Methane and Natural Gases Kinetic and Equilibrium Adsorption Comparison on Synthesised Porous Coconut Shell Kernel Activated Carbon

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Instability of diesel and gasoline market price with the generation of environmental pollution attracted world attention in looking towards natural gas (NG) as a means of alternative fuel. This research work presents an investigation of experimental adsorption uptake of pure methane (CH_4) and NG onto a hybrid of coconut shell and polyetheretherketone (PEEK) porous carbon. The hybrid porous carbon was prepared by KOH microwave-assisted activation of a coconut shell with PEEK. The Porous carbon (M33P15) was used as a potential sorbent to investigate the adsorption characteristics of the two gasses. The adsorption is applied at an ambient and 5 °C adsorption temperatures and at a pressure of 3.5 MPa. The comparison is based on measuring adsorption uptake differences between the two gases onto porous carbon. The ideal CH_4 and NG adsorption uptake on porous carbon are investigated using volumetric adsorption method. The CH_4 adsorption capacity of 9.7045 and 9.9958 mmol CH_4 adsorbed/g adsorbent was achieved at an ambient and 5 °C adsorption temperature. While NG adsorption capacity of 9.9432 and 10.0901 mmol NG adsorbed/g was achieved at an ambient and 5 °C adsorption temperatures. In conclusion, the results show that NG adsorption uptake is slightly higher than CH_4 adsorption uptake. This is due to the ability of the adsorbent to adsorb other components of the NG other than CH_4. It is also suggested that applying heat management strategies, by lowering the temperature of adsorbent during the adsorption process, can significantly improve the storage capacity of CH_4 and NG.

1. Introduction

Instability of conventional fuel market price with its generation of environmental pollution has attracted world attention in looking natural gas (NG) as a means of it alternative (El-Sharkawy et al., 2015). NG reduces nitrogen oxide, sulfur oxide and carbon monoxide emissions, in a required area especially in densely populated areas (Blanco et al., 2016). It consists of CH_4 (70 – 90 %), CO_2 (0 – 5 %) and other hydrocarbons (0 – 20 %) namely; butane, propane, and ethane (Patil and Sahoo, 2018). NG or CH_4 are available and contribute less environmental pollution to the environment when compared with conventional fuels such as diesel and gasoline (Rios et al., 2011). Currently, compressed natural gas (CNG) and liquefied natural gas (LNG) are the most matured technology that used for the transportation system. Changtao et al. (2018)

reported that CNG system operates at very high-pressure ranges between 20 to 30 MPa that sustains high costs of manufacturing and filling the vessels coupled with the need for specially designed pressure vessels. While LNG system requires a huge amount of energy for cryogenic cooling of the gas to a temperature of −163 °C.

Storage of gas using carbonaceous materials is proposed to overcome the limitation exist in the above-mentioned technologies. Carbonaceous materials are attractive for CH_4 or NG storage due to its low cost, availability, high thermal stability and low sensitivity to moisture (Rashidi et al., 2013). Adsorbed natural gas (ANG) is an efficient technology, which requires cheap carbonaceous material to adsorb and store the gases (NG or CH_4) at relatively low pressures between the 3.5 - 4 MPa and at ambient temperature (Patil and Sahoo, 2018).

In most of the researches achieved in ANG system using dry activated carbon, CH_4 used as the test gas. In the real practical application, NG is used as fuel for the ANG system. CH_4 adsorption mechanism onto a porous carbon is different from NG adsorption mechanism, despite CH_4 the main component of NG. Components constituted NG other than CH_4 have a strong attraction with a carbon material, which cannot easily desorb totally on discharge, and gradually affect the adsorption uptake of the gas for the subsequent adsorption-desorption process (Pourmahdi and Maghsoudi, 2017). This is because larger molecules in the NG cannot easily diffuse out through the pores (Hamza et al., 215). The amount of the gas left can only be discharged by unnatural means using vacuum or heating. In addition, carbon adsorbents usually have a higher selectivity for CO_2 and higher alkanes (non-methane components) over pure CH_4. The high affinity (attraction) of the adsorbate towards carbon adsorbent makes the discharge more difficult, causing its accumulation in the porous adsorbent, which reduces the performance of the system storage on successive charge and discharge cycles (Rios et al., 2011).

Most of the previous research focused on adsorption of pure CH_4 onto different activated carbon and limited research on adsorption of commercial NG. Therefore, the objective of this paper is to investigate the adsorption characteristic of pure CH_4 and NG commercially available in Malaysia market, onto the synthesised adsorbent. The novelty of this work is focused on adsorbent preparation and adsorption kinetic modeling. Adsorbent for most CH_4 or NG adsorption is developed from a single precursor (coconut shells, palm kernel shells, bamboo etc.) and to the best of my knowledge the use of a hybrid of coconut shells and PEEK for this purpose has not been exploited.

2. Experimental

2.1 Materials and methods

Potassium hydroxide (KOH), hydrogen chloride (HCl), CO_2, N_2, pure CH_4 and NG were supplied by Merck chemical Malaysia and coconut shell was acquired from local vendors in Johor, Malaysia. Coconut shell was carbonised using the procedure adapted from Hayatu et al. (2017) under a flow of nitrogen at 1,000 mL/min at the rate of heating 10 °C/min from ambient temperature to 700 ± 20 °C. PEEK was also carbonised. The carbonisation lasted for 45 min which leads to the formation of char. Prior to activation, the char of coconut shell and PEEK were sieved to a particle size ranges between 0.841 mm - 0.425 mm (20 - 40) mesh. PEEK char 15 % was blended with coconut shell char to form coconut-PEEK char. The blended chars were mixed with an impregnating agent (KOH) in the ratio of 2 : 1. Conditions of sample impregnation, microwave irradiation, and application in CH_4 adsorption are given elsewhere (Hamza et al., 2015). The final samples containing 15 % of PEEK which was irradiated at 300 W was denoted as M33P15. The activated sample was washed thoroughly with distilled water until a neutral pH is attained and stored in a dry environment.

2.2 Gas adsorption procedure

Prior to the adsorption and desorption processes, the sample was dried at 120 °C for 12 h then cooled (El-Sharkawy et al., 2015), the experiment conducted using the set-up shown in Figure 1. The adsorption procedure adopted from the work of Hayatu et al. (2017). The adsorption cell was fed with 3 g of adsorbent while load cell fed with adsorbate to a pressure of 3.5 MPa. The valve between loading and adsorption cells was closed to avoid movement of the gas from load cell to adsorption cell while loading the gas. The valve between the loading and adsorption cell is then open for the gas to adsorb onto the surface of the adsorbent, while the valve below the adsorption cell is closed. The result obtained based on measuring the quantity of gas adsorbed between two equilibrium adsorption states. The equilibrium state reached when the pressure of both cells maintained constant pressure values for at least 20 min. The amount of gas adsorbed determined using the mass balance as in Eq(1).
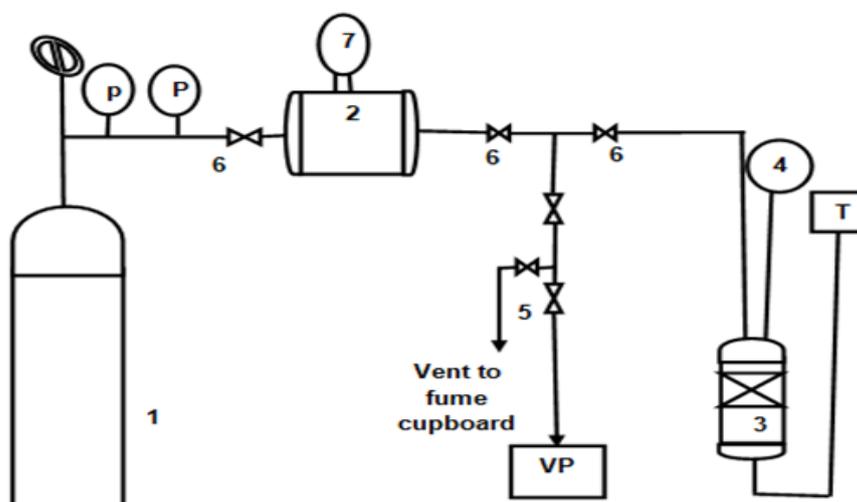
Figure 1: Schematic diagram of volumetric adsorption set-up

Where 1 = Natural gas cylinder, 2 = Loading cell, 3 = Adsorption cell, 4 = Digital pressure transducer, 5 = Safety valves, 6 = Valves, 7 = Analog pressure gauge, T = adsorption cell temperature, p = Gas supply pressure gauge, VP = Vacuum pump.

$$\frac{1}{m}\left[\left(\frac{PV}{ZRT}\right)_{L1} - \left(\frac{PV}{ZRT}\right)_{L2} + \left(\frac{PV}{ZRT}\right)_{A1} - \left(\frac{PV}{ZRT}\right)_{A2}\right] \tag{1}$$

Where P = Pressure, V = Volume, R = Gas constant, m = Adsorbent mass, Z = Compressibility factor, q = Amount adsorbed, L = load cell, A = Adsorption cell, 1 = the state prior to adsorption equilibrium and 2 = the final equilibrium state.

2.3 Modelling of adsorption kinetics

The kinetics of CH_4 and NG onto the activated carbon were measured at ambient temperature and at a pressure of 3.5 MPa. The kinetic behavior of CH_4 and NG onto the synthesised activated carbon were simulated to validate the adsorption rate profile obtained from the experiment. This was conducted by fitting the results obtained from experiment to the frequently used kinetic model's equations in order to select the model that best fits (described) the experimental results. Two kinetic models were selected based on their suitability in predicting gas-solid interaction during adsorption, which is the pseudo-1st order and pseudo-2nd order.

3. Results and discussions

3.1 Pure methane and natural adsorption characteristics

In this research, work, CH_4, and NG adsorption measurement on to synthesised porous carbon (M33P15) is conducted for comparison. The adsorption measurements achieved at a pressure of 3.5 MPa and at ambient temperature. Natural gas is favorably adsorbed at relatively higher amount than methane as depicted in Figure 2. This is due to the presence of other components other than methane (ethane, propane and heavier hydrocarbons) which favorably adsorbed into the adsorbent (Wu et al., 2017). High-pressure adsorption of natural gas is more concerned in this research work owing to the high-pressure streams of natural gas. This experimental data obtained at high pressure are more suitable for possible industrial applications. It is commendable to mention that methane and natural gas adsorption characteristics investigated by most of the previous studies showed similar characteristics. The natural gas and methane adsorption characteristics of this study are similar; however, natural adsorption uptake is slightly higher than methane adsorption uptake. This is due to the ability of the adsorbent to adsorb other components of the NG.

Their higher affinity towards the carbonaceous materials makes their adsorption more efficient, causing faster accumulation in the porous medium, increasing the efficiency of the storage system (Hayatu et al., 2017).
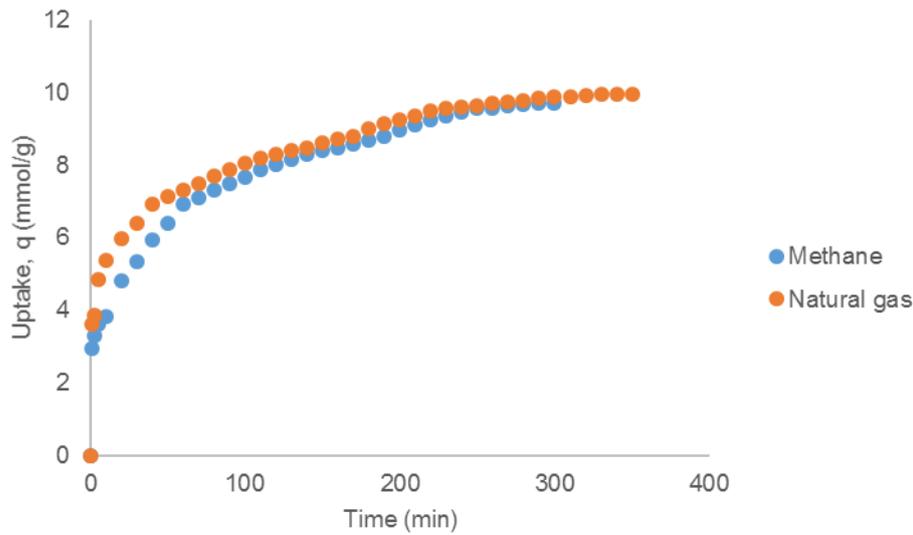
Figure 2: Comparison plots of CH₄ and NG adsorption capacity at ambient temperature and at 3.5 MPa

3.2 Behavior and performance of adsorbent at a low temperature

To evaluate the effect of temperature on adsorption rate, the comparison of each gas adsorption characteristics onto M33P15 at ambient and 5 °C temperature under a pressure of 3.5 MPa were investigated. The plots of the experimental data for adsorption of CH_4 and NG at ambient and 5 °C were shown in Figure 3 and 4. The plots reveal that the equilibrium time tends to longer at a lower temperature due to the slow movement of the of the gas molecules onto the adsorbent. Increasing temperature give the adsorbent molecules extra energy to overcome the van der Waals' force holding them in the condensed-phase and lead migrating them in a faster motion. A similar trend was observed by Xing et al. (2015) for adsorption of CH_4 onto a block anthracite at a temperature range of 20 °C to 56 °C, decreased in time to reach equilibrium with an increase in temperature. The results also reveal that at a temperature (5 °C) the CH_4 and NG uptake is slightly higher than at an ambient temperature (Figure 3 and 4), as decreasing the temperature leads to removal of heat of adsorption.
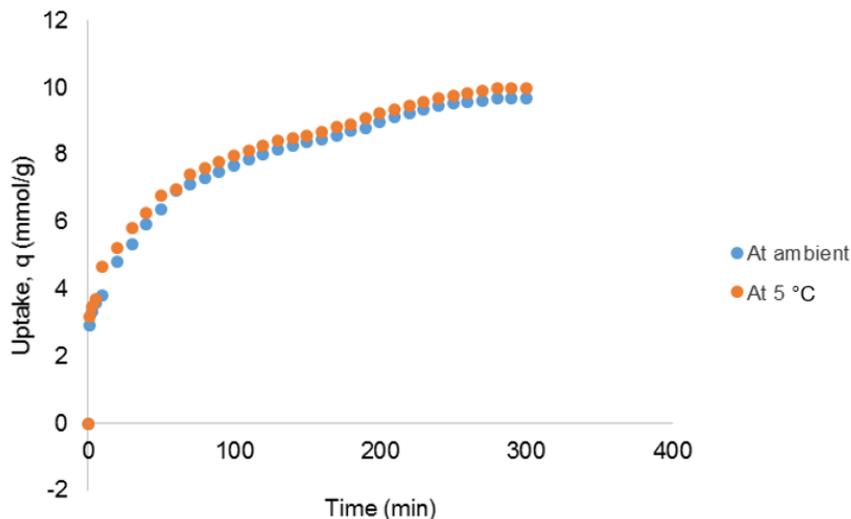

Figure 3: CH₄ uptake with time on M33P15 for pressure 3.5 MPa at two different temperatures
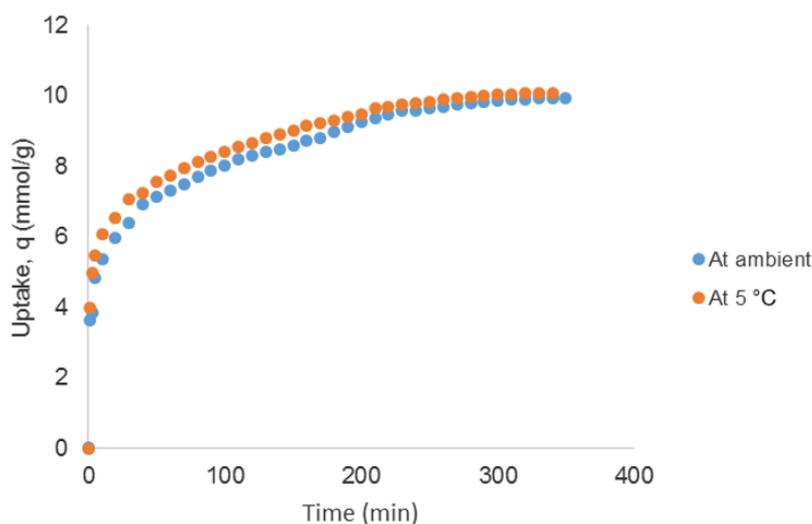
Figure 4: NG uptake with time on M33P15 for pressure 3.5 MPa at two different temperatures

3.3 Kinetic models fitting

In order to examine the controlling mechanism of CH_4 and NG adsorption on synthesised porous carbon such as gas molecules movement, adsorption capacity and reaction rate, kinetic equations were applied to analyse the experimental data. The experimental data obtained were fitted to pseudo-1st order and pseudo-2nd order kinetic models as shown in Figure 5 to predict the theoretical relationship between the rate of mass transfer of CH_4 and NG by adsorption and the time taken to do so. The linear forms of the two models were depicted in Figure 4a - 4d to determine their respective kinetic model parameters. The suitability of the models in fitting experimental data was evaluated by the coefficient of determination (R^2) value. Based on the R^2, the pseudo-second-order kinetic model fitted best in both of the gases. Considering this result, repulsion among adsorbate molecules play an important role in the adsorption process. According to the tradition of the pseudo-second-order model, the adsorption process involves mechanisms of repulsion among adsorbate molecules (Dil et al., 2016).
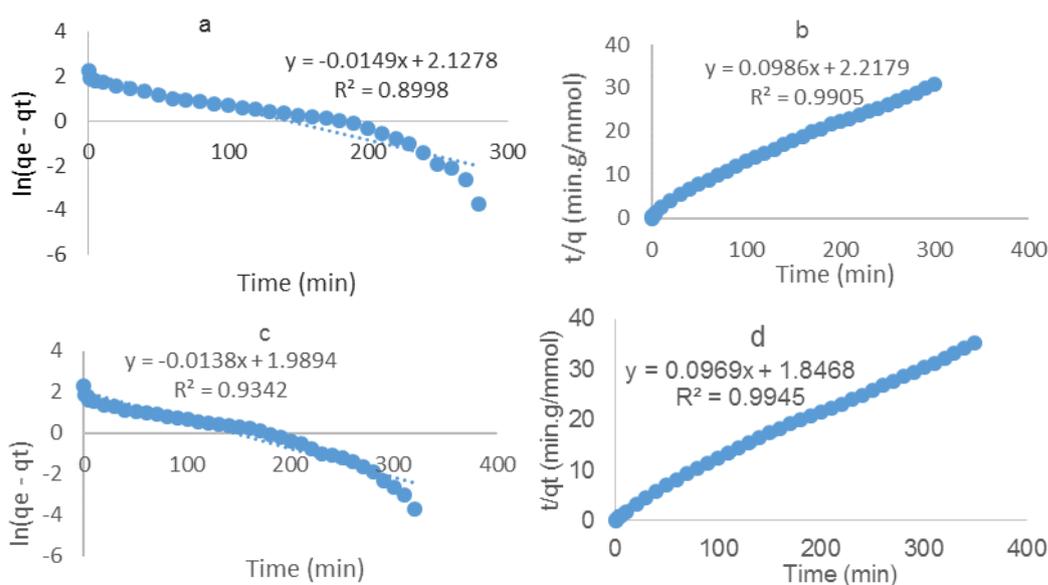

Figure 5: Linearised plots of kinetic modeling with (a) Pseudo-1st order for CH_4 at ambient, and Pseudo-2nd order for CH_4 at ambient (c) Pseudo-1st order for NG at ambient and (d) Pseudo-2nd order for NG at ambient.

4. Conclusions

The kinetic behavior of porous carbon impregnated with potassium hydroxide in adsorption of CH_4 and NG was studied using two different adsorption reaction models namely: pseudo-1st order and pseudo-2nd order models. The study compared the adsorption of CH_4 and NG available in Malaysian market onto coconut-PEEK porous carbon. The CH_4 and NG adsorption capacities were tested at ambient temperature and 5 °C using the volumetric static method and fitted with pseudo-1st and pseudo-2nd order models. In all conditions, the NG uptake is higher than CH_4 uptake. The CH_4 adsorption capacity of 9.7045 and 9.9958 mmol CH_4 adsorbed/g adsorbent was achieved at an ambient and 5 °C adsorption temperature. While NG adsorption capacity of 9.9432 and 10.0901 mmol NG adsorbed/g was achieved at an ambient and 5 °C adsorption temperatures.

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