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Adsorption of pure and predicted binary (CO_2:CH_4) mixtures on 13X-Zeolite: Equilibrium and kinetic properties at offshore conditions

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ABSTRACT

The growth in energy demand for natural gas has led to the exploration of sub-quality natural gas reserves with high CO_2 content up to 80% at the offshore condition with temperature and pressure approximately 50 °C and 70 bar. In this work, a gravimetric technique is used to study CO_2 and CH_4 adsorptions on 13× zeolites at 50 °C and up to 70 bar pressure as an adequate range for offshore operations. 13× zeolite shows high CO_2 adsorption capacity with 5.226 mmol/g at 50 °C compared to 4.29 mmol/g at 70 °C. The same trend is noticed for CH_4 adsorption on both temperatures. Four equilibrium isotherm models are used to analyze the adsorption data i.e. Langmuir, Freundlich, Toth, and Sips. Virial isotherm model is applied on the experimental data to illustrate the isosteric heat of adsorption and it shows an excellent agreement with R^2 = 0.998 for 13× MSZ. Henry's law constant is estimated utilizing Virial coefficients, which shows higher molar selectivity ratio for CO_2 on 13× with α ˜ 3.957 at 50 °C as compared to the α ˜ 3.736 at 70 °C. Extended Langmuir (EL) Model and Multisite Langmuir (MSL) models are applied for 30:70, 50:50, and 70:30 CO_2:CH_4 binary mixtures. The outcomes of MSL exhibit high agreement with the quadrupole and polarizability of the single component and the mixtures. The kinetic rate constant is estimated according to the applied LDF model at higher operational regions. The 13× MSZ shows feasibly good isosteric heat of adsorption, which might refer to the large surface area and pore volume that can accommodate CO_2 at higher speed and quantity at offshore conditions.

1. Introduction

Fossil fuels and natural gas remain the major energy source for mankind and their developed lifestyle as these energy sources are affordable and cost-effective. The demand for energy is increasing day by day with depleting oil and gas reservoirs that are economically accessible. In the current era, researchers concentrate on finding new feasible and economical ways of exploiting marginal and unconventional natural gas fields. Increasing energy costs and growing demand for natural gas have driven the development of sour gas fields around the world. About 40% or 2600 Tcf of the world's natural gas reserves are in the form of sour gas with high CO_2 content (≈80%) in the raw natural gas [1]. Natural gas contains contaminants which include heavy hydrocarbons, mercaptans, mercury, water and the acid gases (H_2S and CO_2). However, the increased CO_2 emission is always considered as the breakdown for the stream feasibility and can cause major issues such as blockage and penetration of the downline transportation pipelines [2–4]. Currently, the conventional technology is economically viable for processing sweet and sour natural gas. Thus, appropriate technology is required before these marginal and unconventional fields become economically viable. The fact that CO_2 separation and capture process at high pressure on offshore is illustrated as a considerable challenge because it may comprise of 75% of the total cost for natural gas purification. This capital cost gives the priority for carbon removal process as compared to other refining pre-treatments, which is a key factor to find better alternatives [5,6].

The chemical solvents utilized for the absorption of CO_2 are usually amine-based solvents such as monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), triethanolamine (TEA), methyldiethanolamine (MDEA). Monoethanolamine (MEA) is one of the most conventional solvents used in CO_2 absorption at low-pressure conditions [7–9]. However, it has several limitations such as, a low CO_2 loading capacity, high degradation, and a tendency to corrode processing equipment. Therefore, solid desiccants are considered as the most attractive alternatives for amine solvents [10].

Several types of adsorbents are studied for selective CO_2 separation such as coal, activated carbon, alumina, metal oxides, and molecular sieves [11–13]. Furthermore, various operating condition are studied to

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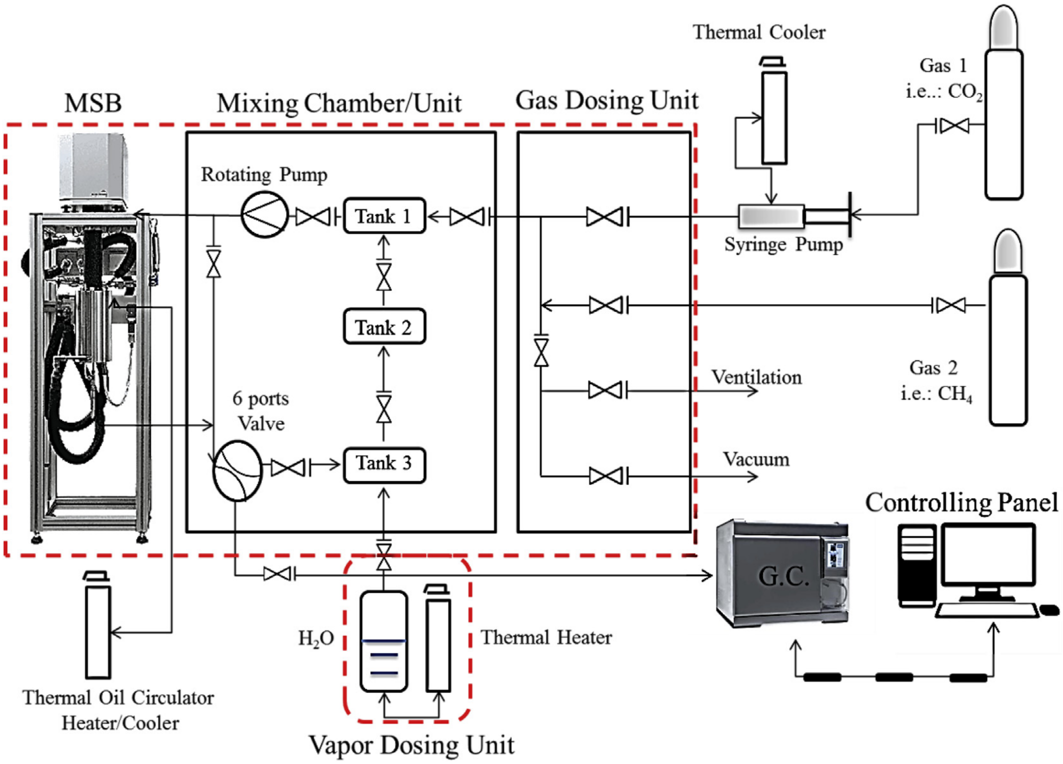

Fig. 1. Experimental Gravimetric Setup main sections and parts.

cater low temperature or low pressure, which is distant from the real case for offshore applications. Numerous solid desiccants such as Metal Organic Frameworks (MOFs) and covalent organic polymers (COPs) were studied for CO_2 adsorption performance or separation from natural gas [14–19]. Whereas, these adsorbents undergo a high synthetic cost and limited studies are found at platform circumstances [20]. Recent studies are investigating newly synthesized and modified adsorbents for the aim of CO_2 separation from natural gas, which are still covering a lower range of operating conditions [21,22]. However, even with the considered high-pressure category studies, the operating pressure condition does not go beyond than 50 bar.

Molecular Sieve zeolites are considered as the most potent-known solid adsorbents for natural gas separation and purification at a viable cost, eco-friendly, with ease of handling and long operating lifetime. However, they still need further investigation in term of platform conditions, selectivity, temperature and pressure effect on adsorption capacity and thermodynamic characteristics [23–26].

Palomino et al. [27] studied the structure modification effect of adsorbents on CO_2 adsorption, focused on several types of zeolites, and investigated the promising kinds for selective CO_2 adsorption from CO_2/CH_4 mixtures, with the regeneration methods at low to moderate conditions. Miyamoto et al. [28] studied the CHA type zeolite in comparison with 13× zeolite at a pressure of 3–4 Mpa, and selective behavior with N_2 existence. Their findings implied that 13× has a promising affinity towards CO_2 adsorption, featuring adsorbents hydrophobicity, and highlighting the significance of water existence on CO_2 adsorption. Cheung and Hedin [29] investigated on zeolites and related narrow pore adsorbents, which were utilized for CO_2 adsorption. They outlined that zeolites could be the best alternatives for CO_2 adsorption and they might need to be investigated thoroughly. Both zeolite and chabazite zeolite are commercially available and the properties of these materials can be improved. They investigated that the zeolites offered high uptake of CO_2.

In this work, a correlation and a detailed comparison of the extensive common adsorbent, 13× molecular sieve zeolites (MSZs), under high-pressure and offshore conditions i.e. 50 and 70 °C and up to 70 bar pressure, utilizing gravimetric technique. The adsorption capacity, excess and absolute adsorption isotherms, with various two and three parameters equilibrium isotherm models are investigated. These parameters are utilized in binary theoretical models. Extended Langmuir (EL) and Modified Multisite Langmuir (MSL) models are applied for CO_2 and CH_4 binary mixtures prediction at various combinations for ideality and intensity validation. Furthermore, kinetic and modeling are also studied at the same operating conditions.

2. Experiments and methods

2.1. Materials

In this work, 13× zeolite (molecular sieve pellets) is used for CO_2 capture equilibrium and kinetic analysis. MSZ is purchased from Sigma-Aldrich, Germany. High purity gases for pre-measurements and experiments i.e. He (99.999%), CO_2 (99.995%), CH_4 (99.995%) are provided by Linde Sdn. Bhd. Malaysia.

2.2. Surface area and pore size

The zeolite sample is characterized to determine pore size and surface area using adsorption apparatus (BELSORP-max, BEL Japan Inc.) at the temperature of liquid nitrogen. The adsorption isotherms of CO_2 and CH_4 are performed in the range of 0–1 bar at 298 K (25 °C). The samples are degassed and reactivated at 130 °C in a vacuum oven for 3 h.

2.3. Experimental setup

The experiments are performed in the specially designed gravimetric system. The IsoSORP MIX FLOW experimental setup is made by Rubotherm, Germany. A detailed flow diagram of the experimental setup is shown in Fig. 1. The setup consists of three main sections: