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# MULTI-COMPONENT SEPARATION AND PURIFICATION OF NATURAL GAS

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## ABSTRACT

Over the past decade, several technical developments (such as hydraulic fracturing) have led to an exponential increase in discovering new domestic natural gas reserves. Raw natural gas composition can vary substantially from source to source. Typically, methane accounts for 75% to 95% of the total gas, with the rest of the gas containing ethane, propane, butane, other higher hydrocarbons, and impurities, with the most common including  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{S}$ . All natural gas requires some treatment, if only to remove  $\text{H}_2\text{O}$ ; however, the composition of natural gas delivered to the commercial pipeline grids is tightly controlled. Sub-quality natural gas reserves, which are defined as fields containing more than 2%  $\text{CO}_2$ , 4%  $\text{N}_2$ , or 4 ppm  $\text{H}_2\text{S}$ , make up nearly half of the world's natural gas volume. The development of sub-quality, remote, and unconventional fields (i.e. landfill gas) can present new challenges to gas separation and purification methods. Adsorbent technologies, such as the use of activated carbons, zeolites, or metal-organic frameworks (MOFs), may hold the key to more efficient and economically viable separation methods.

This work proposes to prove the applicability of the multi-component potential theory of adsorption (MPTA) to a real world natural gas adsorbent system to properly characterize the adsorbent's selectivity for an individual gas component using only the single component isotherms. Thus, the real-world gas separation/purification application of a specific adsorbent for a given gas stream can be obtained simply and effectively without the need for large experimental efforts or costly system modifications until after an initial computational screening of perspective materials has been completed. While the current research effort will use natural gas, which is the world's largest industrial gas separations application, to validate the MPTA, the tools gained through this effort can be applied to other gas separation effort.

## INTRODUCTION

Over the past decade, several technical developments (such as hydraulic fracturing) have led to an exponential increase in discovering new domestic natural gas reserves. In 2010, nearly 24% of the world's energy demands were supplied by natural gas, which is an increase of 7.4% from the previous year [1]. Raw natural gas composition can vary substantially from source to source. Typically, methane accounts for 75% to 95% of the total gas, with the rest of the gas containing ethane, propane, butane, other higher hydrocarbons, and impurities, with the most common including  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{S}$ . All natural gas requires some treatment, if only to remove  $\text{H}_2\text{O}$ ; however, the composition of natural gas delivered to the commercial pipeline grids is tightly controlled. Natural gas processing is the largest industrial gas separation application in the world, with an estimated \$5 billion natural gas separations equipment market in 2008 [2]. Even with the economic and environmental incentives, as much as 20% of the worldwide natural gas reserves require extensive treatment (2008 estimate) and remain unusable due to high costs of purification and delivery to the commercial pipeline grid [2]. Sub-quality natural gas reserves—defined as fields containing greater than 2%  $\text{CO}_2$ , 4%  $\text{N}_2$ , and/or 4 ppm  $\text{H}_2\text{S}$ —make up an estimated 50% of the world's natural gas volume [1]. The development of sub-quality, remote, and unconventional fields (i.e. landfill gas) can present new challenges to gas separation that require more efficient and economically viable approaches to the conventional  $\text{CO}_2$  and  $\text{N}_2$  removal processes [1]. Adsorbent technologies, such as the use of activated carbons, zeolites, or metal-organic frameworks (MOFs) are already widely used in the natural gas industry for separation of impurities [3]. “Central to the development and implementation of adsorption-based processes are the various selectivity mechanisms that give rise to the separation of components within the gas mixture.” [1]

The selectivity of an adsorbent depends on the interactions between various components with the adsorbent surface, as well as on the intermolecular interactions between components themselves. For this reason, estimating the selectivity and describing the thermal response and transport processes of a gas mixture in a specific adsorbent requires much more than knowledge of single component adsorption isotherms; although the individual single-component isotherms do play a critical role in predicting the adsorbent-mixture behavior. There are several theoretical approaches to understanding and predicting mixture adsorption—Density Functional Theory (DFT), Ideal Adsorption Solution Theory (IAST), Real Adsorbed Solution Theory (RAST), Vacancy Solution Theory (VST), Corrected Langmuir Model (CLM), and others. While some of these approaches can describe the properties of mixture adsorption reasonably well, they typically describe ideal systems that behave very differently from actual adsorbents whose pore structures and surface areas vary significantly from ideality [4]. However, Dunbar et al. (2012) presented a very promising and versatile new approach for modeling the

properties of non-ideal real gas mixture adsorption called Multi-component Potential theory of Adsorption (MPTA). MPTA considers the mixture as a heterogeneous substance segregated in the external field of the adsorbent as shown Figure 1. A crucial advantage of MPTA is its capacity to accurately predict excess adsorption of various gases on adsorbents with very few fitting parameters due to the use of the same equations of state for both the bulk and adsorbed phases. For this and other reasons, MPTA and proving its capabilities in predicting real world gas separation applications—specifically, natural gas separation/purification through adsorption—is the focus of the current work.

Through the results of the current work and the subsequent continuation of this work, new adsorbents can be tested computationally in specific separation applications without the need for hundreds of costly experimental efforts. In addition, existing gas separation technologies, such as pressure swing adsorption (PSA) and temperature swing adsorption (TSA) systems, will be improved through process intensification by accurately modeling these real-world gas separation operations and testing new operating conditions, components, and/or adsorbent materials. Finally, the performance of new separation operations that combine existing technologies, such as temperature-assisted pressure swing adsorption (TAPSA) systems, can be modeled accurately to predict their performance without the need for excessive experimental efforts.

## NOMENCLATURE

AC	Activated carbon
ANG	Adsorbent natural gas
ARPA-E	Advanced Research Projects Agency – Energy
CLM	Corrected Langmuir model
DFT	Density functional theory
GT	Georgia Institute of Technology
HSECoE	Hydrogen Storage Engineering Center of Excellence
IAST	Ideal adsorption solution theory
MOF	Metal organic framework
MPTA	Multi-component potential theory of adsorption
$n_{ex}$	Excess adsorption
NIST	National Institute of Standards and Technology
PSA	Pressure swing adsorption
RAST	Real adsorbed solution theory
SRC	Savannah River Consulting
SRNL	Savannah River National Laboratory
TAPSA	Temperature assisted pressure swing adsorption
TSA	Temperature swing adsorption
UQTR	Université du Québec à Trois-Rivières
VST	Vacancy solution theory
$x$	Composition of the adsorbed phase
$y$	Composition of the gas phase
$z_0$	Limiting micropore volume
$\alpha_{ij}$	Selectivity, the ratio of permeability of species i with relation to species j
$\varepsilon$	Fluid-surface interaction potential
$\varepsilon_0$	Characteristic energy of adsorption
$\mu_{Ad}$	Density of the fluid in the adsorbed phase
$\mu_B$	Density of the fluid in the bulk phase
$\rho_{Ad}$	Chemical potential of the fluid in the adsorbed phase
$\rho_B$	Chemical potential of the fluid in the bulk phase

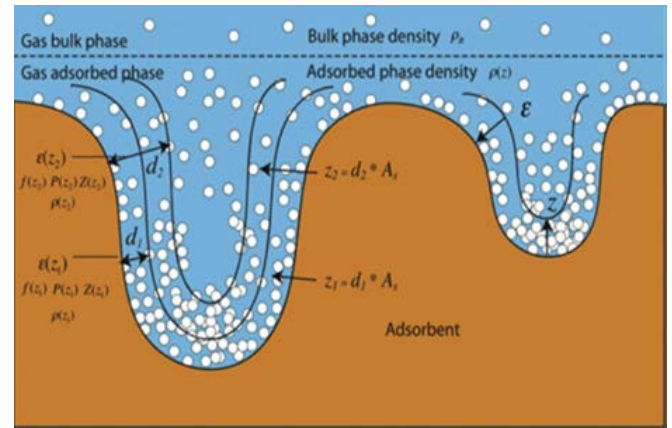
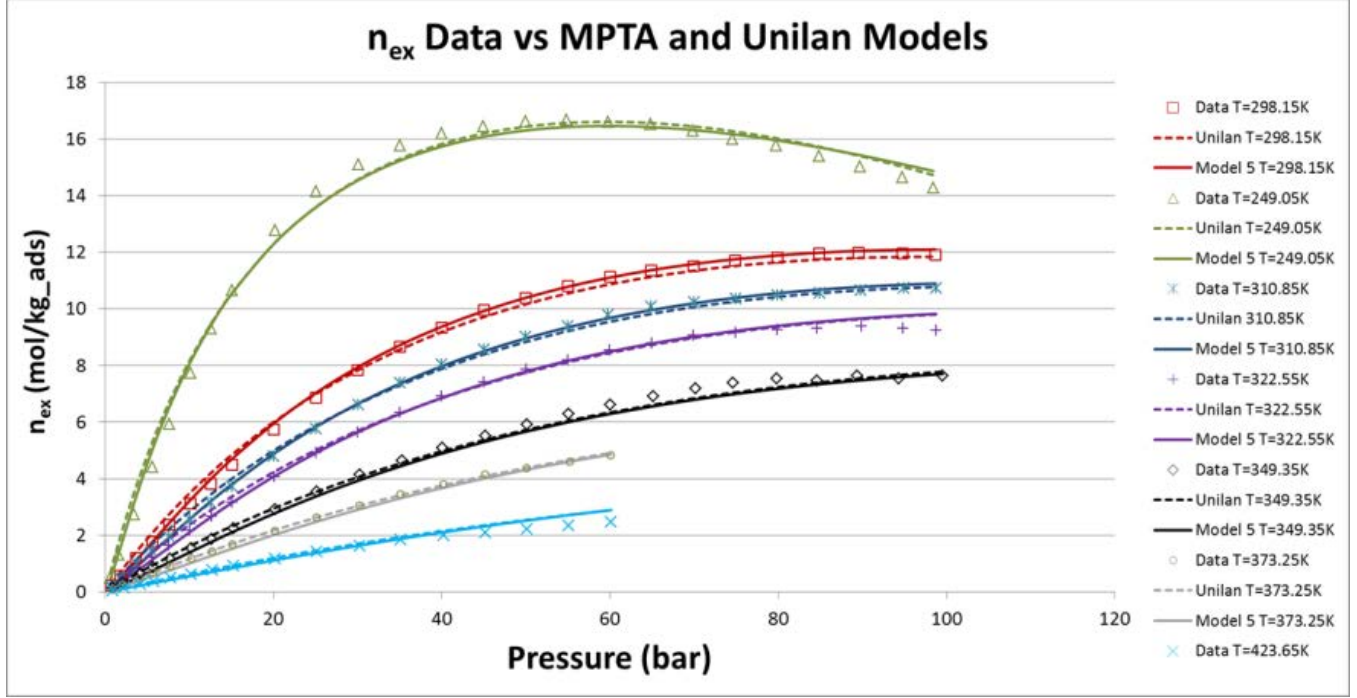


Figure 1. Basic principles of MPTA [4]

## APPROACH

This work can be broken into two efforts: 1) theory derivation and adaptation and 2) experimental measurements and application. The first effort consists of an initial derivation of the MPTA and its adaptation to a specific gas composition. The mass and energy balances together with equations for the multicomponent isotherms and excess internal energy will be coupled to the real gas properties (compressibility, enthalpy, viscosity, etc.) to create a global model describing an ANG system. The second effort consists of adsorbent selection, gas composition selection, and experimental set-up. From the over fifty adsorbents currently in use by the petrochemical industry for natural gas separation, UiO-66, MOF-5, and AC were chosen for analysis based on their availability, their ease of synthesis, and the availability of literature data. These two efforts will merge together as the experimental data is taken and the models are validated. The remainder of the project will then consist of model validation and augmentation using both single-component and multi-component



**Figure 1. MPTA fits and UNILAN model of CH<sub>4</sub> on MOF-5 isotherm data.**

isotherm measurements. The single-component experimental data will then be fed into the MPTA model to predict and compare with the multi-component data for validation. As necessary, the MPTA model will be updated to correct for discrepancies and improve accuracy. By validating the MPTA model's viability to describe the adsorption selectivity of an individual component of a gas mixture using only single component isotherm data, this work will prove the predictive capability of using specific adsorbents for specific gas separation applications.

## RESULTS AND DISCUSSION

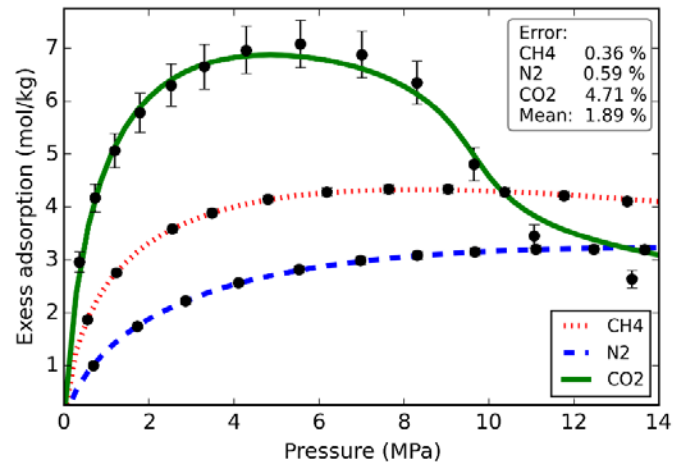
MPTA is a two parameter thermodynamics model used to predict gas mixture adsorption using only pure gas adsorption isotherms. A literature review of MPTA, including but not limited to, the initial development by Polanyi from 1920, and subsequent work by Shapiro, Stenby, Benard, and Dunbar has been completed. A mathematical formulation for the MPTA has been developed at SRNL and has been programmed into Mathcad® using the NIST REFPROP database to describe the thermodynamic properties of the fluids. REFPROP is considered the most accurate equation of state to describe pure fluids and mixtures.

The constitutive equation of the MPTA is given by:

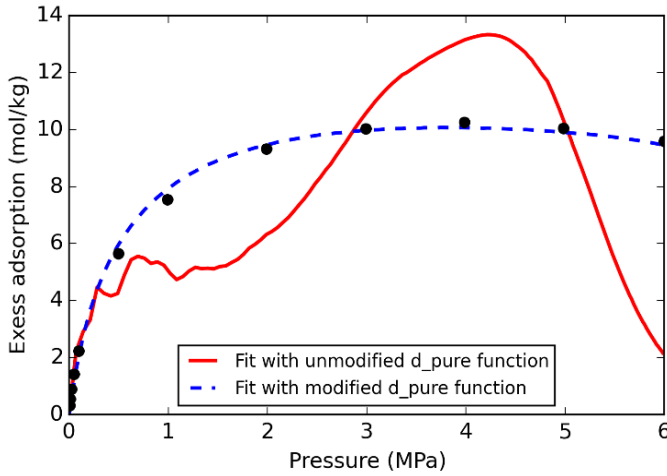
$$\mu_B(\rho_B) = \mu_{Ad}(\rho_{Ad}) - \varepsilon \quad (1)$$

where  $\mu_B$  and  $\rho_B$  are the chemical potential and density of the fluid in the bulk phase, respectively, while  $\mu_{Ad}$  and  $\rho_{Ad}$  are the chemical potential and density of the fluid in the adsorbed phase, respectively. The fluid-surface interaction potential is represented by  $\varepsilon$ . The bulk phase is defined as the region far from the surface, where the potential  $\varepsilon$  is negligible. Conversely, the adsorbed phase is defined as the region near the surface, where the fluid is significantly affected by the presence of the surface via the potential  $\varepsilon$ .

For the present work, the potential  $\varepsilon$  is modeled using the Dubinin-Radushkevich-Astakhov potential given by:



**Figure 3. MPTA model vs. experimental data [5] for pure CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> on activated carbon at 45 °C.**



**Figure 4. Direct (red) and finely tuned (blue) MPTA model implementation vs experimental data [6] for subcritical CO<sub>2</sub> at 25 °C on AC.**

$$\varepsilon(z) = \varepsilon_0 \left( \ln \frac{z_0}{z} \right)^{\frac{1}{2}} \quad (2)$$

where  $\varepsilon_0$  is the characteristic energy of adsorption and  $z_0$  is the limiting micropore volume. These are the fitting parameters of the model. The equation for the potentials can be solved to get  $\rho_{Ad}(z)$ , and then the excess adsorption  $n_{ex}$  is evaluated using:

$$n_{ex}(\rho_B) = \int_0^{z_0} (\rho_{Ad}(z) - \rho_B) dz \quad (3)$$

Note that the potential  $\varepsilon$  lacks a near field repulsion term. It was found that either a lower limit must be imposed on the approach of a gas to the adsorbent surface or an upper limit must be applied to the density of the adsorbate as the surface of the adsorbent is approached. The limiting distance from the adsorbent surface would be representative of the molecular radius of the adsorbed gas, while the limiting density would be related to the condensed form of the adsorbate. Figure 2 shows MPTA fits of CH<sub>4</sub> on MOF-5 compared with UNILAN isotherm model fits. Note that the MPTA fits the isotherm data as well, if not better than the UNILAN model, which is the accepted standard for the

HSECoE and the ARPA-E natural gas research programs.

Figures 3 and 4 provide examples of the implementation of the MPTA model on experimental data for various gases on two different activated carbons. Supercritical fluids such as pure CH<sub>4</sub>, N<sub>2</sub>, and CO<sub>2</sub> at 45 °C on Calcon F-400 activated carbon [5] are relatively straightforward and provide good agreement with the source experimental data, as shown in Figure 3.

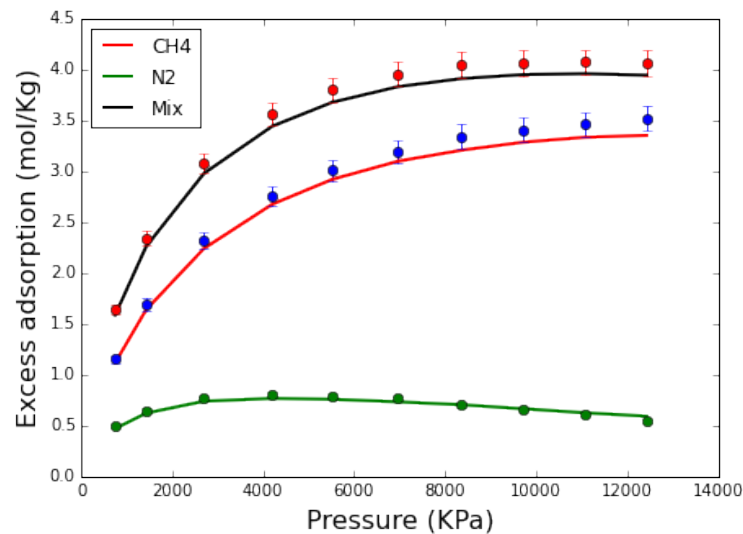
In the subcritical region for the adsorbed phase, the initial assumption of the root finding routines for the fluid density must be carefully adjusted. Otherwise, the algorithm may fail to converge to the proper density. Figure 4 shows the results of the fit for a direct implementation of the MPTA model (red line) and of an improved implementation where the initial guess for density is finely tuned based on the fluid nature and phase (blue dashed line). This is done by starting with the bulk phase, where the fluid properties are well known, and then dividing the adsorbed phase into small intervals ( $\Delta z$ ). For each step  $\Delta z$ , the fluid density is computed using the density of the previous step as starting point. For supercritical fluids, this approach is enough because the fluid density is assumed to vary smoothly. For subcritical fluids, the fluid phase must be verified and the initial density assumption should be set to a value greater than the liquid density of the fluid. Figure 4 illustrates this for subcritical CO<sub>2</sub> at 25 °C on Norit R1 activated carbon [6].

Once MPTA is properly fitted on pure gas isotherms (i.e. once the optimal values for parameters  $\varepsilon_0$  and  $z_0$  are found), the model can

be used to predict mixture adsorption. Figure 5 shows the agreement between the implementation of the MPTA model and experimental data for a fluid mixture constitute of a 60/40 mixture of CH<sub>4</sub> and N<sub>2</sub> at 45 °C on activated carbon [5]. Table 1 provides the model mean error and experimental uncertainties of this data.

**Table 1. Mean MPTA implementation error for 60/40 CH<sub>4</sub>/N<sub>2</sub> mixture on AC, with experimental uncertainties [5].**

	Mean Model Error	Experimental Uncertainties
CH <sub>4</sub>	4.63%	2.6%
N <sub>2</sub>	3.56%	4.5%
Mixture	4.11%	2.5%



**Figure 5. MPTA model and experimental data fit for a 60/40 mixture of CH<sub>4</sub> and N<sub>2</sub> at 45 °C on AC.**

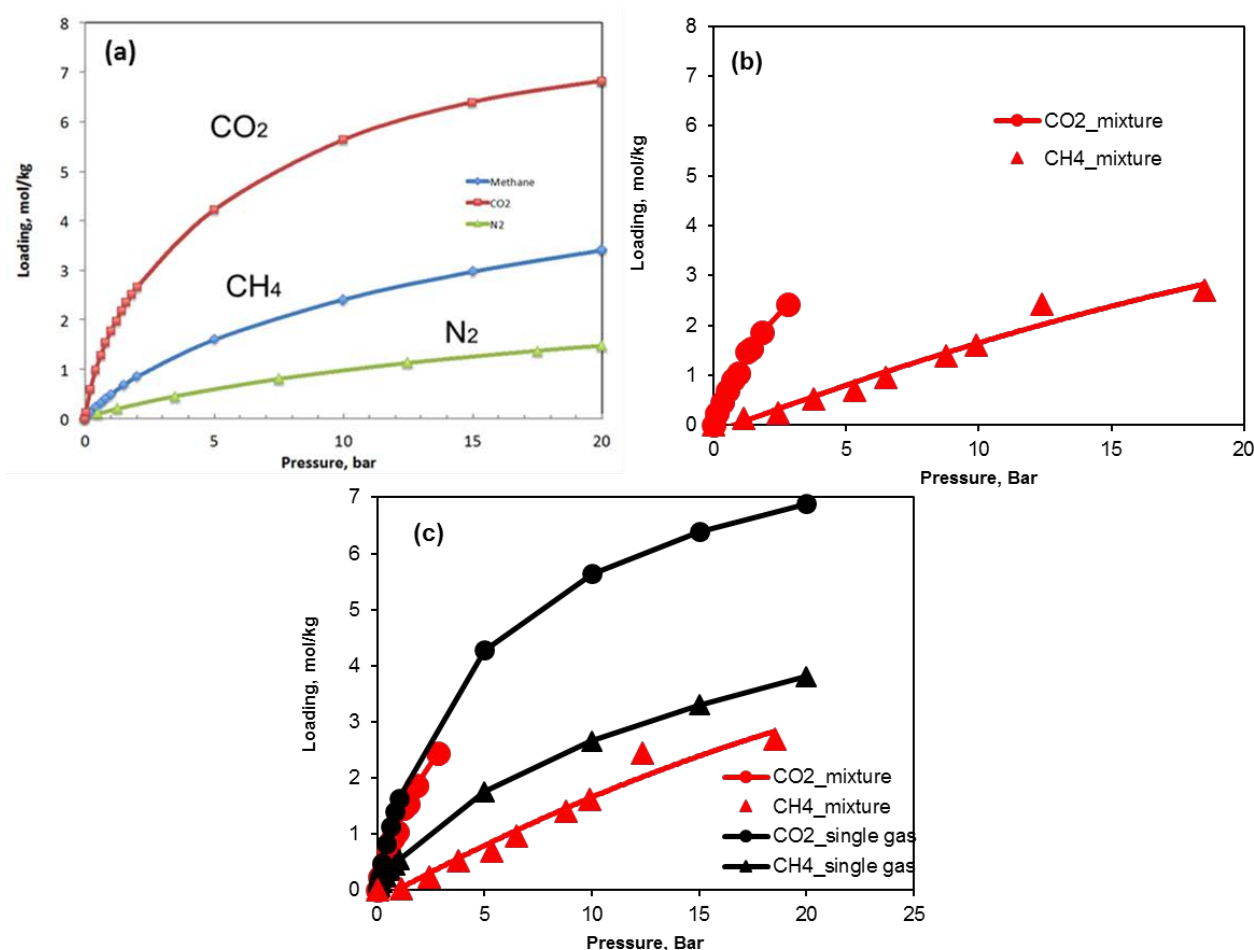
Due to its robust nature and resistance to degradation in the presence of water vapor, UiO-66 was chosen as the primary adsorbent for the multi-component measurements. As noted by Rufford *et al.* (2010), the most common natural gas impurities are H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>S. For simplicity, the impurities CO<sub>2</sub> and N<sub>2</sub> were chosen to compare with CH<sub>4</sub>. Single component

adsorption isotherms indicate a preferential for CO<sub>2</sub> as compared to CH<sub>4</sub> and N<sub>2</sub>. To validate the MPTA multi-component adsorption model, the MOF UiO-66 was also studied with a binary gas of CO<sub>2</sub>/CH<sub>4</sub> with a 15/85 mixture in order to best simulate the average composition of natural gas, as shown in Figure 6. The multi-component isotherms differ from those of the single component, most notably for CO<sub>2</sub>, due to the percent composition of the binary gas.

**Table 2. Surface area of UiO-66-based adsorbents tested for multi-component gas adsorption.**

Adsorbent	BET Surface Area (m <sup>2</sup> /g)
Parent UiO-66	1329
UiO-66-DM	785
UiO-66-NO <sub>2</sub>	914
UiO-66-NH <sub>2</sub>	1501
Defective UiO-66 Type I	1690
Defective UiO-66 Type II	1922
Defective UiO-66 Type III	1654
Defective UiO-66 Type IV	1617

To further understand the selective adsorption of multi-component gas streams, additional UiO-66 based adsorbents were also examined. Alteration to the parent UiO-66 allows for potential improvement to the material's surface area, which in turn may enhance adsorption and selectivity. The additional MOFs synthesized, based on UiO-66, consisted of functionalized versions with either amine (-NH<sub>2</sub>), nitrogen dioxide (-NO<sub>2</sub>) and dimethyl (-DM) groups. Defective UiO-66 was also synthesized that created vacancies in the parent



**Figure 6. (a) Single and (b) multi-component adsorption isotherms of UiO-66 at 25 °C. (c) Together on one graph.**



compound through additional work-up during the synthesis process. Table 2 list the UiO-66 based adsorbents and their related surface area as measured using the widely accepted Brunauer-Emmett-Teller theory (BET). Multi-component isotherms were then collected for the functionalized UiO-66-DM, -NO<sub>2</sub> and -NH<sub>2</sub> for the same gas composition (15% CO<sub>2</sub>: 85% CH<sub>4</sub>). Figure 7 shows the single component isotherms and the multi-component equivalent. Note that the defective UiO-66 work is still ongoing and will be included in future work.

As the main focus of this project is to study the separation of gases on an adsorbent and to validate the MPTA model, it is important to examine the isotherm adsorption data of UiO-66 and its derivatives for selectivity. As with any natural gas stream, the ideal scenario is to capture undesirable gases and allow the desired gas (methane) to continue. To more closely compare the adsorbents studied and their selectivity of CO<sub>2</sub> over CH<sub>4</sub>, the following equation was considered:

$$\alpha_{ij} = \frac{x_i}{y_i} \times \frac{y_j}{x_j} \quad (4)$$

where  $i = \text{CO}_2$ ,  $j = \text{CH}_4$ ,  $x$  = composition in adsorbed phase, and  $y$  = composition in the gas phase.

The above equation for selectivity is used by the membrane industry to determine the optimum membrane require for a separation process where the selectivity,  $\alpha_{ij}$ , is defined as the ratio of permeability of species  $i$  with relation to species  $j$ . It was modified for this project due to the two phases that occur during solid-state adsorption. **Figure 8 (Fig 7 in Report)** shows the preferential selectivity for CO<sub>2</sub> on the UiO-66 adsorbents that have been studied thus far. Note that the data for original UiO-66 does not follow the trend shown for its variants. This is believed to be a data acquisition error and the data will be retaken to prove/disprove this belief. Also note that the -DM variant shows a higher selectivity than the other versions, which was an unexpected result. At this time, no explanation is available without additional study.

## CONCLUSIONS AND FUTURE WORK

This work proposed to prove the applicability of the multi-component potential theory of adsorption (MPTA) to real-world natural gas adsorbent-based separation/purification systems. MPTA was shown to fit single-component isotherm data as well as the UNILAN

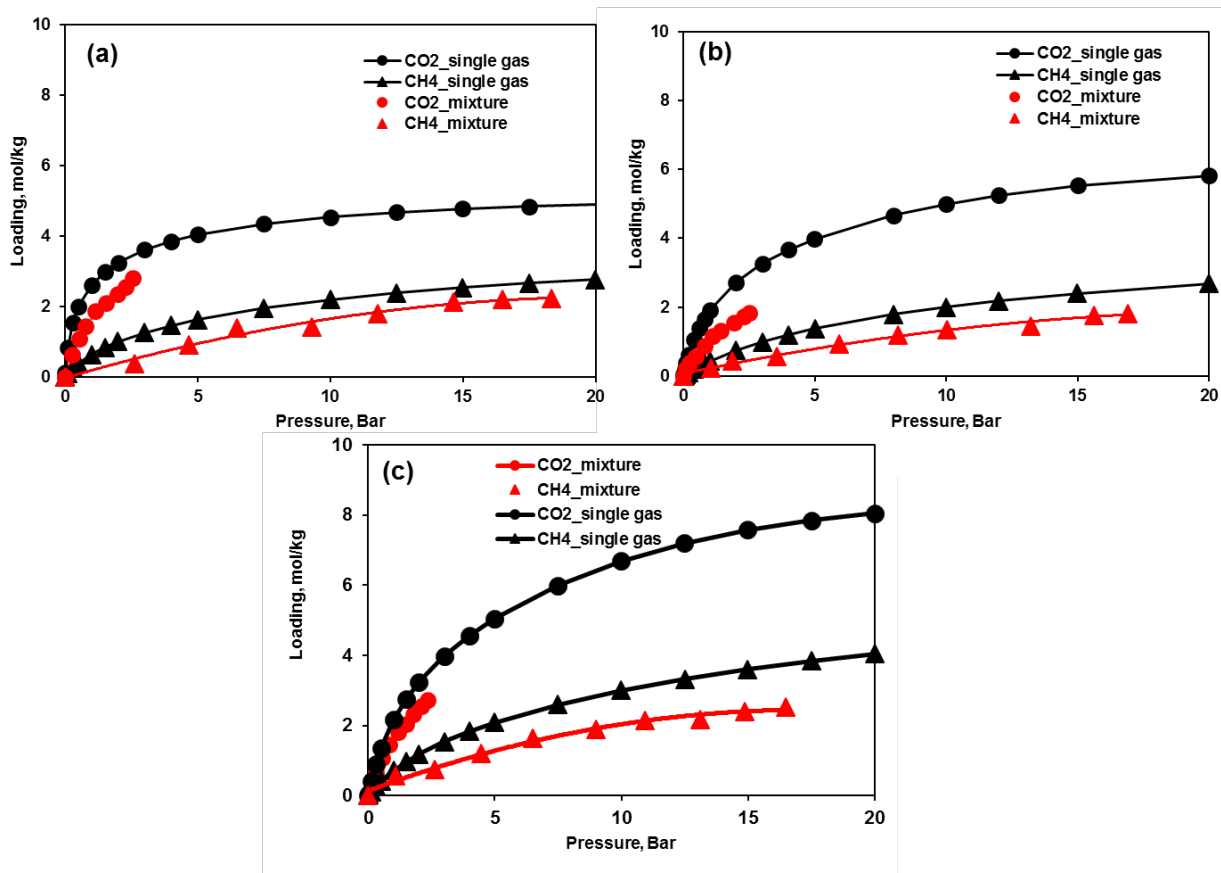
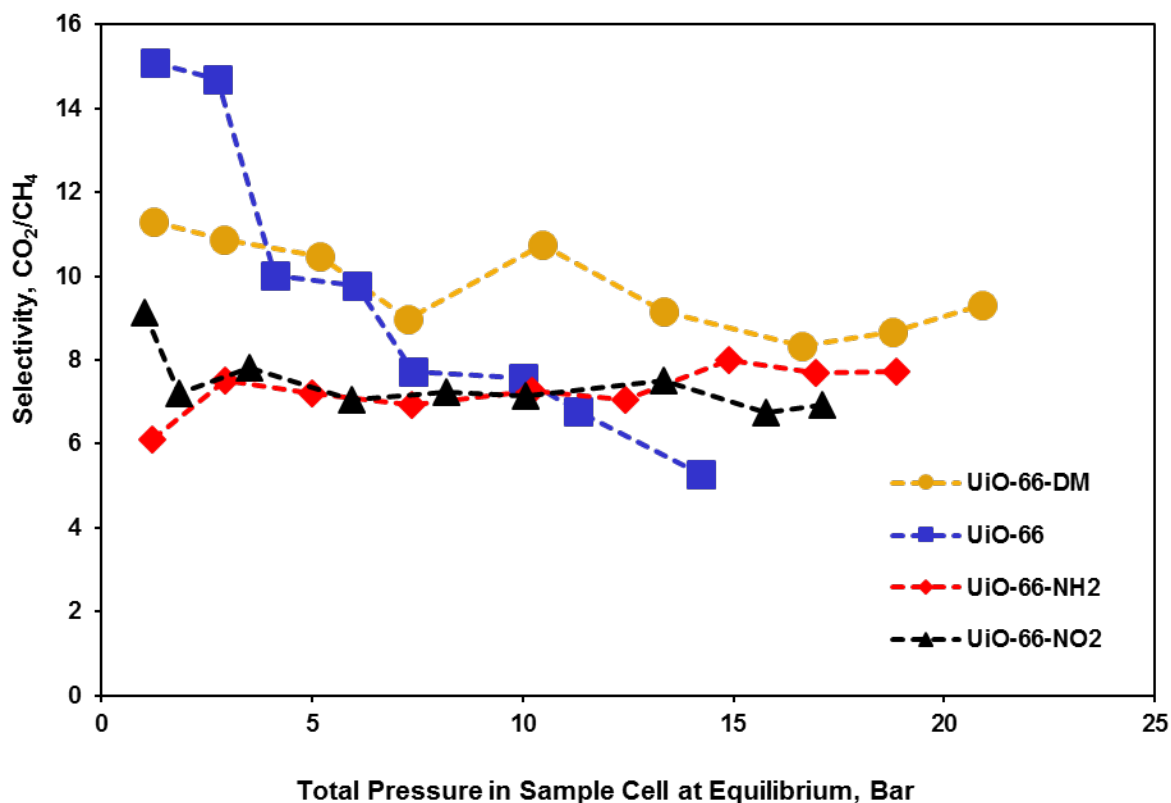


Figure 7. Methane and carbon dioxide single and multi-component isotherms of UiO-66 functionalized with (a) -DM, (b) -NO<sub>2</sub>, and (c) -NH<sub>2</sub>.



**Figure 8. Preferential selectivity ( $\alpha_{\text{CO}_2/\text{CH}_4}$ ) for CO<sub>2</sub> over CH<sub>4</sub> of the variants of UiO-66.**

isotherm theory, which is an accepted standard. The MPTA potentials found for single-component gas streams were used to fit multi-component gas mixture isotherms, and were shown to fit multi-component isotherms well. Note that MPTA was validated using both literature data and experimental data taken for the current project. Borrowing the selectivity equations from the membrane industry, the preferential selectivity of both UiO-66 and several functionalized versions of it.

While much has been accomplished, there is still much to be done for this project. Further improvements can be made the implementation of the MPTA fitting routines to aide in convergence. There are also several two-component and three-component gas mixtures that should be examined to further prove the applicability of MPTA to real-world natural gas streams. Several non-natural gas based gas mixtures may also be examined, depending upon the funding organization's research needs. Finally, additional variations of UiO-66 will continue to be examined, with specific emphasis on defective UiO-66 that is synthesized with missing linkers from the parent compound.

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