



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 CO 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 provided a prediction of adsorption behavior of the gas mixtures containing CO₂, CO and H₂ gases

Introduction

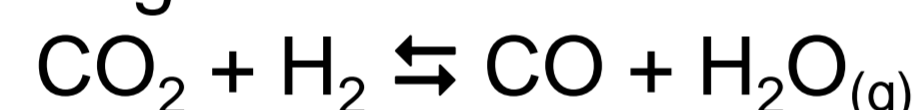
Recycle of CO₂:

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 synthetically valuable CO from cheap CO₂.

- Captured CO₂ can be converted to CO using the reverse water-gas shift reaction:



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 $n\text{CO} + (2n+1)\text{H}_2 \rightleftharpoons \text{C}_n\text{H}_{(2n+2)} + n\text{H}_2\text{O}$

Adsorption:

Adsorption is a surface phenomenon where one or more species of a fluid selectively adsorb 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

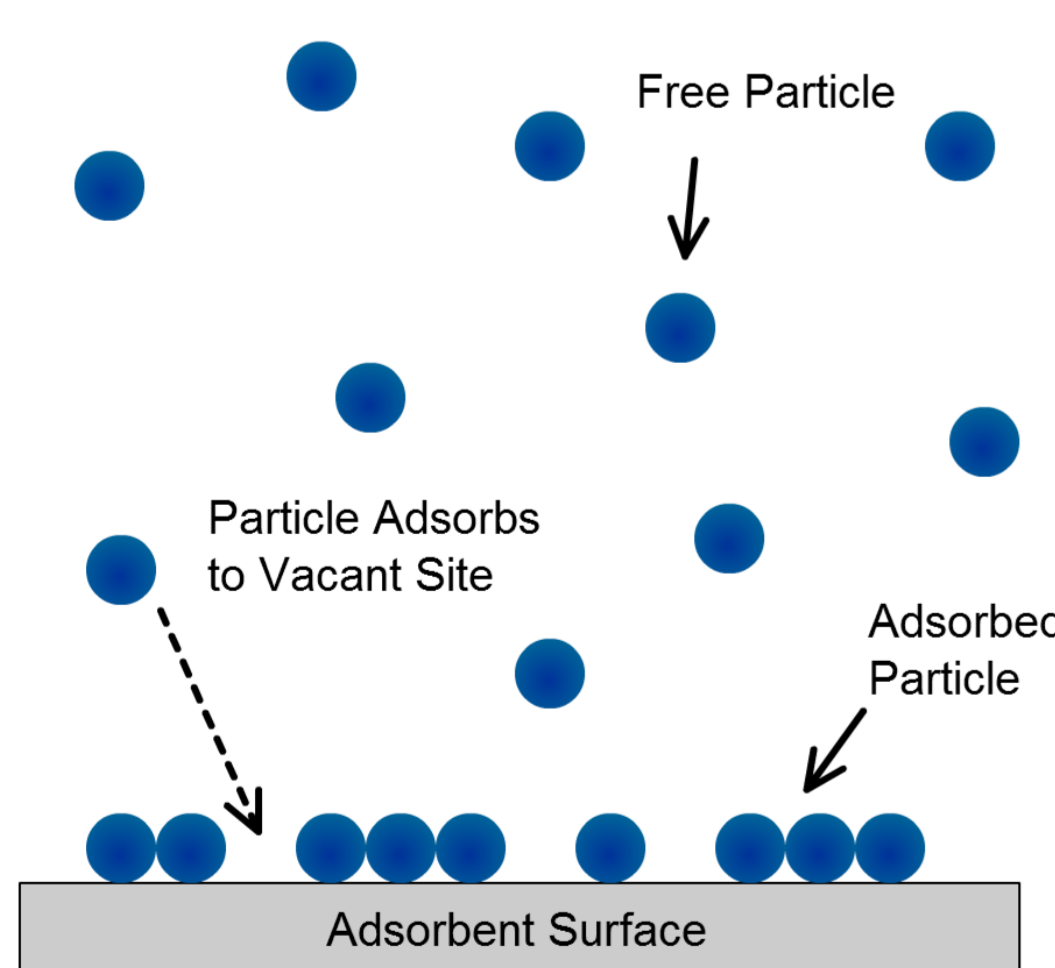


Figure 1: Adsorbate (CO₂ and CO) are attracted to the surface of the adsorbent (activated carbon) which it bonds to. [1]

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

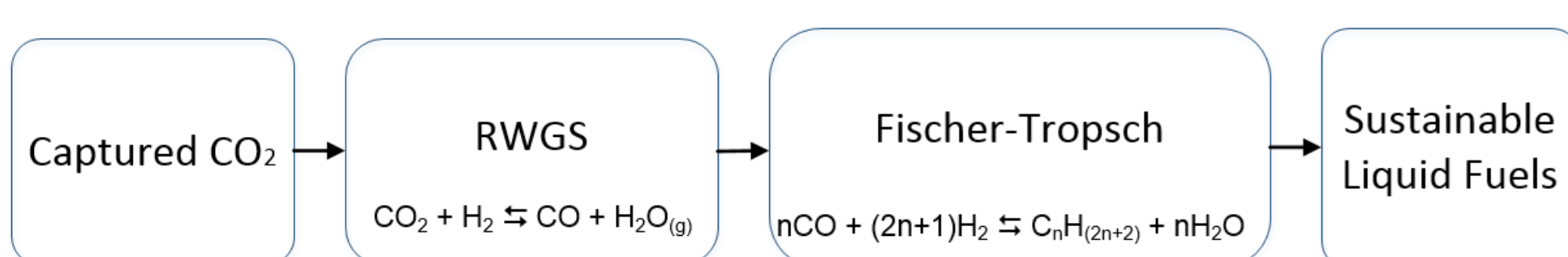


Figure 2: Simplified schematic for a system that incorporates RWGS reaction to produce Fischer-Tropsch sustainable liquid fuels from captured CO₂

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.



Figure 3: XTRUSORB A754



Figure 4: XTRUSORB HP115



Figure 5: BPL

Table 1: List of adsorbents studied with some important properties. [2]

Adsorbent	Supplier	Surface Area (m ² /g)	Particle Size (mm or μm)
XTRUSORB A754	Calgon, Mississauga, ON	850	4 mm
XTRUSORB HP115	Calgon, Mississauga, ON	850	6.7 mm, 1.5 mm *
BPL	Calgon, Mississauga, ON	850	450-600 μm

*Extrudes: (Length, Diameter)

Apparatus

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

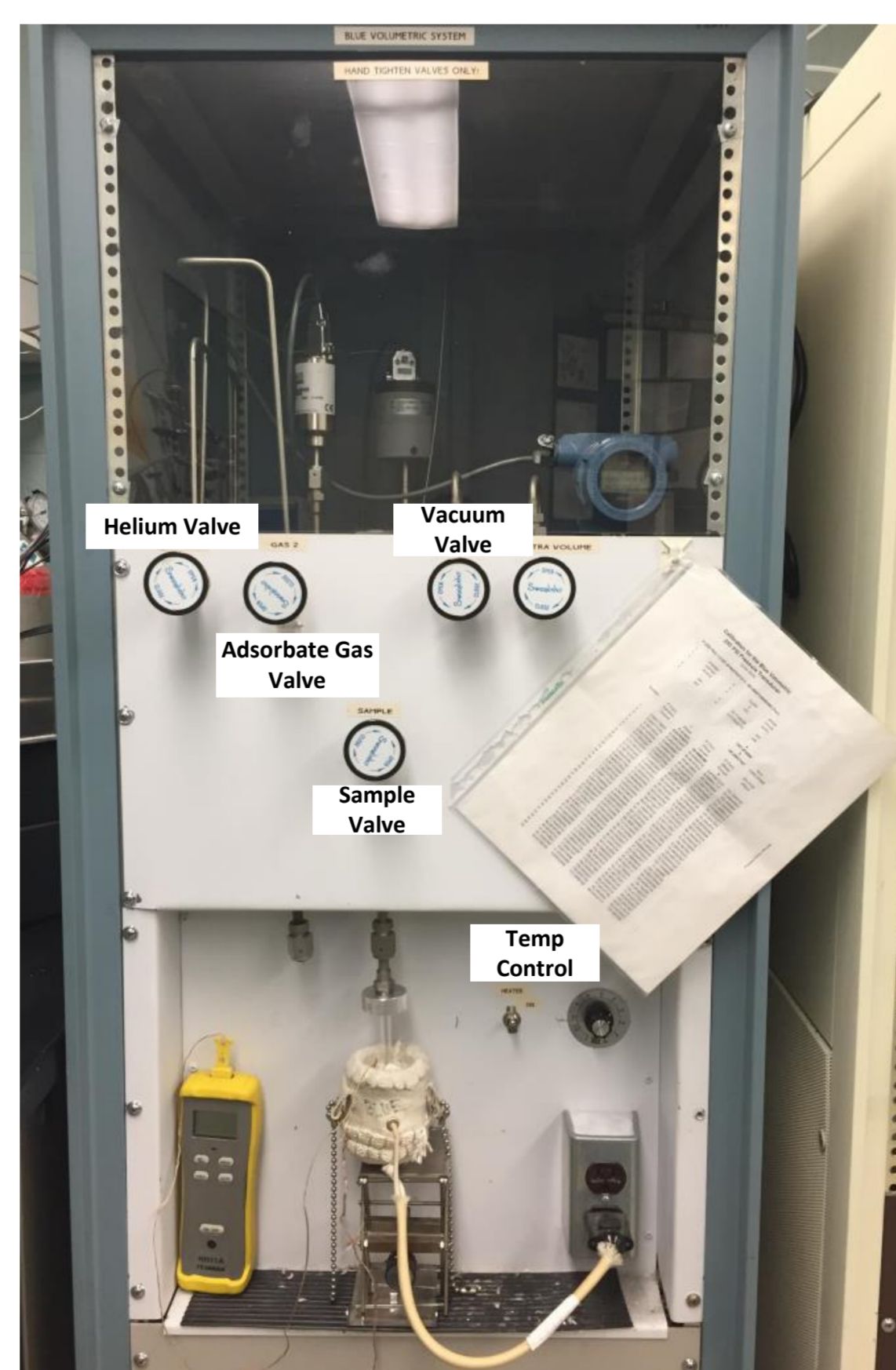


Figure 6: AccuSorb 2100E Physical Adsorption Analyser

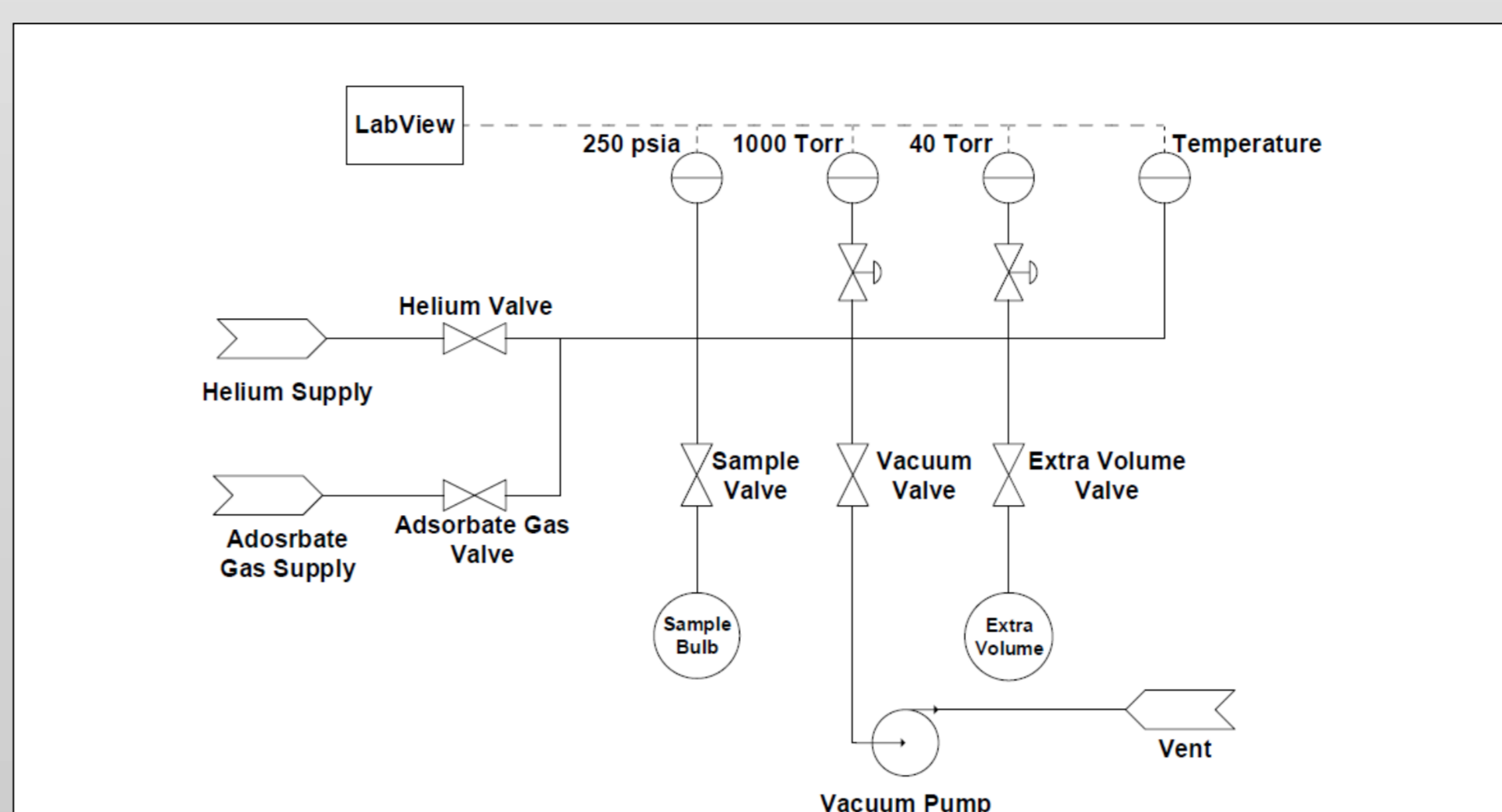


Figure 7: AccuSorb 2100E Process Flow Diagram. The sample bulb is where the adsorbent is placed and is then dosed by the adsorbate gas supply.

Results

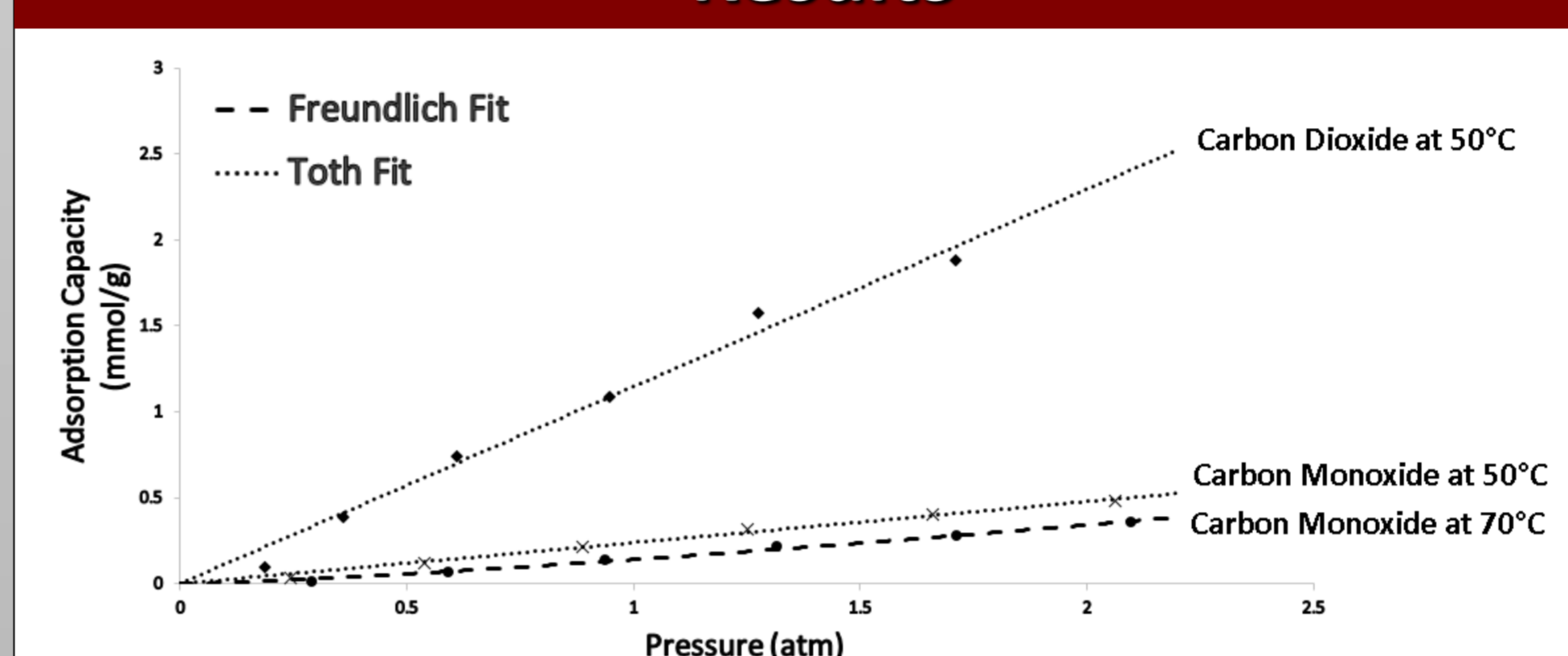


Figure 8: Isotherms for activated carbon BPL for CO₂ and CO at temperatures of 50°C and 70°C

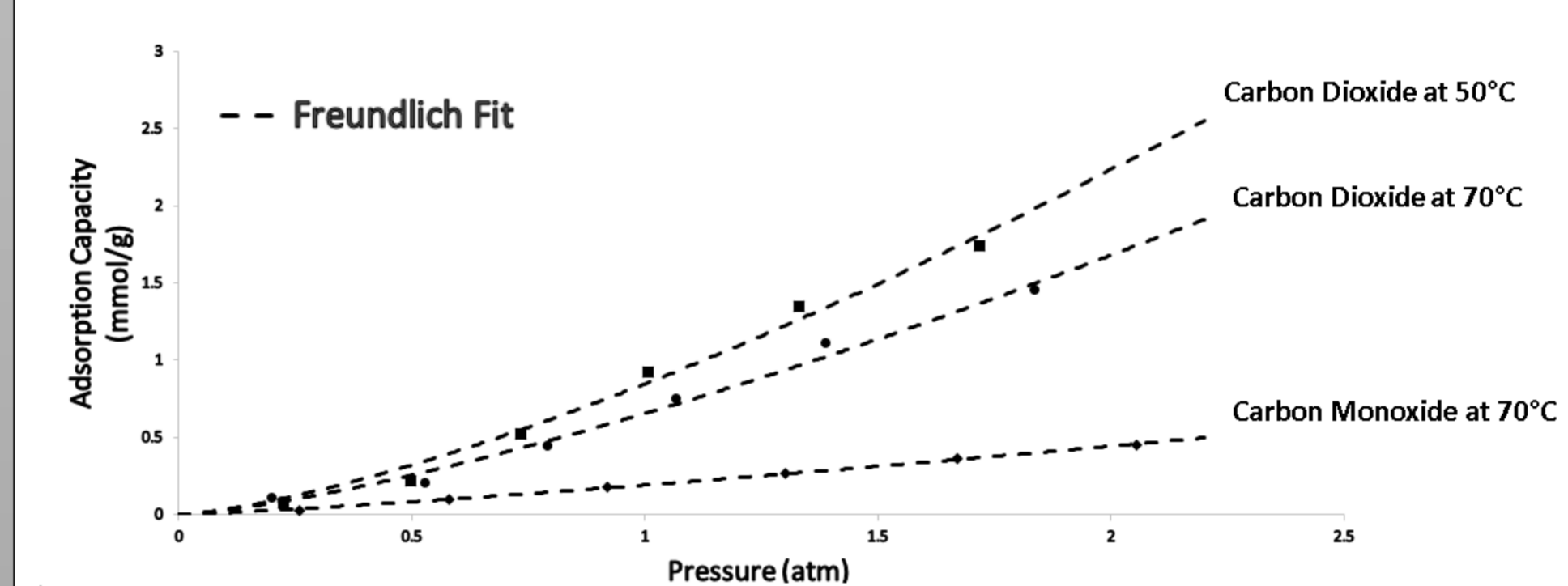


Figure 9: Isotherms for activated carbon XTRUSORB A754 for CO₂ and CO at temperatures of 50°C and 70°C

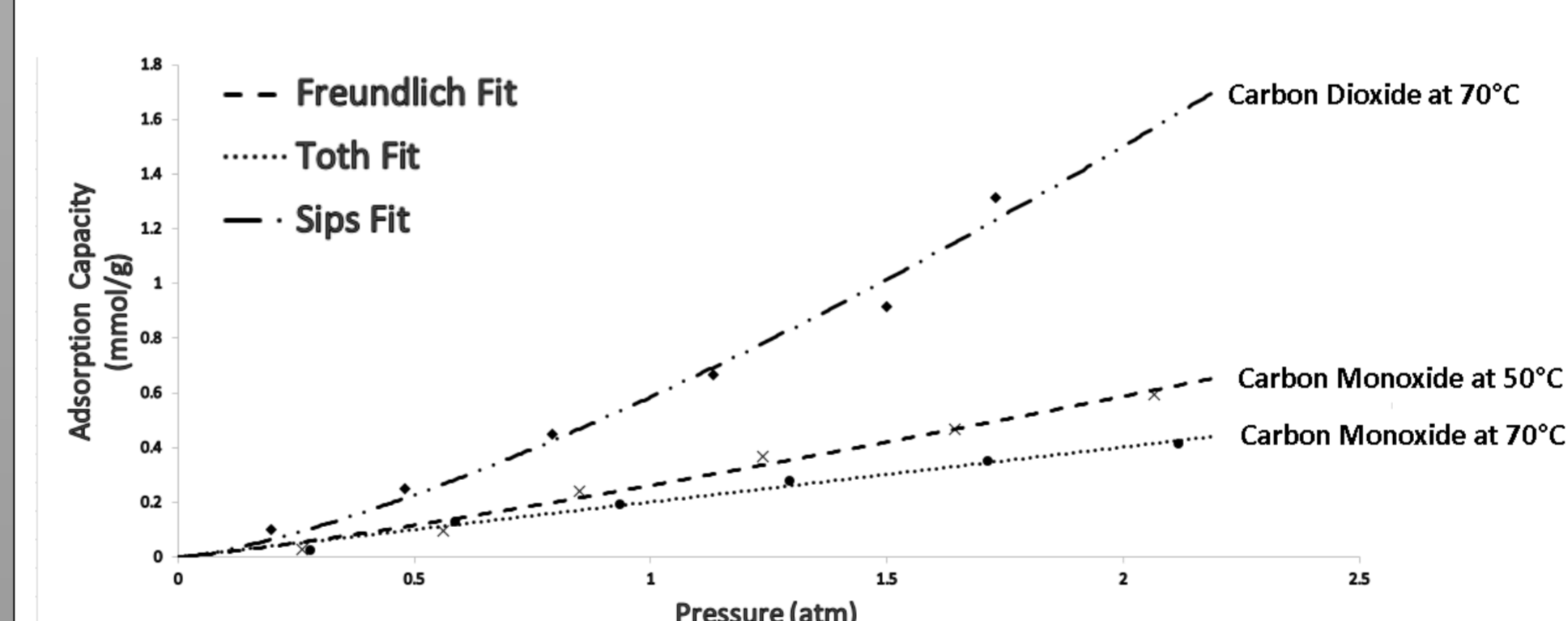


Figure 10: Isotherms for activated carbon XTRUSORB HP115 for CO₂ and CO at temperatures of 50°C and 70°C

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

$$\begin{aligned} \text{Freundlich Isotherm Model} & q = KP^{1/a} \\ \text{Toth Isotherm Model} & q = \frac{q_s \beta P}{(1 + (\beta P)^\tau)^{1/\tau}} \\ \text{Sips Isotherm Model} & q = \frac{q_s (\beta P)^\alpha}{1 + (\beta P)^\alpha} \end{aligned}$$

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

Adsorbents	Freundlich Isotherm			Toth Isotherm model			Sips Isotherm Model		
	K	a	τ	q _s	β	τ	q _s	β	α
CO Adsorbate									
BPL 50°C	0.238	0.984	28.774	0.0083	29328.35	0.840	0.579	1.589	
BPL 70°C	0.140	0.777	23.655	0.0068	29328.35	0.677	0.498	1.878	
XTRUSORB A754	0.191	0.825	27.073	0.0078	29328.36	1.457	0.285	1.489	
XTRUSORB HP 115	0.262	0.859	31.317	0.0090	29328.36	0.926	0.643	1.930	
XTRUSORB HP 115	0.202	1.009	26.418	0.0076	29328.35	0.719	0.569	1.546	
CO ₂ Adsorbate									
BPL 50°C	1.150	1.008	63.072	0.0182	29328.36	3.241	0.726	1.554	
XTRUSORB A754	0.585	0.735	47.821	0.0138	29328.38	65.73	0.033	1.376	
XTRUSORB HP 115	0.847	0.714	57.310	0.0165	29328.37	2.677	0.756	2.395	
XTRUSORB HP 115	0.655	0.736	26.418	0.0076	29328.35	2.463	0.645	2.209	

Overall Comparison:

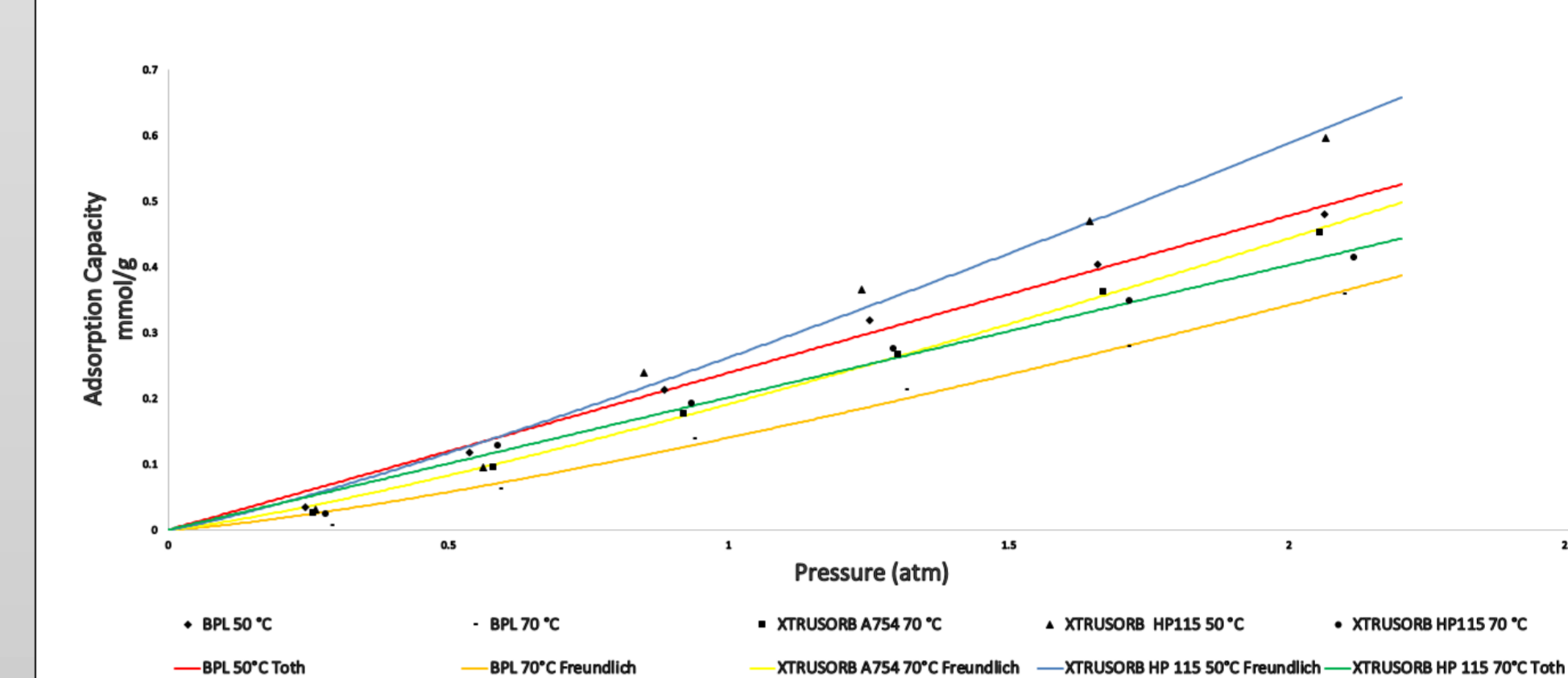


Figure 11: Pure CO isotherms for the three activated carbon at 50°C and 70°C

Top CO Performer:

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

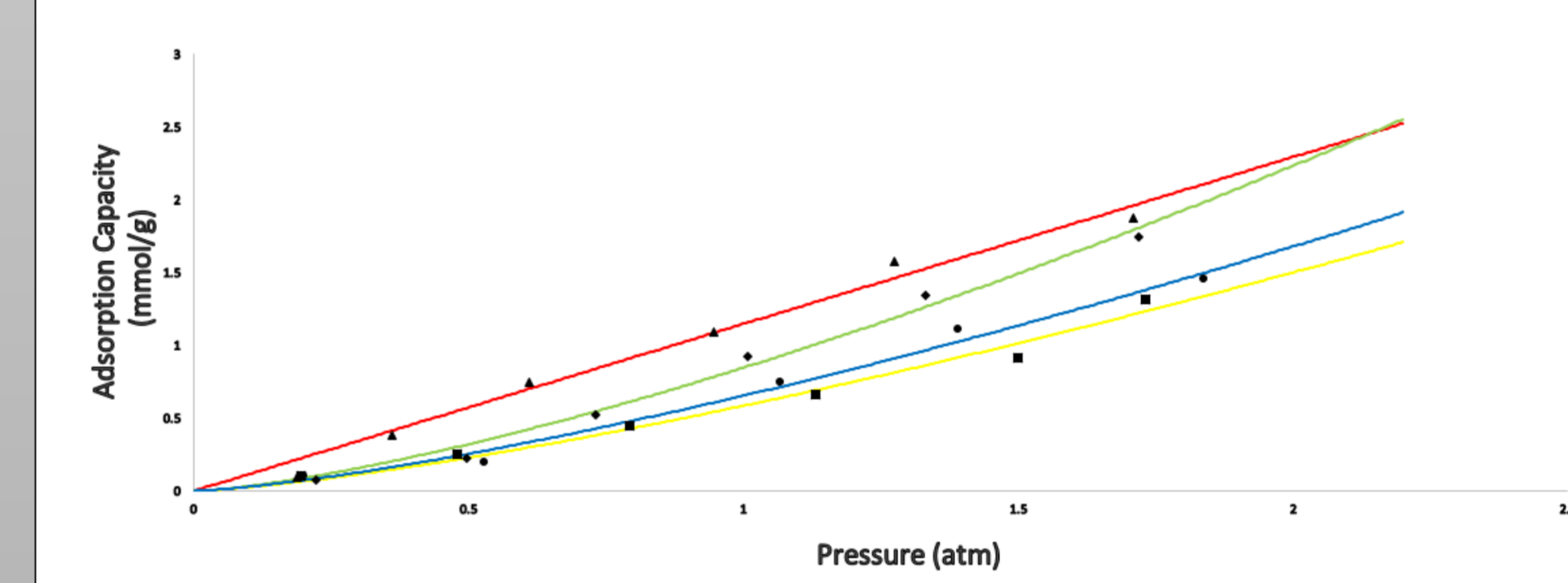


Figure 12: Pure CO₂ isotherms for the three activated carbon at 50°C and 70°C

Top CO₂ Performer:

- Greatest adsorption capacity is achieved by XTRUSORB A754 and BPL

Selectivities:

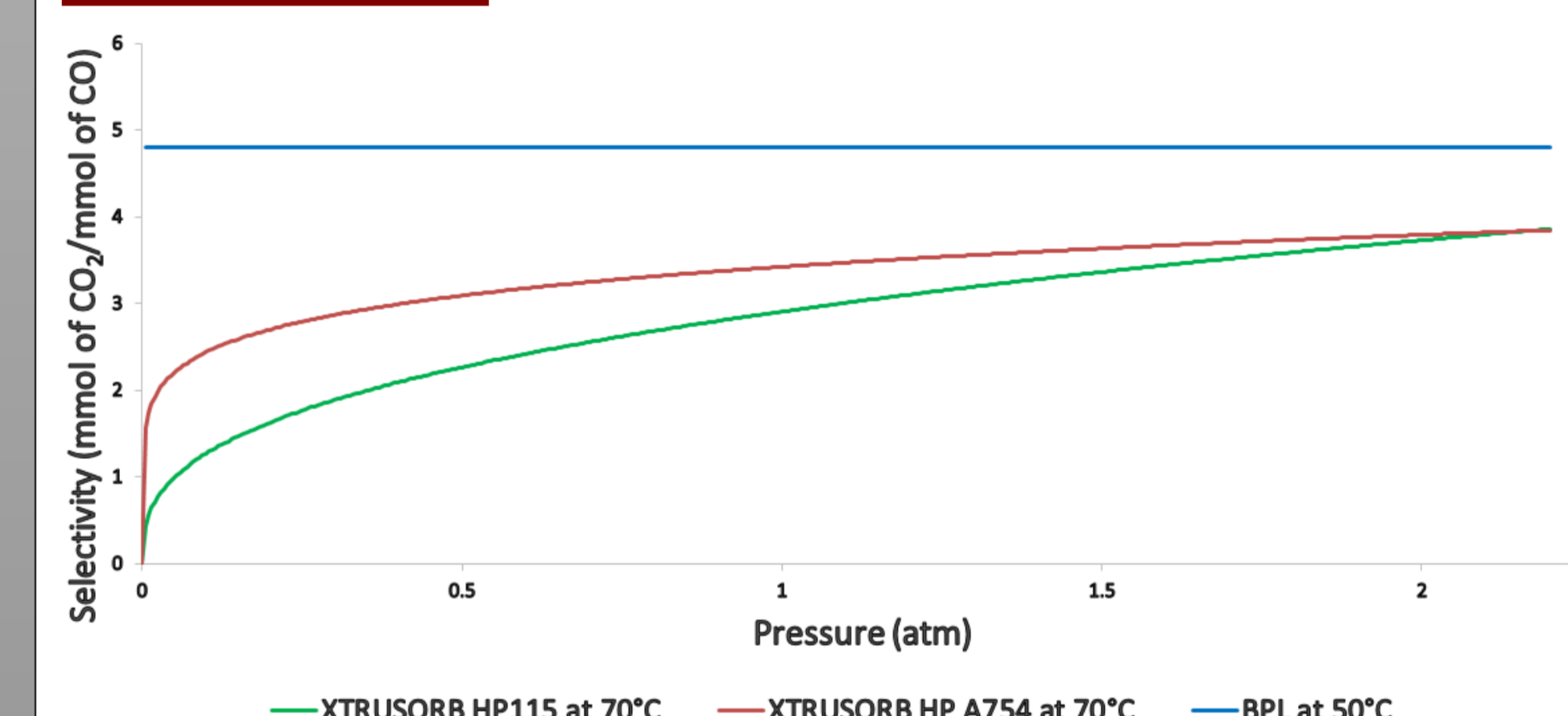


Figure 13: Selectivity ratio of CO₂/CO adsorption on the three adsorbents tested

- Adsorption capacity decreases as temperature increases indicating an exothermic adsorption process
- CO adsorption capacity is lower than CO₂ for all adsorbents.

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.

Acknowledgements

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References:

- [1] Robert Tyssen, *Gas-Solid Adsorption of Carbon Dioxide*, B.A.Sc. Thesis, University of Ottawa, 2014
- [2] Rudy Jones, *Enhanced Ethanol Production: In-Situ Ethanol Extraction Using Selective Adsorption*, Ph.D. thesis, University of Ottawa, 2012

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