Temperature based Enhanced Desorption of Adsorbed Biomethane Stored on Sustainable Nanoporous Materials

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Abstract. In recent years, adsorbed natural gas storage has been seen as a better alternative to storing methane-rich gas on porous materials. Especially when these porous materials can be derived from a source like biomass whole process becomes valuable development. However, the problem of lower delivery capacity and the amount of gas released upon releasing the pressure remains unsolved. The micropores developed on the activated carbons retain the gas as they cannot get the activation energy to detach from the surface. The thermodynamics of the desorption process discourages the overall technological development of the system. We have carried out studies under particular temperatures by placing material and gas-filled cylinder in a water bath to overcome this challenge. Coconut based activated carbons were used in the study, which were procured from the market. Adsorption isotherm and other characteristics were performed for activated carbons. The desorption amount of the gas was recorded for different temperatures of 40, 45, 50 and 55 °C. At room temperature, nearly 54% of adsorbed gas is being released. Whereas, at 55 °C, approximately 80% of the gas is being recovered. This work will be useful for the externally cylinder fitted vehicles where the exhaust stream can be channelised to warm the surrounding of the cylinder to facilitate the higher discharge of the adsorbed gas.

1. Introduction

Adsorption based storage has paved a better alternative to compressed based storage technology for methane gas, especially utilization in vehicular fuel [1]. However, methane-rich gas is relatively cleaner fuel, not a carbon neutral [2]. Methane burning still has emissions but they are far lesser than crude oil-based fuels. Interestingly, it can be obtained from a renewable source like biomass via anaerobic breakdown of organic matter. This sustainable production source gives an advantage and encourages to utilize the methane-based fuel judiciously [3].

Adsorption of methane-rich gas on porous materials has been advantageous in reducing the pressure requirements substantially. As per the DoE (department of energy, US) targets, adsorbed gas systems should have 263 v/v energy density at 3.5 MPa, equivalent to compressed methane at 25 MPa at STP. A variety of materials like Metal-organic frameworks (MOFs), porous organic frameworks (POFs), zeolites, carbon-based materials etc., has been analysed for this purpose [4,5]. MOFs have been one of the most investigated materials and shown greater storage, and even some have crossed the DoE targets [6,7]. However, their chemical synthesis, cost, disposal and non-renewability remains doubtful. Moreover, most of the reports are limited to crystallographic theoretical studies. Apart from MOFs,
carbon-based materials are most studied for methane adsorption. Especially, biomass-based activated 
carbons (AC) have been vital as they are abundantly available, have low-cost preparation, negative 
impact disposal etc. [8]. Nevertheless, their performance has been comparable to the best performing 
MOFs due to which they remain potential materials for application [9,10].

ACs provide a balance between gravimetric and volumetric uptake capacity possessing good packing 
density[11]. However, having high adsorption capacity is not related to good delivery capacities. Almost 
all materials suffer from a poor release percentage of the uptake amount. Altawala et al. report nearly 
60-62% of working capacity on their best performing ACs [10]. Whereas Casco et al. record nearly 73- 
78% working capacity for MOFs and ACs [12]. We also recorded around 76% release of the adsorbed 
amount of gas [11]. All variety of materials faces this problem of low delivery capacity.

Delivery capacity further decreases when the experiments are performed on large volume cylinders. 
This decrease in the capacity is mainly attributed to two reasons (i) micropore gas retention and (ii) 
endothermic desorption process. Adsorption hysteresis curves represent the pore blocking/percolation 
phenomena while the desorption takes place, leading to gas retention in the material pores [13]. The 
temperature reduction while the gas desorption disfavours the gas release from the adsorbent bed of 
porous materials. However, it can be possibly overcome by supplying heat to the storage cylinder from 
outside, maintaining the temperature drop while desorption. We have performed experiments to increase 
desorption efficiency from the materials at different elevated temperatures with this idea. The cylinder 
was placed into a water bath with at 40, 45, 50 and 55 °C, and the gas release amount was recorded.

2. Materials and methods
The Norit granular activated carbons (GAC) were purchased from Garjiya Chemtech Inc., which 
reported iodine value of 950 mg/g. These activated carbons were directly used without any chemical 
modification for gas uptake and release measurement. Activated carbons were first degassed under hot 
air over at 105 °C for 24 h. These oven dried GACs were placed in the 3 litre stainless steel cylinder. 
This cylinder was designed to use at a working pressure of maximum upto 10 MPa. The gas adsorption 
measurements are based on our previously described methodology[11]. Volumetric uptake capacity was 
measured in the Sievert type apparatus. Pressure for adsorption was 6.5 MPa, as per our previous 
experiments. A vacuum was applied to the cylinder after filling the material. The cylinder was then 
subjected to the gas till 6.5 MPa pressure, and the difference in weight was recorded. Based on the 
weight recorded the volume of the gas at STP was calculated. The gas-filled cylinder was then placed 
in the water bath maintained at a particular temperature and released measurements were also taken. The 
gas was released to the atmospheric pressure and again the difference in weight was noted.

\[
\text{Volumetric energy of gas} = \frac{\text{Volume of gas in the cylinder (cm}^3\text{)}}{\text{total volume of a cylinder (cm}^3\text{)}}
\]

There were 6 cycles performed at each temperature, and the ACs were not subjected to any degassing 
during these cycles. After recording the delivery capacity for six cycles at a particular temperature the 
activated carbons were replaced with fresh. The temperature changes while the gas desorption is also 
recorded. Packing density of ACs in 3 L cylinder is nearly 0.60 g/cm³. The gas composition has ~90% 
methane and remaining CO₂ and air which was obtained by our in house biogas production and 
enrichment facility. The delivery percentage was calculated by the formula below:

\[
\text{Delivery \%} = \left( \frac{\text{Volume of the gas released}}{\text{Volume of the gas adsorbed}} \right) \times 100
\]

3. Results and discussion
The volumetric uptake of the gas was 85 v/v at room temperature in empty cylinder in compressed form 
as per our laboratory experiments. The gas uptake in the cylinder filled with materials was carried out 
at room temperature. The first round of release was recorded at room temperature. The material-gas-
filled cylinder was placed into a water bath with maintained temperature from the second round onwards.

3.1. Delivery at 40 °C
Freshly activated carbons can store ~163 v/v of the gas in the cylinder, whereas under NTP, it desorbs 
nearly ~88 v/v gas while pressure is released. Figure 1 represents the results of heated discharge at 40 °C. 
This records almost 54% of the adsorbed gas release, whereas the remaining gas is present in the cylinder, 
stuck in the micropores. From the second cycle onwards the adsorption capacity is decreased in
subsequent cycles. From 163 v/v in the first cycle, it reaches to 155 v/v in the sixth cycle. The desorbed amount of gas also reduces in subsequent cycles. The discharge is recorded under 40 °C of the surrounding temperature from the second cycle onwards. The desorption percentage has changed from 54% to 55%, whereas it remains similar in subsequent cycles. However, heated discharge at 40 °C has not shown any noticeable improvements.

![Figure 1. Uptake and volumetric delivery ratio on activated carbons in the cylinder and heated discharge recorded at 40 °C from the second and subsequent cycle.](image1)

3.2. Delivery at 45 °C
For this studied cycle of studies, the GACs were fresh and degassed under a hot air oven, and vacuum was applied to the cylinder before gas uptake measurements. Heated discharge capacities at 45 °C are represented in figure 2. The second cycle discharge was under 45 °C surrounding temperature, where the desorption capacity is increased from 54% to 62%. Second and all subsequent discharge percentage follow the trends and remains higher than the unheated discharge. However, the last sixth cycle has little increased from 62.12% to 63.32% delivery of stored gas.

![Figure 2. Uptake and volumetric delivery ratio on activated carbons in the cylinder and heated discharge recorded at 45 °C from the second and subsequent cycle.](image2)

3.3. Delivery at 50 °C
Significant margins increase the delivery percentage when the surrounding temperature is 50 °C presented in figure 3. The highest delivery recorded was 74% which nearly 37% higher than the discharge at room temperature. However, no pattern is found in the percentage discharge between the cycles.
3.4. Delivery at 55 °C
When the surrounding temperature increases to 55 °C, the delivery percentage rises to 79%. Results are being represented in figure 4 of heated discharge at 55 °C. The adsorption capacity is comparatively lower in the second cycle since this and subsequent cycle adsorption is taken on the fresh GACs. Here as well there is no trend between process and delivery percentage. However, there is 46% increase in delivery of the adsorbed gas compared to the room temperature delivery.

4. Conclusion
The above experiments show higher adsorbed gas release in the material packed in cylinders upon increasing the temperature. Heated discharge at 40 °C does not offer much increment, but further temperature increases release more gas from the cylinder. The delivery capacity has been increased from 54% at room temperature to 79% at 55 °C. Lower adsorption and desorption is found in all the subsequent cycles; however there is no relative change in the delivery percentage. The lower working capacity of adsorbed gas technology can be overcome by applying heat in the surrounding of the material packed cylinder.

This particular method can be helpful to in vehicles with gas storage cylinders in open spaces like three and four wheeler goods vehicles. The cylinder can be placed in a shell where exhaust gases emitted from vehicles can be channelized, maintaining the temperature in the cylinder surroundings. This shell can have insulation to prevent heat loss and maximum heat transfer to the cylinder surrounding. This overall would improve the low delivery drawback of adsorbed gas systems.
5. References

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