



Enhancement of Mineralized Hydrocarbon Formation in Biogas by Fe-Cement Based-Sand from Anaerobic Fermentation of Agricultural Wastes Catalyzed by Rumen Fluid

Preecha Sriprapakhan¹, Pisit Maneechot², and Ritchard Artkla^{3,*}

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ABSTRACT

In order to produce biogas through anaerobic fermentation for immediate use, it is essential to carefully select cellulosic and lignocellulosic materials to ensure an adequate supply of substrates and avoid reliance on waste food with varying compositions. This experiment used five different types of organic substrates, namely pineapple peel, maize stover, banana peel, rice straw, and Kankrao leaves. All of these were found to be suitable for digestion and production of reducing sugars at the reflux temperature of acids for 30 minutes, with hydrolysis using 2% v/v H₂SO₄ and HCl. Pineapple peel and corn stover produced slightly more reducing sugar (19.93 and 19.80 mg/L respectively) compared to other raw materials. All organic substrates and 0.2 g of reducing sugars were successfully fermented anaerobically for 5,760 minutes at 42°C to produce biogas. While the cellulosic substrate (pineapple peel) yielded the maximum volume of 1.06 mL in 2,880 minutes, the lignocellulosic materials (Kankrao leaves, maize stover, and rice straw) produced biogas volumes ranging from 0.60-0.74 mL within 5,760 minutes (96 hours). The substrate of starch and saccharides (banana peel) produced 0.63 mL of biogas within 1,440 minutes of fermentation. All reducing sugars performed exceptionally well in biogas production, with total amounts of fermented biogas ranging from 0.5-1.6 mL within 5 minutes. CO₂ and CH₄ were the major components of the biogas, with quantities of 0.75 and 0.16 mL respectively. The use of Fe/Cement-based sand for adsorption or reduction decreased CO₂ to 11.41%, while simultaneously increasing CH₄ to 8.10%.

1. INTRODUCTION

As a result of the burgeoning population and the swift growth of economies worldwide, energy, a crucial factor in global prosperity, experienced a surge in demand and was speedily utilized. The global populace is projected to hit 9-10 billion individuals by 2040 [1, 2]. In order to attain sustainable living avenues, every government across the globe must furnish a substantial quantity of energy (comprising of both renewable and fossil fuels).

At present, Thailand is one of the foremost countries in agricultural production both for export and subsistence, with an estimated population of 66 million. To meet the needs of its people, the government and investors have prioritized agro industries and basic infrastructure. However, these endeavors have resulted in the excessive burning of fossil fuels. The consumption of fossil fuels is equally divided between home and transportation use. In 2013, the country consumed an average of 22,000 tons per day of liquid-pressured gas (LPG) [3]. Our dependence on fossil fuels as

the primary energy source has led to various issues such as human health concerns, environmental degradation, and global climate change [4, 5]. Furthermore, the recent surge in fossil fuel prices may prompt a shift in the economy towards alternative energy sources like biogas, which can replace LPG. Biogas can be produced from a variety of sources such as food waste, agricultural crop residues, municipal solid wastes, sewage sludge, and forestry residues [6], [7], [8], [9]. Normally, the relative relationship between organic matter and anaerobic microorganisms in animal excrement during a range of hours to weeks of reaction time leads to effective biogas generation from organic refuse under anaerobic conditions [10], [11]. As there are numerous catalogues of organic waste applications, including nutrient supplements for fish farms and organic feed for poultry and pigs, the generation of biogas from food waste has experienced a slight decrease in recent times. Food wastes consist of diverse compounds, some of which are detrimental to anaerobic bacteria and pose a challenge to

¹Takasila Research and Development Center of Energy, Department of Physics, Faculty of Science, Maha Sarakham University, Kantara Wichai, Maha Sarakham, 44150, Thailand.

²School of Energy Research and Technology (SERT), Naresuan University, Muangpitsanulok, Pitsanulok, 65000, Thailand.

³Renewable Energy Research Unit (RERU), Faculty of Liberal Arts and Science, Roi-Et Rajabat University, Selaphum, Roi-Et, 45120, Thailand.

*Corresponding author: Ritchard Artkla; E-mail: Surachaiartkla@Reru.ac.th.

regulate [12]. As per this hypothesis, alternative sources for anaerobic fermentation have been put forward, such as farm by-products like cellulosic and lignocellulosic remnants. However, the primary stage of anaerobic digestion, which is the restricted pace of hydrolysis of cellulosic and lignocellulosic compounds, has raised apprehension, leading to extended fermentation periods and lower yields [13], [14], [15]. To accelerate the hydrolysis rates, acid hydrolysis was employed to transform the chemical and physical arrangements of lignocellulosic materials into oligo- or monosaccharides [16].

The effective conversion of cellulosic or lignocellulosic materials into biogas products was illustrated through the incorporation of rumen fluid, an innate cellulose-degrading mechanism discovered in mammals [17]. The research indicated that rumen bacteria exhibited remarkable acidogenic and hydrolytic capabilities, and reaction durations were considerably reduced [17], [18]. As the concentration of mineralized hydrocarbons (60%) increased, the by-product CO₂ (40%) became more dominant [19]. This study focuses on finding alternative sources for anaerobic fermentation, as well as increasing the yield of fermentation. Materials such as rice straw, pineapple peel, corn stover, banana peel, lignocellulosic agricultural waste (organic matter), and Kankrao (*Fagraea fragrans* Roxb.) leaves were examined. To create reducing sugars, half of the organic matter was treated with acid hydrolysis (HCl and H₂SO₄) before anaerobic fermentation. Both organic matter and reducing sugars were used as source materials, and both were fermented anaerobically with the presence of rumen fluid. Additionally, it is expected that the adsorption of Fe₂O₃/cement-based sand will significantly increase mineralized hydrocarbons. After CO₂ molecules are adsorbed onto cement-based sand [20], Fe [21] will reduce the C₂-C₄ hydrocarbons.

2. EXPERIMENTAL

2.1 Materials and Methods

Five different types of organic materials and crop residues, including banana peel, maize stover, Kankrao leaves, pineapple peel, and rice straw, were selected for the study. These samples were collected from the sufficiency economy demonstration farm located in the northeast region of Thailand at Roi Et Rajabhat University. The fresh samples were collected in duplicate and weighed before being dried for 72 hours at 65°C in a hot air oven. After drying, the materials were cut into smaller pieces of 2 mm length for use in anaerobic fermentation. The dried materials were divided into two groups for anaerobic fermentation in the presence of rumen fluid. The first group was used immediately in a solid condition, while the second group underwent acid hydrolysis to produce reducing sugars before the reaction.

2.2 Acid hydrolysis of organic matters by HCl and H₂SO₄ to reducing sugar

Various concentrations of H₂SO₄ and HCl (1:20 g/mg of substrates: acids) were used to acid hydrolyze five organic materials, namely pineapple peel, corn stover, banana peel, rice straw, and Kankrao leaves, at reflux temperatures of acids for a duration of 5 to 60 minutes. The acids were first heated to their reflux temperature (almost 100.00 g), and then organic matter (nearly 5.0 g) was cut into pieces about 2 mm long. The chopped organic material was added in stages to the refluxed acid and continuously stirred for 5 to 60 minutes to ensure complete dissolution. To determine the pH of the dissolved solution and naturally occurring salt, the dissolved substrate was neutralized using 10 M NaOH. Prior to undergoing three rounds of acetone cleaning, the liquid was filtered to remove the salt. The reducing sugar solution was subsequently subjected to mild drying at a temperature of 60°C for a duration of three hours. The desiccated substrate was then scrutinized for the existence of reducing sugars by means of the DNS technique. The quantitative assessment of a distinct reducing sugar was gauged and ascertained at the wavelength of utmost absorption through employment of a UV/VIS spectrophotometer.

2.3 In vitro gas production and fermentation technique

Prior to the morning feeding, rumen fluid (also known as rumen liquor) was collected from the center of the rumen of a ruminant cow (Native x Brahman) in a quantity of 1,000 mL. The fluid was quickly transported to the laboratory for use as inoculable bacteria. It was then filtered through four layers of cheesecloth in sequence and placed into a heat-retaining bottle that had been purged with N₂. The procedures outlined by Divya et al. [22] and Jin et al. [23] were adapted to create the synthetic media used in the rumen fermentation batch experiments. This included an upgraded ingredient consisting of NaHCO₃ (5.88), Na₂HPO₄ (2.22), NaCl (0.282), KCl (0.342), MgCl (2.6 H₂O) (0.0768), and Ca (2.2 H₂O) (0.0318). To carry out rumen fermentation on organic materials, 100 mL bottles filled with nitrogen gas were used. The bottles contained 5 mL of reduced sugar, 6 mL of rumen fluids, and 50 mL of media (10% v/v). The anaerobic fermentation was incubated at 39 °C for 96 hours. Biogas products were observed and noted at different intervals of 0, 5, 15, 30, 60, 90, 120, 180, 360, 420, 600, 720, 1,080, 1,440, 2,160, 2,880, 3,600, 4,320, and 5,760 minutes. Simultaneously, 50 mL of media (10% v/v), 5 mL of distillation water, 6 mL of rumen liquid, and approximately 0.2 g of chopped organic matter (roughly 0.2 g of dry matter) were added to each 100 mL bottle of nitrogen gas. The anaerobic fermentation of reduced sugars and the conversion of chopped organic matter to biogas products were measured under the same conditions and at the same time intervals.

2.4 Analysis of biogas compositions

The complete amount of biogas was estimated by utilizing a 100-microliter syringe attached to a bottle for anaerobic

fermentation. An Agilent Technologies 6890 N gas chromatograph was utilized for a meticulous analysis of biogas, which was equipped with two columns (molecular sieve; Porapak), flame ionization detection (FID), and thermal conductivity detection (TCD). In order to perform a quantitative calibration using standard gas combinations, helium was employed as the carrier gas. The gas chromatography device, operating at a detection temperature of 300 °C and an oven temperature of 270 °C, was administered with the 10- μ L biogas injection via the sample port. Helium was furnished at a rate of 26 mL/min and 80 psi, hydrogen at a rate of 30 mL/min and 40 psi, and air at a rate of 300 mL/min and 60 psi [24].

2.5 Preparation of Fe/Cement based sand

A cement-based sand (which acts as an adsorbent) was created by combining the components in a mass ratio of 2.00 sand to 1.00 cement (a fine binding powder) to 1.00 H₂O. The resulting slurry was placed in a mortar, leveled, and punched through the center to form a cement-based sand. The cement-based sand was then aged at room temperature on a level surface for 48 hours. Next, a mass ratio of 8.25 As-cement-based sand was mixed with 0.486 FeCl₃.6H₂O: 3.00H₂O and soaked for 1 hour to add Fe to the As-cement-based sand. The resulting mixture was dried in a hot air oven for 24 hours to create Fe/As-cement-based sand. Finally, the Fe/As-cement-based sand was activated on its surface by soaking it in a sodium hydroxide solution with a mass ratio of 0.36NaOH: 8.25Fe/As-cement-based sand: 3.00H₂O. To use the Fe/As cement-based sand as a functional adsorbent for minimizing and adsorbing CO₂ from biogas, the mixture was left to propagate for 24 hours and then the Fe/As cement-based sand with NaOH was dried overnight at ambient temperature.

2.6 Adsorption and reduction of produced biogas on Fe/Cement based sand

The 100-microliter container underwent anaerobic fermentation of reducing sugars facilitated by 10% v/v rumen fluid to increase the production of mineralized hydrocarbons (mainly CH₄) and CO₂. The procedure may be repeated, with the addition of 10 grams of Fe/Cement-based sand to the cylindrical neck of the fermenting container. At intervals of 0, 5, 15, 30, 60, 90, 120, 180, 360, 420, 600, 720, 1,080, 1,440, 2,160, 2,880, 3,600, 4,320, and 5,760 minutes, the biogas products were observed and documented. The total biogas volume was determined using a 100-microliter syringe connected to the anaerobic fermentation container. Quantitative analysis of the biogas was conducted using a gas chromatograph (Agilent Technologies 6890 N) under the same conditions as the previous experiment.

3. RESULTS AND DISCUSSION

3.1 Effects of acid concentration on the digestion of organic substrates

The acid hydrolysis of pineapple peel, maize stover, banana peel, rice straw, and Kankrao leaves was conducted at reflux temperature with varying times of 5 to 60 minutes. The substrates were treated with H₂SO₄ and HCl at concentrations ranging from 2-4% v/v (1:20 g/mg of substrates: acids). For this research, all organic materials were subjected to acid hydrolysis using 2% v/v of H₂SO₄ and HCl, which resulted in higher sugar content compared to 3 or 4% v/v at reflux temperature of acids for 30 minutes. The yields of all five organic compounds were nearly the same, at 19.5 mg/L. Pineapple peel and maize stover produced slightly higher reducing sugar yields than other raw materials, at 19.93 and 19.80 mg/L, respectively. The fundamental constituents consist of significant proportions of cellulose and glucose, which unite to generate substantial quantities of sugar (Figure 3). As per the findings of Raudhatussyarifah et al. [25], rice straw pulp was subjected to hydrolysis in an oven using sulfuric and hydrochloric acids for a duration of 10 to 50 minutes. The hydrolysis process using 1.5 M sulfuric acid for 50 minutes resulted in a yield of 55.91% and produced the highest proportion of crystalline cellulose fraction, which amounted to 63.23%. By utilizing hydrochloric acid, a yield content of 59.16% and a fraction of 60.70% crystalline cellulose were attained under identical circumstances. Furthermore, a 350-L batch reactor containing a 1% H₂SO₄ concentration was able to generate sugars and by-products from rice straw in just 27 minutes at a relatively low temperature (121 °C) and achieved a high output of xylose (77%) [26], [27]. This theory suggests that using 2% v/v of both HCl and H₂SO₄, as opposed to the customary 3-4% v/v, contributed to the appropriate rate of degradation for crystalline cellulose, hemicellulose, and lignocellulose (Figure 1). The resolution would transform into a dark brown shade due to the excessively acidic concentrations, leading to the generation of byproducts such as carbon and mineralized inorganic substances. Roman and Winter [28] demonstrated that an increased acidic synthesis of sulfate resulted in the production of more brown-colored glucose, and the solution turned dark brown upon the formation of carbon in significant amounts. Furthermore, it was demonstrated that catalysts with higher acidities (Brønsted and Lewis acid sites) accelerated the rehydration procedure, leading to the formation of several unwanted secondary products [27].

3.2 Effects of time interval on the digestion of organic substrates with acid solutions

In the previously mentioned trial, maize stover and pineapple peel displayed greater concentrations of reducing sugars than the other substances when subjected to acid hydrolysis. To further investigate the effects of time

intervals, an additional experiment was conducted using hydrochloric and sulfuric acid with concentrations of 2% v/v for durations of 5, 10, 15, 30, 45, and 60 minutes. At the 30-minute time interval, the hydrolysis of pineapple peel and maize stover exhibited the highest concentrations of reducing sugars, which were 52.2 and 48.9 mg/mL, respectively. Furthermore, the diminishing sugar levels at 30, 45, and 60 minutes did not exhibit any significant variation from each other with a confidence level of 99% (p-value of 0.01). The optimal conditions for the hydrolysis digestion of 2% v/v at reflux temperature for 30 minutes were sustained throughout the experiment (as depicted in Figure 2), as the relatively high sugar concentration acquired under these circumstances could be cost-effective and energy-conserving. As per the consensus, the liberation of reducing sugar was prolonged during the pretreatment process as the concentration of diluted acids escalated. Following 48 hours of incubation with 10% biomass loading and 2% (w/v) acid in the native biomass, which resulted in a TRS concentration of 64 mg/g individually, the highest TRS concentration surged from 163 mg/g in a 0.4 (% w/v) diluted acid treatment to 457 mg/g [28]. Furthermore, diluted sulfuric acid was selected, and enzymatic breakdown was employed to evaluate the efficiency of the pretreatment. The most favorable hydrolysis conditions resulted in the production of 0.651 g/g of reducing sugar, which involved introducing the biomass at a rate of 11.25% (w/w), using 50 FPU of industrial cellulase, adding 0.125% (w/w) of Tween-80 as a surfactant, and allowing the mixture to incubate for 42 hours [29].

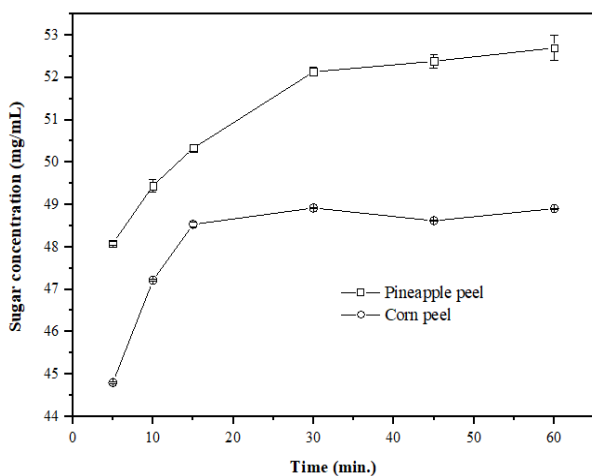


Fig. 1. Reducing sugar formation from the acid hydrolysis of pineapple peel and corn stover with 2% v/v H₂SO₄ at the reflux temperature for the time interval of 5 - 60 minutes.

Figure 2 presents a comparison of the effects of 2% v/v HCl and H₂SO₄ on the acid hydrolysis of pineapple peel, maize stover, banana peel, rice straw, and Kankrao leaves under reflux temperature for 30 minutes. The results showed that H₂SO₄ produced higher concentrations of reducing

sugars compared to HCl. Nevertheless, HCl, which lacks acidic groups, can be considered as an alternative option. Nonetheless, the use of HCl was problematic due to the aggregation of cellulose crystals resulting from the hydrolysis process, which was caused by the absence of surface charges [28]. To avoid a significant decrease in degradation temperature caused by hydroperoxide functional group (ROOH) during hydrolysis, the thermal auto-oxidation of cellulose should be restricted. Hence, when performing acid hydrolysis of organic materials, it is advisable to use low acid concentration, a low acid-to-cellulose ratio, and a quick reaction time. The presence of sulfate groups in large quantities resulted in considerably lower activation energies for the processes, indicating that H₂SO₄ catalyzed degradation reactions directly through acid molecules or indirectly by promoting dehydration reactions.

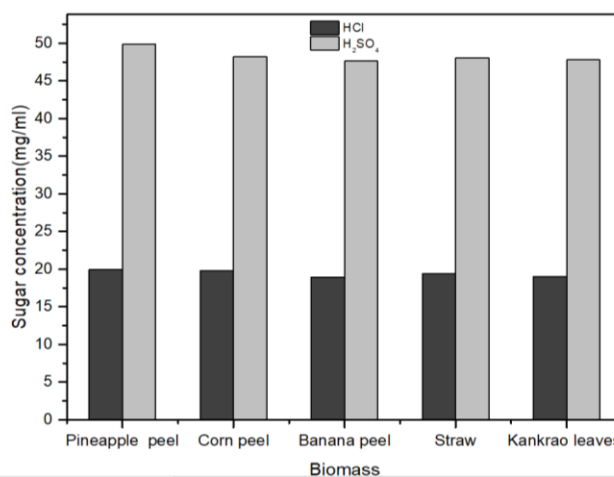


Fig. 2. Comparison on acid hydrolysis of pineapple peel, corn stover, banana peel, rice straw and Kankrao leaves between 2% v/v of HCl and H₂SO₄ at the reflux temperature for 30 minutes.

3.3 Biogas fermentation from organic substrates and reducing sugars

The biogas fermentation process utilized various organic materials, including pineapple rind, corn stalks, banana skins, rice husks, and Kankrao foliage. These materials were classified into three groups based on their composition: lignocellulose, cellulose, and starch. An amount of 0.2 g of finely chopped organic matter was subjected to anaerobic fermentation in vitro for 5,460 minutes at 42 °C, using 10% v/v rumen fluid. Results indicated that the performance of methanogens was significantly influenced by variations in the fermented organic substrates.

Lignocellulosic substrates such as Kankrao leaves, rice straw, and maize stover contain a significant amount of crystalline cellulose, which is resistant to natural decomposition due to its crystalline structure that makes it difficult for microorganisms to penetrate and digest [30].

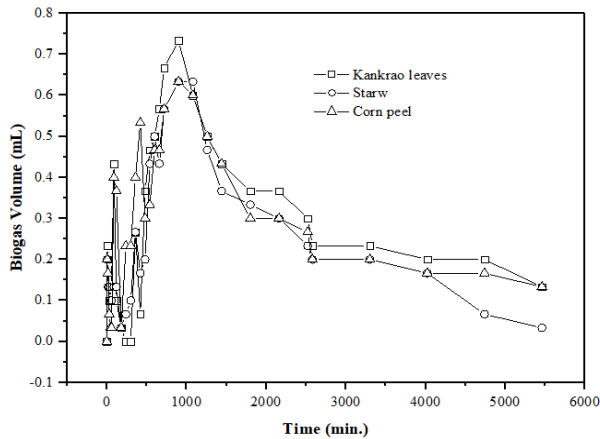


Fig. 3. Anaerobic fermentation of 0.2 g lignocellulosic substrates including corn stover, rice straw and Kankrao leaves (in solid state) catalyzed by 10% v/v of rumen fluid at 42 °C for 5,460 minutes.

These natural materials were capable of substantially breaking down and producing a noteworthy quantity of biogas within a time span of 600 to 1,440 minutes when combined with rumen fluid containing microorganism biocatalysts (methanogen). The highest biogas yields were observed from the fermentation of Kankrao leaves, maize stover, and rice straw, measuring 0.74, 0.60, and 0.62 mL, respectively. Following a 5-minute reaction time, the slow fermentation phase was initiated, indicating that sugar fermentation had already begun to decline. During the subsequent 500–4,320 minute period, starch fermentation resulted in significant methane production. However, as the reaction progressed, the volume of biogas gradually decreased. After 5,760 minutes, the fermentation was halted, as it takes 72 to 96 hours for lignocellulose to decompose into intermediate molecules of VFAs and acetate before being mineralized into biogas (CO_2 , CH_4 , or H_2) (Figure 3). Just like Phoungngoen et al. [31], the authors utilized methanogen from cow rumen fluid to ferment the raw materials in 50-mL volumetric flasks of 20 mL volume to investigate the production of biogas from seaweed cells as opposed to Napier grass. Both algae and Napier grass yielded biogas at rates of 5.75 and 2.68 mL per day, respectively. The results of biogas fermentation tests using 0.2 g of chopped pineapple peel (in a solid form) in 10% v/v rumen fluid at 42 °C for 5,460 minutes (or 96 hours) are shown in Figure 4. Microorganisms immediately consumed the biogas produced from pineapple peels for a short duration. The maximum volume of biogas produced was 1.06 mL, which occurred between 240 and 600 minutes. As a result of the decline in substrate, the biogas fermentation process achieved saturation after 1,000 minutes, leading to a delayed response rate. This organic substrate is effortlessly broken down to generate intermediates, acetate derivatives, and mineralized hydrocarbon products of biogas. It comprises a variety of nutrients (sugars) for microorganisms

(CO_2 , CH_4 , etc.). The findings aligned with Yao et al. [30], who employed laboratory-scale anaerobic digestion to transform solid pineapple wastes into energy-rich biogas. Pineapple waste had a remarkable potential for biogas production, generating an effective amount of 3 liters at a pineapple waste to cow dung ratio of 1:2.4. During a 92-day hydraulic retention period, the resulting methane output was 113.8 L/kg ODM. The biogas produced had a methane content that varied from 41.0 vol% to 70.5 vol%.

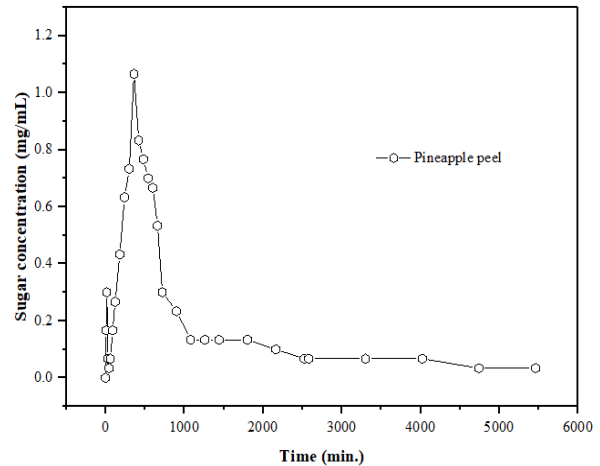


Fig. 4. Anaerobic fermentation of 0.2 g cellulosic substrate (pineapple peel in solid state) catalyzed by 10% v/v of rumen fluid at 42 °C for 5,460 minutes.

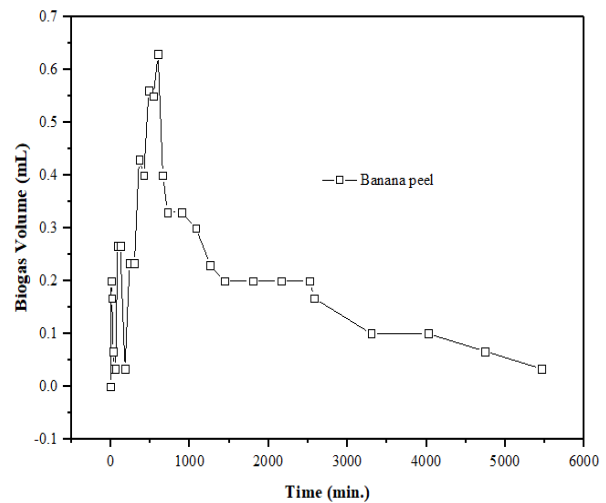


Fig. 5. Anaerobic fermentation of 0.2g starch and derivative (banana peel in solid state) catalyzed by 10% v/v of rumen fluid at 42 °C for 5,460 minutes.

A chopped banana peel, which includes monosaccharides, oligosaccharides, starch, and by-products (0.2 g, solid), underwent anaerobic fermentation for 5,460 minutes (equivalent to 96 hours) at 42 °C. Biodegradable substances from this raw material may be available for biogas production in 500–900 minutes, with a maximum

biogas volume of 0.63 mL. Biogas production gradually decreased until it stabilized, and ultimately there was no more formation of biogas (Figure 5). Nathoa et al.'s study [32], which employed batch reactors for biogas fermentation under mesophilic incubation with varying feedstock to microbial inoculum (F/M) ratios from 2.5 to 10.0 F/M ratios, supported this conclusion. At an F/M of 5.0 and methane production of 251.3 mL g⁻¹ VS, methane fermentation demonstrated optimal results.

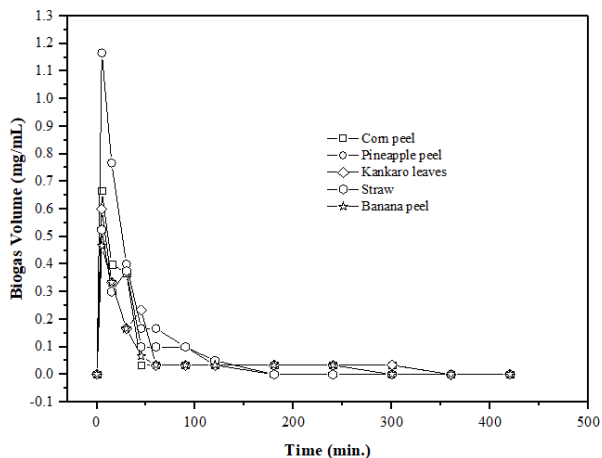


Fig. 6. Anaerobic fermentation of 5.0 mL reducing sugars (equally 0.2 g of substrates in solid state) from pineapple peel, corn stover, banana peel, rice straw and Kankrao leaves catalyzed with 10% v/v of rumen fluid at 42 °C for 5,460 minutes.

An exploration into anaerobic fermentation of hydrolyzed products (liquid state, comprising reducing sugars) derived from pineapple peel, corn stover, banana peel, rice straw, and Kankrao leaves was undertaken. This was achieved by introducing 2% v/v H₂SO₄ to the substrates, and under the conditions of 5.0 mL (equating 0.2 g of solid-state substrates) reducing sugars catalyzed with 10% v/v rumen fluid at 42 °C for 420 minutes. The findings showed that all organic substrates underwent swift anaerobic fermentation, resulting in the production of various types of biogas within 5 minutes. The highest volumes of biogas produced were 1.16, 0.60, 0.46, 0.50, and 0.60 mL for pineapple peel, maize stover, banana peel, Kankrao leaves, and rice straw, respectively. The quantity of biogas produced was dependent on the amount of reducing sugar present in the organic substrate. After exceeding the reaction time, there was a sharp decline in the rate of biogas production, which then stabilized after 120 minutes (Figure 6). This finding is consistent with Manzoor's study [33], which investigated the delignification of sugar cane bagasse using different concentrations of sulphuric acid (ranging from 0.5% to 5% per 10 g of dry matter) as an impregnating agent at 121 °C for intervals of 30, 60, 90, 120, 150, and 180 minutes. The results indicated that the most significant

delignification, weight loss, and production of total and reducing sugars occurred after 180 minutes in 4% sulphuric acid. The 4% sulphuric acid pretreatment resulted in 82% delignification after 180 minutes, which could increase ethanol production.

During the process of anaerobic fermentation of a reducing sugar such as banana peel, 10% v/v rumen fluid was used as a catalyst and the temperature was maintained at 42°C for a duration of 5,460 minutes. To enhance the purification of mineralized hydrocarbons, specifically CH₄, Fe/Cement-based sand was introduced which facilitated the adsorption of CO₂ and unsaturated molecules. The results indicated that initially, all fermented products displayed a higher volume of CO₂ (0.75 mL) compared to CH₄ (0.16 mL). However, after 48 hours, the volume of CH₄ gradually increased in the absence of Fe/Cement-based sand. However, the combination of Fe/Cement-based sand and anaerobic fermentation resulted in a significant increase in the volume of CH₄ (0.027 mL) by approximately 11.41%, while there was a notable decrease in the volume of CO₂ (0.67 mL) by approximately 8.10% (refer to Figure 7). This suggests that CO₂ molecules could be adsorbed on cement-based sand [20], while active Fe species (which are impregnated on cement-based sand) could transform CO₂ molecules into mineralized hydrocarbons. Liu [21] demonstrated that catalysts made of iron were capable of converting CO₂ into C₂-C₄ hydrocarbons. Based on this theory, it is feasible to produce pure biogas with a high concentration of methane and a low concentration of CO₂, which can be used immediately.

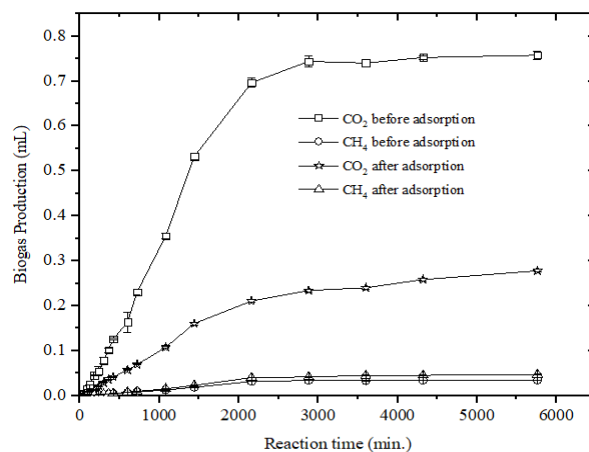


Fig. 7. Adsorption and reduction of CO₂ on Fe/Cement-based sand from anaerobic fermentation of 5.0 mL reducing sugars (banana peel) catalyzed with 10% v/v of rumen fluid at 42°C for 5,460 minutes.

4. CONCLUSIONS

Five distinct varieties of organic substrates were proficiently synthesized for the purpose of anaerobic fermentation. All

of these organic substrates were able to undergo digestion within a 30-minute acid hydrolysis process utilizing 2% v/v H₂SO₄ and HCl, which also led to the production of reducing sugars at reflux temperature. Pineapple peel and corn stover produced slightly higher amounts of reducing sugar (19.93 and 19.80 mg/L, respectively) compared to other raw materials. Biogas was produced through anaerobic fermentation of the organic substrates and 0.2 g of reducing sugars. The yield of the cellulosic substrate (pineapple peel) was optimized to 1.06 mL within 2,880 minutes, while the anaerobic fermentation of lignocellulosic material (Kankrao leaves, maize stover, and rice straw) resulted in biogas volumes ranging from 0.60-0.74 mL within 5760 minutes (96 hours). In the span of 1,440 minutes, the substrate consisting of starch and saccharides (banana peel) generated 0.63 mL of biogas. Notably, all types of reducing sugars were highly effective in producing biogas. In just 5 minutes, the total amount of fermented biogas ranged from 0.5 to 1.6 mL. CO₂ and CH₄ comprised the largest portion of the biogas, with quantities of 0.75 and 0.16 mL, respectively. Through adsorption or reduction on Fe/Cement-based sand, the CO₂ content was reduced to 11.41%, while the CH₄ content increased to 8.10%.

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REFERENCES

- [1] Budiyo, I.N. Widiyasa, S. Johari, Sunarso, Increasing Biogas Production Rate from Cattle Manure Using Rumen Fluid as Inoculum, *International Journal of Science and Engineering*, 6 (2014) 31-38.
- [2] S. Srinonil, V. Nittivattananon, P. Noithammaraj, R. Nitisoravut, Tourism governance for coastal urbanization and environment with changing climate on Koh Chang Island, Thailand, *GMSARN Int. J.*, 14 (2020) 82-88.
- [3] E.P.a.P. Office, Energy statistics, in: M.o. Energy (Ed.), 2013.
- [4] F. Perera, Pollution from Fossil-Fuel Combustion is the Leading Environmental Threat to Global Pediatric Health and Equity: Solutions Exist, *International Journal of Environmental Research and Public Health*, 15 (2018) 16.
- [5] S. Thoumavongsa, X. Bounsou, Sustainable management of hydropower in Lao PDR, *GMSARN International Journal*, 7 (2013) 1-12.
- [6] B. Morero, R. Vicentin, E.A. Campanella, Assessment of biogas production in Argentina from co-digestion of sludge and municipal solid waste, *Waste Management*, 61 (2017) 195-205.
- [7] A. Teghammar, G. Forgács, I. Sárvári Horváth, M.J. Taherzadeh, Techno-economic study of NMMO pretreatment and biogas production from forest residues, *Applied Energy*, 116 (2014) 125-133.
- [8] F. Valenti, Y. Zhong, M. Sun, S.M.C. Porto, A. Toscano, B.E. Dale, F. Sibilla, W. Liao, Anaerobic co-digestion of multiple agricultural residues to enhance biogas production in southern Italy, *Waste Management*, 78 (2018) 151-157.
- [9] M. Ebrahimi-Nik, A. Heidari, S. Ramezani Azghandi, F. Asadi Mohammadi, H. Younesi, Drinking water treatment sludge as an effective additive for biogas production from food waste; kinetic evaluation and biomethane potential test, *Bioresource Technology*, 260 (2018) 421-426.
- [10] P. Ormaechea, L. Castrillón, E. Marañón, Y. Fernández-Nava, L. Negral, L. Megido, Influence of the ultrasound pretreatment on anaerobic digestion of cattle manure, food waste and crude glycerine, *Environmental Technology*, 38 (2017) 682-686.
- [11] Y. Noorollahi, M. Kheirrouz, H.F. Asl, H. Yousefi, A. Hajinezhad, Biogas production potential from livestock manure in Iran, *Renewable and Sustainable Energy Reviews*, 50 (2015) 748-754.
- [12] C. Mao, Y. Feng, X. Wang, G. Ren, Review on research achievements of biogas from anaerobic digestion, *Renewable and Sustainable Energy Reviews*, 45 (2015) 540-555.
- [13] A. Barakat, F. Monlau, J.-P. Steyer, H. Carrere, Effect of lignin-derived and furan compounds found in lignocellulosic hydrolysates on biomethane production, *Bioresource Technology*, 104 (2012) 90-99.
- [14] A. Bayané, S.R. Guiot, Animal digestive strategies versus anaerobic digestion bioprocesses for biogas production from lignocellulosic biomass, *Reviews in Environmental Science and Bio/Technology*, 10 (2011) 43-62.
- [15] Ç. Akyol, E.G. Ozbayram, O. Ince, S. Kleinstueber, B. Ince, Anaerobic co-digestion of cow manure and barley: Effect of cow manure to barley ratio on methane production and digestion stability, *Environmental Progress & Sustainable Energy*, 35 (2015) 589-595.
- [16] P. Kumar, D.M. Barrett, M.J. Delwiche, P. Stroeve, Methods for Pretreatment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofuel Production, *Industrial & Engineering Chemistry Research*, 48 (2009) 3713-3729.
- [17] Z.-B. Yue, W.-W. Li, H.-Q. Yu, Application of rumen microorganisms for anaerobic bioconversion of lignocellulosic biomass, *Bioresource Technology*, 128 (2013) 738-744.
- [18] J. Procházka, J. Mrázek, L. Štrosová, K. Fliegerová, J. Záborská, M. Dohányos, Enhanced biogas yield from energy crops with rumen anaerobic fungi, *Engineering in Life Sciences*, 12 (2012) 343-351.
- [19] W. Jin, X. Xu, F. Yang, C. Li, M. Zhou, Performance enhancement by rumen cultures in anaerobic co-digestion of corn straw with pig manure, *Biomass and Bioenergy*, 115 (2018) 120-129.

- [20] J. Cai, S. Wang, Z. Xiao, A study on the CO₂ capture and attrition performance of construction and demolition waste, *Fuel*, 222 (2018) 232-242.
- [21] J. Liu, A. Zhang, X. Jiang, M. Liu, Y. Sun, C. Song, X. Guo, Selective CO₂ Hydrogenation to Hydrocarbons on Cu-Promoted Fe-Based Catalysts: Dependence on Cu-Fe Interaction, *ACS Sustainable Chemistry & Engineering*, 6 (2018) 10182-10190.
- [22] D. Divya, L.R. Gopinath, P.M. Christy, A review on current aspects and diverse prospects for enhancing biogas production in sustainable means, *Renewable and sustainable energy reviews*, 42 (2015) 690-699.
- [23] W. Jin, X. Xu, Y. Gao, F. Yang, G. Wang, Anaerobic fermentation of biogas liquid pretreated maize straw by rumen microorganisms in vitro, *Bioresource Technology*, 153 (2014) 8-14.
- [24] P.D. Florendo, Sharma-shivappa, V. VFellner, Cattle rumen microorganisms hydrolysis for switchgrass saccharification, volatile fatty acids and methane production, *International Journal of Agricultural Technology*, 14 (2018) 31-43
- [25] R. Raudhatussyarifah, W.B. Sediawan, M.M. Azis, I. Hartati, Microcrystalline cellulose production by acid hydrolysis of hydrotropic rice straw pulp, IOP Publishing, pp. 012055.
- [26] I.C. Roberto, S.I. Mussatto, R.C.L.B. Rodrigues, Dilute-acid hydrolysis for optimization of xylose recovery from rice straw in a semi-pilot reactor, *Industrial Crops and Products*, 17 (2003) 171-176.
- [27] P.B. Kasangana, N. Auclair, R. Daassi, K. Durand, D. Rodrigue, T. Stevanovic, Impact of Pre-extraction on Xylose Recovery from Two Lignocellulosic Agro-wastes, *BioResources*, 17 (2022).
- [28] M. Roman, W.T. Winter, Effect of Sulfate Groups from Sulfuric Acid Hydrolysis on the Thermal Degradation Behavior of Bacterial Cellulose, *Biomacromolecules*, 5 (2004) 1671-1677.
- [29] R. Sindhu, M. Kuttiraja, P. Binod, R.K. Sukumaran, A. Pandey, Bioethanol production from dilute acid pretreated Indian bamboo variety (*Dendrocalamus* sp.) by separate hydrolysis and fermentation, *Industrial Crops and Products*, 52 (2014) 169-176.
- [30] L. Yao, H. Yang, C.G. Yoo, Y. Pu, X. Meng, W. Muchero, G.A. Tuskan, T. Tschaplinski, A.J. Ragauskas, Understanding the influences of different pretreatments on recalcitrance of *Populus* natural variants, *Bioresource Technology*, 265 (2018) 75-81.
- [31] T. Phoungngoen, N. Yodsuwan, N. Sinbuathong, W. Panutai, S. Sirisansaneeyakul, Biogas production from microalgal cell debris derived from lipid extraction, *Agro-Industry*, 6 (2014) 419-426.
- [32] C. Nathoa, U. Sirisukpoca, N. Pisutpaisal, Production of Hydrogen and Methane from Banana Peel by Two Phase Anaerobic Fermentation, *Energy Procedia*, 50 (2014) 702-710.
- [33] A. Manzoor, Z.-U. Khokhar, U. Athar Hussain, S.A. Ahmad, Dilute sulfuric acid: a cheap acid for optimization of bagasse pretreatment, cellulose, 10 (2012) 100.