Supplement the Amount of Biogas Volume by Adsorption of VFAs on SiO₂ and MCM-41 from Anaerobic Fermentation of Rice Straw

Preecha Sriprapakhan[1], Pisit Maneechot[2], and Surachai Artkla[3,*]

ARTICLE INFO

ABSTRACT

The purpose of this investigation is to offer enough organic substrates. For anaerobic fermentation to produce biogas, rice straw was investigated as a source of lignocellulosic material. The adsorbent SiO2 is produced through the process of acid leaching. The hydrolysis of rice straw using 2% v/v H2SO4 proved successful. In comparison to rice straw under the same conditions, the anaerobic fermentation of rice straw accelerated by 10% v/v rumen fluid at 42 °C for 420 minutes was roughly 1.60 times greater. SiO2 and MCM-41 adsorbents enhanced biogas levels by around 2.07 mL over the control when added (13.1 mL). During anaerobic fermentation, VFA concentrations titrating with 0.01 M NaOH were also noticeably greater than those of the non-adding adsorbent (0.29 M). The amount of CO2 (3.76 mL) and CH4 (2.94 mL) significantly increased when adsorbents were added compared to when they weren't (0.74 mL). However, there was no discernible difference between CO2 formation on SiO2 (3.76 mL) and MCM-41 (2.94 mL), whereas CH4 formation was not (approximately 0.62 mL on both SiO2 and MCM-41). SiO2 and MCM-41 have kinetic constants of k_{SO_2} and k_{MCM-41} were 3.0208 and 0.8875 s-1 mol-3, respectively, and half-lives of 3.31 and 11.3 minutes.

1. INTRODUCTION

The current environmental, financial, and social awareness of sustainable energy has sparked efforts to locate a more ideal, renewable, and sustainable resource given the rapid growth of our global population [1]-[3]. As we all know, non-sustainable energy sources (fossil fuels) are largely non-renewable, can have negative impacts on the environment, and present new threats to humans [4, 5]. As a result, we will never again be able to fulfill our passion for diverse chemicals. However, unlike fossil fuels, lignocellulose, for example, is prevalent in domestic garbage and agricultural residuals [6, 7]. Numerous sources including farming (bagasse, corn stover, rice straw, etc.), agroforestry (bark, sawdust, pulpwood, branches, foliage, etc.), energy harvesting (Napier grass, French weed, etc.), household green (grass cutting, shrubberies, etc.), and other sources have combined to produce enormous amounts of lignocellulosic residues [8]. Considering these facts, rice straw stands out as one of the most prevalent grain crop leftovers in many nations, with an annual production of roughly 973.9 million metric tons [9]. During the 2015–2016 crop season, Thailand produced about 26 million metric tons of rice straw [10]. Rice straw can be reused in a variety of ways, although the practical utilization rate has remained below 50% [11]. Currently, a sizable portion of rice straw is frequently disposed of by decomposing in landfills or unnecessarily burning outside, which releases large amounts of harmful gases like carbon monoxide, polycyclic aromatic hydrocarbons, volatile organic compounds, nitrous oxide, and suspended particulate matter [12]. This approach reduces the success of agricultural resource recovery because of nutrient loss [13, 14]. Numerous feedstocks (such rice straw) are available for the environmentally friendly generation of biofuels such as biogas, bioethanol, volatile fatty acids (VFAs), and saccharides. The anaerobic fermentation of rice straw has recently been proposed as one of the environmentally acceptable processes for degrading lignocellulose to produce biogas (hydrocarbons C_1-C_4, CO_2, H_2, H_2S, and other gases). Generally speaking, rice straw has strong anaerobic fermentation capacity and can yield biogas with a high methane content. Contrarily, rice straw has a high degree of polymerization and branching low molecular weight hemicellulose, which makes it resistant to anaerobic bacteria's ability to degrade it [7]. Pretreatment of rice straw before to anaerobic fermentation has been judged essential to increase biodegradability and biogas production [15, 16]. Chemical pretreatment is a promising method for

[1]*Faculty of Science, Mahasarakham University, Kamrieng Rd, Kantarawichai District, Maha Sarakham, 44150, Thailand.*

[2]*School of Renewable Energy and Smart Grid Technology (SGTech), Naresuan University, Pitsanulok, 65000, Thailand.*

[3]*Faculty of Liberal Arts and Science, Roi-Et Rajabhat University, 113 Moo 12, Koh Koae Selaphum, Roi Et, 45120, Thailand.*

Corresponding author: Surachai Artkla; Phone: +66-43-556-111; E-mail: Surachaiartkla@yahoo.com.

accelerating cellulose biodegradation and getting rid of rigid lignin structures. Acid hydrolysis is one of the most often used pretreatment methods because it is economical and has acceptable digestibility for a range of feedstocks. The logical justifications for this evident accumulation are the displacement of amorphous hemicellulose and lignin and the subsequent decoration in the concentration of crystalline cellulose [17]. Glucose and xylose from the acid hydrolysis of lignocellulose (rice straw) were anaerobically fermented under mild conditions of the microbial metabolism process and with varied glucose to xylose ratios in order to increase methane generation for this study. 1% HCl, 7.5% rice straw (solid loading), 60 °C, and 48 hours were the appropriate acid hydrolysis conditions. The metabolic process with the 40:60 glucose to xylose ratio showed excellent butyrate intermediate and a high rate of Chemical Oxygen Demand (COD) removal (88.9%) during anaerobic fermentation [18]. Rice straw was subjected to rumen fluid-based anaerobic fermentation for 30 days at 39 °C with biological pretreatment by Zhang et al. [19] and Warade et al. [20]. The results demonstrated that a 24-hour fermentation period was appropriate, with increases of 66.5% and 82.6% over the control, respectively, in total biogas and pure methane. These findings showed that rumen fluid presented an exciting opportunity to enhance lignocellulose anaerobic fermentation.

Unavoidably, high levels of VFAs, intermediate metabolites of anaerobic fermentation, could obstruct methanogenesis. It has been demonstrated that total VFA concentrations higher than 4 g/l prevent glucose fermentation [21]-[23]. However, propionic (3,000 mg l^{-1}) acids are more inhibitory to the methanogens [22], [24] because the methanogens won't be able to metabolize the acetate produced by the acetogenic organisms until there are enough of them. Acetic acid is typically present in higher concentrations during anaerobic digestion than other fatty acids [25]. Effective cellulolytic bacteria require the removal of VFAs from fermented products. These intermediary products are efficiently absorbed by the rumen epithelium [26, 27]. The wayside grass that was fed into the anaerobic hydrolysis reactor almost entirely hydrolyzed in less than 4 days, allowing for the preservation of the microbial biocommunity in the rumen media [28, 29]. Additionally, at 750 °C during the steam reforming reaction, which mostly comprised the decarboxylation of acetic acid to CH_4 and CO_2, the performance of the 5% Cu and 5% Ni-based MCM-41 was demonstrated. The results showed that in the presence of copper, acetic acid decarboxylation activities predominated and produced considerable volumes of methane. Active species of 5% Ni-based 25Zr-MCM-41 were good catalysts for the production of hydrogen during the steam reforming of acetic acid [30].

The main objective of this experiment was the 96-hour anaerobic fermentation of rice straw at 42 °C with 10% v/v rumen fluid. The organic substrate (rice straw) was subjected to the aforementioned circumstances with both small grains (chopped solid rice straw that was 2 mm in length) and reducing sugar (2% v/v H_2SO_4 hydrolysis) to compare their efficacy in the production of biogas (mainly CH_4 and CO_2). Two different adsorbents, SiO_2 (silica) and MCM-41 (Mobil Crystalline Materials No.41), were used to increase the rates of CH_4 and CO_2 fermentation in order to remove VFAs. The kinetics of anaerobic fermentation of rice straw were made clearer by the correlation of the observed data, including catalyst content, decreasing sugar concentration, reaction rate, and time.

2. 2. EXPERIMENTAL

2.1 Materials and Methods

Around the sufficiency economics demonstration farm at Roi Et Rajabhat University in northern Thailand, rice straw was gathered. A second fresh sample (0.5 kg) was dried in a hot air oven for 72 hours at 65 °C before being weighed. For use in anaerobic fermentation, the material was then divided into smaller bits and spread out on a 2 mm long. The dried materials were split into two groups before anaerobic fermentation in the presence of rumen fluid: 1) half of them were employed immediately in the solid state, and 2) the other group underwent acid hydrolysis to create reducing sugars before reaction. Prior research indicates that MCM-41 was created using rice husk silica [31].

2.2 Preparation of SiO₂ and MCM-41

According to Artkla et al. [31], SiO_2 (rice husk silica) was created by acid hydrolysis and employed as a silica source for the synthesis of MCM-41. First, a solution of cetyltrimethylammonium bromide (CTAB) was mixed with the sodium silicate produced from rice husk silica in 3.33 mol/L NaOH solution to make a sol-gel matrix with the molar ratios of 1.0SiO$_2$: 3.0NaOH: 0.25CTAB: 180H$_2$O. Before the sol-gel matrix was crystallized at 100 °C for 24 hours, filtered, dried, and calcined at 540 °C for 6 hours, the pH solution in the blender was changed to a pH solution of 11.5 before the process.

2.3 Catalyst characterization

Using a Bruker Axs D5005 diffractometer and CuKα radiation, powder X-ray diffraction (XRD) was used to examine the crystalline phases of bare SiO_2 and RH-MCM-41. A sample holder was used to press the catalyst powder (0.20 g), which was then scanned from 1.5 to 15 degrees (2θ) in steps of 0.05 degree per minute. To compare the diffraction intensities of multiple samples, the diffraction patterns of distinct powder samples were recorded with the same sample mass.

Using a Micromeritics ASAP 2010 (ASAP 2010 V4.00 H) N$_2$ adsorption-desorption isotherm at -196 °C and relative pressures ranging from 0.01 to 0.99, the surface area and pore structure of the samples were calculated. Each

sample was degassed at 250 °C for three hours before to the measurement. The N_2 adsorption data in the relative pressure range of 0.02 to 0.2 were used to calculate the BET surface area. The desorption branches were used to compute the pore diameter using the Barrett-Joyner-Halenda (BJH) method.

2.4 Acid hydrolysis of rice straw by H_2SO_4 to reducing sugar

Rice straw was acid hydrolyzed at reflux temperatures for 30 minutes using a concentration range of 2-4% v/v H_2SO_4 (1:20 g/mg of substrates: acids). At first, H_2SO_4 (almost 100.00 g) was heated to its reflux temperature while organic matter (about 5.0 g) was divided into pieces about 2 mm long. To ensure full breakdown, the chopped rice straw was progressively added to the refluxed acid and stirred continuously for 5 to 60 minutes. The dissolved substrate was neutralized by 10 M NaOH in order to get the pH of the dissolved solution and naturally occurring salt. The fluid was filtered to remove the salt before being washed three times in acetone. The reducing sugar-containing solution was then analyzed using the DNS method to identify the presence of multiple reducing sugars in the dry substrate after being gently dried at 60 °C for three hours. The quantitative analysis of particular reducing sugars was tracked and measured at the wave length of maximum absorption using a UV/VIS spectrophotometer.

2.5 In vitro gas production and fermentation technique

A ruminant cow's central rumen was sampled for 1,000 mL of rumen fluid (rumen liquor) before the morning feeding (Native x Brahman). Rumen fluid was shipped to the lab as inoculable bacteria as soon as possible. The mixture was next progressively filtered through four layers of cheesecloth before being put into a heat-retaining bottle that had been N_2-gassed. For the production of the synthetic medium supplied to the rumen fermentation batch trials, the methods of Suassuna et al. [32] and Jin et al. [33] were adapted. An improved ingredient consisted of $NaHCO_3$ (5.88), Na_2HPO_4 (2.22), NaCl (0.282), KCl (0.342), $MgCl$ (2.6 H_2O) (0.0768), and Ca (2.2 H_2O) (0.0318). 100-mL bottles of nitrogen gas were filled with 5 mL of reducing sugar, 6 mL of rumen fluids, and 50 mL of medium (10% v/v) for the rumen fermentation of organic materials. The anaerobic fermentation was kept at 39 °C for 96 hours. The biogas products were observed and noted at 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. Each 100 mL bottle of nitrogen gas was coupled with 50 mL of media (10% v/v), 5 mL of distillation water, 6 mL of rumen liquid, and around 0.2 g of chopped organic matter (roughly 0.2 g of dry matter). The conversion of chopped organic matter to biogas products and the anaerobic fermentation of reducing sugars were assessed under the same conditions and at the same intervals. Under comparable conditions as in the prior work,

the adsorbents SiO_2 and MCM-41 (0.01-2.00 g) were used to extract the intermediate products of VFAs. VFA concentrations were measured using KOH titration, and total quantities and quantitatively distinct species of biogas products were introduced using gas chromatography.

2.6 Analysis of biogas compositions

The entire volume of biogas was calculated using a 100-mL syringe linked to an anaerobic fermentation bottle. A gas chromatograph (Agilent Technologies 6890 N) outfitted with two columns (Porapak; molecular sieve), flame ionization detection (FID), and thermal conductivity detection was used to perform a quantitative determination of biogas (TCD). Helium served as the carrier gas for the quantitative calibration using standard gas combinations. The gas chromatography equipment, which ran at a detection temperature of 300 °C and an oven temperature of 270 °C, received the injection of the 10-μL biogas through the sample port. Helium was supplied at a flow rate of 26 mL/min and 80 psi, hydrogen at a flow rate of 30 mL/min and 40 psi, and air at a flow rate of 300 mL/min and 60 psi [34].

3. 3. RESULTS AND DISCUSSION

3.1 XRD of SiO_2 and MCM-41

The XRD pattern of SiO_2 is depicted in Figure 1, and the board peak, which is typical of amorphous silica [35], was revealed at 2 of 22.5-30°. Figure 1 displays the MCM-41 XRD patterns. At 2.32, 4.05, and 4.69°, respectively, there were three MCM-41 characteristic peaks, confirming the presence of an organized structure with a hexagonal pore array comparable to that of MCM-41 [36].
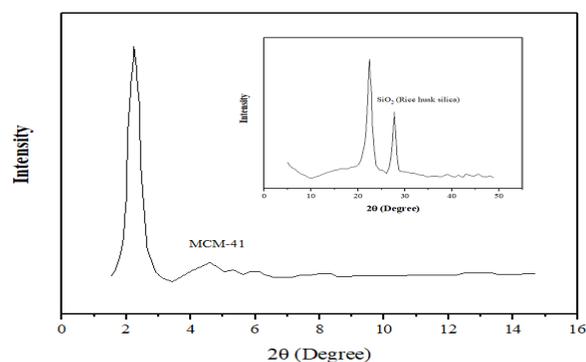

Fig.1. XRD patterns of characteristic peaks of SiO_2 and MCM-41.

The nitrogen adsorption-desorption isotherms of SiO_2 and MCM-41 are shown in Figure 3.2. According to Wang et al. [37], the BET surface area and BJH pore volume of SiO_2 were 167.9 ± 12 m²/g and 1.05 ± 0.02 cm³/g, respectively. The BET surface area of MCM-41's adsorption-desorption isotherm matched type IV, which is typical of mesoporous material isotherms [38]. The

adsorption at low relative pressure (P/P = 0.2) significantly enhanced as a result of the adsorption on monolayers of an external surface. N_2 adsorption volume increased once more before approaching constant levels. Nitrogen was adsorbed in the mesopores at relative pressures of 0.2 to 0.4 [39]. The specific surface areas and BJH pore volumes of MCM-41 were 973 ± 25 m^2/g and 4.57 ± 0.03 cm^3/g, respectively, whereas the BJH equation's estimate of its pore diameter was in the range of 25–50 Å. This meant that the textural properties of MCM-41 had all been improved to be better than those of the precursor (SiO_2), which promoted the adsorption of VFAs molecules in the ensuing anaerobic fermentation.
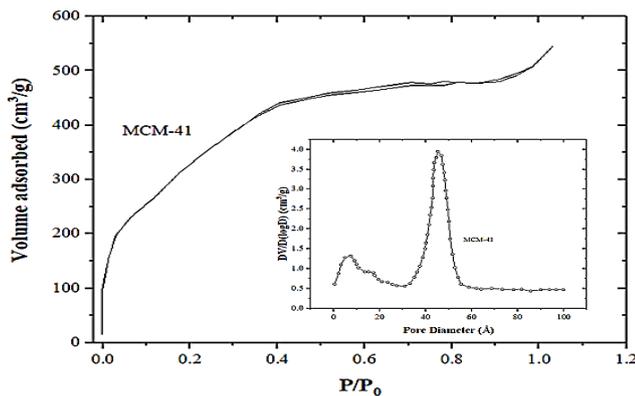

Fig.2. N$_2$ adsorption-desorption isotherm and pore diameter of MCM-41.

3.2 Biogas fermentation from rice straw (solid vs reducing sugar)

The maximum yield of 28.9 mg/mL reducing sugar was obtained for this investigation when 0.5 g of rice straw was digested with 2% v/v H_2SO_4 at refluxed temperature for 30 minutes [40]. In order to increase the biogas production, anaerobic fermentation of rice straw (solid) vs. reducing sugars (from acid hydrolysis of rice straw) was done at 0.2 g substrates and 10% v/v rumen fluid at 42 °C for a duration of 5,670 minutes. It was discovered that within 5 minutes, reducing sugars and solid rice straw produced 0.2 and 1.25 mL of biogas, respectively (Figure 3). Both biogas volumes did not have substantially different variances in the F-Test two-sample at the p value of 0.01. This outcome was in line with Teghammar et al. 's research [41], who changed rice straw by treating it with N-methylmorpholine-N-oxide (NMMO or NMO) prior to anaerobic fermentation and discovered that the fraction of methane increased by 400–1200%. The cellulose, lignin, and hemicellulose fibers' porosity was able to be increased by rice straw that had been digested with weak acid. As a result, fermentation times were shortened, response rates were greatly increased, and bacterial performance was improved [42].
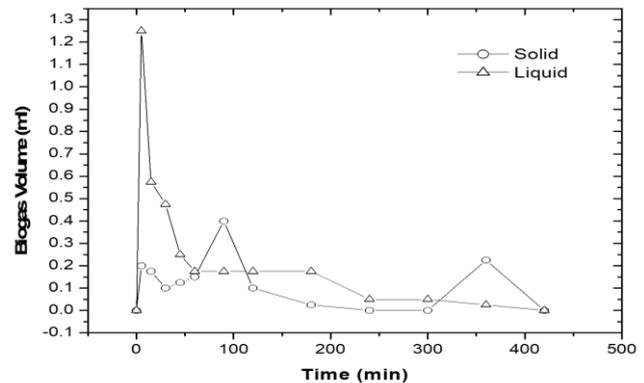

Fig. 3. Comparison on the effectiveness of anaerobic fermentation of 0.2 g rice straw (solid) vs reducing sugar.

3.3 Adsorption of VFAs from anaerobic fermentation with and without SiO$_2$

With 0.2 g of reducing sugars, 10% rumen fluid, and 0.01-2.00 g of SiO_2 at 42 °C for 420 minutes, biogas can be produced under anaerobic circumstances. 16.9, 17.1, 18.5, 27.5, 27.1, 22.2, and 21.2 mL of biogas were created cumulatively by adding 0.01 to 2.0 g SiO_2, respectively (as shown in Figure 4). The cumulative volumes of biogas produced under these circumstances were equivalent to those of SiO_2 additions of higher concentrations, making the addition of 0.1 g SiO_2 the best choice for further testing. As a result, 0.1 g of SiO_2 will be used in this study's experiment to completely remove VFAs. However, when the maximum cumulative volume (27.1 mL) with SiO_2 was compared to the experimental fermentation of methane in anaerobic fermentation under the same conditions as without SiO_2 (13.1 mL) [43], adding SiO_2 to fermentation resulted in a greater cumulative volume that was 2.1 times higher. The possibility existed that adding 0.1 g more SiO_2 might help the adsorbent [35] have enough surface area to effectively bind to the VFAs that were generated. SiO_2 was added in amounts greater than 0.1 g, which resulted in an increase in both the adsorptive area and the adsorptive efficiency. VFAs were added in amounts that remained constant.
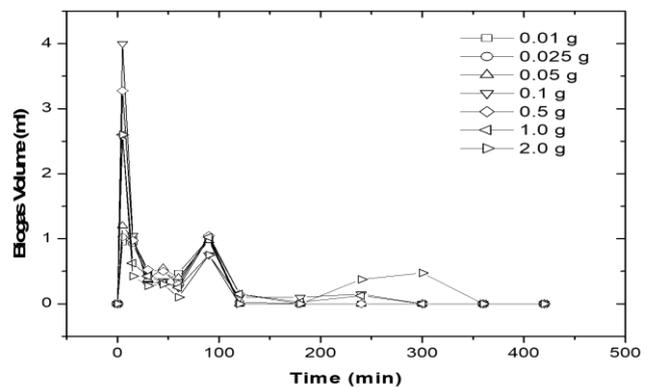

Fig. 4. Cumulative volumes of biogas under the anaerobic fermentation of 0.2 g reducing sugar (from acid hydrolysis of rice straw).

For Figure 5, the maximum cumulative biogas quantities at 5 minutes were, respectively, 1.25 and 4.0 mL for both tests (with and without 0.1 SiO_2). When compared to anaerobic fermentation without the adsorbent, the adsorption of VFAs from an anaerobic fermentation system with 0.1 SiO_2 was outstandingly increased to 68.75%. According to this theory, removing VFAs helped extend the life cycles of methanogens and other vital microbes [26]. According to a different study, the initial stages of the operation under anaerobic conditions saw a reduction in pH due to the synthesis of VFAs [44, 45]. The pH range of 6.5 to 7.5 is where most methanogens proliferate. A low pH spreads throughout the system as a result of VFA production as metabolic intermediates, which is known to inhibit methanogens [45]. Sequentially, the large improvement in fermenting efficiency (glucose digestion) strongly suggested that a favorable environment has been identified, and it is feasible to carry out the experiment further.
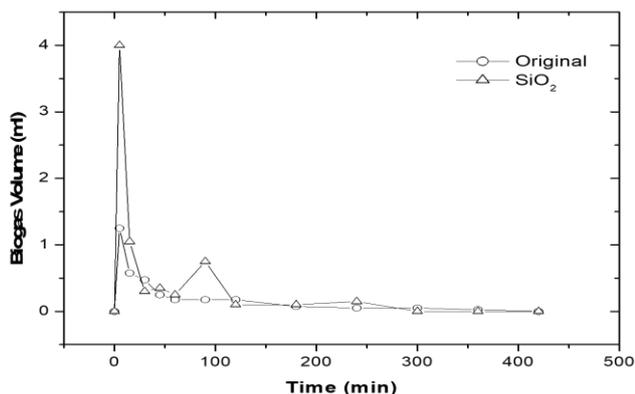

Fig. 5. Cumulative volumes of biogas under anaerobic fermentation of 0.2 g reducing sugar (from acid hydrolysis of rice straw).

3.4 Effect of SiO₂ and MCM-41 adsorbents on reducing sugar fermentation

To assess the adsorptive effectiveness of MCM-41 and SiO_2 for the removal of VFAs, the two adsorbents were added to a sequential reaction in the same quantity of 0.1 g each. The trials used 0.2 g of precursor at 10% v/v at 42 °C for 420 minutes in an environment suitable for anaerobic fermentation. The overall biogas accumulative volumes between the SiO_2 and MCM-41 adsorbents were insignificantly 27.5 and 28.2 mL, respectively (Figure 6). At the p value of 0.01, the F-Test on two-sample data for variances concluded that there was no significant difference. Compared to SiO_2 (600 m^2/g), MCM-41 has a surface area between 800 and 1,400 m^2/g [39], but it also has a higher absorptive capacity. The hydroxyl-functionalized groups of particular adsorbents are the basis for the adsorption of polar molecules, such as H_2S and acidic compounds [46]. MCM-41 and SiO_2 are consistently crucial parts of exclusive and absorptive molecules [47]. This information allowed it to

explain why VFA absorption should be successful on the surface of MCM-41. However, due to the limitation of VFA synthesis from fermentation, the adsorptive portions on MCM-41 and SiO_2 were not considerably different.
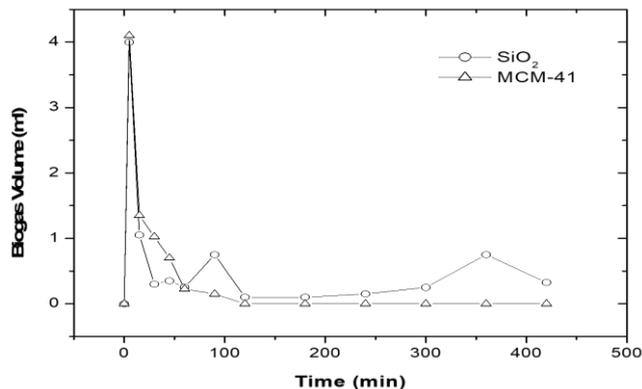

Fig.6. Cumulative volumes of biogas under the anaerobic fermentation of 0.2 g reducing sugars (from acid hydrolysis of rice straw).

Following the equal addition of 0.1 g of adsorbents, the VFA concentrations computed were 1.00 M and 0.95 M, respectively, according to the results of the VFA concentration determination from the titration of biogas liquid with 0.1 M NaOH. This was greater than the untreated fermentation's level (the VFAs determined were 0.29 m). The outcomes suggest that VFAs absorbed during anaerobic fermentation can be used (see Fig. 7). This meant that while the acute VFAs were removed from the solution and the crucial microbes could function effectively, a higher level of fermented efficacy was attained [26,48].
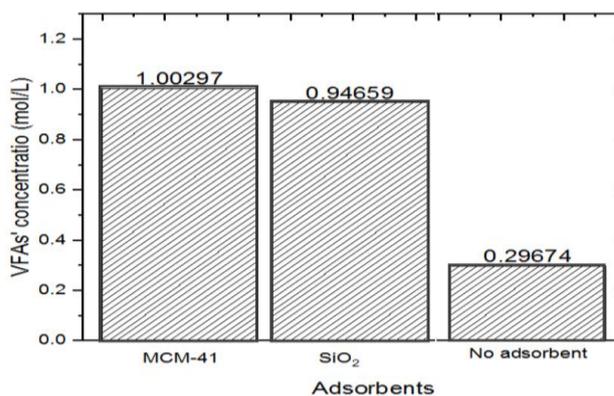

Fig.7. Comparison of VFAs' removal efficiencies between added 0.1 g adsorbents (MCM-41 and SiO₂) and without the adsorbent of anaerobic fermentation of 0.2 g reducing sugar (from acid hydrolysis of rice straw).

3.5 Kinetics of biogas fermentation from reducing sugars

At 0.2% v/v at 42 °C for 420 minutes, the kinetics of biogas fermentation from reducing sugars were tested. 0.1 g of

reducing sugars given to the fermentation process were equally absorbed by SiO_2 and MCM-41. The solution demonstrates that after 120 minutes of fermentation, the quantities of reducing sugars were practically constant. The paucity of nutrients to digest and other biogas components as a result of the decline in reducing sugars may help to explain this [49] (Figure 8).
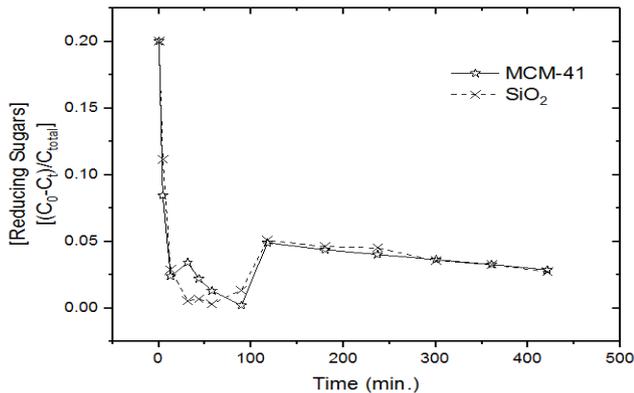

Fig.8. Digestion rate of reducing sugar fermentation carried out on the condition of 1.0g MCM-41 and SiO₂ adsorbents, 2.0 g reducing sugars, %10v/v of rumen fluid at 42°C for 420 minutes.

Figure 9 depicts the generation of CO_2 and CH_4 during the adsorption of VFAs on SiO_2 and MCM-41 adsorbents as well as on adsorbentless surfaces. According to the solution, adding adsorbents significantly raised the amount of CO_2 (3.76 mL) and CH_4 (2.94 mL) over 3.97 times when compared to not using an adsorbent (0.74 mL). SiO_2 (3.76 mL) and MCM-41 (2.94 mL) both produced small differences in CO_2 formation, but not in CH_4 formation (approximated 0.62 mL on both SiO_2 and MCM-41). It can be inferred from the -OH functionalized groups on both adsorbents that MCM-41 has a significant amount of active groups that were used to adsorb polar molecules [39]. Additionally, Shavi et al. [50] found that montmorillonite, a zeolite family related to MCM-41, adsorbed CH_3COO^- and CH_3COOH on the O atoms of its surface. This demonstrated that VFAs, as intermediate products, could indeed be continuously transformed to biogas on the surfaces of SiO_2 and MCM-41 [26].

The pseudo-second order was used to calculate the link between lowering sugar decreases and reaction time, as seen in Figures 10A and 10B. The half-lives of the reactions were 3.31 and 11.3 minutes, respectively, while the reaction constants of k_{SO_2} and k_{MCM-41} were 3.0208 and 0.8875 s^{-1} mol^{-3}, respectively. The reaction was well-fitted using quadratic regression, and these fit-well kinetic models were identical to anaerobic reducing sugar fermentation (banana peel under pretreatment conditions) [51].
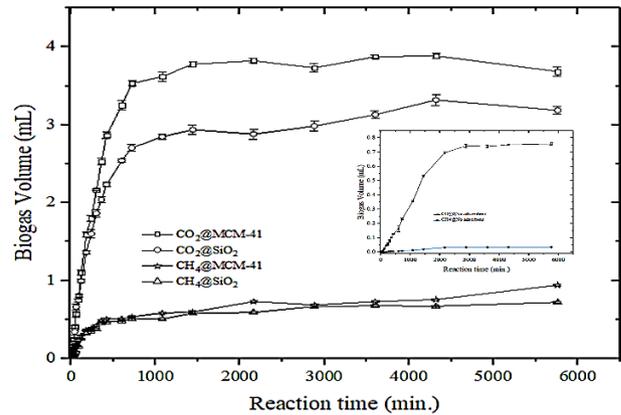
Fig. 9. Adsorption of VFAs on SiO₂ and MCM-41 to form CH₄ and CO₂ for anaerobic fermentation of reducing sugars (rice straw) catalyzed with 10% v/v of rumen fluid at 42 °C for 5,460 minutes.
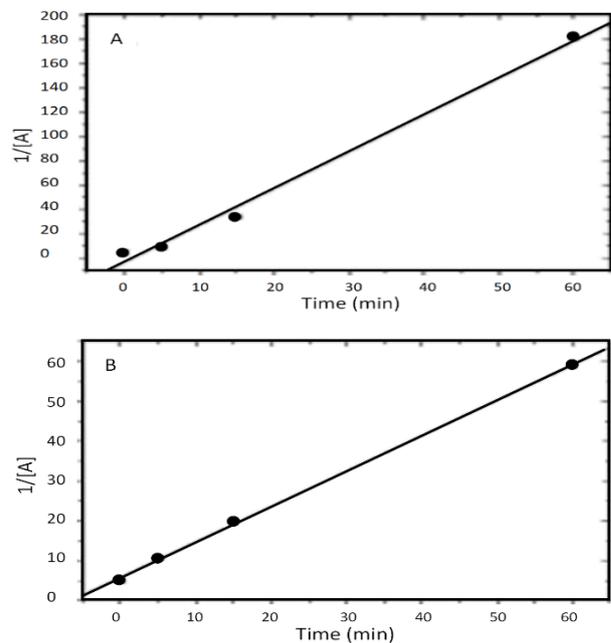
Fig. 10. Pseudo-second reaction of reduce sugar fermentation carried out on the condition of 1.0g SiO₂ adsorbent.

4. CONCLUSIONS

SiO_2 adsorbents made using the acid leaching approach and MCM-41 made using the hydrothermal method both worked well for VFA adsorption. At low angles of 2θ, XRD revealed the MCM-41 and SiO_2 characteristic peaks (1.5-22.5 degrees). Using BET and molecular adsorption, surface areas of 167.9 and 973 m²/g for SiO_2 and MCM-41 (pore sizes of 25–50 Å) were determined. With an average yield of 28.9 mg/L, acid hydrolysis made rice straw easily accessible. The anaerobic fermentation of rice straw (reducing sugars) reached a level that was roughly 1.60 times higher than that of solid rice straw in 420 minutes. The biogas levels were considerably increased by around 2.07 mL over that of the non-added adsorbent (Produces 13.1 mL

of CH_4) by adding 0.1 g SiO_2 (Produces 27.1 mL of CH_4) and 0.1 g MCM-41 (Produces 28.2 mL of CH_4). During anaerobic fermentation, the concentrations of VFAs adsorbed on 0.1 g of MCM-41 (Removes the VFAs' concentration of 1.00 M) and SiO_2 (Removes the VFAs' concentration of 0.95 M) were both significantly higher than those of the non-adding adsorbent (Removes the VFAs' concentration of 0.29 M). The amount of CO_2 (3.76 mL) and CH_4 (2.94 mL) significantly increased when adsorbents were added compared to when they weren't (0.74 mL). However, there was no discernible difference between CO_2 formation on SiO_2 (3.76mL) and MCM-41 (2.94 mL), whereas CH_4 formation was not (approximated 0.62 mL on both SiO_2 and MCM-41). For kinetics, k_{SO_2} and k_{MCM-41} were 3.0208 and 0.8875 $s^{-1}mol^{-3}$, with the half-life values of 3.31 and 11.3 minutes, respectively. Quadratic regression or pseudo-second order was used to fit the anaerobic fermentation of reducing sugars.

ACKNOLEDGEMENT

REFERENCE

[1] F. Carvalheiro, L.C. Duarte,; and F.M. Gírio, 2008. Hemicellulose biorefineries: a review on biomass pretreatments, Journal of Scientific & Industrial Research, (67) : 849-864

[2] A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R.A. Dixon, P. Gilna, M. Keller, P. Langan, A.K. Naskar, J.N. Saddler, T.J. Tschaplinski, G.A. Tuskan,; and C.E. Wyman, 2014. Lignin Valorization: Improving Lignin Processing in the Biorefinery, Science, (344) : 55.

[3] A. Barwińska Małajowicz, M. Knapková, K. Szczotka, M. Martinkovičová,; and R. Pyrek, 2023. Energy Efficiency Policies in Poland and Slovakia in the Context of Individual Well-Being, Energies, (16) : 116.

[4] S. Mirmohamadsadeghi, Z. Chen,; and C. Wan, 2016. Reducing biomass recalcitrance via mild sodium carbonate pretreatment, Bioresource Technology, (209) : 386-390.

[5] N. Armaroli,; and V. Balzani, 2006. The Future of Energy Supply: Challenges and Opportunities, Angewandte Chemie International Edition, (46) : 52-66.

[6] S. Wang, G. Zhang, P. Zhang, X. Ma, F. Li, H. Zhang, X. Tao, J. Ye,; and M. Nabi, 2018. Rumen fluid fermentation for enhancement of hydrolysis and acidification of grass clipping, Journal of Environmental Management, (220) : 142-148.

[7] Y. Zheng, J. Zhao, F. Xu,; and Y. Li, 2014. Pretreatment of lignocellulosic biomass for enhanced biogas production, Progress in Energy and Combustion Science, (42) : 35-53.

[8] H. Chen, J. Liu, X. Chang, D. Chen, Y. Xue, P. Liu, H. Lin,; and S. 2017. Han, A review on the pretreatment of lignocellulose for high-value chemicals, Fuel Processing Technology, (160) : 196-206.

[9] R. Singh, M. Srivastava,; and A. Shukla, 2016. Environmental sustainability of bioethanol production from rice straw in India: A review, Renewable and Sustainable Energy Reviews, (54) : 202-216.

[10] P. Cheewaphongphan, A. Junpen, O. Kamnoet,; and S. Garivait, 2018. Study on the Potential of Rice Straws as a Supplementary Fuel in Very Small Power Plants in Thailand, Energies report.

[11] A. Satlewal, R. Agrawal, S. Bhagia, P. Das,; and A.J. Ragauskas, 2016. Rice straw as a feedstock for biofuels: Availability, recalcitrance, and chemical properties, Biofuels, Bioproducts and Biorefining, (12) : 83-107.

[12] W. Wang, X. Wu, A. Chen, X. Xie, Y. Wang,; and C. Yin, 2016. Mitigating effects of ex situ application of rice straw on CH4 and N2O emissions from paddy-upland coexisting system, Scientific Reports, (6) : 37402.

[13] S. Negi, H. Dhar, A. Hussain,; and S. Kumar, 2018. Biomethanation potential for co-digestion of municipal solid waste and rice straw: A batch study, Bioresource Technology, (254) : 139-144.

[14] R. Guan, X. Li, A.C. Wachemo, H. Yuan, Y. Liu, D. Zou, X. Zuo, ; and J. Gu, 2018. Enhancing anaerobic digestion performance and degradation of lignocellulosic components of rice straw by combined biological and chemical pretreatment, Science of The Total Environment, (638) : 9-17.

[15] Y. Wei, X. Li, L. Yu, D. Zou,; and H. Yuan, 2015. Mesophilic anaerobic co-digestion of cattle manure and corn stover with biological and chemical pretreatment, Bioresource Technology, (198) : 431-436.

[16] K. Hussaro, J. Intanin,; and T. Sombat, 2014. Biogas Production of Animal Manure with Wastewater From Toddy Palm Process with Circulate System for The Community: Case Study Phechaburi Province.

[17] R. Agrawal, A. Satlewal, M. Kapoor, S. Mondal,; and B. Basu, 2018. Investigating the enzyme-lignin binding with surfactants for improved saccharification of pilot scale pretreated wheat straw, Bioresource Technology, (224) : 411-418.

[18] D. Wang, H. Shi, Y. Xin, Y. Zhang,; and P. Ai, X. Li, 2018. Mild Acid Hydrolysis of Rice Straw for Highly Efficient Methane Generation with Hydrolysates, BioResources; Vol 13, No 4.

[19] H. Zhang, P. Zhang, J. Ye, Y. Wu, W. Fang, X. Gou,; and G. Zeng, 2016. Improvement of methane production from rice straw with rumen fluid pretreatment: A feasibility study, International Biodeterioration & Biodegradation, (113) : 9-16.

[20] H.M. Warade, R.A. Daryapurkar,; and P.B. Nagarnaik, 2021 Impact of Micronutrients on Bioenergy Production with Addition of Animal Dung—A Pilot-Scale Study, Advances

in Civil Engineering and Infrastructural Development, Springer (1) : 427-436.

[21] S. A., 2005. Enhancement of biogas production from biomass using hydrothermal conditioning and partial oxidation, University of Sharjah journal of pure and applied sciences, (2) : 59-74.

[22] X. Gómez-Quiroga, K. Aboudi, C.J. Álvarez-Gallego,; and L.I. Romero-García, 2022. Successful and stable operation of anaerobic thermophilic co-digestion of sun-dried sugar beet pulp and cow manure under short hydraulic retention time, Chemosphere, (293) :133-484.

[23] D. Divya, L.R. Gopinath,; and P.M. Christy, 2015. A review on current aspects and diverse prospects for enhancing biogas production in sustainable means, Renewable and sustainable energy reviews, (42) : 690-699.

[24] A.J. Mawson, R.L. Earle,; and V.F. Larsen, 1991. Degradation of acetic and propionic acids in the methane fermentation, Water Research, (25) : 1549-1554.

[25] I.H. Franke-Whittle, A. Walter, C. Ebner,; and H. Insam, 2014. Investigation into the effect of high concentrations of volatile fatty acids in anaerobic digestion on methanogenic communities, Waste Management, (34) : 2080-2089.

[26] B.A. Dehority, 2002. Gastrointestinal Tracts of Herbivores, Particularly the Ruminant: Anatomy, Physiology and Microbial Digestion of Plants, Journal of Applied Animal Research, (21) : 145-160.

[27] C.M.B. Membrive, 2016. Anatomy and Physiology of the Rumen, Rumenology, Springer, 1-38.

[28] Dalhoff, R., Rababah, A., Sonakya, V., Raizada, N.,; and Wilderer, P.A., 2003. Membrane separation to improve degradation of road side grass by rumen enhanced solid incubation, Water Sci Technol (48) : 163-168.

[29] K.-U. Do,; and X.-Q. Chu, 2022. Performances of membrane bioreactor technology for treating domestic wastewater operated at different sludge retention time, Development in Wastewater Treatment Research and Processes, Elsevier, (1) :107-122.

[30] N. Cakiryilmaz, H. Arbag, N. Oktar, G. Dogu,; and T. Dogu, 2018. Catalytic performances of Ni and Cu impregnated MCM-41 and Zr-MCM-41 for hydrogen production through steam reforming of acetic acid, Catalysis Today.

[31] S. Artkla, W.Y. Choi,; and J. Wittayakun, 2010. Comparison of TiO2/RH-MCM-41 and TiO2/TEOS-MCM-41 Hybrid Catalysts in Characteristics and Photodegradation of Tetramethylammonium, Advanced Materials Research,(1) : 93-94.

[32] J. Suassuna, A.P.d. Andrade, D.R. Menezes, Y.C.F. Teles, C.M. Araujo, L.K.S. Lima, P.M.G. Beelen, A.L.R. Magalhães, B. Fernandes,; and A.N. Medeiros, 2023. Accuracy of Techniques for Predicting Gas Production by Ruminants Associated with Diet, Fermentation, (9) : 39-40.

[33] W. Jin, X. Xu, Y. Gao, F. Yang,; 2014. G. Wang, Anaerobic fermentation of biogas liquid pretreated maize straw by rumen microorganisms in vitro, Bioresource Technology, (153) : 8-14.

[34] P.D. Florendo, Sharma-shivappa,; and V. VFellner, 2018. Cattle rumen microorganisms hydrolysis for switchgrass saccharification, volatile fatty acids and methane production, International Journal of Agricultural Technology, (14) : 31-43.

[35] S. Artkla, 2012. Photodecomposition of polyphenols in E.

[36] P. Schacht, L. Noreña-Franco, J. Ancheyta,; and S. Ramírez, 2004. I. Hernández-Pérez, L.A. García, Characterization of hydrothermally treated MCM-41 and Ti-MCM-41 molecular sieves, Catalysis Today, (98) : 115-121.

[37] H. Wang, Z. Chen, X. Deng, S. Wu, Q. Yu, W. Yang,; and J. Zhou, 2018. Template-Free Synthesis of Macroporous SiO2 Catalyst Supports for Diesel Soot Combustion, Industrial & Engineering Chemistry Research, (57) :11600-11607.

[38] A. Surachai,; and W. Jatuporn, 2009. Enhancement of Catalytic Performance of MCM-41 Synthesized with Rice Husk Silica by Addition of Titanium Dioxide for Photodegradation of Alachlor, EnvironmentAsia, (2) : 41-48.

[39] S. Artkla, W. Kim, W. Choi,; and J. Wittayakun, 2019. Highly enhanced photocatalytic degradation of tetramethylammonium on the hybrid catalyst of titania and MCM-41 obtained from rice husk silica, Applied Catalysis B: Environmental, (91) : 157-164.

[40] Pisit, M. Sriprapakhan, P.; and Artkla , S., 2018. Highly enhancement of mineralized hydrocarbon formation in biogas by Fe-Cement based sand from anaerobic fermentation of agricultural wastes catalyzed by rumen fluid, The Grand GMSARN International Conference 2018 on "Energy, Environment, and Development in GMS" Nanning, Guangxi , China.

[41] A. Teghammar, K. Karimi, I. Sárvári Horváth,; and M.J. Taherzadeh, 2012. Enhanced biogas production from rice straw, triticale straw and softwood spruce by NMMO pretreatment, Biomass and Bioenergy, (36) : 116-120.

[42] Z. Anwar, S. Akram,; and M. Zafar, 2023. Production of Bioethanol from Mixed Lignocellulosic Biomass: Future Prospects and Challenges, Agroindustrial Waste for Green Fuel Application, (1) : 313-326.

[43] A. Srisathat, 2017. Investigation of kinetics and thermodynamics of anaerobic fermentation enhanced by rumen fluid catalyst, Chemistry, Roi-Rajabhat University, unpublished, pp. 61.

[44] K. Chandrasekhar, K. Amulya,; and S. Venkata Mohan, 2015. Solid phase bio-electrofermentation of food waste to harvest value-added products associated with waste remediation, Waste Management, (45) : 57-65.

[45] A.S. Deval, H.A. Parikh, A. Kadier, K. Chandrasekhar, A.M. Bhagwat,; and A.K. Dikshit, 2017. Sequential microbial activities mediated bioelectricity production from distillery wastewater using bio-electrochemical system with simultaneous waste remediation, International Journal of Hydrogen Energy, 42 : 1130-1141.

[46] H. Sheng, D. Chen, N. Li, Q. Xu, H. Li, J. He, ; and J. Lu, 2017. Urchin-Inspired TiO2@MIL-101 Double-Shell Hollow Particles: Adsorption and Highly Efficient Photocatalytic Degradation of Hydrogen Sulfide, Chemistry of Materials, (29) : 5612-5616.

[47] S. Artkla, K. Wantala, B.-o. Srinameb, N. Grisdanurak, W. Klysubun,; and J. Wittayakun, 2009. Characteristics and photocatalytic degradation of methyl orange on Ti-RH-MCM-41 and TiO2/RH-MCM-41, Korean Journal of Chemical Engineering, (26) : 1556-1562.

[48] K. Hussaro, J. Intanin,; and S. Teekasap, 2017. Biogas production from food waste and vegetable waste for the

Sakaew Temple Community Angthong Province Thailand, GMSARN International Journal, (11) : 82-89.

[49] S. Park, Y. Li, 2012. Evaluation of methane production and macronutrient degradation in the anaerobic co-digestion of algae biomass residue and lipid waste, Bioresource Technology, (111) : 42-48.

[50] R. Shavi, J. Ko, A. Cho, J.W. Han,; and J.G. Seo, 2018. Mechanistic insight into the quantitative synthesis of acetic acid by direct conversion of CH4 and CO2: An experimental and theoretical approach, Applied Catalysis B: Environmental (229) : 237-248.

[51] P. Pei, C. Zhang, J. Li, S. Chang, S. Li, J. Wang, M. Zhao, J. Li, M. Yu,: and X. Chen, 2014. Optimization of NaOH Pretreatment for Enhancement of Biogas Production of Banana Pseudo-Stem Fiber using Response Surface Methodology, BioResources; Vol 9, (3): 25-26