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Hydrogen capture using zeolite 3A for pipeline gas deblending

Jianing Yang, Leila Dehdari, Yalou Guo, Jining Guo, Ranjeet Singh, Penny Xiao, Jin Shang, Ali Zavabeti, Gang Kevin Li

Abstract

Less than 20% of hydrogen gas can be co-transported with natural gas (NG) and distributed to end-users using existing gas pipelines. However, most industrial gas turbines can only tolerate up to 1% by volume of hydrogen in natural gas. A separation process is needed to selectively capture the minor component such as hydrogen. Herein, we report the design of a deblending process to meet the requirements of these specific industries. We demonstrated that zeolite 3A which is believed to be a trapdoor zeolite has a selectivity towards hydrogen molecules based on the laboratory experiment results. A multiple-bed pressure swing adsorption (PSA) using zeolite 3A was subsequently modelled for removing hydrogen at various concentrations from the blended gas. The results indicate that high pressure and high purity methane (>99%) can be obtained by the 3A PSA, making products suitable for gas turbines. When a methane PSA with activated carbon (AC) adsorbents is used for comparison, the process needs to do separation work towards the major component methane and an overwhelming pump work is required to repressurize the desorbed methane gas. Therefore, a hydrogen capture PSA process with zeolite 3A stands out in terms of product purity, recovery and energy consumption, for low concentration H₂ deblending from NG.

Keywords:
Hydrogen separation
Natural gas
VPSA simulation
Energy consumption and productivity

1. Introduction

In the last two centuries, due to rapid technological development, gradual industrialization and urbanization, the greenhouse gas levels in the atmosphere have increased, leading to climate change and sea level increase [1]. In response to these, governments are committing to carbon neutrality and countries such as Germany, New Zealand, the United Kingdom and the United States have set net-zero emission targets [2,3]. As a result, there is a mounting imperative worldwide to decrease society’s reliance on fossil fuels as a source of energy and instead move to renewable sources.

Hydrogen is one of the critical factors in addressing energy transition, which has attracted much attention. Hydrogen can be produced from multiple sources of clean energy [4] with low (i.e. as “green” hydrogen) or even zero-emission [5]. To handle large hydrogen flow over a long distance, the existing natural gas pipeline can be employed for hydrogen transportation with a maximum hydrogen concentration of 15%-20% in volume in view of the current gas system [6]. For instance, the project “Hydrogen Park South Australia (Hyp SA)” commenced in May 2021 is blending 5% hydrogen with natural gas [7]. After the co-transportation, the hydrogen and natural gas mixture can be separated or used directly according to the quality requirements of different end-users. For instance, hydrogen product has to be extracted with purity levels higher than 98% to satisfy combustion applications and higher than 99.97% to feed road vehicles according to the ISO 14687 standard [8–10]. On the contrary, for a typical blended gas with less than 15% hydrogen, there is no need to further separate gases after transportation for household heating or cooking purposes.

Traditional hydrogen separation technologies entailing adsorption techniques [11,12], membrane techniques [13], cryogenic techniques [14] and selective absorption techniques [15] are well-known and widely used in industry [16]. Among all of these, adsorption processes such as pressure swing adsorption (PSA) and vacuum pressure swing adsorption (VPSA) are projected as promising solutions to gas separation [17] due to their high energy efficiency, low cost, and excellent design flexibility [18].

There have been commercial adsorption units for industrial hydrogen purification, for example, removal of contaminants/traces for the production of ultrahigh purity hydrogen [19]. In most cases, they used adsorbents such as activated carbon, zeolite 5A, and alumina...
instead of any hydrogen selective materials to remove impurities. For instance, Lopes, Grande, Ribeiro, Loureiro, Evaggelos, Nikolakis and Rodrigues [23] designed a multiple-bed PSA process for hydrogen purification with activated carbon at the bottom layer and zeolite 5A at the top layer. The activated carbon was a guard layer to remove CO₂ and CH₄, and zeolite 5A was used to adsorb CO and N₂ so that pure H₂ could be obtained. Yang and Doong [24] performed a multiple-bed PSA process filled with activated carbon to separate the gas mixture with 50/50% H₂/CH₂. Zhang, Xiao, Bénard and Chahine [25] employed zeolite 5A and built dynamic adsorption models for H₂ and CO separation (70% H₂ in the mixture) to study the effects of different numbers of adsorption beds. In many cases, the separation processes are designed and operated at high hydrogen concentrations [17, 26, 27], in which hydrogen is the major component and the other component is considered an impurity and adsorbed preferentially.

However, no adsorption processes exist for hydrogen capture, where hydrogen is the minor component. For example, hydrogen needs to be removed from no more than 20% in blended NG, to less than 1% in the feed to turbines [28]. To our best knowledge, physisorbents with selectivity towards hydrogen are rare till now, because hydrogen is extremely weak adsorptive, featuring one of the smallest molecular sizes amongst all gases. In a gas mixture with hydrogen, the adsorption selectivity is always towards the other gas components rather than hydrogen. Nevertheless, the advantage of using hydrogen selective materials for pipeline gas with low feed concentration H₂/NG mixture is obvious in that it can effectively adsorb the minor component (H₂) from the gas mixture, potentially more energy efficient and cost competitive.

The main objective of this work is to investigate a novel hydrogen selective adsorbent namely 3A trapdoor zeolite and assess the performance of PSA processes using 3A for deblending H₂/NG mixture containing diluted (<20%) hydrogen. Herein, we report isotherms of hydrogen and other competing gases on zeolite 3A and a benchmark adsorbent namely activated carbon. We then design and evaluate the (V) PSA cycles for the H₂/NG deblending using our in-house process simulation tool. The performance of the (V) PSA processes using zeolite 3A is benchmarked against that using activated carbon in terms of product purity, recovery, energy consumption, and adsorber bed size. The outcomes of this work will shed a light on the hydrogen capture from industrial gas mixtures.

2. Modelling of hydrogen P/VSA

To investigate the large-scale separation performance and energy consumption of the materials, the process was simulated using a specialized in-house developed simulator MINSA (Melbourne Integrated Numerical Simulation of Adsorption). The software used is customized to simulate the PSA process for a specified absorbent material. The model is built based on dynamic conservation equations of mass, momentum and energy over a series of column beds [29–31]. Simulation convergence could be obtained when a cyclic steady state (CSS) is achieved. For the designed PSA experiment, the software simulation convergence could be obtained when a cyclic steady state (CSS) is achieved. The rate of mass transfer during the adsorption on adsorbent is described by the LDF model:

\[
\frac{dq}{dt} = K_l (q' - q_i) 
\]

Where \(q_i\) denotes equilibrium loading on the adsorbent and mass transfer constant \(K_l\) is calculated by:

\[
K_l = k D / \pi^2 
\]

Where \(r\) is the pellet diameter, \(k\) is an empirical mass transfer coefficient and \(D\) is the diffusion coefficient. There is a lack of information on the diffusion of H₂ and CH₄ within zeolite 3A probably because it is not easy to measure due to the low adsorption capacity. Based on the referenced small molecule kinetics in narrow porous materials such as the kinetics of O₂ and N₂ in CMS-T3A (with nominal diameter less than 4 Å) [32] and zeolite 4Å [33], the \(k\) is from 10² to 10³ s⁻¹. \(k\) is 15 according to Glueckauf [34, 35]. Thus, in this simulation, the \(K_l\) is set to 0.1 (1/s).

The H₂ equilibrium loading on zeolite 3A (\(q'_i\)) was modelled by the DLS equation. The six Dual-site Langmuir parameters \((m, n, b_h, d_0, Q_i, Q_{2i})\) were determined using standard non-linear regression of the experimentally measured adsorption isotherms at three different temperatures, as tabulated in Table 3.

\[
q'_i = m_i \exp \left( \frac{Q_{si}^*}{RT} \right) \quad \text{and} \quad d_i = d_{si} \exp \left( \frac{Q_{2i}^*}{RT} \right) 
\]

Where \(q'_i\) is adsorption amount (mmol/g), \(m_i\) and \(n_i\) are the saturated adsorption amounts of the two adsorption sites, \(P_i\) is equilibrium pressure (kPa), \(b_h\) and \(d_i\):

\[
b_i = b_{hi} \exp \left( \frac{Q_{si}}{RT} \right) \quad \text{and} \quad d_i = d_{si} \exp \left( \frac{Q_{2i}}{RT} \right) 
\]

Where \(b_{hi}\) and \(d_{si}\) represent coefficient (1/kPa), \(Q_{si}\) and \(Q_{2i}\) represent adsorption heat on the two sites (J/mol).

For zeolite 3A, the adsorption amount of H₂ can be well represented by the Dual-site Langmuir model while the amount of both N₂ and CH₄ is too small for reliable measurement using ASAP 2050 at 25, 40 and 60 °C, and thus in this work, they were assumed to be the inert gas.

Cycle performance criteria, including product purity, product recovery rate, and productivity were calculated at CSS based on these equations:

\[
H_2 Purity (%) = \frac{\int_0^{t_c} C_{H_2 \text{H}_i} F_{ad} dt}{\int_0^{t_c} F_{ad} dt} \times 100 
\]

\[
H_2 Recovery (%) = \frac{\int_0^{t_c} C_{H_2 \text{H}_i} F_{ad} dt}{\int_0^{t_c} F_{ad} dt} \times 100 
\]

\[
CH_4 Purity (%) = \frac{\int_0^{t_c} C_{CH_4 \text{H}_i} F_{ad} dt}{\int_0^{t_c} F_{ad} dt} \times 100 
\]
Specific energy consumed in the separation process when a vacuum is required (vacuum pump needed). Energy consumption occurs only when a vacuum is required to drive the PSA process, there is no need to compress inlet gas. Hence, included in the process. As feed pressures from the pipeline are sufficient, the specific energy used in the separation process when a vacuum is required is negligible.

\[ CH_4 \text{Recovery} = \frac{\int_0^{t_{ads}} C_{CH_4, CH_4} F_{feed} dt - \int_0^{t_{rep}} C_{CH_4, CH_4} F_{rep} dt}{\int_0^{t_{ads}} C_{CH_4, CH_4} F_{feed} dt} \times 100 \] (9)

Where \( F_p, F_{rep}, F_{feed} \) and \( F_{ads} \) denote the instantaneous gas flow rate of the product, product for repressurization, feed and desorption, respectively. \( C_p, C_{feed} \) and \( C_{ads} \) represent the concentration of the product, feed gas and desorption gas. \( t_{ads}, t_{rep} \) and \( t_{rep} \) are the time of adsorption, desorption and repressurization.

\( CH_4 \) productivity can be calculated by using the following equation:

\[ CH_4 \text{Productivity} = \frac{\int_0^{t_{ads}} C_{CH_4, CH_4} F_{feed} dt}{W_{cycle}} \times CH_4 \text{Recovery} \times MW_{CH_4} \times \rho_b \] (10)

Where \( MW_{CH_4} \) represents the molecular weight of \( CH_4 \), \( t_{cycle} \) and \( W_{cycle} \) represent cycle time and weight of absorbent, respectively.

Another critical indicator to evaluate the separation performance is the specific energy used in the separation process when a vacuum is included in the process. As feed pressures from the pipeline are sufficient to drive the PSA process, there is no need to compress inlet gas. Hence, energy consumption occurs only when a vacuum is required (vacuum pump needed).

\[ \text{Specific energy} = \frac{J}{\text{kg CH}_4} = \frac{\int_0^{t_{ads}} \frac{C_{CH_4, CH_4} F_{feed} dt}{MW_{CH_4}}}{\int_0^{t_{ads}} \frac{C_{CH_4, CH_4} F_{feed} dt}{MW_{CH_4}} - \frac{\left( \frac{P_{ads}}{P_{vac}} \right)^{\gamma} - 1}{\gamma} dt} \] (11)

Where \( \gamma \) is the ratio of heat capacities of the gas mixture at constant pressure and volume (\( C_p/C_v \), assumed to be 1.3 for \( CH_4 \) and 1.4 for \( H_2 \)). \( \eta \) is the vacuum pump efficiency and it was assumed to be 0.7 here. \( F_{ads} \) is the instantaneous gas flow rate of the vacuum and \( F_{vac} \) is the vacuum pressure.

3. Process description

3.1. The necessity of hydrogen capture from blended NG

Natural gas is primarily methane with smaller quantities of other hydrocarbons [36]. To simplify the process modelling, the pipeline gas is assumed to be a binary mixture of methane (instead of natural gas) and hydrogen gas in this work.

Once the blended gas arrives at the destination, the gas mixture can be used directly or separated to meet the requirements of different customers. The end-user to be served in this study is the gas turbine in power plants. As the operation of conventional gas turbines is highly sensitive to the hydrogen content with an upper limit of 1% [28,37,38], surely the objective of this deblending work is to remove the hydrogen gas in the mixture of gas and to obtain a methane product with purity above 99%.

3.2. Simulation conditions

The scope of this study is determined by the currently operated hydrogen injection plant configurations and the \( H_2 \) concentrations within the mixture are from 3% to 15%. Simulations were performed at a temperature of 298.15 K and the feed gas flow rate was 100 sm\(^3\)/h (1.24 mol/s) of a typical pilot-scale PSA plant. Fig. 1 illustrates the configuration of the pipeline gas network of the state of New South Wales, Australia. The pressure at different industrial nodes of the pipeline ranges from 68.95 bar in the trunk main pipeline to 35 bar in the primary main, and 10.5 bar in the secondary main. In our modelling, we chose 50, 30 and 10 bar, for the feed gas pressure, respectively.

3.3. Cycle design

Multiple design strategies can be considered to meet the purity requirements for the turbines in power plants. Firstly, the number of beds should be determined according to the feed gas conditions and separation target. The greater number of beds usually leads to more pressure equalization steps and better separation performance but higher capital cost correspondingly. Secondly, the adsorption time influences the PSA performance to a great extent. The adsorption time is set according to the adsorption capacity of the bed, adsorption kinetics, feed flow rate and product concentration target. In VPSA or VSA, vacuum level is an important parameter to determine the separation performance and energy consumption.

Based on these considerations, designs are customized according to different feed gas pressures for PSA and VPSA processes. When feed gas pressures were 10 bar and 30 bar, five-bed (V)PSA processes were designed. For inlet gas with a pressure of 50 bar, a more complex design known as a six-bed PSA process was utilized. The scheme and cyclic
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4

configurations are listed below in Table 1 (The connection of each column is shown in Supplementary Information Figs. S1 and S2).

In terms of the 10 bar VPSA process, the designed system consists of 5 beds and each of them undergoes 10 steps in each cycle, which is shown in Table 1. Each cycle starts with two adsorption steps, followed by three pressure equalization (PE) steps, a vacuum desorption step, three receiving pressure equalization (RPE, countercurrent introducing the effluent gas from previous PE steps) steps and a repressurization (RP) step from the top using gas from the CH\textsubscript{4} product tank. The RP step is to exclude the adsorbed gas from the bed so that the bed is fresh and ready for the next cycle. When the feed gas pressure is raised to 50 bar, a six-bed twelve-step PSA process is employed for the gas separation. The purpose of the additional PE steps is to minimize the CH\textsubscript{4} gas losses within the bed as it can reduce the initial pressure of the desorption step. More PE steps can be considered steps that save product, and these steps result in a considerable increase in CH\textsubscript{4} recovery while causing only a minor reduction in CH\textsubscript{4} purity. The (V)PSA column and adsorbent characteristics used in the simulation are summarized in Table 2. For all the inlet pressures, the column height is 1.8 m, which is a commonly used height for this flow rate (100 sm\textsuperscript{3}/h). Various diameters were tested, and the criterion is to select the minimum diameter while ensuring that CH\textsubscript{4} product purity is higher than 99% for all the feed H\textsubscript{2} concentrations.

As hydrogen within the mixture is captured (Fig. 2), the high purity and high pressure CH\textsubscript{4} product can be obtained from the top (the target product) of a hydrogen PSA process. On the contrary, the CH\textsubscript{4} product with ambient pressure can be obtained from the bottom of a CH\textsubscript{4} PSA process, which means that the energy of the gas is lost during this process.

4. Results and discussion

4.1. Properties of adsorbent materials

4.1.1. Materials selection and characterizations

The design, performance and cost of an adsorption process predominantly depend on the properties of adsorbent materials. Being one of the smallest gas molecules and among those with the lowest binding affinity, hydrogen barely adsorbs on any known commercial porous adsorbent materials at standard temperature and pressure. To capture hydrogen, the key challenge is to identify a hydrogen selective adsorbent.

As one of the commonly used groups of zeolites, LTA zeolites including K-LTA (zeolite 3A), Na-LTA (zeolite 4A) and Ca-LTA (zeolite 5A) have been commercially deployed for many years [40]. Zeolite 3A is known to have a nominal pore aperture size of 3 Å, and it is believed to only allow for the admission of molecules smaller than 3 Å, such as water (dynamic diameter 2.8 Å) and hydrogen (dynamic diameter 2.9 Å). Zeolite 3A is commercially used for the dehydration of natural gas and alcohol [41]. On the contrary, zeolite 4A and 5A with larger
nominal pore aperture sizes are typically applied for the removal of contaminants such as $N_2$ for gas purification and air separation [42,43]. In terms of pipeline gas deblending, we propose to use zeolite 3A as a candidate to selectively adsorb hydrogen gas molecules but exclude the larger molecule $CH_4$ (dynamic diameter 3.8 Å).

To characterize the morphology and crystal structure of commercial binder-free zeolite 3A (UOP®), the precursor beads shown in (Fig. 3(a)) were ground using a mortar and pestle and sonicated in ethanol for 10 min. The samples were then prepared by drop cast onto silicon substrates for scanning electron microscopy (SEM) and holey carbon grid for transmission electron microscopy (TEM). SEM and TEM images both revealed the cubic morphology of the zeolite 3A (Fig. 3(b) and (c)). The powder obtained from the grinding process was used for X-ray diffraction (XRD) analysis. As elucidated in Fig. 3(d), the XRD pattern confirmed the cubic crystal structure $K_{12}Al_{12}Si_{12}O_{48}$ with space group $Pm3m$ and peaks matching with lattice parameter $a = 12.2962$ Å. High-resolution TEM (HRTEM) micrograph obtained from an edge of a sample showed a spacing of 0.507 nm with regular atomic arrangement corresponding to $(211)$ plane (Fig. 3(e)). Selected area electron diffraction (SAED) of the sample was indexed as $(110)$ and $(311)$ according to the

**Fig. 2.** Adsorption and desorption process configuration using $H_2$ selective material - zeolite 3A (a) and $CH_4$ selective material - activated carbon (b).

**Fig. 3.** Characterization of adsorption materials zeolite 3A. Optical image of zeolite beads (a), SEM micrographs of the zeolite cubes (b), TEM image confirming cube morphology of the zeolite (c), XRD pattern reference JCPDS 04-009-4204 (d), HRTEM image of the zeolite 3A showing lattice fringes (e), TEM SAED micrograph of zeolite featuring indexed reflections (f) and aperture of zeolite 3A and hydrogen selectivity configuration (g).
measured spacings of 0.869 and 0.374 nm, respectively (Fig. 3(f)).

4.1.2. Adsorption equilibria

As mentioned before, zeolite 3A has the same framework structure (LTA) as zeolite 4A but they differ in extra framework cations. By comparing the adsorption isotherms of zeolite 3A and 4A (Fig. 4(a) and (b)), we demonstrate that only 3A has hydrogen selectivity because of its molecular trapdoor effect. It indicates that with the change of cations from Na⁺ (in 4A) to K⁺ (in 3A), the LTA zeolite will surprisingly become hydrogen selective. Because of its selectivity, zeolite 3A is proposed as a good candidate for gas separation in this study.

In order to find a suitable working temperature, H₂ adsorption isotherms on zeolite 3A at different temperatures were measured to plot adsorption isobars (Fig. 4(c)). As depicted in Fig. 4(c), after 298 K, H₂ uptake declines with temperature, which is consistent with the conventional thermodynamics, while below 298 K, the pattern shows opposite trends. The phenomenon below 298 K can be explained by the mechanism of “molecular trapdoor” which means that the accessibility of adsorption sites of zeolite 3A to H₂ gas is nonmonotonically temperature dependent. The H₂ gas could be adsorbed by zeolite 3A beyond a specific temperature range, which is denoted as critical admission temperature (T_C), also called pore-blockage temperature for H₂ gas.
Acting as the door-keeper, the $K^+$ only accepts part of $H_2$ at lower temperatures, but at higher temperatures, the $K^+$ can be deviated to allow substantial $H_2$ admission. For $H_2$ adsorption on zeolite, the critical admission temperature should be below 298 K. Similar temperature-dependent behaviours have been found in zeolites [44–46]. Furthermore, the adsorption measurements agree with the in-situ TEM results, which are shown in Fig. 4(d). The crystals expand upon heating from 248 to 303 K and an extra pore aperture size expansion occurs at 298 K.

<table>
<thead>
<tr>
<th>Component</th>
<th>$m_i$ (mol/kg)</th>
<th>$n_i$ (mol/kg)</th>
<th>$b_0$ (1/kPa)</th>
<th>$d_0$ (1/kPa)</th>
<th>$Q_{1,i}$ (J/mol)</th>
<th>$Q_{2,i}$ (J/mol)</th>
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</thead>
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<tr>
<td>$H_2$</td>
<td>47.04</td>
<td>8.37</td>
<td>2.3E-06</td>
<td>1.25E-27</td>
<td>289.15</td>
<td>128852.57</td>
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</table>

Table 4
Summary of the 10 bar VPSA simulation results.

<table>
<thead>
<tr>
<th>Desorption pressure (kPa)</th>
<th>Feed $H_2$ concentration (%)</th>
<th>Cycle time (s)</th>
<th>$H_2$ downstream concentration (%)</th>
<th>$CH_4$ upstream concentration (%)</th>
<th>$H_2$ recovery rate (%)</th>
<th>$CH_4$ recovery rate (%)</th>
<th>Energy consumption (kJ/kg $CH_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3</td>
<td>560</td>
<td>8.20</td>
<td>99.00</td>
<td>76.06</td>
<td>73.67</td>
<td>97.50</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>470</td>
<td>9.82</td>
<td>99.00</td>
<td>83.51</td>
<td>68.03</td>
<td>126.25</td>
</tr>
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<td></td>
<td>5</td>
<td>410</td>
<td>11.50</td>
<td>99.02</td>
<td>87.96</td>
<td>64.38</td>
<td>167.50</td>
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<tr>
<td></td>
<td>10</td>
<td>275</td>
<td>17.89</td>
<td>99.03</td>
<td>95.46</td>
<td>51.31</td>
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<td></td>
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<td>97.66</td>
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<td>99.01</td>
<td>97.58</td>
<td>40.74</td>
<td>275.63</td>
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Fig. 5. Example pressure profile (a) and temperature profile (b), gas (c) and solid (d) phase concentration profiles of 10 bar VPSA process over one cycle at CSS condition. (Feed $H_2$ concentration = 5%, desorption pressure = 20 kPa).
To avoid pore blockage and fully utilize the capacity of zeolite 3A, the working temperature of the PSA process for gas separation was set to 298 K. The adsorption and desorption isotherms at this temperature are shown in Fig. 4(e). It shows that the H₂ adsorption amount on zeolite 3A increases linearly with elevated partial pressure with a value of 0.47 mol/kg at 950 kPa and H₂ desorption is easily achieved by decreasing the pressure.

### 4.1.3. Calculation of dual-site Langmuir parameters

Based on the adsorption data at three temperatures: 298 K, 303 K and 313 K (Adsorption isotherms at other temperatures are in Supplementary Information Fig. S3), the Dual-site Langmuir equation was used to model the H₂ adsorption isotherms. The results of the simulation are consistent with the experimental data, as shown in Fig. 4(f). The isotherm parameters are listed in Table 3.

### 4.2. Hydrogen capture performance of (V)PSA processes

#### 4.2.1. Separation performance of zeolite 3A

The processes were simulated in three configurations, entailing 10, 30, and 50 bar feed pressures, denoted in Sections 4.2.1.1 to 4.2.1.3 below.

**4.2.1.1. 10 bar VPSA.** The simulation for the VPSA study was conducted at a feed pressure of 10 bar and desorption pressures below 1 bar. Additional energy was required to operate the vacuum pressure. For different feed H₂ concentrations, the adsorption time could be adjusted to achieve the target of 99% CH₄. Since the separation performance depends highly on the desorption pressure level, different desorption pressures (10, 20 and 30 kPa) were analyzed to study the effect of vacuum levels.

The simulated separation performance is shown in Table 4. CH₄ product purity of 99% can be successfully attained for all scenarios, which indicates the product complies with the specifications for conventional turbines and is amenable for direct usage. Adsorption time changes with feed concentration, that is, a shorter adsorption time is necessary for higher concentrations of H₂ in the feed. Meanwhile, shorter adsorption time results in lower recovery of CH₄. It is also observed that with the reduction of CH₄ recovery, energy consumption is increased. Therefore, both energy consumption and recovery indicate that the PSA design is superior especially for lower H₂ feed concentrations.

The pressure, temperature and concentration profiles of bed I for one cycle of the 10 bar VPSA process at CSS are shown in Fig. 5. As illustrated in Fig. 5(a) changes in pressure are minimal in the adsorption step. After that, the bed pressure declines gradually in the first, second and third PE steps to around 7.4 bar, 5.8 bar and 3.9 bar, respectively and then decreases to an ultimate pressure of 0.2 bar in the desorption step. Following that, the pressure increases over the RPE steps and reaches the peak at the end of the RP step. Fig. 5(b) shows the corresponding temperature profile for the same process. Akin to most adsorption processes, H₂ adsorption on zeolite 3A is an exothermic reaction, so temperatures at the top are climbing during the adsorption step, while the temperature is stable at the bottom due to the continuous flow. During the PE steps, with the pressure drop, the H₂ adsorbed is partially released, leading to a temperature decrease. Concerning the desorption step, more H₂ adsorbed are released from the bottom, resulting in a marked temperature decline. Subsequently, the temperature increases as H₂ is reabsorbed in the RPE and RP steps. In terms of the whole cycle, the temperature swings between 295.7 K and 298.5 K near the bottom of the bed. Because of the higher adsorption amount, the temperature fluctuation at the bottom is greater than that at the top of the bed.

Fig. 5(c) illustrates the H₂ concentration in the gas phase at the end of the adsorption, PE, and desorption steps, respectively. It shows that the H₂ front in the gas phase reaches nearly the top of the bed at the end of the adsorption step so that the adsorption column is saturated. Regarding the PE step, the H₂ concentration drops against the length of the bed. This pattern indicates the impacts of the PE steps. They make the H₂ front move up and CH₄ release from the bed column, resulting in a high H₂ purity downstream and a high CH₄ recovery. Fig. 5(d) shows the H₂ concentration profile in the solid phase. At the end of the adsorption step, H₂ adsorption reaches the maximum value and then during PE steps, the pressure is decreased and H₂ is partially desorbed. In the desorption step, the H₂ adsorbed is released as expected and the

![Fig. 6. CH₄ product recovery (a) and energy consumption (b) of various vacuum levels in 10 bar VPSA processes.](image-url)

**Table 5**

<table>
<thead>
<tr>
<th>Feed H₂ concentration (%)</th>
<th>Cycle time (s)</th>
<th>H₂ downstream concentration (%)</th>
<th>CH₄ upstream concentration (%)</th>
<th>H₂ recovery rate (%)</th>
<th>CH₄ recovery rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>425</td>
<td>6.59</td>
<td>99.01</td>
<td>78.90</td>
<td>65.44</td>
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<tr>
<td>4</td>
<td>375</td>
<td>7.96</td>
<td>99.05</td>
<td>87.65</td>
<td>58.33</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>9.17</td>
<td>98.98</td>
<td>89.61</td>
<td>53.27</td>
</tr>
<tr>
<td>10</td>
<td>250</td>
<td>15.27</td>
<td>98.95</td>
<td>96.13</td>
<td>40.74</td>
</tr>
<tr>
<td>15</td>
<td>180</td>
<td>19.79</td>
<td>99.08</td>
<td>73.85</td>
<td>31.43</td>
</tr>
</tbody>
</table>
Regarding the effect of vacuum level, deeper vacuum pressure usually leads to greater VPSA performance with high CH\textsubscript{4} purity and recovery (Fig. 6(a)) because the bed can be more appropriately regenerated. However, a deeper vacuum would cost higher energy as shown in Fig. 6(b). Meanwhile, for large-scale applications, it is difficult to achieve very deep vacuum pressures (below 10 kPa) without multiple-stage vacuum pumps. Therefore, the real application should be performed at a mild vacuum condition, and it is a tradeoff between separation performance and operational flexibility.

4.2.1.2. 30 bar PSA. The separation performance including recovery and product concentration is summarized in Table 5. As discussed previously, no electrical energy is needed in the PSA processes. Similar to the 10 bar VPSA process, higher feed H\textsubscript{2} concentrations lead to a lower CH\textsubscript{4} recovery rate for this specific design. Greater than 53% CH\textsubscript{4} in the mixture can be recovered for 5% H\textsubscript{2} in the feed, while only 31% can be recycled for 15% H\textsubscript{2} in the feed. This may be due to the insufficient amount of adsorbents in the bed as more H\textsubscript{2} needs to be adsorbed for a mixture with high H\textsubscript{2} feed.

Fig. 7 shows the pressure swing, the temperature swing and concentration variation over one cycle for the case of 5% feed 30 bar PSA. Fig. 7(a) indicates that the pressure in the bed falls after the adsorption step and the desorption pressure is 1 bar. The bed undergoes regeneration in the desorption step and after that, the pressure increases due to the influx of the gas mixture. The temperature at the bottom fluctuates between 292.8 K and 298.9 K (Fig. 7(b)). The temperature drops in both PE and desorption steps and grows afterwards which exhibits an analogous tendency with the pressure profiles. Also, compared with the 10 bar VPSA process, the temperature variation is greater. Fig. 7(c) and (d) represent the gas and solid phase concentrations within the column. Due to the elevated H\textsubscript{2} partial pressure, the amount of H\textsubscript{2} adsorbed in the solid phase is notably greater compared with the VPSA process.

### Table 6
Simulation results of 50 bar PSA.

<table>
<thead>
<tr>
<th>Feed H\textsubscript{2} concentration (%)</th>
<th>Cycle time (s)</th>
<th>H\textsubscript{2} downstream concentration (%)</th>
<th>CH\textsubscript{4} upstream concentration (%)</th>
<th>H\textsubscript{2} recovery rate (%)</th>
<th>CH\textsubscript{4} recovery rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>780</td>
<td>6.36</td>
<td>98.95</td>
<td>77.97</td>
<td>64.54</td>
</tr>
<tr>
<td>4</td>
<td>750</td>
<td>7.66</td>
<td>99.06</td>
<td>82.99</td>
<td>58.45</td>
</tr>
<tr>
<td>5</td>
<td>690</td>
<td>8.98</td>
<td>99.00</td>
<td>90.11</td>
<td>51.91</td>
</tr>
<tr>
<td>10</td>
<td>510</td>
<td>13.80</td>
<td>99.01</td>
<td>97.12</td>
<td>32.56</td>
</tr>
<tr>
<td>15</td>
<td>432</td>
<td>17.54</td>
<td>98.99</td>
<td>99.03</td>
<td>17.84</td>
</tr>
</tbody>
</table>
4.2.1.3. 50 bar PSA. Since the temperature and pressure profiles of the 50 bar PSA process are analogous to the previous 30 bar PSA scenario, the pressure, temperature and concentration profile are not presented here (reported in the Supplementary Information Fig. S4). The simulation results are shown in Table 6. As expected, the product purity can reach 99% by processing this designed configuration. Also, energy consumption in the PSA process is negligible in this process.

Regarding the downstream gas product of the 3A PSA, it is still a blended gas with an increased hydrogen concentration. The enriched hydrogen gas could be directly supplied to end users without purity requirements (such as for heating or cooking purposes of households) or

### Table 7


<table>
<thead>
<tr>
<th>Component</th>
<th>Mᵦ (mol/kg)</th>
<th>Mₒ (mol/kg)</th>
<th>Bₒ (1/kPa)</th>
<th>Dₒ (1/kPa)</th>
<th>Qᵦ (J/mol)</th>
<th>Qₒ (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>8.49E-02</td>
<td>2.97</td>
<td>7.26E-05</td>
<td>2.64E-07</td>
<td>17.66</td>
<td>24.01</td>
</tr>
<tr>
<td>H₂</td>
<td>4.90</td>
<td>–</td>
<td>1.24E-06</td>
<td>–</td>
<td>10.10</td>
<td>–</td>
</tr>
</tbody>
</table>

![Fig. 8. Scheme and cyclic configuration of the designed 30 bar PSA system using activated carbon for 10% and 15% H₂ feed input (a). The PU (purge) step was designed to increase the CH₄ product purity. Pressure profile of 5% feed H₂ concentration (b) and 15% feed H₂ concentration (c) activated carbon PSA as a function of cycle time.](image)

![Fig. 9. Comparison between activated carbon and zeolite 3A in terms of recovery, productivity (a) and power consumption (b). (Adsorption pressure = 30 bar.)](image)
pressure for other applications. After pressurization, the $H_2$ can be injected back into the NG pipeline for transportation, or further separated for example another stage of the PSA process, to obtain pure hydrogen. More details including enriched hydrogen product utilization, and energy consumption for compression are illustrated in Supplementary Information Figs. S5–S7.

### 4.2.2. Zeolite 3A PSA VS activated carbon PSA

Since activated carbon is one of the most commonly used adsorbents in (V)PSA for CH$_4$ adsorption, we compared the separation performance of zeolite 3A with that of activated carbon. Isotherms of H$_2$ and CH$_4$ adsorption on activated carbon were measured by our group and published previously (Table 7) [17]. Based on these, we could simulate and compare zeolite 3A with activated carbon. 30 bar feed gas pressure scenario was selected to study the impact of adsorbents on PSA processes.

To evaluate the performance of these two adsorbents, the same design with a consistent physical size should be employed. However, activated carbon is unable to achieve the separation target of CH$_4$ product purity above 99% when the feed H$_2$ concentration is equal to 10% or 15%; therefore, the design was upgraded. (Fig. 8(a)). High purity CH$_4$ from the product tank was used to purge the adsorption column (step No.5) which can effectively improve the outlet purity. Despite differences in design, the number of beds and column size were kept constant to ensure comparability.

As shown in Fig. 8(b) and (c), the pressure profiles of 5% and 15% feed H$_2$ concentrations show different patterns. For feed H$_2$ concentration of 15%, the pressure increase during the PU step indicates the impact of the CH$_4$ purge. With the small amount of CH$_4$ product purge, the purity of the CH$_4$ product tank could reach 99% but the recovery rate of CH$_4$ may drop slightly because of this.

As shown in Fig. 9, when the feed H$_2$ concentration is 5%, more CH$_4$ can be recovered by using zeolite 3A than activated carbon. In the case of 10% feed H$_2$ concentration, the recovery of zeolite 3A is still higher than activated carbon, and also extra energy is required for activated carbon. Therefore, zeolite 3A is more efficient for the separation of gas mixtures with H$_2$ below 10%. If the feed H$_2$ concentration is further increased to 15%, activated carbon is marginally better than zeolite 3A but the energy consumption of activated carbon spikes.

### 5. Conclusion

In this study, H$_2$ adsorption isotherms on zeolite 3A were measured and PSA separation processes with 3A were modelled at three feed pressures (10, 30 and 50 bar) with low H$_2$ concentrations (3%-15%). The separation target was determined by the industry requirement, which is to ensure that the CH$_4$ product purity is higher than 99%. Based on this, the (V)PSA cycles were designed and customized. With the validated MINSA simulation tool, the H$_2$ separation from the real pipeline gas distribution was simulated. The key findings in the study are:

- Zeolite 3A is one of only a few physisorbents having selectivity towards H$_2$ and can be used for H$_2$ capture from blended pipeline gas using PSA processes at room temperature.
- The designed PSA system shows promising technical feasibility to produce a high purity CH$_4$ product (>99%) using zeolite 3A adsorbent.
- Zeolite 3A has advantages over activated carbon for the same separation tank in terms of recovery, productivity and energy consumption especially when the feed H$_2$ concentration is low (<10%).

This work’s significant contribution entails reporting a physisorbent material with an unprecedented H$_2$ selectivity used in the (V)PSA process for gas separation. Meanwhile, results predict the separation performance of zeolite 3A surpasses traditional adsorbent (i.e., activated carbon) in some scenarios. This work provides a vision for H$_2$ separation technologies, as this material can also be applied for H$_2$ capture from nitrogen, ethane, carbon dioxide, and other gases.

Regarding this framework’s limitations and challenges, simplifying the gas blend (CH$_4$ and H$_2$, not NG and H$_2$) may limit the exact analysis to this particular mixture. Also, the reactor column height and the amount of materials used may require optimization due to the specific zeolite 3A adsorption capacity range. Generally, H$_2$ selective materials are left underexplored, and the critical role of H$_2$ in the energy transition, envisages this framework as an enormous potential for clean energy management.

### 6. Material and methods

The zeolite 3A and zeolite 4A beads with a diameter of 1.6 mm were sourced from UOP®. SEM measurements were performed using FEI Verios high-resolution electron microscope equipped with Elstar in-lens secondary electron detector in immersion mode working with 13 pA and 2 kV current and acceleration voltages, respectively. As purchased zeolite 3A includes ~ 1 at% Na$^+$ revealed by large area energy dispersive X-ray spectroscopy (EDS). Tecnai F20 TEM with 200 kV acceleration voltage was used for low magnification, HRTEM and SAED imaging. A liquid nitrogen cryo sample holder was used together with Gatan SmartSet cold stage temperature controller for the in-situ diffraction analysis. The TEM sample and holder were placed in heat controlled vacuum station overnight prior to the cryo experiment to ensure the effective removal of moisture and contamination. A Bruker D8 Advance Powder Diffractometer, Germany was utilized for XRD measurements.

Around 1 g of zeolite 3A in a stainless-steel tube was heated under vacuum to 100 °C for 6 h and then increased to 350 °C for another 12 h for activation. Following that, the material was cooled down under Helium protection before isotherm measurement. Adsorption isotherms of pure methane and H$_2$ on zeolite 3A were measured using a volumetric apparatus ASAP 2050 (Micromeritics, USA) in the pressure range of 0 to 1000 kPa at different temperatures.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

### Acknowledgement

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2023.143224.

### References


