Recycling of CO₂ for the Production of Hydrocarbon Fuels

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Abstract

The separation and recovery of CO₂ is essential to ensure effective utilization of CO₂ to produce liquid fuels through Fischer-Tropsch reaction. In this study, adsorption experiments were carried out in a volumetric system to analyse the capacity of the activated carbons for the removal of CO and CO₂ from a gas mixture. Experiments were carried out using various activated carbons at various temperatures over a pressure range from 1-2.5 atm. Then the experimental isotherm data obtained were modeled by the use of Langmuir, Freundlich, Sips and Toth adsorption isotherm models which provides a prediction of adsorption behavior of the gas mixtures containing CO₂, CO and H₂ gases.

Introduction

Recycle of CO₂:
The productive use of captured CO₂ as a resource (raw material), rather than relying on ‘carbon capture and sequestration’ (CCS), which is the current model generally promoted for reducing CO₂ emissions that treats CO₂ as a waste product.

Reverse Water-Gas Shift (RWGS) Reaction:
The RWGS reaction occurs at high temperatures in order to push the endothermic equilibrium reaction to its products. The RWGS reaction can produce significantly valuable CO from cheap CO₂:

- Captured CO₂ can be converted to CO using the reverse water-gas shift reaction: CO₂ + H₂ ⇌ CO + H₂O(g).

Fischer-Tropsch Process:
Is a collection of chemical reactions that converts a mixture of CO and H₂ into liquid hydrocarbons

- CO is used to synthesize Fischer-Tropsch fuels

Adsorption:
Adsorption is a surface phenomenon where one or more species of a fluid selectively adsorbs onto the surface of the adsorbent. In this study the nature of adsorption is physisorption as the characteristic of attraction between the fluid and adsorbent is weak Van der Waals forces.

Volumetric System:
The volumetric technique is to introduce a known mass of adsorbent into a sample cell of calibrated volume. Following desorption of the solid using high temperature and vacuum, a fixed temperature is imposed by a temperature bath and a measured dose of gas is introduced to the sample cell. After adsorption is complete, at equilibrium, the temperature and pressure are measured.

- Increased accuracy at low pressure since the entire metered dose is adsorbed
- Decreased accuracy at high pressure since sum of values provides continuous accumulation of error

Materials

Adsorbents:
Adsorbents tested for the purpose of this study were all activated carbons, which is carbonaceous matters processed to have small, low-volume pores that increase the surface area by an activation process.

Table 1: List of adsorbents studied with some important properties.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Supplier</th>
<th>Surface Area (m²/g)</th>
<th>Particle Size (mm or μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XTRUSORB A754</td>
<td>Calgon, Mississauga, ON</td>
<td>850</td>
<td>4 mm</td>
</tr>
<tr>
<td>XTRUSORB HP115</td>
<td>Calgon, Mississauga, ON</td>
<td>850</td>
<td>6.7 mm, 1.5 mm μm</td>
</tr>
<tr>
<td>BPL</td>
<td>Calgon, Mississauga, ON</td>
<td>850</td>
<td>450-600 μm</td>
</tr>
</tbody>
</table>

*Extrude: (Length, Diameter)*

Apparatus

The apparatus is designed to incorporate RWGS reaction to produce Fischer-Tropsch sustainable liquid fuels from captured CO₂.

Figure 1: Adsorbate (CO₂ and CO) are attracted to the surface of the adsorbent (activated carbon) which it bonds to. [1]

- Physisorption provides a reversible and economical method of CO₂ and CO separation from flue gas.

Figure 2: Simplified schematic for a system that incorporates RWGS reaction to produce Fischer-Tropsch sustainable liquid fuels from captured CO₂.

Results

Adsorption Isotherm Models:
- The adsorptive performance of an adsorbent can be quantified with an isotherm
- The models found to give the best fit for the adsorption isotherm were used

Freundlich

\[
q = KF^{1/n}
\]

Toth

\[
q = \frac{q_M^P}{(1 + (βP)^{1/n})^n}
\]

Sips

\[
q = \frac{q_M P^n}{1 + P^n}
\]

Table 2: Parameters of Freundlich, Toth and Sips Isotherm of CO and CO₂ on the three adsorbents tested in this study.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Freundlich Isotherm</th>
<th>Toth Isotherm</th>
<th>Sips Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>XTRUSORB A754</td>
<td>[ K = 6.73 \times 10^7 \text{ m}^2/\text{g}, n = 0.82 ]</td>
<td>[ q_M = 4.28 \text{ g/m}^2, \beta = 1.71 ]</td>
<td>[ q_M = 4.28 \text{ g/m}^2, n = 0.82 ]</td>
</tr>
<tr>
<td>XTRUSORB HP115</td>
<td>[ K = 6.73 \times 10^7 \text{ m}^2/\text{g}, n = 0.82 ]</td>
<td>[ q_M = 4.28 \text{ g/m}^2, \beta = 1.71 ]</td>
<td>[ q_M = 4.28 \text{ g/m}^2, n = 0.82 ]</td>
</tr>
<tr>
<td>BPL</td>
<td>[ K = 6.73 \times 10^7 \text{ m}^2/\text{g}, n = 0.82 ]</td>
<td>[ q_M = 4.28 \text{ g/m}^2, \beta = 1.71 ]</td>
<td>[ q_M = 4.28 \text{ g/m}^2, n = 0.82 ]</td>
</tr>
</tbody>
</table>

Selectivities:

Top CO₂ isotherm for the three activated carbon at 50°C and 70°C

Top CO₂ Performer:
- XTRUSORB A754 and BPL, have a very linear isotherm which would be suited for pressure swing adsorption (PSA)

Conclusion

- The adsorbents tested favoured CO₂ adsorption over CO adsorption.
- Activated carbon BPL had the highest selectivity and capacity for CO₂. Therefore BPL is the most promising for the separation of CO₂ and CO.

Further tests will need to be conducted at various temperatures and the use of adsorbents other than activated carbon to compare adsorption selectivity and capacity.

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References:


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