Improvement of Biogas Production by Sequential Pretreatment of Rice Straw and Coconut Shell for Power Generation Applications

A Magomnang¹ and S Capareda²

¹Mechanical Engineering Department, University of Science and Technology of Southern Philippines, Cagayan de Oro City, Philippines
²Biological and Agricultural Engineering Department, Texas A&M University, College Station, Texas, USA

E-mail: a_magomnang@yahoo.com

Abstract. Different pretreatment methods (milling, ultrasonication, liquid hot water, and alkali hydrolysis) were evaluated on rice straw and coconut shell biomass as a substrate for biogas production for vehicle fuel, provide heat and generate electricity. This was achieved by the sequential combination of ultrasonication, hot water, and alkali hydrolysis treatment at (4% and 5% w/v) concentration was evaluated. Additionally, Fourier Transform Infrared (FT-IR) spectroscopy was used in identifying structural differences and identification of compounds in the treated biomass. The results show 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. Moreover, the Fourier-transform infrared spectroscopy (FT-IR) methodology identified modifications in the biomass structure after different types of pretreatment and conditions. 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.

1. Introduction

Renewable energy produced from lignocellulosic materials (i.e. agriculture and forest residues), non-food crops (i.e. algae and grasses) or industrial waste and residue streams have considerably lower greenhouse gas emissions (GHGs) due to its closed carbon cycle. The use of second-generation feedstocks will diminish the concern over competition between food versus fuel and will lessen the potential impact on food supply.

At present, feedstocks 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 feedstock sourced from a variety of crops like palay, corn, sugarcane, cassava, and coconut; and livestock such as 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 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.
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. But the current status of biogas production and utilization varies largely among continents.

To overcome the issues related to the utilization of lignocellulosic materials like rice straw and coconut shells 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 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 type of research on the pretreatment of biomass wastes similar to paddy straw using sodium hydroxide-microwave pretreatment. 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.

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 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.

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 Mindanao, Philippines by utilizing as a fuel for the stationary non-road engines and engine-generator units.

2. Materials and Methods

2.1. Biomass waste pretreatment for anaerobic co-digestion process

In this research, three different pretreatments (alkaline-ultrasonication, hot water) and their combinations were evaluated to obtain the best biogas production from rice 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 1 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.

Figure 1. Schematic diagram of the biomass pretreatment experimental procedure conducted in this study

2.2. Sequential pretreatment process
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 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 1, 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 that 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 1. 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     | 2,000 mL              | 250 g            | 1 hour, 100%, cycle (1) | 121 °C, 15 psi, 1 hour    |
| Coconut Shell T1  | 3% w/v     | 2,000 mL              | 250 g            | 1 hour, 100%, cycle (1) | 121 °C, 15 psi, 1 hour    |
| Coconut Shell T2  | 4% w/v     | 2,000 mL              | 250 g            | 1 hour, 100%, cycle (1) | 121 °C, 15 psi, 1 hour    |
2.3. Anaerobic co-digestion process

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. Biomass analysis using Fourier Transform InfraRed (FTIR) Spectroscopy

The structural composition of the rice straw biomass before and after the pretreatments be determined using the analytical protocols NREL LAP was followed. The Fourier Transform InfrarRed (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 Discussions

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 basic hydrolysis using different concentrations of NaOH (3 and 4% w/v) and control of untreated rice straw as shown in Table 2. The pretreatment of rice straw and coconut shell with 3% w/v NaOH concentration, yielded the highest heating value, followed by the 4% NaOH.

**Table 2.** 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                        |
|                            | 23.79                      | 24.79                         |
| C/N ratio                  | 27.05                      | 27.03                         |
| Biogas Yield (L)           | 18.18                      | 12.54                         |
| Methane Yield (L)          | 9.88                       | 6.96                          |
| Average Methane content (%)| 53.80                      | 53.00                         |

Furthermore, the results are shown in Figure 2 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. This implies that the fermentation/anaerobic digestion process properly converts the waste organic matter into a mixture of carbon dioxide and methane gas. Hence, the co-digestion of pretreated biomass helps to overcome the deficiencies of mono-digestion, which typically becomes the rate-limiting step for the AD process \[8]-[9]. Thus, anaerobic co-digestion of different organic materials may enhance the stability of the anaerobic processes because of better carbon-to-nitrogen balance. Besides, the co-digestion of rice straw and coconut shell at 4% w/v reduce the methane yield due to the inhibitory effect of high ammonia and sulfide concentrations [10] and exhibits a more stable biogas production.
Figure 2. Methane concentration after 45-day anaerobic digestion of cattle manure, treated rice straw & coconut shell.

3.1. Biomass waste pretreatment
As shown in Tables 3 and 4, 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 [14]. 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], [11].

| 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 |                      |                 |                      |                            |
| 3             | 3% w/v |                      |                 |                      |                            |
| 4             | 4% w/v |                      |                 |                      |                            |

Table 4. Data for the Coconut Shell Pretreatment Experiments

| Treatment No. | Conc. | Vol of NaOH Solution | Wt of CS | 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 |                      |         |                      |                            |

Table 5. 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         |
Analysis and tests were conducted for the untreated and treated rice straw 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 5. 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 than the pretreated rice straw by 7 - 8 percentage points for 3% and 4% NaOH+U+LHW pretreatment respectively.

### Table 6. 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                 |

As shown in Table 6, 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.

#### 3.2. Analysis of the pretreated biomass using FTIR

As shown in Figures 3 and 4, the analyzed peaks for the pretreated samples of rice straw and coconut shell spectra's. In all of the samples, 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 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 in 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 wavenumber 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 wavenumbers are enumerated, identified and presented in Tables 7 and 8.

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. Likewise, the hydrolysis of lignocellulosic biomass is the rate-limiting step in anaerobic digestion and pretreatment improves digestion efficiency and biogas production [12].
3.3. Anaerobic co-digestion process: methane quality

The biogas production from rice straw and coconut shell subjected for sequential pretreatment were shown in Figure 6, 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 twenty-three (23) liters of biogas was produced (Table 2). 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 5, the biogas produces methane components higher than the 50% concentration mark except for the cow manure as observed on the 10th to the 12th day. Likewise, parallel reports were reported [13] in the 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 8 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.

### Table 7. 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 |
Table 8. Wave numbers of IR vibration frequencies used for coconut shell characterization

| Wave Number (cm\(^{-1}\)) | Compound     | Functional Groups                                      |
|---------------------------|--------------|--------------------------------------------------------|
| 3340                      | \(\alpha\)-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    | \(\beta\)-D-cellulose                                 |

On all the biogas treatments, the methane concentration level reaches above 50% on its fourth day and readings maintain with slight variations and reported the same levels with other publications [9], [12] presented. This implied the conversion of the waste organic matter through an anaerobic digestion process into a mixture of carbon dioxide and methane gas [9].

The biogas production trends of the biomass (pretreated and untreated) as shown in Figure 5 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 thrice than the untreated ones. Hence, the co-digestion of pretreated biomass helps to overcome the deficiencies of mono-digestion, which typically becomes the rate-limiting step for the AD process [11], [13].

3.4. Scanning electron microscopy (SEM) of the pretreated biomass samples

The rice straw and coconut shell samples (Figures 7 and 8) subjected to sodium hydroxide ultrasonication and liquid hot water treatment 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 the 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).

![Figure 7. Scanning Electron Microscopy image of Rice Straw](image-url)
3.5. Statistical analysis of various pretreatment

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. shown in Tables 3 and 4, 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 [14]. 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 pretreated rice straw digestibility and biogas production presented in various publications [11],[12].

4. Conclusion
The sequential pretreatment of agricultural biomass helps to increase the cellulose and lignocellulose conversion and resulted in a significant increase in biogas (methane) yields from the 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, hemicellulose, 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 the 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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