

Analysis of Dual, Onboard Storage and Separation of Biogas in Carbon-Based Adsorbed Gas Systems

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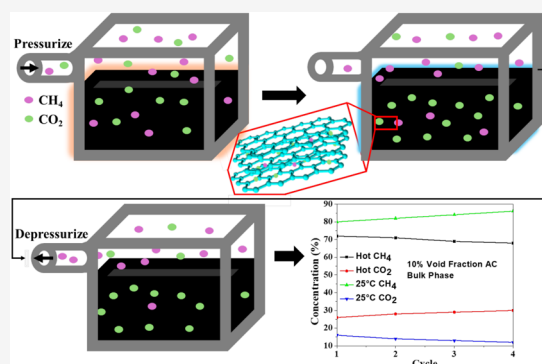
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ABSTRACT: Direct utilization of “low-grade” biogas, as an important sustainable energy resource, provides a viable approach to avoid the energy-intensive upgrading step that is often required to separate CO₂ from CH₄ in order to produce a pipeline-grade fuel gas. This study investigated dual, onboard storage and separation of biogas in an adsorbed gas system (AGS) over two highly porous carbon sorbents, Br-318 and Nuchar, in the pressure range of 0–55 bar. The AGS was pressurized with a 50/50 vol % CH₄/CO₂ feed, and working capacities as a function of charge–discharge pressures and temperatures were determined and compared with those obtained from the pure CH₄-pressurized AGS. Also, the outlet composition of the discharged gas during depressurization was determined experimentally as a function of vessel void fraction. Both sorbents exhibited an acceptable storage and separation performance; but Br-318 outperformed Nuchar by displaying a 20% higher storage capacity at a 40% void fraction. This, however, only improved the purity of delivered CH₄ by 10% at elevated temperatures. As the void fraction of the Br-318-filled AGS decreased from 40 to 10%, the weight of biogas stored increased by 35.3% and the purity of CH₄ at the outlet increased to 89%. Analysis of the temperature profiles indicated large temperature fluctuations of 52.0 and 40.3 °C during charge and discharge steps, respectively, necessitating a proper thermal management to maintain the vessel’s temperature. Additionally, cyclic test results showed capacity losses of 7.4 and 5.7% for Br-318 and Nuchar, respectively, after the fourth cycle, highlighting the importance of consistent regeneration to maintain the storage/separation performance of the biogas-filled AGS. Lastly, the biogas-filled vessel demonstrated an increased gas storage performance compared to the pure CH₄-filled vessel by exhibiting 61.8% higher storage capacity under the same conditions.



INTRODUCTION

Renewable fuel is becoming a popular topic in various industries, as more countries are implementing stricter policies and taxes on greenhouse gases, such as carbon dioxide. European countries rely heavily on the importation of fuel from countries such as Ukraine and Russia, which caused countrywide shortages of natural gas in 2022, but many of these countries are predicted to increase their biogas demand by 2050.^{1,2} Other countries such as China and India depend heavily on natural gas from nonrenewable local resources to fuel their economy.³ The use of biogas as a renewable fuel source can significantly reduce the reliance on fossil-based fuels, specially for countries with abundance of feedstocks, including waste products, food waste, and plant waste that can be easily turned into fuel.^{4,5} Once the feedstock goes through methanation from anaerobic digestion, the affluent gas comprises 50–70% CH₄, 30–40% CO₂, and ppm concentrations of H₂S.^{4,6} This exponentially increases the market for biogas as the alternate contender for high-purity CH₄ production once the upgrading (purification) step is complete. Despite this, biogas upgrading to separate CO₂ from CH₄ is an

energy-intensive process, which makes the use of biogas uneconomical in most places.⁷ Introducing fuel vessels that can simultaneously purify and store biogas could potentially address this issue and increase the accessibility to biogas fuel sources, in particular for onboard applications.^{4,8–10} However, direct storage of raw biogas in onboard vessels can cause issues such as reduced brake power due to high concentrations of CO₂ that accompany CH₄.¹¹ Therefore, capturing CO₂ in high quantities while leaving CH₄ in the bulk phase could pave the way toward direct use of raw biogas in onboard applications.

Storage of CH₄ is an energy-intensive process, with the most common forms being liquified natural gas (LNG) at –162 °C and compressed natural gas (CNG) at 200 bar. However,

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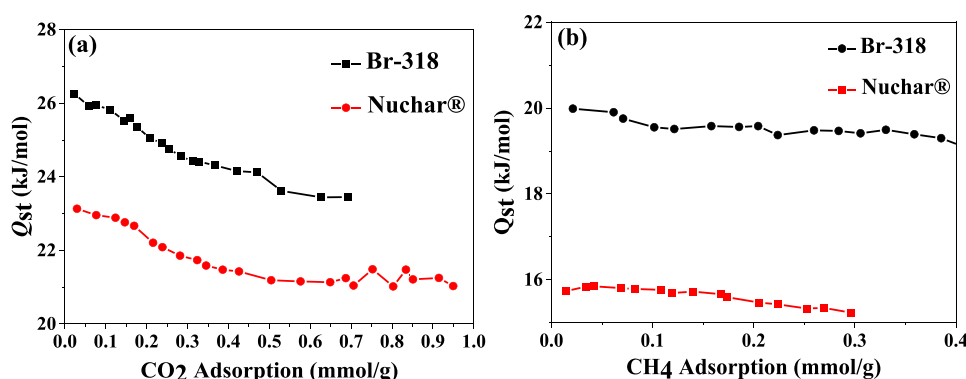


Figure 1. Heat of adsorption of (a) CO_2 and (b) CH_4 over Br-318 and Nuchar sorbents.

similar quantities of CH_4 can be stored in adsorbed vessels at much moderate temperature/pressure conditions (e.g., 25 °C and 65 bar), thereby increasing safety at lower pressures and minimizing energy losses at higher temperatures.¹² In fact, adsorption-based gas storage has become a more viable option due to the lower energy cost and smaller footprint compared to traditional liquefaction and compression options. Such systems not only enable onboard biogas storage but also allow for building small biogas plants on-site, which will in turn allow the fuel to be sourced and used directly from the farm. Once CH_4 is consumed, the remaining CO_2 can then be retrieved and sold at a higher purity.

There have been many materials developed for CH_4/CO_2 separation, including zeolites, activated carbons (ACs), metal-organic frameworks (MOFs), amine-functionalized silica/alumina, and many more.^{13–17} However, most of these candidates do not meet specific requirements for dual, onboard separation/storage, in particular, with respect to the storage capacity and durability under highly pressurized conditions.¹⁵ In particular, although ACs have been widely evaluated in CO_2/CH_4 separation or pure CH_4 storage applications, much is still relatively unknown about how these sorbents would perform under dual separation/storage conditions.^{18–20} Understanding how highly porous ACs with hierarchical pore structure perform under dual separation/storage conditions can open new avenues for accelerating the development of adsorbed gas systems (AGSs) that can run on biogas for onboard applications.²¹

In this work, we assessed the viability of two AC sorbents, namely, commercially available Nuchar (from Ingevity) and lab-made Br-318 in the context of dual separation/storage of low-grade biogas. These materials were chosen on the basis of their superior CH_4 storage performance. In particular, a record storage of 4.2 kg of CH_4 in a 40 L vessel holding 21 kg of Br-318 was previously demonstrated and reported by Rash et al.²² Our working hypothesis was that while the addition of CO_2 would reduce CH_4 storage, it could lead to enhanced fuel viability for mixed gases. The high-pressure adsorption runs were conducted in a 0.5 L vessel under various temperature, pressure, and feed conditions. Cyclic tests were also carried out to better understand the dynamics of the AC vessel under charge–discharge conditions. Additionally, the effect of the vessel's void fraction (VF) on its separation/storage efficiency was evaluated to determine the most effective loading of AC sorbents.

EXPERIMENTAL SECTION

Materials. The AC sorbents were obtained from University of Missouri, Columbia and Ingevity, known as Br-318 and Nuchar, respectively, as seen in Figure S1 of the Supporting Information. Br-318 is a compressed activated carbon–boron mixture in the form of a highly porous monolith whose synthesis procedure is reported by Rash et al.²² Ingevity's Nuchar sample uses a binder to form large clusters of pellets. The ultrahigh-purity (UHP) N_2 , CH_4 , and 50/50 vol % CH_4/CO_2 gas cylinders were all obtained from Airgas.

Material Characterization. The surface area, pore volume, and pore size distribution (PSD) of the two AC sorbents were analyzed via N_2 physisorption isotherms at 77 K on a 3Flex gas analyzer from Micromeritics. The Brunauer–Emmett–Teller (BET) and nonlocal density functional theory (NLDFT) methods were used to calculate the BET surface area and PSD, respectively. For these runs, the samples were first degassed at 350 °C under vacuum for 6 h at a ramp rate of 10 °C/min. The same instrument was used to obtain unary adsorption isotherms of CO_2 and CH_4 at 25, 35, and 55 °C. The Clausius–Clapeyron equation was then used to estimate the heat of adsorption (Q_{st}) for each of the gases. In addition, a BELSORP gas analyzer from Microtrac was used to obtain high-pressure isotherms for CO_2 and CH_4 . The skeletal densities of the AC samples were also measured by a He pycnometer in a Micromeritics AccuPyc II 1340 instrument at room temperature.

Pressurized-Vessel Separation/Storage Experiments.

The schematic of the high-pressure storage setup originally designed for pure CH_4 storage has been provided in an earlier work by Prosniewski et al.,²³ with modifications to the adsorption vessel of 0.5 L using a pressure gauge, thermocouple, scale, and sample port. An MKS mass spectrometer was used to analyze the composition of the vessel's bulk phase. For these analyses, sample bags were collected from the vessel and fed into the mass spectrometer. The quantity of Br-318 and Nuchar sorbents was set to 162 g in the 0.5 L vessel using a mesh to reduce the loss of samples from the influx and outflux of gas. For additional experiments with VFs of 10 and 25%, 190 and 220 g of Br-318 were used, respectively. In a typical run, the sorbent material was regenerated at 350 °C for 6 h in a vacuum oven before it was quickly transferred into the 0.5 L vessel, then pulling a vacuum on the vessel for 2 h. Once the room temperature was attained and the vacuum level was stable, the AGS was filled with the pressurized adsorbate gas set to a pressure of 55 bar using a gas regulator. Upon reaching the target pressure, the

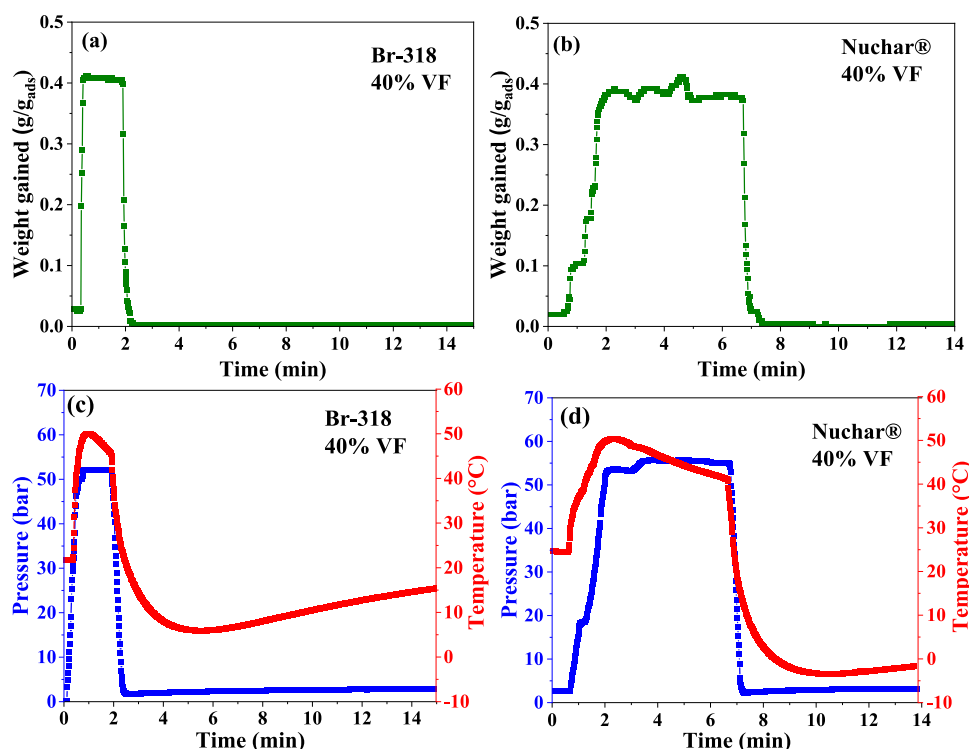


Figure 2. (a, b) Weight and (c, d) pressure/temperature profiles of the vessel pressurized with pure CH₄ at a 52–2 bar range for Br-318 and Nuchar sorbents.

valves were closed, allowing the system to stabilize. The temperature and pressure of the system were monitored for the bulk of the vessel and the weight of the system was monitored using an industrial scale. The weight gain during pressurization was used to estimate the amount of gas uptake (storage). The bulk phase of the vessel was also sampled at the target pressures using a needle sample port after stabilizing the pressure. Once the target pressure and temperature were reached, the vessel was depressurized using an evacuation valve to a target pressure of 2 bar, giving time for the temperature stabilization. The cyclic process repeated the pressurization and depressurization (charge–discharge) steps accordingly.

RESULTS AND DISCUSSION

Heat of Adsorption Estimation. Understanding the evolution of heat of adsorption (Q_{st}) for both CH₄ and CO₂

Table 1. Unused Weight of the Vessel Filled with Pure CH₄ and 50/50 vol % CH₄/CO₂ at a Discharge Pressure of 2 Bar

sorbent	feed	unused weight (g)
Br-318	CH ₄	11
	CH ₄ /CO ₂	29
Nuchar	CH ₄	9
	CH ₄ /CO ₂	22

in biogas-pressurized AGSs is important to properly manage the temperature of the vessel during charge–discharge steps, especially for onboard applications. From the unary adsorption isotherms at different temperatures (see Figure S3 of the Supporting Information), the Q_{st} data, as seen in Figure 1, were calculated for CO₂ and CH₄ gases, using the Clausius–Clapeyron method.²⁴ In the case of Nuchar, noncoverage Q_{st} values of 23.2 and 15.2 kJ/mol were estimated for CO₂ and

CH₄, respectively, whereas in the case of Br-318, the values were found to be 26.1 and 19.4 kJ/mol. These values are consistent with those reported in the literature, confirming a higher binding strength for CO₂ than CH₄, with Br-318 displaying a higher affinity toward both gases than Nuchar (ca. 12.0 and 20.3%, respectively).^{25,26} This helps predict that when loading into an AGS, a Br-318 vessel would heat to a much higher temperature and cool to a lower temperature, requiring more temperature control than a Nuchar vessel. It should also be mentioned here that Br-318 possesses a higher surface area and total pore volume than its counterpart Nuchar at 2310 m²/g (vs 1750 m²/g) and 1.20 cm³/g (vs 1.14 cm³/g), as listed in Table S1 of the Supporting Information, which can justify its slightly higher adsorption capacities for the gaseous species.

Pressurized-Vessel Separation/Storage Profiles. As a control, we analyzed the sorbents with the pure CH₄ feed alongside the mixed CO₂/CH₄ feed under the same temperature/pressure conditions to have a baseline for comparison. The vessel pressurization to 52 bar was carried out for 1 cycle of fast filling and quick release of the gas to estimate the temperature, storage capacity, and bulk phase composition at 40% VF. The pressure sensor and sample port were in the bulk section of the vessel, while the temperature sensor was buried in the sorbent section. The pure CH₄ profiles are shown in Figure 2, where the amount of CH₄ stored in the system was found to be approximately 0.41 and 0.39 g/g_{ads} for Br-318 and Nuchar, respectively. This 6.3% higher CH₄ uptake over Br-318 relative to its commercial analogue was due to its higher surface area and porosity, as demonstrated by the N₂ physisorption profiles shown in Figure S2 and the corresponding data listed in Table S1 of the Supporting Information. It should also be noted that Br-318 filled and stabilized at a higher rate compared to Nuchar (Figure 2), primarily due to the difference in their pore structures, further indicating that

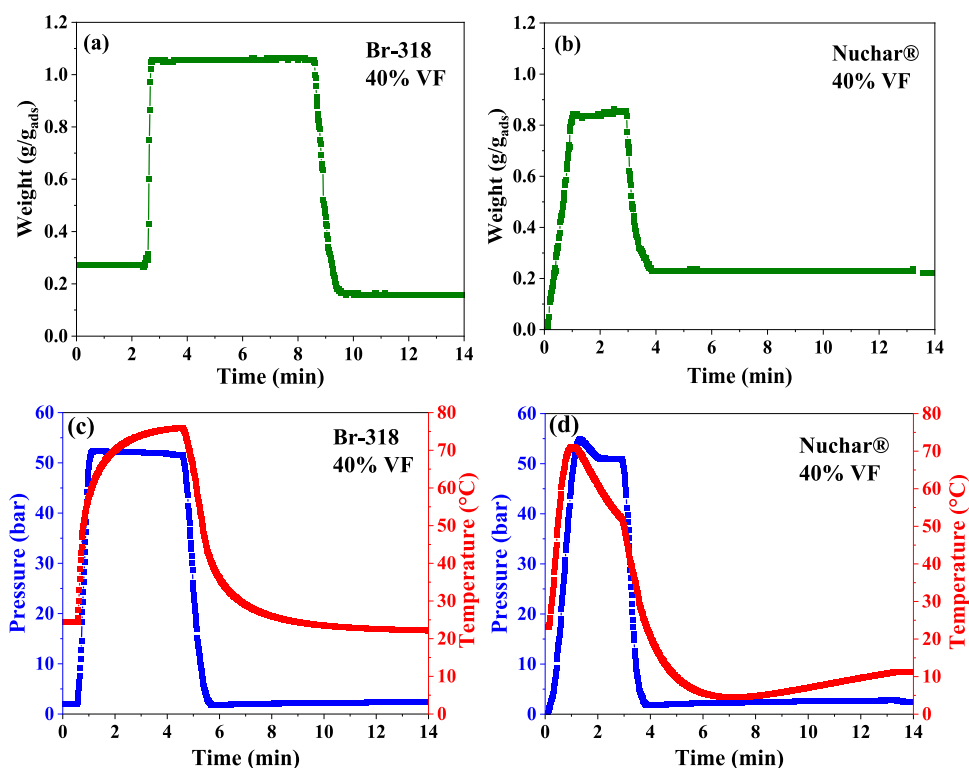


Figure 3. (a, b) Weight and (c, d) pressure/temperature profiles of the vessel pressurized with 50/50 vol % CH_4/CO_2 at a 52-2 bar range for Br-318 and Nuchar sorbents.

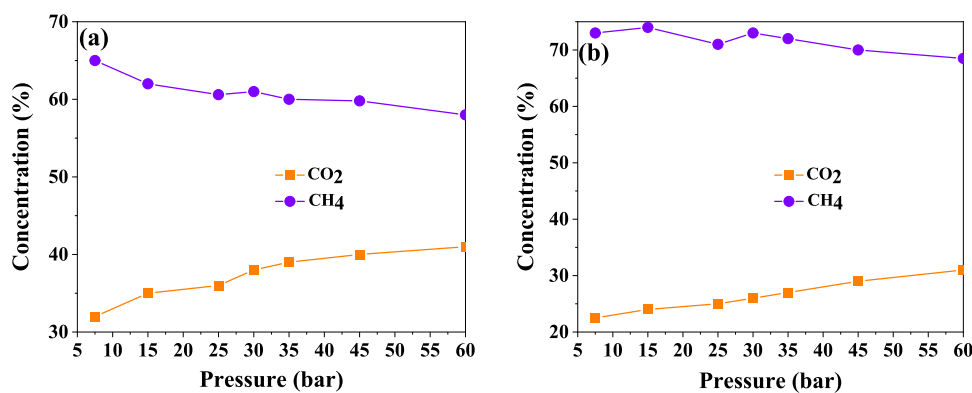


Figure 4. CH_4 and CO_2 compositions in the bulk phase of the pressurized vessel over a 7.5–60 bar pressure range for (a) Br-318 and (b) Nuchar sorbents.

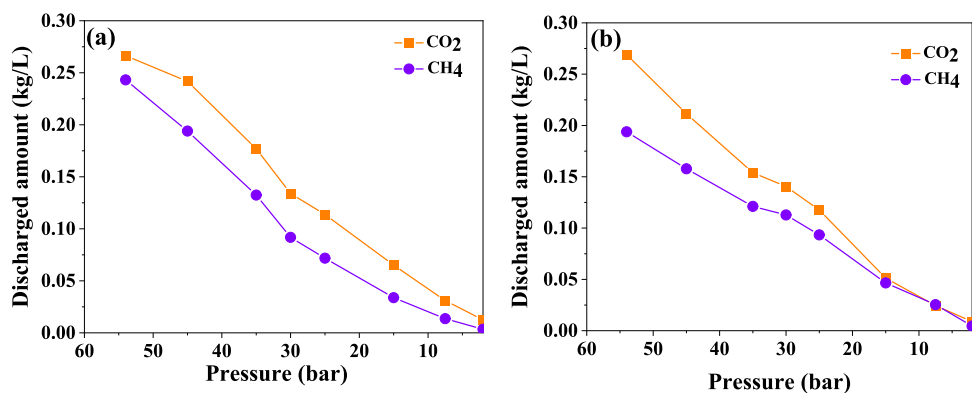


Figure 5. Quantities of CH_4 and CO_2 discharged during vessel depressurization for (a) Br-318 and (b) Nuchar sorbents.

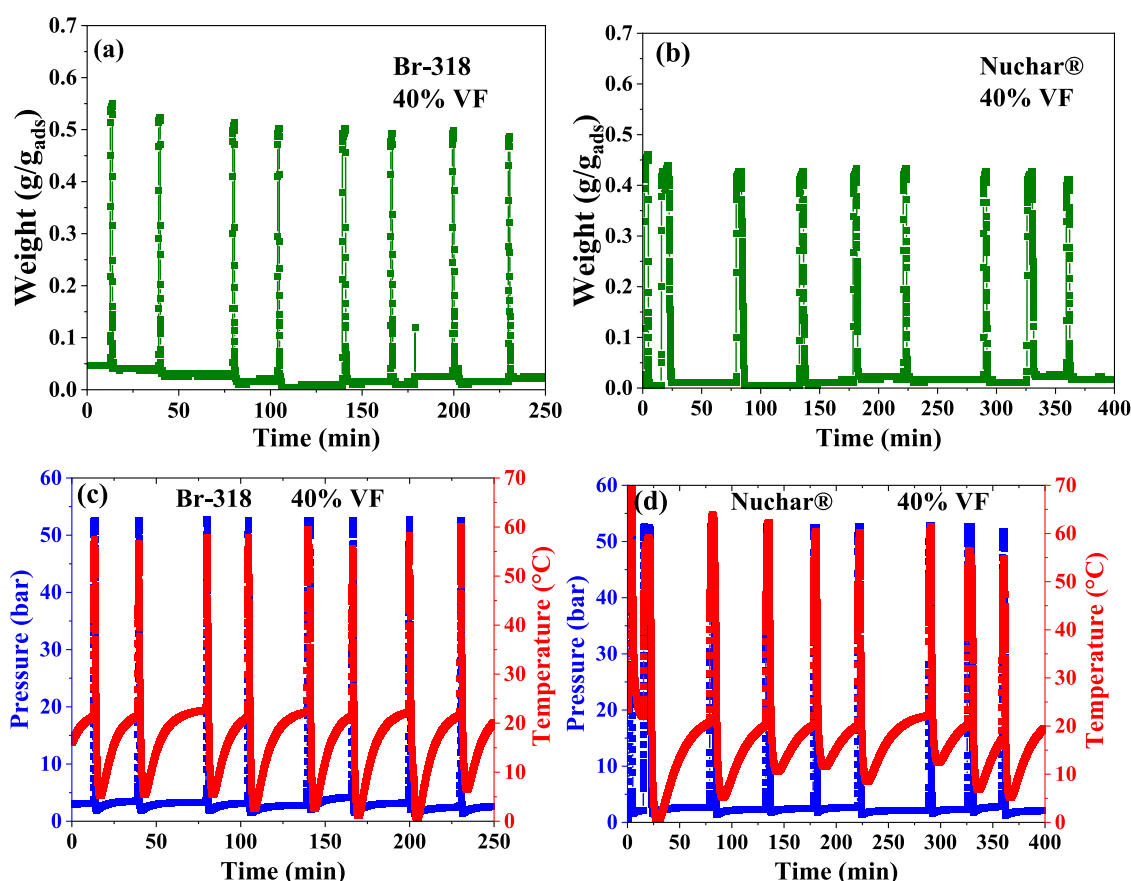


Figure 6. Cyclic (a, b) weight and (c, d) pressure/temperature profiles of the vessel pressurized with pure CH₄ at a 52–2 bar range for Br-318 and Nuchar sorbents.

the Br-318-loaded vessel requires less time to charge (pressurize). The “non-working capacity”, or unused fuel weight left in the vessel at the end of depressurization (discharge), was also estimated for the system and the corresponding values are presented in Table 1. The data confirmed minimal waste in fuel usage across the two AC sorbents for the pure CH₄ system, at the end of the discharge step. Moreover, examination of the temperature profiles for both Br-318 and Nuchar showed an increase in temperature during pressurization of 28.4 and 25.6 °C, respectively, whereas during depressurization, the temperature decreased by 39.6 and 44.6 °C, respectively. As noted earlier, the greater degree of adsorption denoted by the Br-318 sorbent resulted in higher temperature gradients when compared with Nuchar. Therefore, Br-318 was concluded to display a higher storage capacity but at the expense of higher vessel temperature (9.86%) compared to that with Nuchar.

The corresponding profiles of the pressurized vessel with the 50/50 vol % CH₄/CO₂ feed are presented in Figure 3. The goal was to separate CO₂ from CH₄, leaving a high percentage of CH₄ in the bulk phase for usage as a fuel source. From these profiles, the pressurized vessel filled with Br-318 displayed a 20% higher weight than that filled with Nuchar (1.05 vs 0.84 g/g_{ads}). Furthermore, due to the increased affinity toward CO₂, there was an increased weight of unused fuel (nonworking capacity) of 29 g during the depressurization step compared to 22 g for Nuchar, as seen in Table 1. Both Br-318 and Nuchar displayed temperature fluctuations of 52.0 and 48.0 °C during the pressurization step, respectively, while upon depressuriza-

tion, the temperature decreased by 40.3 and 44.2 °C, respectively. The drastic temperature changes indicated that vessel discharge can cause subzero temperatures for the pressurized vessel, thereby reducing the storage efficiency. Similarly, the temperature rise during pressurization led to significant storage efficiency losses, reducing the storage capacity of CO₂ and CH₄ by 1.77 and 2.20%/°C for Br-318 and by 2.99 and 2.37%/°C for Nuchar, respectively.²⁷ Compared with the pure CH₄ system, the weight of the vessel measured during the course of pressurization was significantly increased by 60.8 and 54.2% for Br-318 and Nuchar, respectively, which indicated that more feed was adsorbed/stored in the vessel. This was expected on account of the higher affinity of sorbents toward CO₂. Despite this, issues arose when comparing the temperature profiles. Specifically, the temperatures of the Br-318-filled and Nuchar-filled vessels were, respectively, 45.5 and 45.9% higher when pressurized with CH₄/CO₂ than with pure CH₄. Such higher temperature gradients demand efficient thermal management of the AGS when pressurized with mixed gas (i.e., biogas).

The bulk phase concentrations of CH₄ and CO₂ sampled from the vessel at different pressure stages across the 7.5–60 bar range are provided in Figure 4. What can be observed here is that at a 52 bar charge pressure, more CO₂ was captured within the system, causing its concentration to drop below 50 vol %. It was also noted that while Br-318 exhibited an overall increased capacity for CH₄ and CO₂, the Nuchar sample displayed a higher selectivity toward CO₂, resulting in a higher

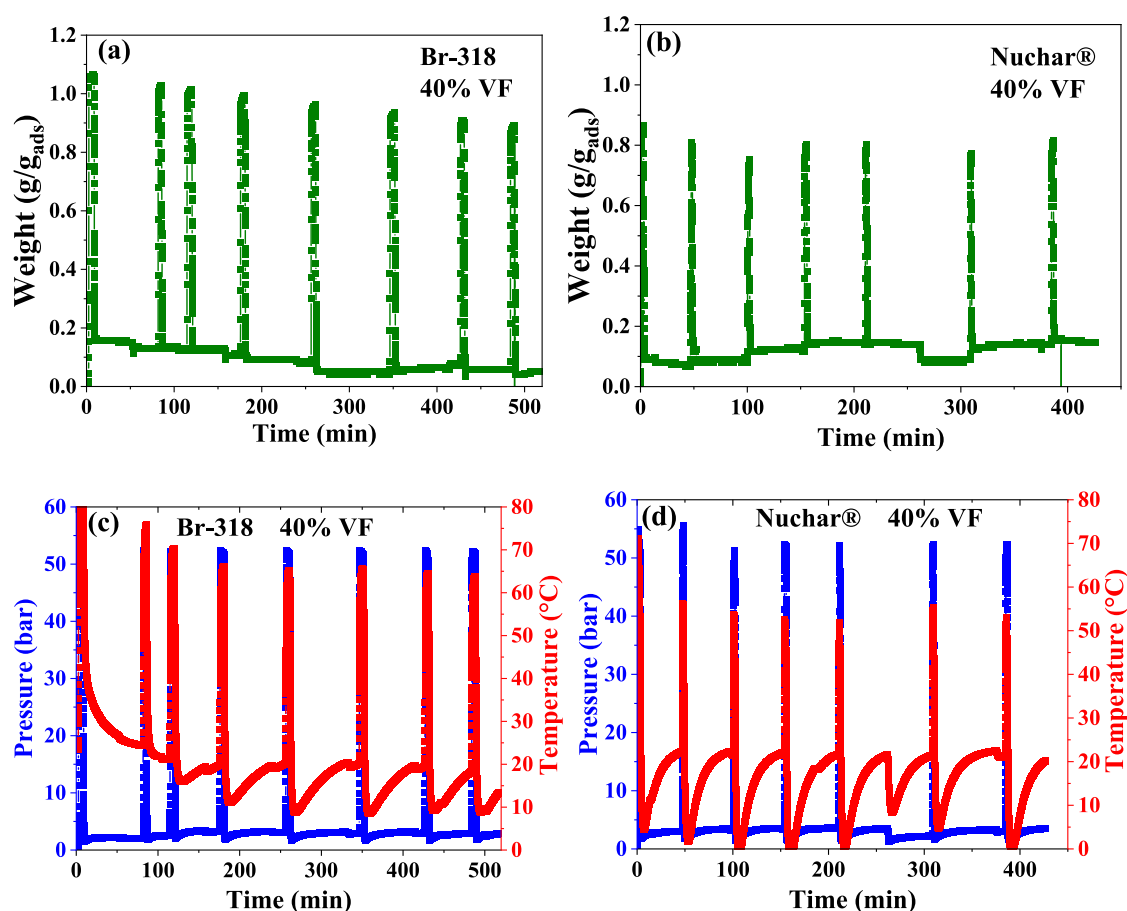


Figure 7. Cyclic (a, b) weight and (c, d) pressure/temperature profiles of the vessel pressurized with 50/50 vol % CH₄/CO₂ at a 52–2 bar range for Br-318 and Nuchar sorbents.

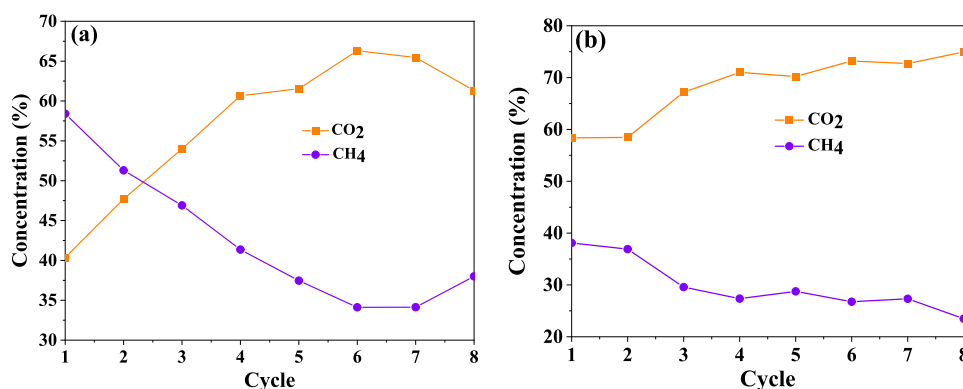


Figure 8. CH₄ and CO₂ compositions in the bulk phase of the pressurized vessel after being depressurized from 60 to 2 bar for (a) Br-318 and (b) Nuchar sorbents.

concentration of CH₄ and a lower concentration of CO₂ in the bulk phase of the pressurized vessel.

The system's discharge profiles during the depressurization step are shown in Figure 5. The values were calculated from the measured changes in the weight and concentration of the vessel. While the molar concentration of CO₂ was lower than that of CH₄, the weight difference between CO₂ and CH₄ led to an increased discharge rate for CO₂. The higher quantity of CO₂ adsorbed in the system gave rise to a higher quantity of discharge during rapid depressurization; however, the CH₄ purity was diminished due to the lower CH₄/CO₂ selectivity (0.72 vs 0.91 for Nuchar).

Cyclic Charge–Discharge Profiles. Assessing the performance of the pressurized AGS under cyclic “charge–discharge” operation is important for understanding their reusability, specially under the dual-mode operation considered here. Therefore, we performed eight charge–discharge cycles with both pure CH₄ and mixed CH₄/CO₂ feeds and the corresponding results are presented in Figures 6 and 7. Among various factors affecting the cyclability of a physisorption system, the strength of the binding between the adsorbate and the sorbent's surface plays a crucial role. From Figure 6, it can be seen that the maximum weight gains were 0.54 and 0.48 g/g_{ads} with a maximum loss in capacity of 14.8 and 10.8% for Br-

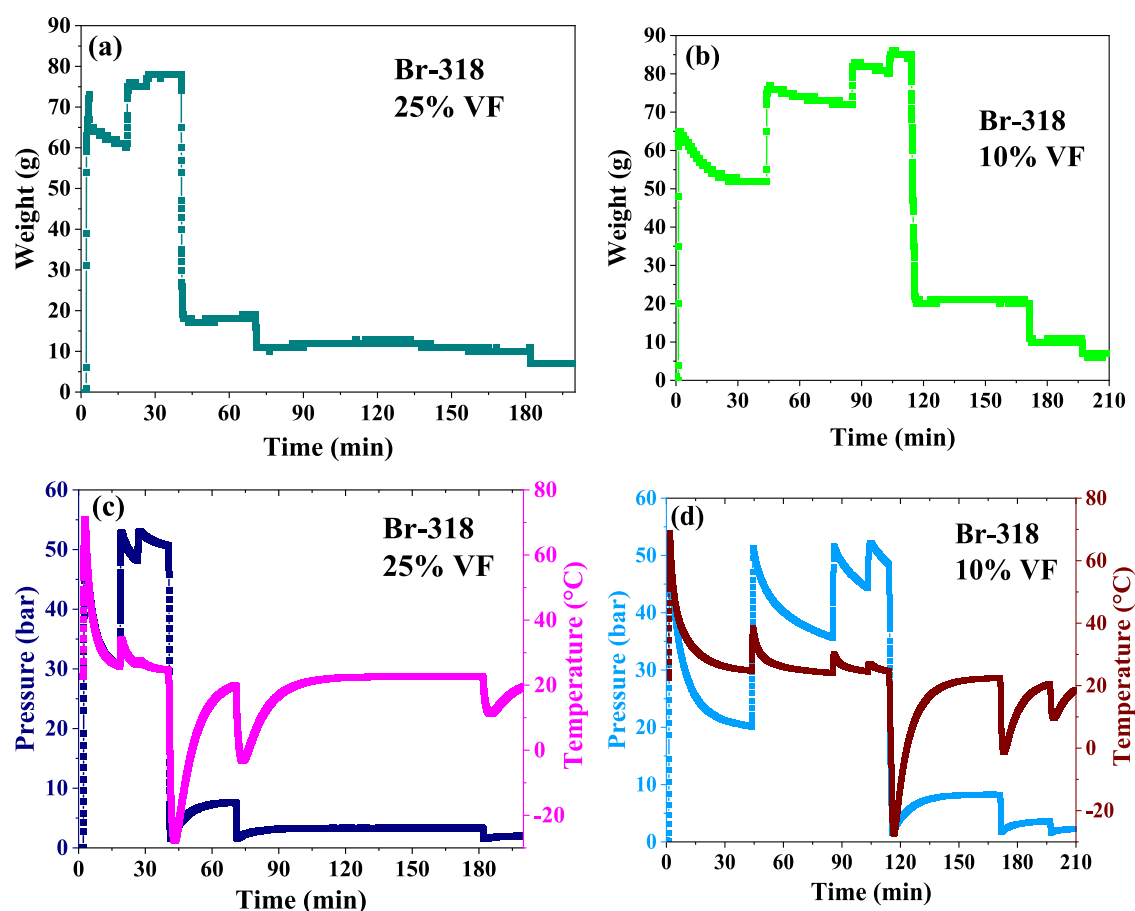


Figure 9. (a, b) Weight and (c, d) pressure/temperature profiles of the Br-318-filled vessel pressurized with pure CH_4 at 52.2 bar and VFs of 25 and 10%.

318 and Nuchar sorbents over 4 cycles, respectively. The weight started to stabilize during cycles 6–7 at 0.46 and 0.43 g/g_{ads} . W-AC and K-AC sorbents with similar surface areas were reported to have lower capacities of 0.30 and 0.38 g/g_{ads} , indicating that these materials are well suited for CH_4 storage.²⁸ Upon CH_4 capture/storage in the first cycle, there was an increase in the bed temperature of 2.1 and 5.1%, as can be seen in Figure 6c,d, which was caused by the working pressure and working capacity difference. Upon depressurization from 55 to 2 bar, average temperature drops of 36.3 and 39.9 °C were observed for Br-318 and Nuchar, respectively. Such large temperature fluctuations indicate that the pressurized vessel needs a temperature controller in order to maintain its effectiveness. Moreover, both Br-318 and Nuchar samples displayed a low nonworking capacity of ~ 0.03 and ~ 0.02 g/g_{ads} , respectively, indicating that the nonworking capacity does not increase over multiple cycles with no apparent change over 8–9 cycles; therefore, high cyclability was achievable with the pure CH_4 system.

The AC sorbents are known to have a stronger bonding energy to CO_2 than CH_4 ; therefore, the driving force will be less effective in terms of working capacity and cyclability. This was evident from the estimated Q_{st} values in Figure 1, and the CO_2 adsorption isotherms shown in Figure S4 of the Supporting Information, which also indicated that there is a high affinity toward CO_2 at high pressures than CH_4 for both sorbents. The weight profiles for the vessel pressurized with the 50/50 vol % CH_4/CO_2 feed, as displayed in Figure 7,

showed a reduction in working capacities by 7.4 and 5.7% after the fourth cycle for the Br-318 and Nuchar samples, respectively, with further reductions of 10 and 12% after cycle 7. As expected, this reduction in the gas uptake gave rise to smaller temperature spikes by approximately 23.5 and 15.9 °C, relative to those observed in the pure CH_4 system. Also, the vessel filled with Br-318 and Nuchar displayed 0.20 and 0.18 g/g_{ads} nonworking capacities, respectively, but with stable average working capacities of 0.85 and 0.66 g/g_{ads} , respectively.

When comparing the performance of the vessels pressurized with pure CH_4 and CH_4/CO_2 , (Figures 6 and 7), significant longer cycle times on the order of 35.5 and 33.6 min were realized for Br-318 and Nuchar sorbents, respectively, for the vessel pressurized with mixed gas. Such longer cycle times were the result of much higher temperature of the biogas-filled vessel, which imposed a longer time to cool down to room temperature. The most striking feature was the reduction in the CH_4 working capacity, which stemmed from the presence of CO_2 with reductions of 15% for Br-318 and 9% for Nuchar by cycle 3, whereas no significant changes were noted for the pure CH_4 system. Overall, these results indicate that under dual storage/separation mode, the biogas-filled AGS would require longer charge–discharge cycles to maintain effective separation.

The concentration profiles of the system depressurized to 2 bar, as shown in Figure 8, indicate the increase in the CO_2 concentration by 15 and 9% after cycle 4, which further increased to 25 and 14% after cycle 6 for the Br-318 and

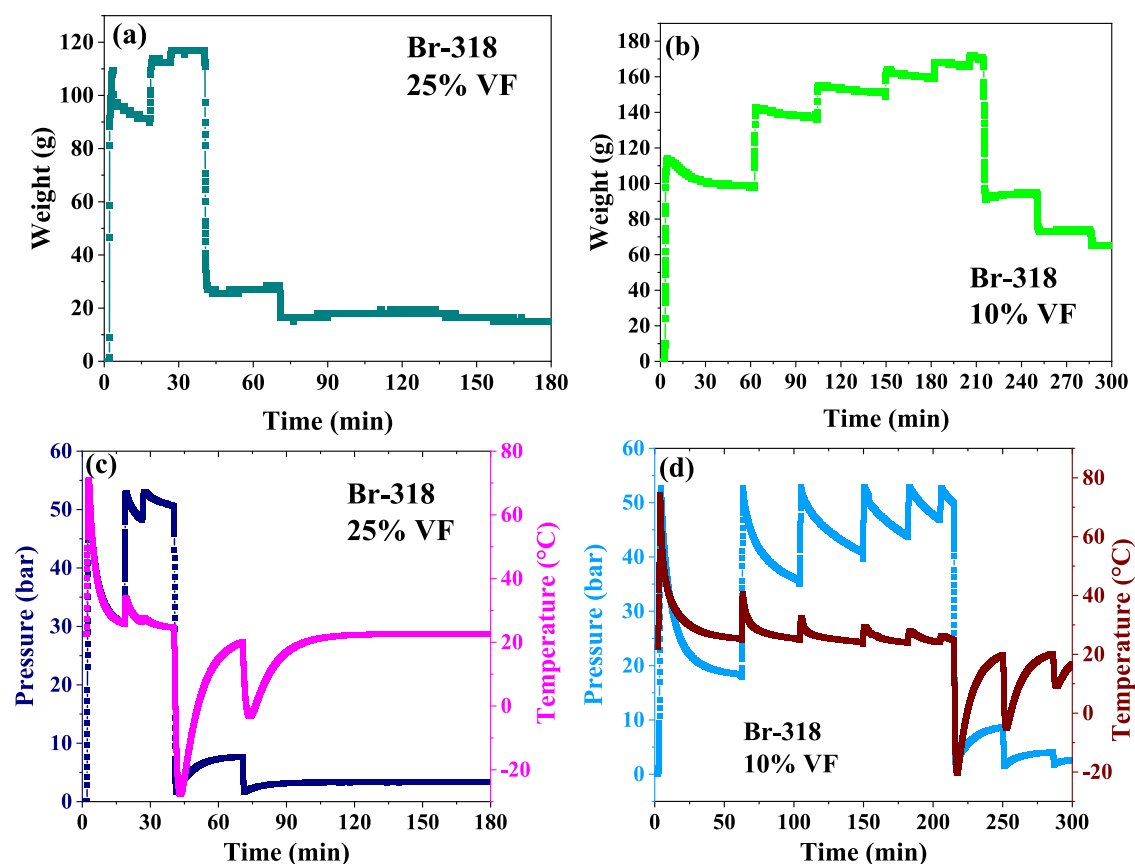


Figure 10. (a, b) Weight and (c, d) pressure/temperature profiles of the Br-318-filled vessel pressurized with 50/50 vol % CH_4/CO_2 at 52–2 bar and VFs of 25 and 10%.

Nuchar samples, respectively. Br-318 and Nuchar exhibited a change in temperature between the first cycle and subsequent cycles on the order of 17.4 and 20.7%, respectively, which stemmed from the reduction in their working capacities, as evident in Figure 7. Dropping the system temperature below 25 °C increased the gas affinity (i.e., the amount of gas adsorbed/stored into the sorbent), and hence restricted the working capacity until the system returned to room temperature. As the vessel heated back to room temperature, its pressure increased, indicating the release of the gas from the sorbent into the bulk phase. Overall, these profiles confirm that the residual CO_2 from depressurization decreases the effective brake power by failing to fully regenerate the system, which further implies that to keep the concentration of CO_2 from building further, it is important to fully regenerate the system after 3 cycles and keep from diluting the fuel source further; otherwise, concentrations of CO_2 will increase and diminish the fuel effectiveness.¹¹

Analysis of the Vessel's Void Fraction. To determine the optimal loading of the sorbent in the pressurized vessel, it is crucial to assess the effect of the VF on the storage/separation performance while determining the saturation limit of the sorbent packed in the AGS. The above results were all obtained with 40% VF. So, for this analysis, we loaded Br-318 into the 0.5 L vessel with two additional VFs at 10 and 25% and evaluated the changes in weight, temperature, full cyclability, and bulk gas compositions. The weight, pressure, and temperature profiles of the vessel pressurized with pure CH_4 for various VF values are illustrated in Figure 9. It should be noted that for this analysis, the sorbent weight was varied to

adjust the vessel's void fraction, therefore, the weight profiles shown in Figure 9a–b were not normalized to the sorbent weight. When Br-318 was rapidly pressurized to 52 bar using CH_4 , the weights were 53 g at 40% VF, 60 g at 25% VF, and 65 g at 10% VF. Compared with the 40% VF case, decreasing the VF to 25% resulted in a 12.4% increase in weight, and a further reduction in the VF to 10% gave rise to a 20.3% weight increase relative to 40% VF. Such a trend highlighted the fact that upon loading more sorbent and decreasing the void fraction of the pressurized vessel, a more efficient fuel storage can be attained. However, the spike in temperature indicated a reduction in the system's effectiveness, as it took 38 more min to fully pressurize the system at 10% VF. Overall, the efficiency of the sorbent decreased by 15.7% when the VF decreased from 25 to 10%; therefore, the increase in the overall gas weight did not effectively translate to a better system. Both VFs required 3 cycles to completely pressurize to the working pressure with total temperature changes of 85.9 and 86.3 °C at 25 and 10% VFs, respectively. Despite the difference in the working capacities, the temperature variance was only 0.5%, indicating that the depressurization step did not prolong the system's cycle time.

The weight, pressure, and temperature profiles of the Br-318-filled vessel, pressurized with 50/50 vol % CH_4/CO_2 at 52–2 bar with 25 and 10% VFs, are presented in Figure 10. A striking feature of this figure is the enhancement in the gas weight upon decreasing the vessel's VF, which can be linked to the presence of CO_2 in the adsorbed phase that is not present in the bulk phase, as shown in Figure 11. This also indicates that controlling the temperature profile is essential to optimally

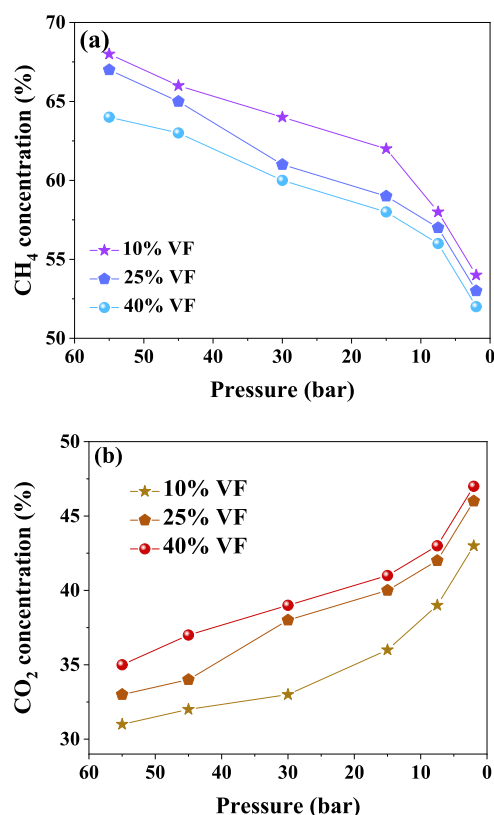


Figure 11. (a) CH₄ and (b) CO₂ gas compositions in the bulk phase of the Br-318-filled vessel pressurized with 50/50 vol % CH₄/CO₂ at VFs of 10, 25, and 40%.

pressurize the vessel. The trend continued for the CH₄/CO₂-pressurized vessel, where, compared with the 40% VF case, the weight increased by 26.1% for 25% VF and 35.3% for 10% VF. Also, as evident from Figure 10, the change in the vessel's temperature dramatically increased by 9.2% when the VF decreased from 25 to 10%, in accordance with the enhanced gas uptake and the large heat of adsorption of CO₂. Moreover, across the 55–2 bar pressure range studied, the bulk phase composition of CH₄ shown in Figure 11 was found to be higher at lower void fractions, indicating that the 40% VF system had a reduced uptake of CO₂, thereby decreasing the concentration of CH₄ in the bulk phase.

Figure 12 displays the concentration profiles of the pressurized vessel at room temperature (RT) and elevated

temperatures, denoted as “hot”, caused by adsorption. Under hot conditions, the vessel contained a higher concentration of CO₂ in the bulk phase, but once the system cooled down to room temperature, the CO₂ was more readily adsorbed out of the bulk phase, resulting in a higher CH₄ concentration in the bulk phase. At 10% VF, the system reached 89% CH₄ at room temperature. While not hitting the mark of 97% CH₄, the 10% VF system surpassed its 25% VF counterpart, reaching a CH₄ purity of 81%. This indicates an increased brake power difference of approximately 10.5%.¹¹

Thermal management of the AGSs is required to maintain the system's performance during charge-discharge cycles, which brings further complications to the system. Thermal management is typically applied by heat exchangers utilizing conductive heat transfer; however, this method has poor thermal kinetics and requires additional weight to incorporate heat exchanger tubes into a pressurized vessel.²⁹ An alternative to control temperature is electrical heating through wires.³⁰ However, this could lead to safety issues related to potential sparks in the system. Both heating methods can be employed during depressurization to help control the system's temperature; however, only the heat exchangers can be used to cool the system during the charge step. The cooling fluid can be introduced through the sorbent unit but requires more energy to run the system. Therefore, adding a proper thermal management system will reduce the mileage of a vehicle due to additional weight, which will require more power to propel a vehicle. Such trade-offs should be carefully optimized and accounted for when designing an onboard AGS.

CONCLUSIONS

In this work, we assessed the possibility of using biogas directly for fueling activated carbon-based AGSs that have the capability of dual, onboard storage/separation. The adsorption experiments considered two cases, one being the pure CH₄-pressurized vessel and the other being the CH₄/CO₂-pressurized vessel. Our results indicated that while the CH₄-pressurized vessel effectively stored CH₄ with a high cycle capability and minimal buildup, the CH₄/CO₂-pressurized vessel achieved a CH₄ purity of 88% when packed with Br-318 at 10% VF. Moreover, reducing the void fraction of the vessel resulted in higher CH₄ storage (higher purity) and lower CO₂ concentration in the bulk phase. The greater CH₄ purity indicates higher potential efficiency of the raw biogas as a direct fuel source. Regarding fuel storage and utilization for the

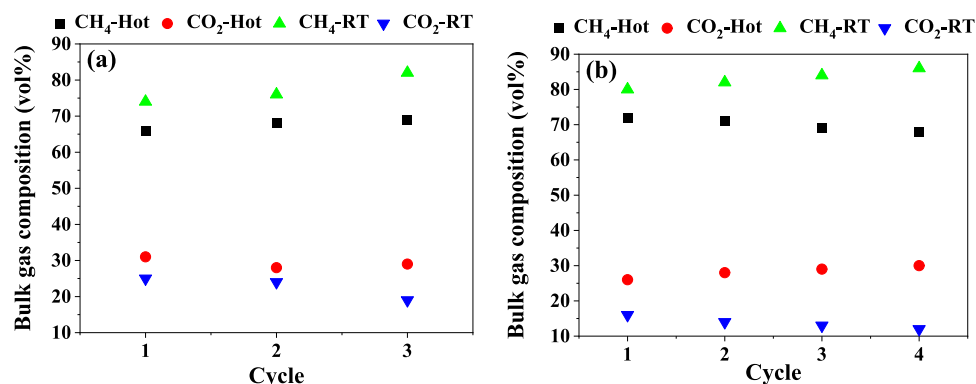


Figure 12. Bulk gas composition of the Br-318-filled vessel pressurized with 50/50 vol % CH₄/CO₂ after pressurization (hot) and after cooling to room temperature (RT) for VFs of (a) 25 and (b) 10%.

onboard separation of CH₄/CO₂, Br-318 outperformed its commercial Nuchar analogue by displaying 9.6% higher CO₂ uptake with under identical conditions. The results highlighted several key factors such as large temperature gradients during charge–discharge cycles for CH₄/CO₂-pressurized AGSs that need to be carefully managed to optimize the cyclability and overall effectiveness of the vessel. Such large temperature fluctuations result in long cycle times, further exacerbated by a decreased VF. The solution would be to modify the AGS to incorporate a heat exchanger to cool the system when charging and heat the system when discharging, thereby reducing the temperature gradient and shortening the overall cycle time. Another important factor affecting the cyclability of the biogas-pressurized tank was found to be the higher binding strength of CO₂, which reduced the overall capacity by 7.4% for Br-318 and by 5.7% for Nuchar after 4 cycles. Overall, this proof-of-concept study demonstrates the feasibility of the dual, separation/storage concept for direct utilization of low-grade biogas in onboard applications, however, the design of such AGSs should be carefully optimized to further improve the purity of the delivered CH₄, while also accounting for large thermal fluctuations during charge-discharge steps.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.4c01868>.

Activated carbon samples, N₂ physisorption isotherms, PSD profiles, low-pressure unary CO₂ and CH₄ adsorption isotherms, and high-pressure unary CO₂ and CH₄ adsorption isotherms (PDF)

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Notes

The authors declare no competing financial interest.

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