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Experimental Investigation on the Sequential Pretreatment of Agricultural Biomass Wastes for Increased Biogas Production

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Abstract

Objectives: In the present work, different pretreatment methods (milling, ultrasonication, liquid hot water, and alkali hydrolysis) were evaluated on rice straw and coconut shell that can be used as a substrate for biogas production for vehicle fuel, provide heat and generate electricity. **Methods**: This was achieved by the sequential combination of ultrasonication, hot water, and alkali hydrolysis treatment at a various concentration (4% and 5% w/v) was evaluated. Additionally, Fourier Transform Infrared (FT-IR) was used as one of the methods in identifying structural differences and identification of compounds in the treated biomass. **Findings**: The results showed that the combination of ultrasonication-alkali hydrolysis, hot liquid water using 3% of NaOH improved methane yield of 150% for rice straw and 290% for coconut shell compared with the original treatment. Additionally, FT-IR identified modifications in the biomass structure after different types of pretreatments and conditions. **Application**: The results of this research are the initial steps for the development of new processes using the Ultrasonication-NaOH LHW pretreatment, for the production of biogas from agricultural biomass waste.

Keywords: Biogas, Co-Digestion, Liquid Hot Water, Methane, Pretreatment, Ultrasonication

1. Introduction

In recent years, the global effects of changing climatic patterns are becoming more evident. Scientists are expecting a continuous rise in global temperatures mainly due to greenhouse gas production. Because of the threatening after math of varying weather conditions, international cooperation among different countries was fostered to achieve the shared goal of reducing greenhouse gas emissions. The Philippines, which is deemed to be highly vulnerable to the impacts of climate change and natural hazards, committed to reducing 70% of its GHG emissions (CO2e) by 2030 based from its Business As Usual (BAU) scenario of 2000-2030. This reduction will come from the energy, transport, waste, forestry and industry sectors. As in any developing nation, energy security is one of the main concerns of the Philippine government for the country to sustain its economic growth and development. The Philippines is highly susceptible to fluctuating global prices since the country is heavily dependent on imported

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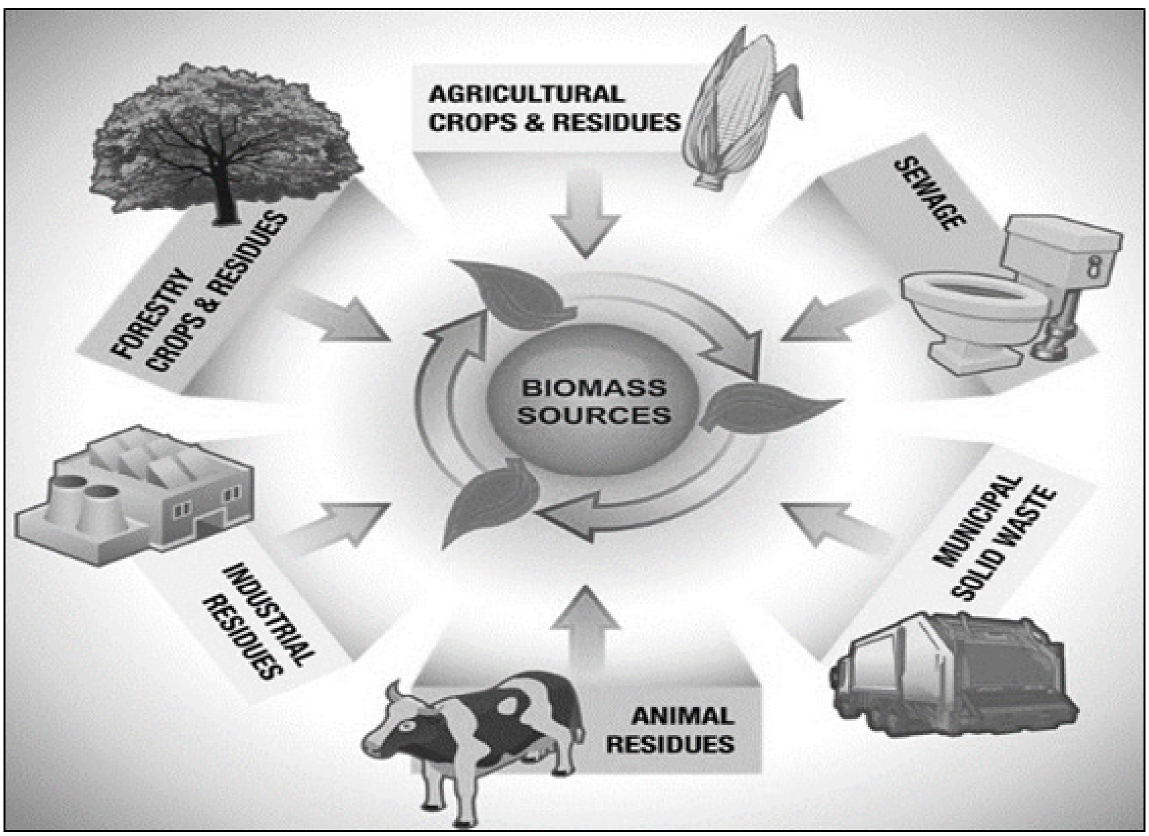
fuels to meet its fuel requirements. Hence, efforts are underway to make the energy sector more sustainable.

The Philippines' continuous efforts towards energy self-sufficiency, climate change mitigation, and poverty alleviation led to the implementation of Republic Act 9367 (R.A. 9367) also known as The Biofuels Act of 2006 which mandates the blending of biofuels to all diesel and gasoline sold in the country. Biofuels have been recognized as very promising alternative fuels because their sources could be indigenous, sustainable and renewable.

Biomass resources are projected to play a major role in mitigating climate change and meeting world energy demand in the future. At present, it is estimated that 10% the world's energy supply comes from biomass.

The Philippines, being an agricultural country, has a vast amount of biomass resources from a variety of its major crops including rice, corn, sugarcane, cassava, and coconut. This biomass sources can be used as a renewable fuel for power generation or as feedstock for advanced biofuels production (biodiesel, bio-ethanol). Given the abundant supply of biomass raw materials 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.

The Biofuels Act of 2006 (R.A. 9367) defined biomass as the organic matter, particularly cellulosic or lignocellulosic matter, which is available on a renewable basis. It is generally defined as biological material from living things that have been part of the carbon cycle for a given duration of time. Biomass comes from a variety of sources (Figure 1) which include wood from natural forests and woodlands, forestry plantations and residues, agricultural residues (straw, stover, cane trash and green agricultural



Source: http://www.bioenergyconsult.com/biomass-energy-introduction/

Figure 1. Different biomass sources.

Table 1. Summary of production of agricultural Crops data

Agricultural Crops	2015 Production (thousand metric tons)	2014 Production (thousand metric tons)	2015 Production (percent)
Palay	18,150	18,968	21.52
Corn	7,519	7,771	8.92
Coconut	14,735	14,696	17.47
Sugarcane	22,926	25,030	27.19
Banana	9,084	8,885	10.77
Pineapple	2,583	2,507	3.06
Mango	902.7	885.0	1.07
Coffee	72	76	0.08

wastes), agro-industrial wastes (sugarcane bagasse and rice husk), animal wastes, industrial wastes (black liquor from paper manufacturing), sewage, Municipal Solid Waste (MSW) and food processing waste. Currently, these types of resources are used to produce power, heat, transportation fuels, food, feeds and other specialized products both for domestic and export use.

In the Philippines, the majority of the generated agricultural residues are from its major crops, namely: sugarcane, palay, coconut, corn, and banana. Tables 1 and

Table 2. Major Crop's percentage production in the Philippines (2015)

Agricultural Crops	Production (in thousand metric tons)	% Distribution of Production		
		Luzon	Visayas	Mindanao
Palay	18,149.84	59.02	18.45	22.53
Corn	7,518.76	43.03	7.87	49.10
Coconut	14,735.19	24.35	13.63	62.10
Sugarcane	22,926.44	14.46	67.8	17.74
Pineapple	2,582.7	9.97	1.17	88.86
Banana	9,083.9	9.39	7.83	82.77
Mango	902.7	50.45	15.37	34.18
Coffee	72.3	14.41	6.44	79.14

2 shows the annual summary and percentage volume of production of major crops and livestock's in 2015[1].

As shown in the table, sugarcane (27.19 %) is the number one agricultural crop produced in the country followed by palay (21.52 %), coconut (17.47 %), banana (10.77 %), and corn (8.92 %), respectively. Also, the percentage distribution is shown in Table 2, Mindanao accounts the distribution of production in the major crops particularly the Pineapple (88.86%), Banana (82.77%), Coffee (79.14%), Coconut (62.10%) and Palay/rice (22.53%).

This study investigated the production of biogas from the anaerobic co-digestion of cattle manure with various feedstocks such as rice straw, coconut shell. Due to ammonia inhibition, different biomass pretreatment methods were employed to increase biogas yield. The feedstocks were subjected to liquid hot water pretreatments with NaOH via ultrasonication. It was noted that methane yields increased by two or threefold from the pretreatments of rice straw and coconut shells, respectively. The results of this study can contribute to the development of new processes using the ultrasonication-NaOH hydrolysis and LHW pretreatment for the production of biogas from agricultural biomass waste.

This study aimed to develop a zero-waste technology that optimizes resource recovery of agricultural wastes to produce bioenergy efficiently and in an environment-friendly approach. This could address the issues of power shortage being observed in the Mindanao, Philippines by utilizing as a fuel for the stationary non-road engines and engine-generator units.

2. Materials and Methods

2.1 Pretreatment of Biomass Feedstocks for AD

In this research, three different pretreatments (alkaline-ultrasonication, hot water) and their combinations were evaluated to obtain the best biogas production from rice

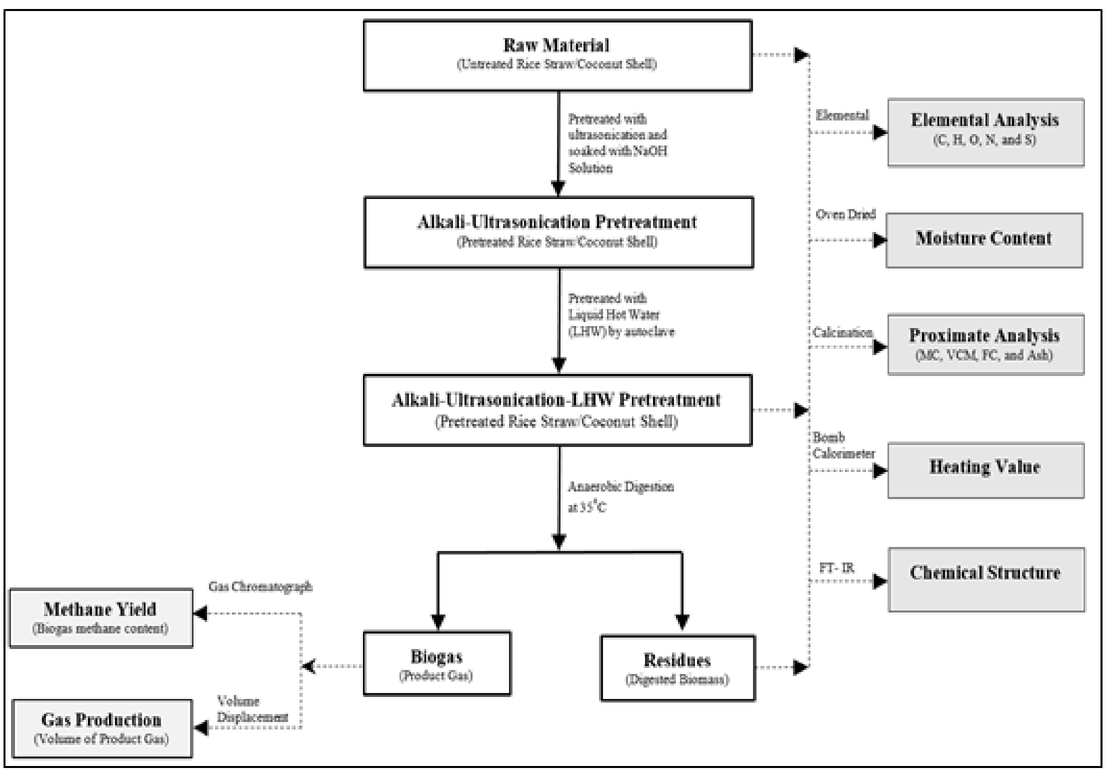


Figure 2. Schematic diagram of the biomass pretreatment experimental procedure conducted in this study.

straw and coconut shell. The experiment followed the selected sequence of pretreatment such as ultrasonication, liquid hot water. However, the ultrasonication step was modified to simultaneously perform basic hydrolysis using the different concentration of NaOH.

The experimental procedure in this study was shown in Figure 2 and the experimental design was completely randomized with the NaOH concentration as a factor with two levels (3 and 4% w/v) control of unpretreated rice straw and coconut shell. All the experiments were developed in two replicates, using yield as response variables.

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 before the hot water treatment, thus remaining particles of NaOH can be present for the hot water treatment. The liquid hot water pretreatment used Erlenmeyer flasks with 10% solution solids at 121°C, 1.02 atm for 1 h in an autoclave.

2.2 Sequential Pretreatment Experiments

The experiment follows a sequence of pretreatments (ultrasonication, liquid hot water, and alkaline treatment) through NaOH[2-7]. However, for this experiment, the ultrasonication step was modified to simultaneously perform basic hydrolysis using different concentrations of NaOH. Moreover, the experiment was completely randomized with the NaOH concentration as the factor of 3 and 4% w/v and a control of untreated (pretreated) rice straw and coconut shell. All the experiments were developed in two replicates and biogas yield considered as response variables.

As shown in Table 3, rice straw and coconut shell samples were subjected to ultrasonication process with a solution of 10% biomass solids. It was set at the highest value of 100% amplitude and full cycle as the waves create cavitation in the liquid medium (NaOH) which contains 250 grams of rice straw sample was placed in 3000 ml Erlenmeyer flask manually stirred, then sonicated for 60 min. After sonication, it was then transferred to the autoclave and subjected it for 121 °C, 15 psi for 1 h. After cooling from the autoclave, it soaked the biomass-NaOH solution for three days at a controlled temperature of 25°C. The liquid solution was drained off and the biomass was filtered and washed with deionized water until the pH becomes neutral. Then, the washed rice straw was dried overnight in an oven dryer at 105 °C. Pretreated and dried rice straw and coconut shell samples were stored in polyethylene bags and stored for the subsequent test such as proximate analysis (total solids, volatile solids, and ash) and compound determination using FT-IR. The control biomass (untreated rice straw and coconut shell) was analyzed simultaneously to determine the extent of degradation.

Table 3. Pretreatment evaluated in the anaerobic co-digestion experiments

Biomass Substrate	NaOH Conc.	Vol. of NaOH Solution	Weight of Biomass	Ultrasound Treatment	Liquid Hot Water Treatment
Rice Straw T1	3% w/v	2,000 mL	250 g	1 hour, 100%, cycle (1)	121 C, 15 psi, 1 hour
Rice Straw T2	4% w/v				
Coconut Shell T1	3% w/v				
Coconut Shell T2	4% w/v				

2.3 Biogas Production: Anaerobic Co-Digestion Processes

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. Furthermore, 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 the pH; it also improves the stability of the process and maximizing the methane due to positive synergistic effects, which can further increase the economic value.

To get a more realistic picture of the biogas production from rice straw and coconut shell substrate that are subject to pretreatments, an anaerobic co-digestion should be employed. In the present study, nine different lab-scale reactors were used to determine the methane yield in a batch process and also to evaluate the effects of the co-digestion processes using the pretreated rice straw and coconut as feedstock (substrates).

2.4 Analytical Methods: FTIR Analysis

The structural composition of the rice straw biomass before and after the pretreatments be determined using the analytical protocols NREL LAP was followed. The FT-IR spectroscopy was then used to evaluate the structural properties of the rice straw and coconut shell with and without pretreatments. Further, the infrared spectra collected range was 4000 to 700 cm^{-1} at a resolution of 4 cm^{-1}.

3. Results and Discussion

3.1 Biomass Characterization

As shown in Tables 4 and 5 the results of the characterization of digestion substrates and inoculum it was established that the coconut shell and rice straw have the potential for increasing biogas production due to lower nitrogen content, factor to consider to avoid ammo-

Table 4. Characteristics of the untreated biomass materials used in the anaerobic co-digestion experiments

Property	Cattle Manure	Sewage Sludge	Rice Straw	Coconut Shell
Moisture (% FW)	77.57	96.43	7.20	22.29
TS (% FW)	54.61	1.92	96.69	81.71
VCM (%TS)	48.54	70.38	66.56	92.42
Ash (%TS)	5.99	3.35	8.49	5.10
TKN (%TS)	5.23	39.48	5.03	5.38
C (%TS)	21.64	36.17	33.71	45.21
H (%TS)	2.83	5.13	4.73	5.93
O (%TS)	73.51	51.36	60.54	47.83
N (%TS)	0.84	6.32	0.81	0.86
S (%TS)	1.18	1.02	0.20	0.17
C:N Ratio	25.86	5.73	41.88	52.57
Heating Value (MJ/kg)	16.99	18.81	13.59	18.51

Table 5. Characteristics of the inoculum used in the anaerobic co-digestion experiments

Property	Inoculum 1 (CM)	Inoculum 2 (CM + SS)	Inoculum 3 (CM + RS)	Inoculum 4 (CM + CS)
Moisture (% FW)	86.88	86.80	80.72	80.36
TS (g/L)	106.88	112.78	158.45	190.03
VS (g/L)	83.05	85.01	107.58	173.74
Fixed Solids (g/L)	23.82	27.77	50.88	16.29
Ash (%TS)	3.52	4.30	16.14	21.97
TKN (%TS)	7.14	7.16	8.61	1.74
C (%TS)	39.02	33.95	37.86	45.05
H (%TS)	0.00	4.71	5.25	5.66
O (%TS)	59.84	59.85	55.14	48.68
N (%TS)	1.14	1.15	1.38	0.28
S (%TS)	0.00	0.34	0.37	0.33
C:N Ratio	34.16	29.63	27.47	162.05
Heating Value (MJ/kg)	17.22	16.48	13.34	16.33

nia inhibition of the anaerobic co-digestion process. However, pretreatment of the said biomass through alkali-ultrasonication and liquid hot water helps to reduce the cellulose that corresponds to the reduction of carbon content. Moreover, the digested cow manure and cow manure with pretreated rice straw produce a biogas volume of 1,100 mL from the mixture of cattle manure with 3% NaOH pretreated rice straw was observed on the 1st day. It reacted efficiently as the pretreated rice straw mixed with mixtures of cow manure and previous batch inoculum as it was already acclimatized to the environment conditions of the digester. This can be shown on the high values of the carbon to nitrogen ratio of the digested manures.

The co-digestion experiments used various mixtures from Cow Manure, Sewage Sludge, and inoculum from previous batch experiments. It was designed to reach a completely randomized experiment to optimized the desired Carbon-to-Nitrogen (C/N) ratio of the mixture of 25. A control run was done using cow manure as a sole substrate.

High volatile solid content from a coconut shell was observed and rice straw is significantly lower, demonstrating the spent microbial activity from the original process. It also showed the disparity of moisture contents, with rice straw having a low content level.

As compared to the reported[8] results by other studies, the ultrasonic irradiation process can reduce ash content, particularly in pretreated rice straw since it enhances the enzymatic hydrolysis. Besides, the results of the characterization of the biomass substrates and inoculum conducted in this study were comparable to the published data[9]. Similarly, a study[10] indicates that the using autoclave pretreatment is effective for enlarging the accessible and susceptible surface area of the cellulose and thus, improving the cellulose degradability to anaerobic microbes and enzymes. Still, the chemical pretreatment by using the NaOH solution is more recommended since the ester bonds (lignin-carbohydrate complexes) were destroyed and the intermolecular linkages and functional groups surrounding the holo celluloses, lignin, cellulose, and hemicellulose were either broken down or destroyed[10,11].

3.2 Pretreated Agricultural Biomass Wastes

As shown in Table 6 and 7, the rice straw and coconut shell biomass were subjected to varying concentrations of NaOH (3 and 4% w/v) and control of untreated rice straw. These were selected to prevent a waste chemical solution and also to reduce the pretreatment cost[12]. Furthermore, 3 to 4% w/v concentration is the optimal dose for five NaOH samples (2, 4, 6, 8, and 10%) as it was used to pretreat rice straw digestibility and biogas production presented in various publications[7,10].

Analysis and test were conducted form the untreated and treated rice strew and coconut shell biomass. The test employed is the percentage of total solids and moisture content determination through proximate and ultimate analysis as the results shown in Table 4. Furthermore, the volatile combustible matter (VCM) content in rice straw is significantly higher than the untreated ones. The untreated rice straw increased VCM content from 18-20 percentage points for the 3% NaOH+U+LHW and 4% NaOH+U+LHW rice straw pretreatments. Moreover, the carbon content of the pretreated coconut shell is higher

Table 6. Data for the rice straw pretreatment experiments

Treatment No.	Conc.	Vol of NaOH Solution	Wt of Rice Straw	Ultrasound Treatment	Liquid Hot Water Treatment
1.	3% w/v	2,000 mL	250 g	1 hour, 100%, cycle (1)	121 C, 15 psi, 1 hour
2.	4% w/v	2,000 mL	250 g	1 hour, 100%, cycle (1)	122 C, 15 psi, 1 hour
3.	3% w/v	2,000 mL	250 g	1 hour, 100%, cycle (1)	121 C, 15 psi, 1 hour
4.	4% w/v	2,000 mL	250 g	1 hour, 100%, cycle (1)	122 C, 15 psi, 1 hour

Table 7. Data for the coconut shell pretreatment experiments

Treatment No.	Conc.	Vol of NaOH Solution	Wt of Coconut Shell	Ultrasound Treatment	Liquid Hot Water Treatment
1.	3% w/v	2,000 mL	250 g	1 hour, 100%, cycle (1)	121 C, 15 psi, 1 hour
2.	4% w/v	2,001 mL	250 g	2 hour, 100%, cycle (1)	122 C, 15 psi, 1 hour

Table 8. Proximate analysis data for the rice straw pretreatment experiments

Sample	Volatile Combustible Matter (%)	Ash Content (%)	Fixed Carbon (%)	Heating Value (MJ/kg)
Pretreated – RS 1 (3% NaOH)	84.73	11.26	4.01	15.62
Pretreated – RS 2 (4% NaOH)	88.18	4.79	7.03	10.32
Pretreated – RS 3 (3% NaOH)	83.00	9.62	7.38	15.90
Pretreated – RS 4 (4% NaOH)	92.42	0.51	7.08	13.08
Pretreated – CS 1 (3% NaOH)	78.85	18.78	2.37	19.28
Pretreated – CS 2 (4% NaOH)	78.19	19.55	2.26	19.33

than the pretreated rice straw by 7 - 8 percentage points for 3% and 4% NaOH+U+LHW pretreatment respectively.

As the results presented in Table 8, the alkaline-ultrasonication and Liquid Hot water using autoclave pretreatment of rice straw and coconut shell biomass with 3% w/v NaOH concentration, yielded the highest heating value, followed by the 4% NaOH.

Moreover, the biomass samples are subjected to combustion and it was shown that it was combustible compared with the untreated rice straw. Consequently, the amount of the combustible matter had increased with 30 percentage points more than the untreated ones. Then, the said pretreatments can be interpreted that the lignin component of the rice straw is degraded during the pretreatments.

3.3 Analysis of the Substrate using FT-IR

As shown in Figures 3 and 4, the analyzed peaks for the pretreated samples of rice straw and coconut shell spec-

Table 9. Wave numbers of IR vibration frequencies used for rice straw characterization

Wave Number (cm^{-1})	Compound	Functional Groups
3335	α-cellulose	Hydrogen bond hydroxyl (Alcohol/Phenol), O-H bond stretch
2920	Lignin	Alkane (alkyl), C-H stretch
1645	Lignin	Conjugated carbonyl (amide), C=O Stretch
1320	Cellulose	C-H plane bending of cellulose I and cellulose II
898	Cellulose	β-D- cellulose

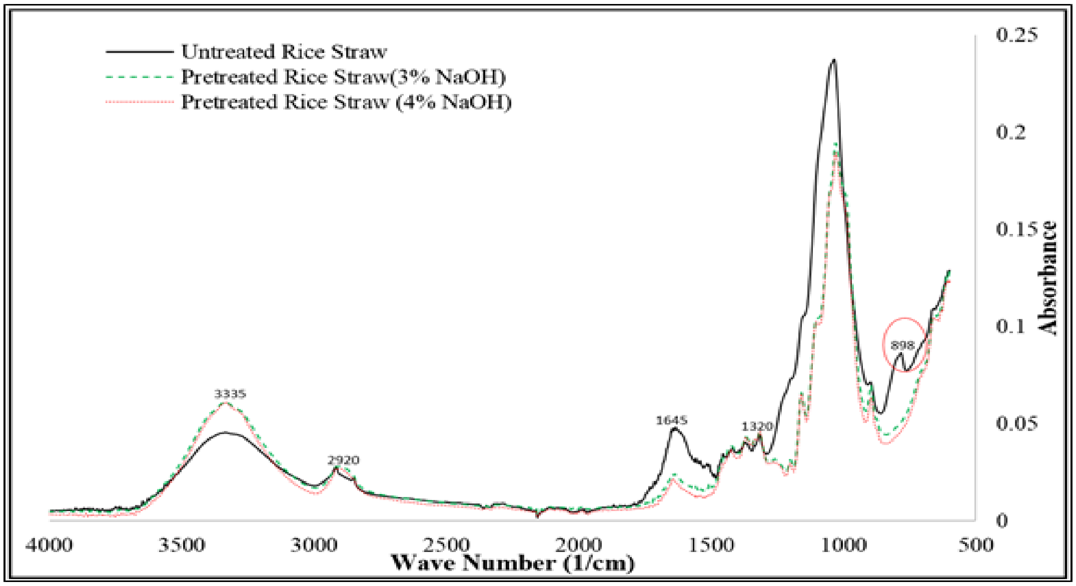


Figure 3. FT-IR spectra of the rice straw subjected to biomass pretreatments.

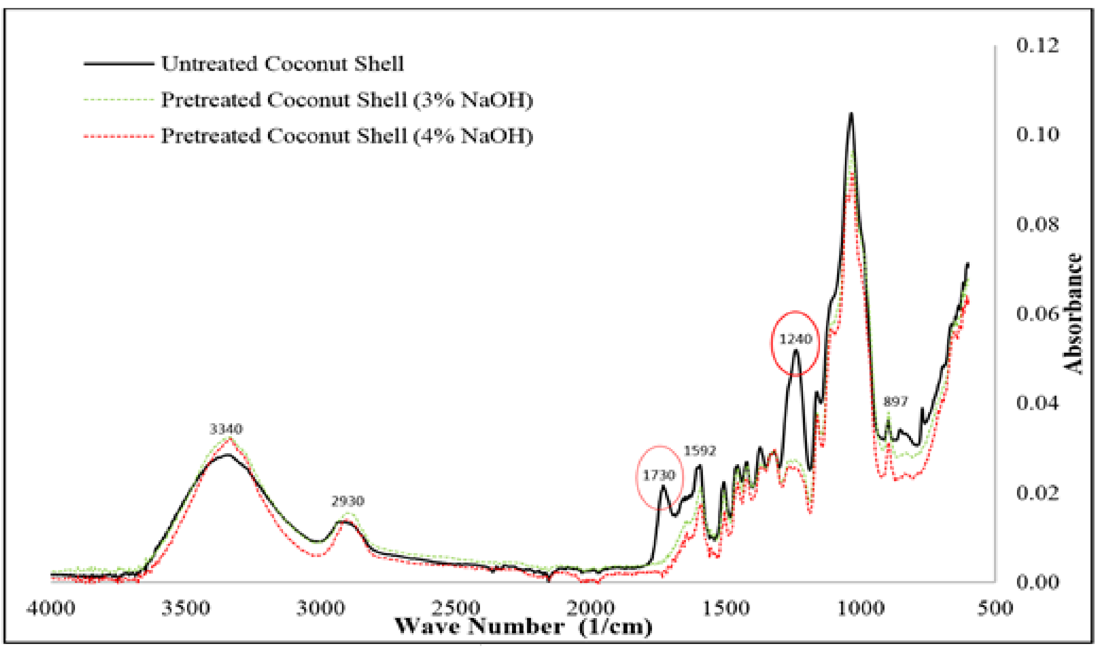


Figure 4. FT-IR spectra of the coconut shell subjected to biomass pretreatments.

tra's. In the entire sample, the highest peaks are the ones related to celluloses for pretreated rice straw biomass, which also has the highest variation among the pretreatments. The principal variation in the cellulose peaks is around 1300 to 1700 $cm^{-1}$for rice straw and similar peaks trends for the pretreated coconut shell biomass. This pretreatment leads to the increased strength of the signal (peaks) as compared with the control of rice straw and

Table 10. Wave numbers of IR vibration frequencies used for coconut shell characterization

Wave Number (cm^{-1})	Compound	Functional Groups
3340	α-cellulose	Hydrogen bond hydroxyl (Alcohol/ Phenol), O-H bond stretch
2930	Lignin	Alkane (Alkyl), C-H stretch
1730	Hemicellulose	Ester Carbonyls, C=O stretch
1592	Lignin	Aromatic, C-H deformation
1240	Hemicellulose	Ester Carbonyls, C=O stretch
897	Cellulose	β-D- cellulose

coconut shell. The NaOH-ultrasonication and liquid hot water pretreatments at varying concentrations showed the highest differences in signals (peaks) as compared with the biomass that was not subjected to any pretreatment.

The increase of improving biogas production due to the biodegradability of pretreated biomass can partly be explained by a decrease in the crystallinity of the cellulose fibers. These characteristics were measured by FTIR, having a wave number of 900 cm^{-1} for rice straw and 1200 to 1700 cm^{-1} for coconut shell (Figure 4). Further, the analyzed compounds and their IR wave numbers are enumerated, identified and presented in Tables 9 and 10.

It was observed in the 1600 cm^{-1} spectrum, the lignin signals of pretreated rice straw were reduced principally. This reduction is related to the modification of the lignin aromatic skeletal structure generated in the pretreatments mixture.

This increase of biogas production due to sequential pretreatments is desirable due to the breakdown of the crystalline structure of the lignocelluloses, and consequently due to the higher accessibility of the bacteria to the cellulose and hemicellulose[13]. Likewise, the hydrolysis of lignocellulosic biomass is the rate-limiting step in anaerobic digestion and pretreatment improves digestion efficiency and biogas production[13].

3.4 Methane Quality

The biogas production from rice straw and coconut shell subjected for sequential pretreatment were shown in Figure 5, where 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 liters of biogas was produced (Table 11). The co-digestion of rice straw increased the biogas by 1.90 times, and 1.50 times higher for the coconut shell as compared with the untreated ones.

As shown in Figure 6, the biogas produces methane components higher than the 50% concentration mark except for the cow manure as observed on 10th to the 12th day. Likewise, parallel reports were reported[14] in the related literature that the anaerobic co-digestion of cow manure at the various time resulted in a methane concentration of around 58% from the co-digestion of cow manure with rice straw. Moreover, the average percent methane concentration for these treatments shown in Table 10 are all in the 50% mark as compared to the untreated rice straw and coconut shell that it took 25 days to reach the 50% methane concentration, which was way slower than the pretreated ones.

On all the biogas treatments (Figure 7 and 8), the methane concentration level reaches above 50% on its

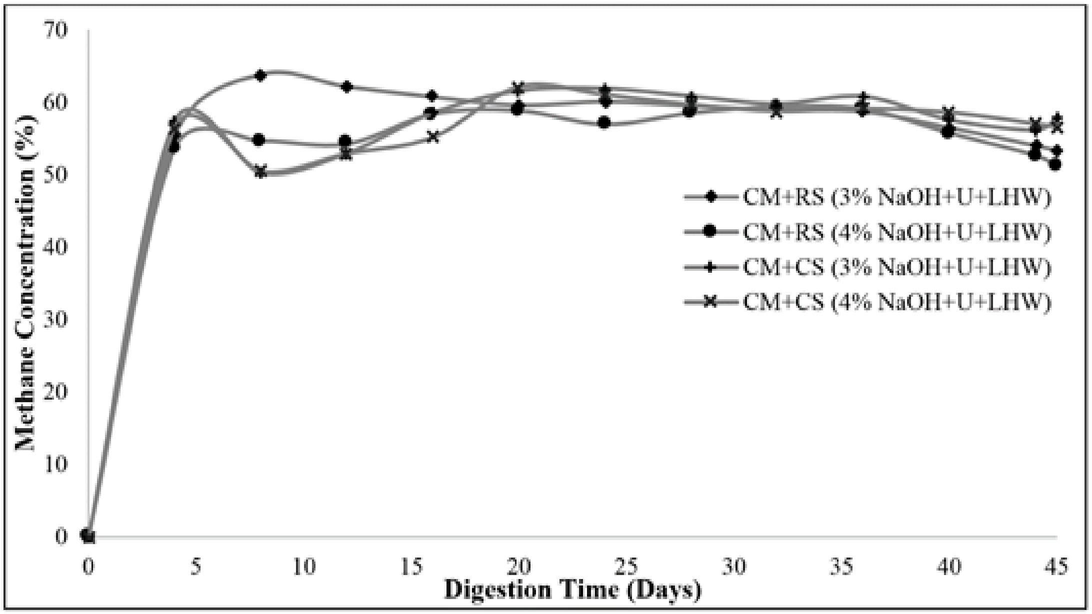


Figure 5. Average methane concentration of different AD treatments.

Table 11. Experimental Results for the different treatments at 45 days digestion time

Parameter	Cow Manure + RiceStraw[a]	Cow Manure + RiceStraw[b]	Cow Manure + Coconut Shell[a]	Cow Manure + Coconut Shell[b]
Digestion Time (d)	45	45	45	45
AD reactor pH	6.87	6.85	7.00	6.83
Biogas Yield (L)	28.84	31.45	26.96	9.06
Methane Yield (L)	15.14	13.69	14.28	4.99
Methane Content (%)	58.98	56.62	57.77	57.19

a Pretreatment with 3% NaOH-Ultrasonication and Liquid Hot water using autoclave (3% NaOH U+ LHW)

b Pretreatment with 4% NaOH-Ultrasonication and Liquid Hot water using autoclave (4% NaOH U+ LHW)

fourth day and readings maintain with slight variations and reported the same levels with other publications[9,13] presented. This implied the conversion the waste organic matter through an anaerobic digestion process into a mixture of carbon dioxide and methane gas[15].

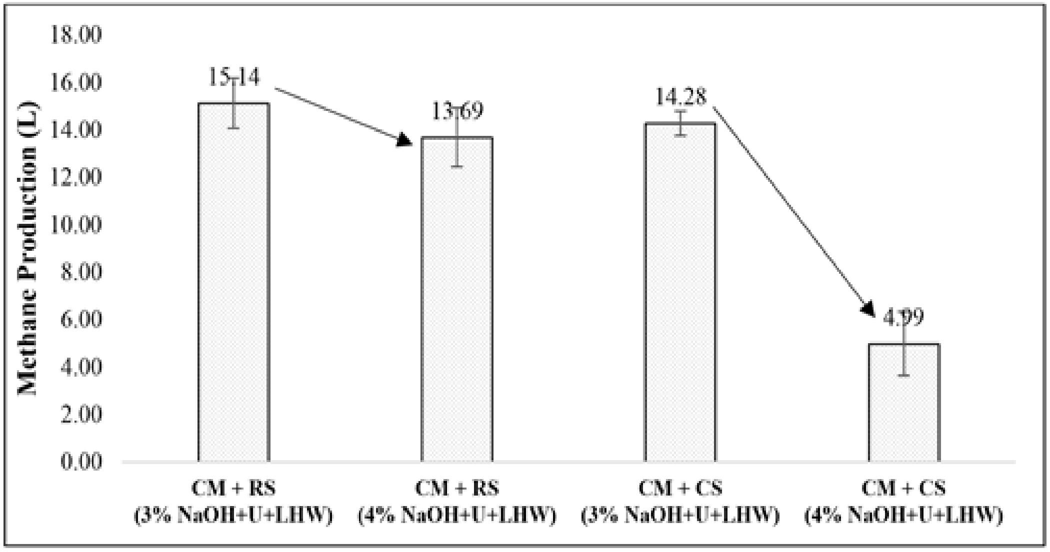


Figure 6. Cumulative methane production for pretreated biomass AD process.

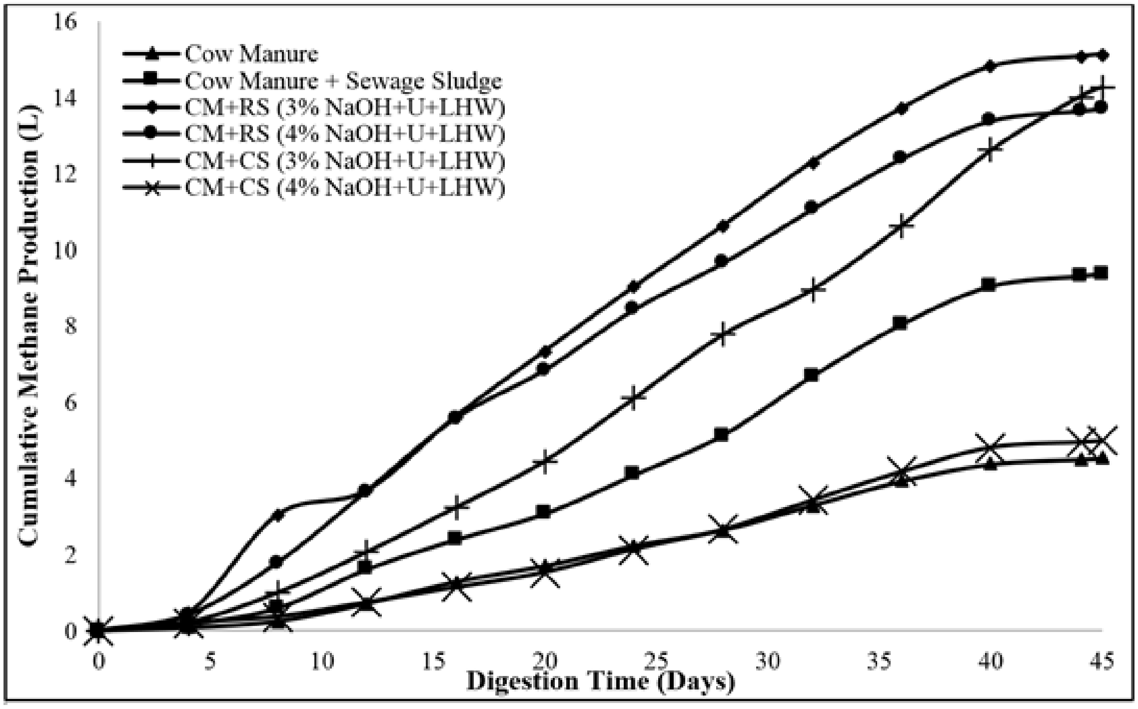


Figure 7. Methane production of different AD treatments.

The biogas production trends of the biomass (pretreated and untreated) as shown in Figure 6 follows similar production trends for all the digesters. In just five (5) days, the methane production rates using treated biomass increases over the initial production rates (Day 4) as compared with the untreated ones for more than

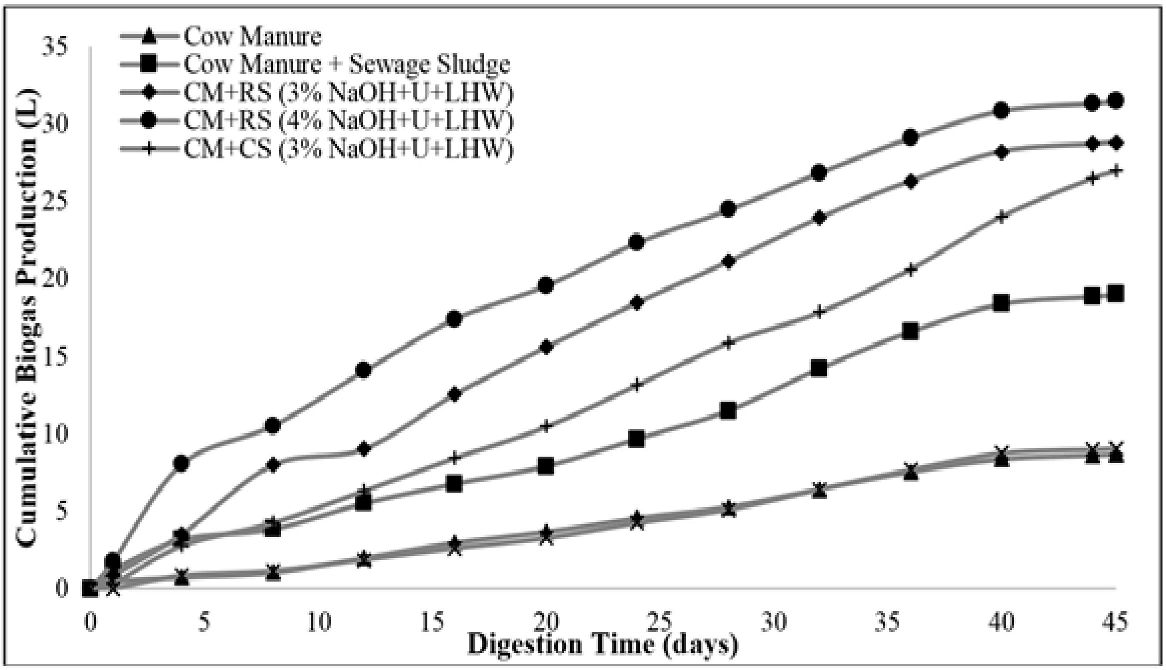


Figure 8. Biogas production of different AD treatments.

thrice than the untreated ones. 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[10,13,16,17].

3.5 Scanning Electron Microscopy (SEM) of the Pretreated Biomass Samples

The SEM of rice straw and coconut shell that re-subjected to sodium hydroxide ultrasonication and liquid hot water

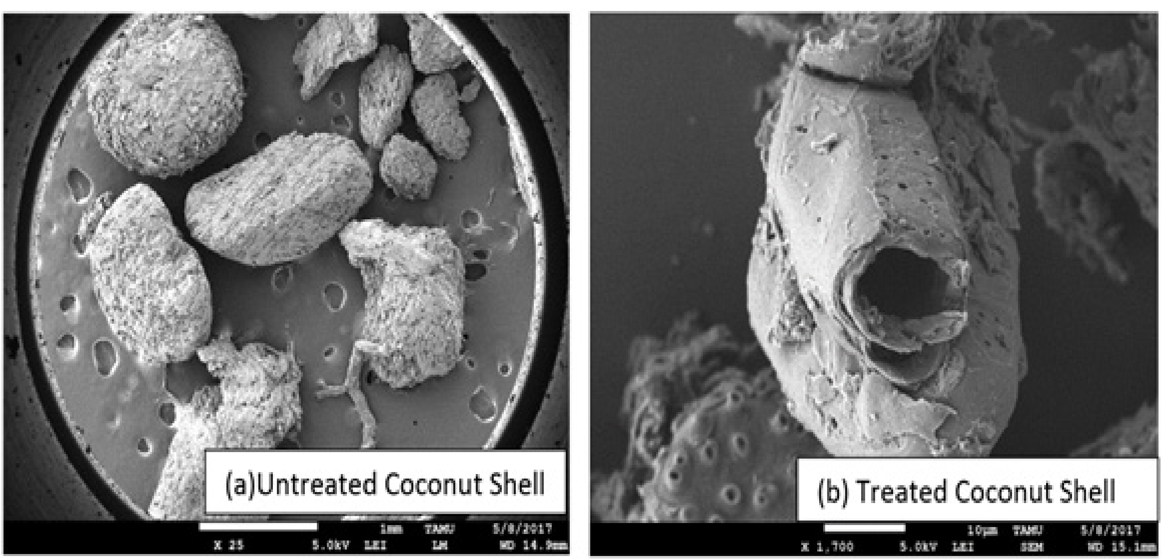


Figure 9. Scanning electron microscopy image of coconut shell.

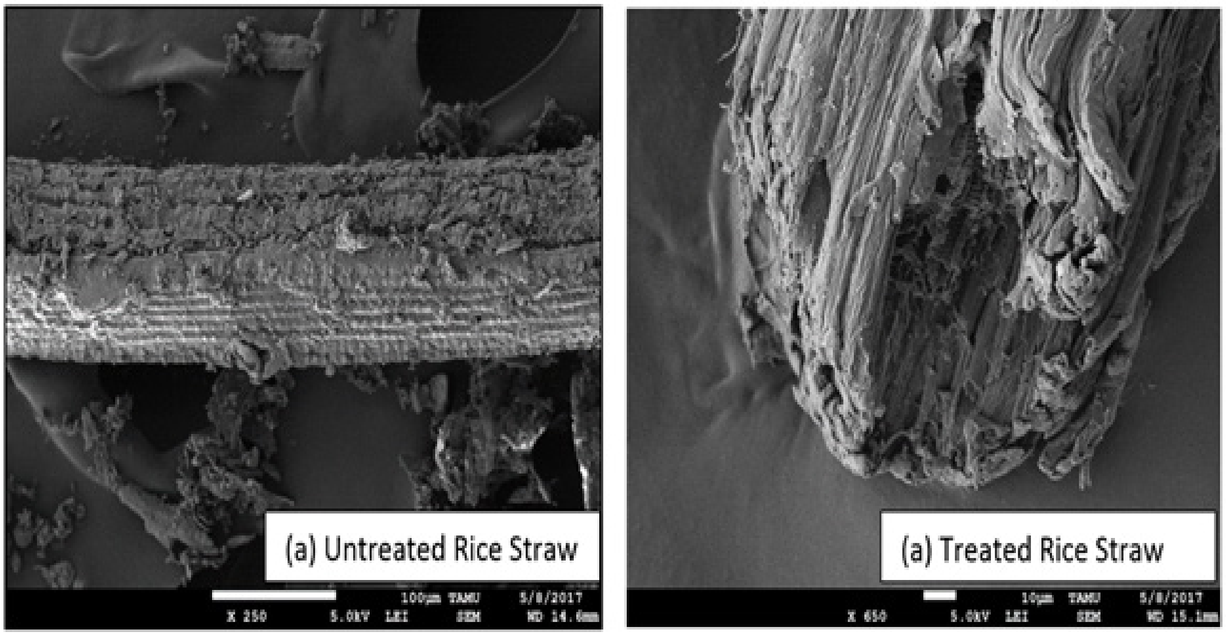


Figure 10. Scanning electron microscopy image of rice straw.

treatment as shown in Figure 9 and 10. The samples were analyzed at the Material Characterization Facility (MCF) at Texas A&M University, College Station, Texas for SEM evaluation. SEM specimens were prepared by spreading particles of each sample on carbon double-stick tabs and subsequently coating it with PtPd (80/20) ~ 10 nm thickness. The carbon tape and film were used for fixation of particles and removal of accumulated charges. Micrographs were taken using a JEOL JSM 7500F field emission scanning electron microscope with a semi-in-lens and equipped with a Gentle Beam to deliver high-resolution. It was operated at a 5 kV acceleration voltage with a working distance of 1-10 mm (coconut shell) and 10-100mm (rice straw).

3.6 Statistical Analysis of Various Pretreatment Applied to Agricultural Biomass Wastes

In this research, considering the possibility of the material characteristics limitation was observed on the pretreatment of coconut shell and rice straw. In fact, by comparing the means of the pretreated coconut shell and rice straw using the paired samples t-test at 95% confidence interval shows that the effect of NaOH concentration is not significant for the rice straw biomass, but it was significant for the coconut shell, and it implies that the results of the said experiments are repeatable at the same time, it tells us that the varying the NaOH concentration (3% and 4%) on the coconut shell. Furthermore, under the alkaline environment of the biomass (pH 11 for RS and pH 13 for CS), it helps to reduce the acidity of the anaerobic digester by increasing the pH into near alkaline range (pH 6.83 – 7.00). Aside from that, the dominant peaks are shown in the FT-IR spectra of the pretreated coconut shell and rice straw qualifies that the cellulose and hemicellulose component is broken down and been reduced due to the presence of NaOH in the mixture since it was carbon-bearing and it greatly helps the digestibility of the biomass material.

Thus, treating the coconut shell biomass will generally increase the biogas production volume at the same time, it will produce high-concentration methane gas, but there is another composition of gases present as by-products during the anaerobic co-digestion process.

4. Conclusion and Recommendations

The sequential pretreatment of agricultural biomass helps to increase the cellulose and lingo cellulose conversion and resulted in a significant increase in biogas (methane) yields from co-digestion of rice straw and coconut shell with cow manure and sewage sludge as inoculum as compared with untreated material. The use of FT-IR helps to identify the variations in the signal of the cellulose, hemi cellulose, and lignin from rice straw and coconut shell after subjecting into different pretreatments. The effect of pretreatment on biomass produces more methane gas due to the increase of biogas volume, and thus digestibility of the biomass feedstocks.

Thus, the study shows how substrate composition, pretreatment methods, and operational parameters during anaerobic digestion affect the microbial consortia working in the digester.

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