared (FT-IR) spectrum. In principle, FT-IR analysis is applied to study qualitatively the modifications in structure and is not utilized for quantitative analysis. However, it can be used to identify the modification in biomass structure after different pretreatments than the conventional structural examination. From a broad perspective, the requirements of the pretreatment are to (1) improve the accessibility of the enzymes to the cellulose and hemicelluloses and thereby the degradability, (2) avoid degradation or loss of the carbohydrates, (3) avoid the production of potential process inhibitors, (4) be cost and energy efficient, and (5) have low negative impact as much as possible on the environment [6].

Anaerobic co-digestion experiments were performed in this study to provide information on the long-term effects, such as eventual inhibition during the digestion of a lignocellulosic substrate. A co-digestion is often beneficial, since it supplies the system with more nutrients, leading to a better balance in the C/N ratio and in the pH. It also improves the stability of the process and increases methane yield due to positive synergistic effects thereby increasing the economic value of the biogas. This study aims to determine the effects of various pretreatment methods (alkalinity using NaOH, ultrasonication, liquid hot water using autoclave) on the biomass properties and biogas yield in the anaerobic co-digestion of agricultural biomass waste utilizing cattle (cow) manure co-digested with different biomass feedstocks such as rice straw, coconut shell, and sewage sludge as inoculum for power generation applications.

2. Materials and methods

2.1. Experimental procedure and analysis

In this study, effects of sequential alkaline-ultrasonication and hot water treatment on biogas production from rice straw and coconut shell were determined. The ultrasonication step was modified. It was simultaneously performed with basic hydrolysis using different concentrations (3 and 4% w/v) of sodium hydroxide (NaOH) solution. The ultrasonicator (Hielscher Ultrasonic Processors, Ringwood, NJ, USA) was set at the highest value of amplitude (100%) and cycle (1). The biomass was not washed prior to hot water treatment using the autoclave, thus remaining particles of NaOH can still be
present adhering with the biomass. The liquid hot water pretreatment was conducted at 121°C, 1.02 atm for 1 hr. in an autoclave using a feedstock concentration of 10% solids. The experimental procedure and analysis conducted in this study are shown in Table 1. Control set-ups were conducted using unpretreated rice straw or coconut shell as a substrate in the digester. All the experiments were done in duplicates, with biogas yield and methane concentration as response variables.

Table 1. Summary of test procedures conducted in this study.

| Test Procedures          | ASTM Standards         |
|-------------------------|------------------------|
| Moisture Content        | E 871 - 82 (2013)      |
| Elemental Analysis      |                        |
| Carbon and Hydrogen     | E 777 - 08             |
| Total Sulfur            | E 775 - 15             |
| Nitrogen                | E 778 - 15             |
| Oxygen                  | By Difference          |
| Proximate Analysis      |                        |
| VCM                     | E 872 - 82 (2013)      |
| Ash                     | E1755 - 01 (2015)      |
| Fixed Carbon            | By Difference          |
| Heating Value           | E 771                  |

2.2. Pretreatment Experiments

The experiment followed the sequence of pretreatments such as ultrasonication [2, 4, 7], with alkaline treatment through NaOH simultaneously [3, 5, 7]; and liquid hot water [2-3, 5]. As shown in Table 2, rice straw and coconut shell samples were subjected to mechanical disruption using the ultrasonication process. A solution containing 10% w/v solid biomass was put in an ultrasonicator (Hielscher Ultrasonic Processors, Ringwood, NJ, USA) with operating conditions set at the highest value of amplitude (100%) and cycle (1). Inside the reactor, ultrasonic waves create cavitation in the liquid medium (NaOH) which contains 250 grams of rice straw sample. Samples in 3,000 ml Erlenmeyer flask were manually stirred, then sonicated for 1 hr. After the ultrasonication process, the biomass was not washed prior to hot water treatment. The liquid hot water pretreatment was performed in an autoclave for 1 hr at a temperature of 121°C and working pressure of 15 psi. The slurry was drained off. The remaining solids were washed with deionized water until the washings were clean, colorless and the pH was neutral. The rice straw was then dried overnight in an oven at 105°C. Dried rice straw and coconut shell were stored in polyethylene bags and were used for proximate analysis (total solids, volatile solids, and ash). Untreated rice straw and coconut shell were also subjected to analysis to determine the extent of their degradation.

Table 2. Pretreatment conditions evaluated in this study.

| Parameters                  | Rice Straw | Coconut Shell |
|-----------------------------|------------|---------------|
| Weight of Biomass (grams)   | 250        | 250           |
| NaOH Concentration (% w/v)  | 3          | 3             |
| Ultrasonication Treatment   | 1 hr., 100%, cycle (1) | 1 hr., 100%, cycle (1) |
| Liquid Hot Water Treatment  | 121°C, 1.02 atm, 1 hr. | 121°C, 1.02 atm, 1 hr. |

2.3. Anaerobic co-digestion experiments

Batch trials were performed to investigate the effects of biogas production from rice straw and coconut shell substrates subjected to pretreatments such as ultrasonication with NaOH simultaneously; and Liquid Hot water treatment. For each batch trial, reactors were filled with the inoculum, which is cattle manure, and sewage sludge; and co-digested simultaneously with various combinations of biomass like rice straw and coconut shell. Control reactors containing only cattle manure, and cattle manure
with sewage sludge were maintained during each batch trial. Feed compositions used for the batch trials are given in Table 2. Each reactor had a total working volume of approximately 4.8 L, and duplicate reactors were used for each feed composition. The trials were performed in an environmental chamber maintained at 35°C. The digesters were mixed daily by turning them upside-down and shaking for about 20 seconds.

Biogas volumes were recorded daily. The gas collectors were marked to provide a direct reading of volume. Biogas was discharged from the gas collectors by lifting the overflow carboy above the collectors to refill the collectors with water and opening the valves on top of the digesters to allow the gas to exit. Gas sampling was done through the use of a tee connection located between the gas collector and digester which were sealed with a rubber stopper. The stopper was removed and a syringe was inserted into the tee to collect a gas sample. While gas was flowing out of the gas collector, the syringe was gradually opened to withdraw a sample. Approximately 60 mL was collected for each biogas sample which was analyzed immediately using gas chromatography unit (SRI Gas Chromatograph). Gas samples were collected daily during the batch trials. Liquid samples were taken only the first and last days of each batch trial to determine solids content characterization. The liquid samples were collected in duplicate, with approximately 75 mL of material collected for each sample. The liquid samples are subjected to moisture content determination, proximate, ultimate and heating value analysis.

3. Results and discussion

3.1. Biomass pretreatment
The rice straw and coconut shell were subjected to a sequence of pretreatments such as ultrasonication with alkaline treatment through NaOH simultaneously; liquid hot water through the autoclave. However, the ultrasonication step for this experiment was modified to simultaneously perform a basic hydrolysis using different concentrations of NaOH (3 and 4% w/v) and a control of untreated rice straw as shown in Table 1. These values were selected to avoid producing a waste chemical solution and also to reduce the pretreatment cost [8]. Another study in the literature reported that 3-4% is the optimal dose for five NaOH samples (2, 4, 6, 8, and 10%) when was used to pretreat rice straw digestibility and biogas production [3, 12]. Series of test and analysis for untreated and pretreated rice straw and coconut shells were conducted, such as % total solids and moisture content determination through proximate and ultimate analysis as shown in Table 3. The analysis shows VCM content in rice straw is significantly higher than the untreated ones. In fact, the untreated rice straw increased VCM content from 66.56% to 84.73% and 88.18%, for the 3% NaOH+U+LHW RS and 4% NaOH+U+LHW RS respectively. Also, the carbon content of the pretreated coconut shell is higher than the pretreated rice straw by 7.25 percentage points and 8.84 percentage points for 3% and 4% NaOH+U+LHW pretreatment respectively. The total solid content determination was conducted in duplicates, while moisture content determination was done in triplicates based on the ASTM E1756 standard.

As shown in Table 3, the pretreatment (using alkaline-ultrasonication and Liquid Hot water using autoclave) of rice straw and coconut shell with 3% w/v NaOH concentration (3% NaOH+U+LHW RS and 3% NaOH+U+LHW CS), yielded the highest heating value, followed by the 4% NaOH (4% NaOH+U+LHW RS and 3% NaOH+U+LHW CS). An additional examination was conducted on the ultimate, proximate analysis and heating value for the untreated and pretreated rice straw and coconut as well as the sewage sludge and cattle manure. Therefore, the said biomass samples are quite combustible in nature, as compared with the untreated rice straw. The amount of the Volatile Combustible Matter increases 30% more than the untreated ones. The said pretreatments can be interpreted that the lignin component of the rice straw is degraded during the pretreatments.

3.2. Biomass pretreatment
The effects of applying pretreatments using the Alkaline-Ultrasonication hydrolysis and Liquid Hot Water on the co-digestion of dairy cattle manure with rice straw and coconut shell, compared with the untreated residues, were determined. The said experiment undergoes 45 days of the anaerobic co-digestion process. The biogas production from rice straw and coconut shell subjected to four (4) pretreatments (i.e. Alkaline-Ultrasonication Hydrolysis and Liquid Hot water using autoclave pretreatments with varying NaOH concentration of 3% and 4% w/v) were monitored.

**Table 3. Pretreatment conditions evaluated in this study.**

| Property     | Rice Straw |               | Coconut Shell |               |
|--------------|------------|---------------|---------------|---------------|
|              | 3% w/v     | 4% w/v        | 3% w/v        | 4% w/v        |
| VCM (%)      | 84.73      | 88.18         | 78.85         | 78.19         |
| Ash (%)      | 11.26      | 4.79          | 18.78         | 19.55         |
| Fixed Carbon (%) | 4.01  | 7.03          | 2.37          | 2.26          |
| C (%TS)      | 39.33      | 37.23         | 46.58         | 46.07         |
| H (%TS)      | 5.76       | 5.48          | 5.77          | 5.64          |
| O (%TS)      | 54.58      | 57.06         | 47.42         | 48.06         |
| N (%TS)      | 0.04       | 0.02          | 0.02          | 0.02          |
| S (%TS)      | 0.28       | 0.22          | 0.20          | 0.22          |
| C:N Ratio    | 936.50     | 2326.56       | 1940.79       | 2879.19       |
| Heating Value (MJ/kg) | 15.76 | 13.08         | 19.28         | 19.33         |

Figure 1 shows that the pretreated rice straw produces higher biogas production than other pretreatments and the same effect was achieved in the pretreatment of the coconut shell, whereas 23.12 L of gas was produced (Table 4). The biogas production with co-digestion of rice straw is 1.89 times higher than the untreated ones and 1.50 times higher than the untreated coconut shell.

**Table 4. 45-days digestion results of pre-treated agricultural residues with cow manure.**

| Parameter     | Cattle Manure & Rice Straw | Cattle Manure & Coconut Shell |
|---------------|----------------------------|------------------------------|
|               | 3% w/v                     | 4% w/v                       | 3% w/v                     | 4% w/v                       |
| C/N ratio     | 27.05                      | 27.03                        | 24.79                      | 24.79                        |
| Biogas Yield (L) | 18.18                   | 12.54                        | 23.12                      | 8.44                         |
| Methane Yield (L) | 9.88                    | 6.96                         | 13.84                      | 4.77                         |
| Average Methane content (%) | 53.80                      | 53.00                        | 55.90                      | 54.50                        |

Similarly, the percent methane concentration on the different treatments shown in Figure 2 maintains in the 50% mark except for the cow manure which slightly decreased as observed on 10th to 12th day. Likewise, similar reports were reported by [9] in the anaerobic co-digestion of cow manure.
at various maceration times which resulted in a methane concentration of 58% from the co-digestion of cow manure with rice straw. Moreover, the average percent methane concentration for these treatments presented in Figure 2 are also in the 50% mark as compared to the untreated rice straw and coconut shell that it took 25 days in order to reach the 50% methane concentration. Likewise, the methane concentration on all the biogas treatments reaches above 50% on its fourth day and readings maintain with slight variations and reported same levels with other publications [9-10]. This implies that fermentation/anaerobic digestion process properly converts the waste organic matter into a mixture of carbon dioxide and methane gas [3]. Methane production trends of the treated and pretreated biomass shown in Figure 3 follows similar production trends for all the digesters. In 5 days, methane production rates using treated biomass had increased over the initial production rates (Day 4) compared with the untreated ones for more than 300%. Hence, co-digestion of pretreated biomass helps to overcome the deficiencies of mono-digestion, which typically become the rate limiting step for the AD process [11-12]. Thus, anaerobic co-digestion of different organic materials may enhance the stability of the anaerobic processes [13] because of better carbon-to-nitrogen balance. In addition, co-digestion of rice straw and coconut shell at 4% w/v reduce the methane yield as shown in table 4 due to the inhibitory effect of high ammonia and sulfide concentrations [13] and exhibits a more stable biogas production.

![Figure 2. Methane concentration after 45-day anaerobic digestion of cattle manure, treated rice straw & coconut shell.](image)

![Figure 3. Methane concentration after 45-day anaerobic digestion of cattle manure, untreated/treated Rice Straw (RS) & Coconut Shell (CS).](image)
4. Conclusion
This study focuses on the possible means of increasing methane production potential from anaerobic co-digestion of agricultural biomass waste. In agreement with results presented, it showed a positive impact on biogas production rate by biomass pretreatment using NaOH-Ultrasonication and Liquid Hot water pretreatment. The alkali-ultrasonication-liquid hot water pretreatment improved the conversion and resulted in methane yields increase of 140% & 290% from anaerobic co-digestion of rice straw and coconut shell with cow manure and sewage sludge as inoculum compared with untreated material. This study also shows how substrate composition, pretreatment methods, and operational parameters during anaerobic digestion affect the microbial consortia working in the digester.

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