Upgrading of Biogas to Methane Based on Adsorption

Jun Liu 1,2,*, Qiang Chen 1 and Peng Qi 2

1 Industrial Center, Harbin Vocational and Technical College, Harbin 150030, China; chenqiang8971@163.com
2 School of Mechanical Engineering, Harbin Vocational and Technical College, Harbin 150030, China; Qipeng0325@163.com
* Correspondence: k___h@163.com; Tel.: +86-451-86617198

Received: 4 July 2020; Accepted: 31 July 2020; Published: 5 August 2020

Abstract: Upgrading raw biogas to methane (CH$_4$) is a vital prerequisite for the utilization of biogas as a vehicle fuel or the similar field as well. In this work, biogas yield from the anaerobic fermentation of food waste containing methane (CH$_4$, 60.4%), carbon dioxide (CO$_2$, 29.1%), hydrogen sulfide (H$_2$S, 1.5%), nitrogen (N$_2$, 7.35%) and oxygen (O$_2$, 1.6%) was upgraded by dynamic adsorption. The hydrogen sulfide was removed from the biogas in advance by iron oxide (Fe$_2$O$_3$) because of its corrosion of the equipment. Commercial 13X zeolite and carbon molecular sieve (CMS) were used to remove the other impurity gases from wet or dry biogas. It was found that neither 13X zeolite nor CMS could effectively remove each of the impurities in the wet biogas for the effect of water vapor. However, 13X zeolite could effectively remove CO$_2$ after the biogas was dried with silica and showed a CO$_2$ adsorption capacity of 78 mg/g at the condition of 0.2 MPa and 25 °C. Additionally, 13X zeolite almost did not adsorb nitrogen (N$_2$), so the CH$_4$ was merely boosted to ac. 91% after the desulfurated dry biogas passed through 13X zeolite, nitrogen remaining in the biogas. CMS would exhibit superior N$_2$ adsorption capacity and low CO$_2$ adsorption capacity if some N$_2$ was present in biogas, so CMS was able to remove all the nitrogen and fractional carbon dioxide from the desulfurated dry biogas in a period of time. Finally, when the desulfurated dry biogas passed through CMS and 13X zeolite in turn, the N$_2$ and CO$_2$ were sequentially removed, and then followed the high purity CH$_4$ (≥96%).

Keywords: biogas; methane; adsorption; 13X zeolite; carbon molecular sieve

1. Introduction

Human civilization relies heavily on the use of fossil fuels, which has resulted in a rapid depletion of natural energy sources, serious environmental pollution and climate change, so there is growing demand to develop renewable energy in the world. Biogas, generated from the anaerobic digestion of organic waste, is considered a renewable energy and can maintain the carbon cycle in nature. Improving biogas projects can not only provide energy but also prevent the emission of CH$_4$, a much more powerful greenhouse gas than CO$_2$, so this field has attracted worldwide attention due to its dual benefits for energy and the environment [1–3]. There are a variety of promising applications for upgraded biogas, such as incorporation in natural gas grids, vehicle fuel or producing chemical feedstock [4]. Take vehicle fuel for example—this field has attracted a growing interest [4–7]. It is now widely acknowledged that transportation is a large energy consuming and CO$_2$ emitting sector. In addition, vehicles burning gasoline and diesel usually give off sulfur dioxide, carbon monoxide and other carcinogenic and toxic substances, such as benzene and lead, that endanger human health. Replacing gasoline and diesel with natural gas or biogas as a vehicle fuel can greatly reduce CO$_2$ emissions and avoid releasing carcinogenic and toxic substances [8,9].

Biogas typically contains CH$_4$, CO$_2$ and some small amount of other impurities such as H$_2$S, N$_2$, O$_2$, etc. It is necessary to remove CO$_2$ and other impurities from biogas to increase the methane
content and thereby the heating value \[10,11\]. The CH\textsubscript{4} content is often required at least to be 95 v/v\% due to application requirements \[12\]. The most common methods for removing CO\textsubscript{2} from biogas include pressure swing adsorption (PSA), high pressure water scrubbing, amine scrubbing and membrane processes \[13\]. Among them, PSA is considered very suitable for biogas upgrading because of its practical advantages, including the simplicity of its equipment, its lower energy expenses in operation and easy operation \[10,14\]. Molecular sieves are conventional commercial adsorbents for PSA technology. 13X zeolite, a Faujasite (FAU) type one, has a tridimensional aluminosilicate framework constituted by Si and Al tetrahedra linked through bridging oxygen atoms, giving rise to a regular distribution of pores and cavities of molecular dimensions. As a consequence of their well-defined crystalline structures, 13X zeolite have uniform pore sizes in the range of molecular dimensions (around 10 Å). Like 13X zeolite, carbon molecular sieve (CMS, a carbon-based material) also has precise pore size \[15\]. 13X zeolite and CMS have been considered as outstanding adsorbents for separating CO\textsubscript{2} from simulated biogas to CH\textsubscript{4}, and the adsorption capacity of CO\textsubscript{2} on them is shown in Table 1. However, the composition of real biogas is much more complicated than simulated biogas and it often changes with the types and properties of the raw materials for fermentation. It is significant to further investigate the situation of 13X zeolite and CMS purifying real biogas into high content of CH\textsubscript{4} (\(\geq 96\) v/v\%).

| Samples    | Gas Composition    | Pressure (MPa) | Temperature (°C) | CO\textsubscript{2} Adsorption Capacity (mgCO\textsubscript{2}/g) | Reference |
|------------|--------------------|----------------|------------------|-----------------------------------------------------------------|----------|
| CMS        | CH\textsubscript{4}/CO\textsubscript{2} 90/10 | 1              | 41.5             | 35.2 \textsuperscript{a}                                       | [16]     |
| CMS        | CO\textsubscript{2} 100 | 0.1            | 25               | 115 \textsuperscript{b}                                       | [17]     |
| CMS        | CO\textsubscript{2} 100 | 0.1            | 25               | 70.8 \textsuperscript{b}                                      | [18]     |
| CMS        | CO\textsubscript{2} 100 | 0.1            | 25               | 132 \textsuperscript{b}                                       | [19]     |
| CMS        | CO\textsubscript{2} 100 | 0.1            | 25               | 207 \textsuperscript{b}                                       | [20]     |
| 13X        | CO\textsubscript{2} 100 | 0.1            | 25               | 210 \textsuperscript{b}                                       | [21]     |
| 13X        | CH\textsubscript{4}/CO\textsubscript{2} 60/40 | 0.1            | 30               | 182 \textsuperscript{a}                                       | [22]     |
| 13X        | CH\textsubscript{4}/CO\textsubscript{2}/H\textsubscript{2}S 59.95/39.95/0.1 | 0.7              | 25               | 298.5 \textsuperscript{a}                                     | [23]     |
| 13X        | CH\textsubscript{4}/CO\textsubscript{2} 35/65 | 0.2            | 25               | 24 \textsuperscript{a}                                        | [14]     |
| 13X        | CO\textsubscript{2} 100 | 0.16           | 25               | 223 \textsuperscript{b}                                       | [24]     |

\textsuperscript{a} CO\textsubscript{2} adsorption capacity calculated by breakthrough curves. \textsuperscript{b} CO\textsubscript{2} adsorption capacity obtained by adsorption isotherms.

Herein, 13X zeolite and carbon molecular sieve (CMS) were used to upgrade the real biogas generated from the anaerobic digestion of food waste for the purpose of exploring new problems encountered by the adsorbents under real biogas condition, purifying the biogas into methane and highlighting the future research directions of promoting the biogas purification technology by adsorption.

2. Materials and Methods

2.1. Materials

Carbon dioxide (CO\textsubscript{2}, 99.99\%) and argon (Ar, 99.99\%) were purchased from Liming Gas Co., Ltd. (Harbin, China). Biogas was produced through the anaerobic fermentation of the food waste from the student cafeteria of the college.

The 13X zeolite and CMS used in this work were purchased from Shanghai Zeolite Molecular Sieve Co., Ltd. (Shanghai, China), and the type A silica (pellets, 2~4 mm) was purchased from Qingdao Haiyang Chemical Co., Ltd. (Qingdao, China). The shape and particle size of each adsorbent are shown in Table 2. The desulfurizing agent (Fe\textsubscript{2}O\textsubscript{3}) was supplied by Jinan Gelun Chemical Co., Ltd. (Jinan, China).
Table 2. Shape and size of adsorbent particles.

|        | CMS          | 13X         | A-Slica     |
|--------|--------------|-------------|-------------|
| shape  | Cylindrical  | Spherical   | Spherical   |
| diameter/mm | 1.7~1.8     | 3~5         | 2~4         |

2.2. Methods

The method flow-process of producing and upgrading biogas is exhibited in Figure 1.

![Method flow-process diagram.](image)

Figure 1. Method flow-process diagram.

2.2.1. Production of Biogas

Pretreatment of Raw Materials

The raw material for producing biogas used in this study was food waste after meals collected in plastic bins by college canteen, which mainly contained rice, wheat, vegetables, meat, toothpicks, etc. The food waste was transferred to the laboratory and the foreign materials that are difficult to ferment such as toothpicks were first removed from the sample. After that, the sample was ground by means of a grinder and then mixed with water at a mass ratio of 1:5. Finally, the sample contained 8 w/w% total solids (TS) and 6.5 w/w% volatile solids (VS), preparing for subsequent anaerobic experiments. The TS and VS were determined according to APHA standard methods (American Public Health Association, 2005).

Production of Biogas

Biogas was produced by two-phase anaerobic fermentation technology and the schematic diagram of gas producing equipment is shown in Figure 2. The pretreated food waste with the inoculation rate of 20% was poured into the acid-generating tank and acidified at 35°C for 24 h. After this, the acidified sample was fed into the methane-generating tank and the amount of feed was kept equal to the output of each methane-generating tank. The pH of the sample in the fermenter was monitored every day to prevent its rancidity and the biogas was collected and stored in an 8 m³ gas bag. The volume fractions of CH₄, CO₂ and N₂ in the biogas were determined by gas chromatograph (Agilent 6890), while the volume fractions of O₂ and H₂S were determined by GASBOARD/3200L portable infrared biogas analyzer produced by Wuhan Sifang Photoelectric Technology Co., Ltd. (Wuhan, China).
After this, CO\(_2\) (22 mL/min) merged with Ar (200 mL/min) controlled by mass flow meters. When the outlet concentration of each gas reached their equal to the output of each methane-generating tank. The pH of the sample in the fermenter was equal to the output of each methane-generating tank. The pH of the sample in the fermenter was 7.4 for methane-generating tank1, 7.6 for methane-generating tank2 and 7.2 for methane-generating tank3. The pH of the sample in the fermenter was determined using a portable pH meter (GASBOARD/3200L, Wuhan Sifang Photoelectric Technology Co., Ltd., Wuhan, China) to ensure that no residual sulfur dioxide was detected.

2.2.2. Purification of Biogas

Desulfurization of Biogas

The collected biogas was first pumped into a desulfurizer that was filled with Fe\(_2\)O\(_3\) and the effluent gas stream was detected by a portable infrared biogas analyzer (GASBOARD/3200L, Wuhan Sifang Photoelectric Technology Co., Ltd., Wuhan, China) to ensure that no residual sulfur dioxide was detected.

Measurement of CO\(_2\) Adsorption Capacity

CO\(_2\) adsorption from gas mixtures of CO\(_2\) and Ar gases (ca. 10 vol% CO\(_2\)) was performed in a single-stage fixed-bed flow system, as shown in Figure 3. In an adsorption process, the adsorbent was filled in the adsorption column (stainless steel tube with length of 250 mm and inner diameter of 11 mm) and Ar was introduced into the system at a flow rate of 200 mL/min to remove the air in the line. After this, CO\(_2\) (22 mL/min) merged with Ar (200 mL/min) controlled by mass flow meters. When the CO\(_2\) concentration of the CO\(_2\)/Ar mixture stabilized, the mixture gas switched to the adsorption column under the condition of 25 °C and 0.2 MPa. CO\(_2\) concentration of the outlet gas was detected by an online gas chromatograph (GC, Agilent 6890, Palo Alto, CA, USA).

![Figure 3. Single stage fixed-bed flow system.](image-url)

For biogas upgrading, a self-assembled fixed bed adsorption system, as shown schematically in Figure 2 (system for purifying), was used to separate CO\(_2\), N\(_2\) or water vapor from the biogas. The adsorption columns (13a, 13b and 13c shown in Appendix A) were responsible for filling the adsorbent for removing water vapor, N\(_2\) and CO\(_2\) respectively. The CO\(_2\), CH\(_4\) and N\(_2\) concentration in the influent and effluent gas streams were analyzed with the online gas chromatograph equipped with a thermal conductivity detector (TCD). The adsorption column(s) was placed in a temperature-controlled water bath. Prior to adsorption measurements, Ar was introduced into the adsorption column and
the pressure in adsorption column rose to 0.2 MPa. When no CO\(_2\) and N\(_2\) could be detected from the outlet, desulfurized biogas was introduced and passed through the adsorbent (in 1, 2 or 3 adsorption columns according to the research needs) at a total flow rate of 200 mL/min. The outlet concentration was determined by GC, until the outlet concentration of each gas reached their inlet state.

The adsorption capacity of CO\(_2\) on an adsorbent was calculated as follows: [25]

\[
Q = \frac{M \times F \times \int_0^t (C_0 - C)dt}{W_a} \times \frac{T_0}{T} \times \frac{1}{V_m},
\]

where \(Q\) represents CO\(_2\) adsorption capacity (mg/g); \(t\) is the adsorption time (min); \(F\) is the flow rate (mL/min); \(W_a\) is the weight of adsorbent (g); \(M\) is the molecular weight (g/mol) of CO\(_2\); \(C_0\) and \(C_t\) are the inlet and outlet concentration (vol\%) of CO\(_2\), respectively; \(T\) represents the gas temperature (K); \(T_0\) is 273 K, and \(V_m\) is the molar volume (22.4 dm\(^3\)/mol).

Regenerating of Adsorbents

After adsorption, desorption was performed with the procedure of vacuuming for 30 min and then another adsorption process followed. The vacuum pump (2xz(s)-1, China) was produced by Shanghai Deying Vacuum Lighting Equipment Co., Ltd. (Shanghai, China). The FTIR spectra of fresh and regenerated adsorbents were recorded on an ALPHA-T spectrometer (Bruker, Karlsruhe, Germany) using the KBr compression method.

3. Results and Discussion

3.1. CO\(_2\) Adsorption on 13X and CMS

CO\(_2\) adsorption performance on 13X zeolite and CMS were investigated at 25 °C under a gas containing 10\%. In order to maintain a stable total flow rate and thus conveniently calculate CO\(_2\) adsorption using Equation (1), inert gas, Ar, was mixed with CO\(_2\). The breakthrough curves are shown in Figure 4, and the corresponding CO\(_2\) adsorption capacities are 75 and 36 mg/g for 13X zeolite and CMS, respectively. Accordingly, both of the adsorbents could effectively adsorb CO\(_2\), while 13X zeolite showed higher CO\(_2\) adsorption capacity.

![Figure 4. CO\(_2\) breakthrough curves based on carbon molecular sieve (CMS) and 13X.](image)

3.2. Purification of the Humid Desulfurized Biogas

The main components of the collected original biogas in this work included CH\(_4\), CO\(_2\), N\(_2\) and H\(_2\)S, and the volume fraction of each component (except for water vapor) is shown in Table 3. In this work, there was a relatively high concentration of N\(_2\) included in the biogas, most of which resulted...
from the mixing of air during the biogas fermentation and collection. Additionally, anaerobic ammonia oxidation might also contribute a small amount of nitrogen.

| Gas     | CH$_4$ | CO$_2$ | N$_2$ | O$_2$ | H$_2$S |
|---------|--------|--------|-------|-------|--------|
| Volume fraction/% | 60.4   | 29.1   | 7.35  | 1.6   | 1.5    |

Table 3. The volume fraction of the main components in the biogas.

The biogas first passed through a large desulfurizer filled with Fe$_2$O$_3$, and the H$_2$S was completely removed, which could be confirmed by the measurement results of a biogas analyzer. Commercial 13X zeolite and CMS were chosen to separate CO$_2$ from the desulfurized biogas using a single adsorption column (only 13a in Figure 2), respectively. Figure 5 shows the breakthrough curves of CH$_4$ and CO$_2$ in desulfurized biogas whose flow was directed to the adsorbents at a flow rate of 200mL/min. It can be seen that both 13X zeolite and CMS could adsorb a certain amount of CO$_2$, because the concentrations of CO$_2$ decreased in the initial period with both of them, but CH$_4$ and CO$_2$ were detected at the same time by using both adsorbents, indicating that there could not be CO$_2$-free methane available and neither of them was able to effectively separate CO$_2$ from the desulfurized real biogas. It is speculated that the low adsorption performance of the adsorbents was caused by competitive adsorption of water vapor in the real biogas. The severely low saturation slopes imply that the rate of adsorbent that reached saturation was very low. The low adsorption kinetics were obtained because the diffusion of gases inside the adsorbent particles might be difficult if water vapor was present, so the biogas was deeply dehydrated in the next test.

![Breakthrough curve of CH$_4$ and CO$_2$ in wet desulfurized biogas](image)

Figure 5. Breakthrough curve of CH$_4$ and CO$_2$ in wet desulfurized biogas at 25 °C and 0.2 MPa.

3.3. Purification of the Dry Desulfurized Biogas

3.3.1. CO$_2$ Separation

In order to solve the problem that 13X zeolite and CMS suffered from water vapor, two adsorption columns were used. One (13a in Figure 2) was used to fill with A-type silica to absorb water vapor and another (13b in Figure 2) was packed with 13X zeolite or CMS to separate CO$_2$. The breakthrough curves of CH$_4$ and CO$_2$ in desulfurized and dehydrated biogas are exhibited in Figure 6. For 13X zeolite, complete adsorption of CO$_2$ was observed and resulted in the CO$_2$ volume fraction close to 0 during the initial period of adsorption (before breakthrough). After this period, the adsorbent began to saturate and a gradual increase in CO$_2$ volume fraction in the outlet gas was observed until complete saturation was achieved. The areas of CO$_2$ adsorption before and after breakthrough were integrated.
to calculate the total adsorption capacity, which was 78 mg CO$_2$/g for 13X zeolite. On the other hand, N$_2$ was still in the outlet gas, which explained the CH$_4$ volume fraction merely reaching ca. 91% when the outlet concentration was essentially free of CO$_2$. 13X zeolite could not effectively separate N$_2$ from the biogas. For CMS, CO$_2$ appeared soon after CH$_4$ was detected, indicating that CMS could not effectively separate CO$_2$ under this condition. However, CMS preferentially adsorbed N$_2$, which could be completely removed from the gas in a period of time, so CMS was a perfect N$_2$ adsorbent instead of CO$_2$ adsorbent if the real biogas contained N$_2$. Therefore, simply using 13X zeolite or CMS could not increase the methane concentration to a very high level, so the next step was to use 13X zeolite and CMS together to obtain a high concentration of methane.

![Graph](image)

**Figure 6.** Breakthrough curves of CH$_4$ and CO$_2$ in dry desulfurized biogas at 25 °C and 0.2 MPa.

3.3.2. Desorption and Adsorption Cycling

13X zeolite and CMS were submitted to regeneration by vacuum treatment and the gas from the outlet of pump was monitored until no CO$_2$ was detected. The total desorption time of 13X zeolite was nearly 29 min, while CMS spent about 25 min desorbing CO$_2$, indicating that CMS was more easily desorbed than 13X zeolite under this desorbing condition. In order to show the regenerability of the adsorbents, they were subjected to two consecutive adsorption/desorption cycles. It can be seen that 13X zeolite showed a significant decrease in CO$_2$ adsorption during the second cycle (Figure 7a) after vacuum treatment for 30 min. One reason for this result is that some adsorbed CO$_2$ was able to form a binary or chelated carbon-containing species with 13X zeolite (a kind of aluminosilicate) [26], which can be proved by infrared spectra (Figure 8) of fresh and regenerated 13X zeolite. As shown in Figure 8, the infrared curve of fresh 13X zeolite (red line) was similar to that of regenerated 13X zeolite (blue line) in most places, but the infrared curve of the regenerated adsorbent had an additional absorption peak at 1373 cm$^{-1}$, which corresponded to binary or chelated carbon-containing species [26]. This confirmed that 13X zeolite could not be completely regenerated by vacuum treatment. In contrast, CMS could be well regenerated, but it exhibited low CO$_2$ breakthrough time, as shown in Figure 7b.

3.4. Upgrading Biogas to CH$_4$

Considering that the ultimate goal is to obtain high-purity CH$_4$, a system including three adsorption columns was used, as shown in Figure 2. The first column (13a in Figure 2) was filled with A-type silica to eliminate water vapor, the second column (13b in Figure 2) was packed with CMS mainly to remove N$_2$, and the third column (13c in Figure 2) was filled with 13X zeolite to separate CO$_2$. Figure 9 represents the breakthrough curves of CH$_4$ and CO$_2$ in the biogas passing through the three adsorption columns at 25 °C and 0.2 MPa with a flow rate of 200 mL/min. It can easily be seen
that CH₄ with high concentration (≥96 v/v%) was obtained after the desulfurized and dehydrated biogas passed through CMS and 13X zeolite in turn. As mentioned above, when there was N₂ in the biogas, CMS will preferentially adsorb N₂, while 13X zeolite could adsorb CO₂ in a large amount. So, in this process, CMS was mainly responsible for adsorbing N₂, but also a part of CO₂, and 13x was responsible for adsorbing CO₂.

![Figure 7](image1.png)

**Figure 7.** Adsorption/desorption cycles: (a) 13X zeolite; (b) CMS.

![Figure 8](image2.png)

**Figure 8.** FTIR spectra of fresh and regenerated 13X zeolite.

![Figure 9](image3.png)

**Figure 9.** Breakthrough curves of CH₄ and CO₂ at 25 °C and 0.2 MPa.
Although the biogas was upgraded to CH$_4$ with high concentration, further research should explore in detail the recovery rate of CH$_4$ and more efficient CO$_2$ adsorbents.

4. Conclusions

One of the promising utilizations of biogas is use as vehicle fuel. Before pumping biogas into the vehicle, it is necessary to remove CO$_2$ and other impurities from biogas to increase the CH$_4$ content and thereby the heating value. This work confirmed that the commercial 13X zeolite and CMS could not efficiently remove CO$_2$ from the desulfurized real biogas due to the impact of water vapor, although the two kinds of adsorbent showed high performance in the removal of CO$_2$ from simulated biogas. For desulfurized dry biogas, CMS would exhibit superior N$_2$ adsorption capacity and low CO$_2$ adsorption capacity if some N$_2$ was present in biogas. 13X zeolite displayed significant CO$_2$ adsorption capacity from the desulfurized dry biogas and did not adsorb N$_2$. High-purity CH$_4$ (≥96 v/v%) could be obtained after the desulfurized and dehydrated biogas passed through CMS and 13X zeolite in turn. However, 13X zeolite exhibited a significant decrease in CO$_2$ adsorption capacity after it was regenerated by vacuum treatment for 30 min, so further research should explore more efficient CO$_2$ adsorbents with high CO$_2$ adsorption capacity and good regeneration performance. Additionally, more attention should be paid to the recovery rate of CH$_4$ in future research.

The results indicate that the CMS material is a perfect N$_2$ adsorbent instead of CO$_2$ adsorbent if the real biogas contained N$_2$ and 13X zeolite exhibited high CO$_2$ adsorption capacity only under dry conditions. This work reveals the shortcomings of existing commercial adsorbents in the purification of real biogas. Therefore, in future work, a new type of CO$_2$ exclusive adsorbent should be developed and overcome its disadvantages of being susceptible to moisture and not easy to regenerate. In this way, the operating cost of purifying biogas by the pressure swing adsorption method can be reduced, the product quality can be improved, and the market competitiveness of this method will be greatly enhanced.

Author Contributions: Conceptualization, J.L.; Formal analysis, J.L. and Q.C.; Investigation, J.L. and P.Q.; Methodology, J.L., P.Q. and Q.C.; Supervision, J.L.; Validation, Q.C.; Writing—original draft, J.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Innovation Team of Automobile Driving Safety Technology of Harbin Vocational and Technical College. This research was also funded by Harbin Science and Technology Bureau, grant number 2015RQQXJ035.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

In Figure 2 (13a–13c) represent adsorption columns which were made of stainless steel tubes and with length of 250 mm as well as inner diameter of 11 mm.

References

1. Gustafsson, M.; Cruz, I.; Svensson, N.; Karlsson, M. Scenarios for upgrading and distribution of compressed and liquefied biogas-Energy, environmental, and economic analysis. J. Clean Prod. 2020, 256, 120473. [CrossRef]
2. Dhanya, B.S.; Mishra, A.; Chandel, A.K.; Verma, M.L. Development of sustainable approaches for converting the organic waste to bioenergy. Sci. Total Environ. 2020, 723, 138109. [CrossRef] [PubMed]
3. Anukam, A.; Mohammadi, A.; Naqvi, M.; Granstrom, K. A review of the chemistry of anaerobic digestion: Methods of accelerating and optimizing process efficiency. Processes 2019, 7, 504. [CrossRef]
4. Yang, L.; Ge, X.; Wan, C.; Yu, F.; Li, Y. Progress and perspectives in converting biogas to transportation fuels. Renew. Sustain. Energy Rev. 2014, 40, 1133–1152. [CrossRef]
5. Karagoz, Y. Analysis of the impact of gasoline, biogas and biogas plus hydrogen fuels on emissions and vehicle performance in the WLTC and NEDC. Int. J. Hydrog. Energy 2019, 44, 31621–31632. [CrossRef]
6. Winslow, K.M.; Laux, S.J.; Townsend, T.G. An economic and environmental assessment on landfill gas to vehicle fuel conversion for waste hauling operations. Resour. Conserv. Recycl. 2019, 142, 155–166. [CrossRef]
7. Scarlat, N.; Dallemand, J.F.; Fahl, F. Biogas: Developments and perspectives in Europe. *Renew. Energy* 2018, 129, 457–472. [CrossRef]
8. Wu, Y.; Huang, X.; Jiang, Z. Composition and sources of aerosol organic matter in a highly anthropogenic influenced semi-enclosed bay: Insights from excitation-emission matrix spectroscopy and isotopic evidence. *Atmos. Res.* 2020, 241, 104958. [CrossRef]
9. Lee, J.; Theis, J.R.; Kyriakidou, E.A. Vehicle emissions trapping materials: Successes, challenges, and the path forward. *Appl. Catal. B-Environ.* 2019, 243, 397–414. [CrossRef]
10. Augelletti, R.; Conti, M.; Annenisi, M.C. Pressure swing adsorption for biogas upgrading. A new process configuration for the separation of biomethane and carbon dioxide. *J. Clean Prod.* 2017, 140, 1390–1398. [CrossRef]
11. Rodero, M.D.R.; Carvajal, A.; Arrib, Z.; Lara, E.; de Prada, C.; Lebrero, R.; Munoz, R.A. Performance evaluation of a control strategy for photosynthetic biogas upgrading in a semi-industrial scale photobioreactor. *Bioresour. Technol.* 2020, 307, 123207. [CrossRef] [PubMed]
12. Ferella, F.; Cucchiella, F.; D’Adamo, I.; Gallucci, K. A techno-economic assessment of biogas upgrading in a developed market. *J. Clean Prod.* 2019, 210, 945–957. [CrossRef]
13. Awe, O.W.; Zhao, Y.; Nzihou, A.; Minh, D.P.; Lyczko, N. A review of biogas utilisation, purification and upgrading technologies. *Waste Biomass Valor.* 2017, 8, 267–283. [CrossRef]
14. Ferella, F.; Puca, A.; Taglieri, G.; Rossi, L.; Gallucci, K. Separation of carbon dioxide for biogas upgrading to biomethane. *J. Clean Prod.* 2017, 164, 1205–1218. [CrossRef]
15. Tagliabue, M.; Farrusseng, D.; Valencia, S.; Aguado, S.; Raven, U.; Rizzo, C.; Corma, A.; Mirodatos, C. Natural gas treating by selective adsorption: Material science and chemical engineering interplay. *Chem. Eng. J.* 2009, 155, 553–566. [CrossRef]
16. Rocha, L.A.M.; Andreassen, K.A.; Grande, C.A. Separation of CO2/CH4 using carbon molecular sieve (CMS) at low and high pressure. *Chem. Eng. Sci.* 2017, 164, 148–157. [CrossRef]
17. Lozano-Castello, D.; Alcaniz-Monge, J.; Cazorla-Amoro, D.; Linares-Solano, A.; Zhu, W.; Kapteijn, F.; Moulijn, J.A. Adsorption properties of carbon molecular sieves prepared from an activated carbon by pitch pyrolysis. *Carbon* 2005, 43, 1643–1651. [CrossRef]
18. Yu, H.; Cho, S.; Bai, B.C.; Yi, K.B.; Lee, Y. Effects of fluorination on carbon molecular sieves for CH4/CO2 gas separation behavior. *Int. J. Greenh. Gas Control* 2012, 10, 278–284. [CrossRef]
19. Wahby, A.; Silvestre-Albero, J.; Sepulveda-Escribano, A.; Rodriguez-Reinoso, F. CO2 adsorption on carbon molecular sieves. *Microporous Mesoporous Mater.* 2012, 164, 280–287. [CrossRef]
20. Wahby, A.; Ramos-Fernandez, J.M.; Martinez-Escandell, M. High-surface-area carbon molecular sieves for selective CO2 adsorption. *ChemSusChem* 2010, 3, 974–981. [CrossRef]
21. Liang, Z.; Marshall, M.; Chaffee, A.L. CO2 adsorption-based separation by metal organic framework (Cu-BTC) versus zeolite (13X). *Energy Fuels* 2009, 23, 2785–2789. [CrossRef]
22. Peter, S.A.; Baron, G.V.; Gascon, J.; Kapteijn, F.; Denayer, J.F.M. Dynamic desorption of CO2 and CH4 from amino-MIL-53(Al) adsorbent. *Adsorption* 2013, 19, 1235–1244. [CrossRef]
23. Alonso-Vicario, A.; Ochoa-Gomez, J.R.; Gil-Rio, S.; Gomez-Jimenez-Aberasturi, O.; Ramirez-Lopez, C.A.; Torrecilla-Soria, J.; Dominguez, A. Purification and upgrading of biogas by pressure swing adsorption on synthentic natural zeolites. *Microporous Mesoporous Mater.* 2010, 134, 100–107. [CrossRef]
24. Cavenati, S.; Grande, C.A.; Rodrigues, A.E. Adsorption equilibrium of methane, carbon dioxide, and nitrogen on zeolite 13X at high pressures. *J. Chem. Eng. Data* 2004, 49, 1095–1101. [CrossRef]
25. Ma, X.; Wang, X.; Song, C. “Molecular Basket” sorbents for separation of CO2 and H2S from various gas streams. *J. Am. Chem. Soc.* 2009, 131, 5777–5783. [CrossRef]
26. Montanari, T.; Busca, G. On the mechanism of adsorption and separation of CO2 on LTA zeolites: An IR investigation. *Vib. Spectrosc.* 2008, 46, 45–51. [CrossRef]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).