MODELLING CRYOGENIC PRESSURE SWING ADSORPTION FOR METHANE AND N2 SEPARATION FOR NATURAL GAS PURIFICATION

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ABSTRACT
Natural gas is processed to control purity and bring it to sales standard. A part of this processing involves the removal of N2 and CO2 which may exist in large quantities in the gas. These impurities are often removed using Cryogenic Pressure Swing Adsorption (CPSA). PSA uses pressure changes to maximise the efficiency of adsorption and desorption. A fundamental mathematical model was developed in MATLAB to describe the adsorption phase of CPSA. This model included simulation of the flow patterns in the column, and the diffusion and adsorption processes occurring in the adsorbent particles to produce information on the composition at the outlet of the column over time. The results of the model were compared to experimental data. The culmination of these four steps was a model that produces relatively accurate results at cryogenic temperature (192K). However, the output when compared to non cryogenic temperature data (at 303K) was less accurate.

INTRODUCTION
With the world in search of cleaner and lower emission fuels, focus has turned to natural gas. The applications for natural gas are numerous and range from heating and cooking on a domestic level, to power generation and fertiliser production on a larger, industrial scale (Gaul & Young, 2003). A large contribution to this growing industry will come from the Gorgon Gas Project. It is a large development project currently in progress with Chevron as the operator (Chevron, 2010). The project is expected to be Australia’s largest resource development project.

Natural gas as used in the above applications is primarily methane (CH4) however when it is extracted from a gas field, it contains large proportions of other compounds. Carbon dioxide (CO2) and nitrogen (N2) are two such components and collectively form up to 17% of the gas in the Gorgon field (Clegg et al., 1990). The processing of natural gas extracted from the Gorgon field will have two main purposes. The first is to remove these impurities and purify the gas stream (in order to achieve the required gas standard). The second function is to liquefy the natural gas (to reduce volume and facilitate transport and storage) and this requires cooling to cryogenic temperatures (Kidnay & Parrish, 2006).

This study focused on the removal of carbon dioxide and nitrogen from natural gas by adsorption processes. This will be achieved using Cryogenic Pressure Swing Adsorption
(CPSA). CPSA is a process which uses low temperatures and changes in pressure to maximise the efficiency of adsorption and desorption and as a result, optimise gas mixture separation. The objective of the study was to produce a mathematical model which accurately describes the characteristics of the adsorption phase of a CPSA cycle for natural gas. Ultimately this model was developed to predict the composition of the gas stream leaving the CPSA unit based on its inlet composition and thermodynamic properties, and the parameters of the equipment used.

BACKGROUND INFORMATION

Cryogenic Natural Gas Processing with PSA

For the Gorgon project, a large proportion of the carbon dioxide in the natural gas stream will be removed using a different unit operation. However PSA can be used to further reduce the proportion of carbon dioxide in the gas. Nitrogen is most commonly removed using cryogenic distillation. However PSA is being investigated as a replacement for cryogenic distillation as it is less expensive in terms of both capital and operating costs (Kidnay & Parrish, 2006; Yang, 1987).

According to Crittenden and Thomas (1998) PSA is analogous to thermal swing adsorption (TSA) where a change in temperature (rather than pressure) is used to optimise adsorption and desorption efficiencies. In this process, temperature is lowered to maximise adsorption and the temperature is raised to maximise desorption. The theory behind this process justifies using PSA under cryogenic conditions. By reducing to cryogenic temperatures there is a decrease in the kinetic energy of the adsorbant, allowing van der Waals forces to be established more readily between the gas particles and the adsorbent surface.

Particle Modelling Techniques

There have been several different approaches to developing mathematical models for PSA cycles throughout the literature. The most effective models typically involve a combination of the pore diffusion model and the equilibrium adsorption model (Yang, 1987). The starting point for the model is some variation of a mass balance for an individual adsorbent particle. Fick’s second law of diffusivity in one dimension can be used to develop a simple mass balance (Yang, 1987).

\[
\frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial x^2}
\]  

[1]

where \( C_i \) is the concentration of component ‘\( i \)’ at a particular position and time [mol/m³], \( t \) is the time since diffusion commenced [s], \( x \) is the distance into the particle from the surface [m] and \( D \) is the diffusion constant for component ‘\( i \)’ in the particle [m²/s]. This equation is relevant in one dimension only, however it can be used to model a three-dimensional particle with some mathematical manipulation.

A more rigorous mass balance for an individual porous particle has been derived by Do (1998) and is given below:

\[
\varepsilon \frac{dC_i}{dt} + (1-\varepsilon) \frac{dC_i}{dt} = -\varepsilon D_p \frac{d}{dr} \left( \frac{dC_i}{dr} \right) - (1-\varepsilon) D_r \frac{d}{dr} \left( \frac{dC_i}{dr} \right)
\]  

[2]
where $\varepsilon$ is the porosity of the particle, $C_{pi}$ is the concentration of component ‘$i$’ on the surface of the adsorbent particle pores [mol/m$^3$], $D_{pi}$ is the diffusion coefficient for component ‘$i$’ in the pores of the adsorbent particle [m$^2$/s] and $D_s$ is the surface diffusivity of component ‘$i$’ on the adsorbent surface [m$^2$/s].

Once the concentration of adsorbate throughout the particle has been determined, the equilibrium adsorption method is adopted. This approach basically views adsorption as being an instantaneous process, meaning that equilibrium is always reached immediately after a change in a component’s partial pressure (Do, 1998). The relationship between the partial pressure of a component and the equilibrium quantity of that component adsorbed is given by adsorption isotherms. Variations of the Langmuir adsorption isotherm have been used in many PSA modelling studies e.g. (Choudary et al., 1995),

$$q_i = \frac{(q_m)_i b_i p_i}{1 + \sum_{i=1}^{n} b_i p_i}$$

[3]

where $q_i$ is the volume of component ‘$i$’ adsorbed [m$^3$], $(q_m)_i$ is the volume required to form a complete monolayer over the adsorbent surface [m$^3$], $b_i$ is the Langmuir constant for component ‘$i$’ [1/Pa] and $p_i$ is the partial pressure or concentration of component ‘$i$’ [Pa]. This model is computationally simple to use once the Langmuir constants have been evaluated. As has been outlined previously, adsorption is highly dependent on both pressure and temperature. There is a standard Arrhenius relationship between the Langmuir constants and temperature which indicates that there is an increase in the quantity of moles adsorbed with a decrease in temperature (Yang, 1987).

$$b_i = b_{\infty,i} \exp\left(-\frac{\Delta H}{RT}\right)$$

[4]

where $b_{\infty,i}$ is the infinite temperature Langmuir constant for component $i$ [Pa$^{-1}$], $\Delta H$ is the heat of adsorption of the component on the adsorbent surface [J/mol], $R$ is the gas constant [J/mol.K] and $T$ is the temperature [K]. An alternative to the Langmuir isotherm is another well established model: the Freundlich isotherm essentially models the same relationship as the Langmuir isotherm using a different functional form (Yang, 1987).

$$\theta = KP^\frac{1}{n}$$

[5]

where $\theta$ is the fraction of the adsorbent surface that is covered by the component, $P$ is the partial pressure of that component [Pa] and the remaining two variables are constants. The Freundlich isotherm is better suited to modelling single component systems (Do, 1998).

**General PSA Modelling Assumptions**

Based on the results of Yang and Doong (1985) and Chahbani and Tondeur (2000) the ideal gas law can be used as an equation of state with the pore diffusion model for ambient to high temperatures. However with there being a lack of adsorption studies at cryogenic temperatures, it is unclear as to whether this assumption is justified for such low temperature applications. An alternative equation that is widely used and accepted for modelling natural gas properties is the Peng-Robinson equation of state (Peng & Robinson, 1976).
where \( v \) is the molar volume \([\text{mol/m}^3]\) and \( a \) and \( b \) are constants.

Ideally we would like the minimum concentration of the adsorbate in an adsorbant particle pore to be as high as possible in order to maximise adsorption rates. As the concentration of a component at a point in the particle increases, the partial pressure of that component increases and therefore, so too does the adsorption of that component. We can maximise the minimum concentration in the particle by minimising the particle size. However this comes at the cost of an increase in pressure drop per unit length of the column as dictated by the Ergun equation for fluid flow through a packed bed (Chahbani & Tondeur, 2000).

\[
-P = \frac{RT}{v-b} \frac{a}{v(v+b) + b(v-b)}
\]  

[6]

where \( P \) denotes the pressure \([\text{Pa}]\), \( z \) is the displacement in the column \([\text{m}]\), \( \varepsilon \) is the packing density in the column, \( \mu \) is the gas viscosity \([\text{Pa.s}]\), \( d_p \) is the average particle diameter \([\text{m}]\) and \( u \) is the gas superficial velocity \([\text{m/s}]\). Increases in the pressure drop result in a decrease in adsorbate partial pressure and consequently adversely affect adsorption. Thus, particle sizes must be chosen by balancing these two effects.

According to Yang (1987), the adsorption of a gas onto a solid surface is an exothermic reaction and consequently the desorption reaction is endothermic. This means that during adsorption there is a localised increase in temperature and there is a localised decrease in temperature during desorption. These effects are detrimental to the adsorption and desorption processes as adsorption is favoured by lower temperatures and desorption by higher temperatures (Crittenden & Thomas, 1998). Depending on the magnitude of these temperature changes, assuming isothermal operation could cause differences between modelled results and reality. An alternative treatment is to introduce a simple energy balance and assume adiabatic operation.

**METHODOLOGY**

The methodology was split into four steps; mathematical modelling, implementation of the mathematical model as a computer simulation, comparison of simulation output to experimental data and iterative improvements to model. Following is a detailed explanation of these four steps.

**Mathematical Modelling**

The first step to building a simulation of this sort is to develop a mathematical model which describes the characteristics of the process in question. This project is focussed on modelling only the adsorption phase of the PSA process due to there being a lack of experimental data available for the other phases of the process. Thus, the adsorption model is the only one which can be verified.

The initial approach to this problem involved developing a highly simplified mathematical model. In order to simplify the model, a series of assumptions were employed. The adsorption column was assumed to operate as a perfect plug flow reactor (although packed with the adsorbent particles) in which there was no mixing between
plugs. This assumption also implies perfect mixing within each of the plugs so there are no radial temperature or composition gradients (Levenspiel, 1999). The relationship between the partial pressure of a component and the amount of that component adsorbed was assumed to correlate with the Langmuir equation. In using this assumption it is implied that equilibrium adsorption is reached instantaneously. Fick’s second law of diffusivity was initially assumed to satisfactorily describe the flow of each component into an adsorbent particle pore by diffusion. It was assumed that the ideal gas law applied throughout the column. The axial pressure gradient through the packed bed was initially assumed to be constant. The column was assumed to operate completely isothermally. Finally, particle size and surface area were assumed to be homogenous.

The mathematical model was constructed in a number of steps. The diffusion profile in an individual pore was modelled and the adsorption isotherm was added to this model to determine the equilibrium amount of each component adsorbed at each point in the pore. This model was extended to model an entire particle. Therefore the total number of moles of each component that are removed from the bulk fluid per particle over a given time period could be calculated. From this point, the total number of moles removed from the bulk fluid due to a single particle was then used to determine the total number of moles removed from an entire plug (or band) of fluid in a given period of time. These calculations were applied to all plugs of gas in the column over multiple time periods to model the dynamic system.

**Simulator Implementation**

The mathematical model was implemented using a MATLAB simulation. MATLAB was chosen as it is well suited to numerical computation and is highly user friendly. The program was written to use the basic mathematical components detailed in the previous section. The simulation divides the adsorption column into multiple bands (as for the PFR model) and uses the mathematical model to determine the number of moles removed in each band over a short time period. The plug of gas then moves on to the next location and this process is repeated. Based on the fraction of each component in the final plug at each period in time, a plot of composition over time is produced.

**Experimental Methodology**

The validity of the resulting model must be tested in order to determine its suitability for modelling practical experiments. This was primarily done by a visual comparison to experimental data. As the only experimental data available was in the form of plots, no statistical analysis was possible. By visually comparing the theoretical data (model output) to the experimental data (experimental output) it was possible to get a qualitative idea of how well the experimental data was represented by the theoretical results.

**Further Iterations of the Model**

The assumptions of the model were revisited to determine whether they should remain in place, be completely omitted, or be replaced with more appropriate assumptions. This was done by changing the assumptions one at a time, modifying the simulator and testing the results against the experimental data. This systematic and iterative approach was used to guarantee that the final model is the best simulation that could be developed using the basic approach of this study.
There were a series of alternative assumptions which were tested and compared to several of the original assumptions as outlined previously. Following the adsorption column being treated as a plug flow reactor, it was remodelled to act as a continuously stirred tank reactor and then as a combination of the two reactor types. The Freundlich adsorption isotherm was tested as a potential candidate to replace the Langmuir isotherm. The more rigorous mass balance which was presented above was tested to determine if it gave more accurate concentration gradients through the adsorbent particles. This was implemented using the Crank-Nicholson method for solving partial differential equations. The Peng-Robinson equation of state was tested as a potential candidate to replace the ideal gas law. Finally, the Ergun equation was introduced to account for the axial pressure drop throughout the column.

RESULTS AND DISCUSSION

The following sections detail the results of this study including an indication of where experimental data and various constants were sourced from. There is also a discussion of the model output and a comparison of the theoretical and experimental results.

Experimentally Obtained Data

The experiments necessary to verify the model are in the process of being carried out by the Centre for Energy at the University of Western Australia. The experimental component of the research was in an early stage during this project so no numerical data was available at that time. However, preliminary results in the form of graphs were provided. These graphs have formed the basis for verifying the model produced in this study. There are a total of four graphs, each of which shows the composition at the outlet of the CPSA column for the adsorption phase of the cycle only. The column is initially flooded with helium before a 50:50 mixture of methane and nitrogen is passed through the column (packed with an activated carbon adsorbant). The plots were all produced under similar conditions with only variations in temperature (between 192K and 303K) and pressure (between 100kPa and 800kPa).

Thermodynamic Constants

With the completed model is largely based on theoretical principles, there were a number of constants which had to be evaluated before the model could carry out the required calculations. Several of these are constants which are specified by the experimenter or found based on experimental reports (including column geometry and particle size). However there were some constants that needed to be estimated. These constants, which included diffusion and Langmuir constants, were estimated using data from a number of sources including Ribeiro et al. (2008) and Perry and Green (1997).

Evaluation of Modelling Assumptions

Reactor Flow Pattern

The reactor flow pattern assumption relates to which basic continuous reactor model the CPSA column model should be based on. As such, models of the flow pattern were constructed for both the plug flow reactor (PFR) model and the continuously stirred tank reactor (CSTR) model. These models were both applied whilst holding the remainder of the simulation constant. While it is noted that the available experimental data was
limited, it was possible to determine that neither of the two flow pattern models produced the sigmoid shaped curve observed in the experimental data (refer to Fig. 1 below).

Levenspiel (1999) notes that the CSTR and the PFR are the two extremes of continuous flow reactor and that there is essentially a continuum of reactors which fall between the two types. This lead to a third model being developed to describe this apparent continuum which was applied to the simulation. The model was developed with the flexibility to simulate the flow pattern at any point along the continuum (so could effectively model a CSTR, a PFR or any combination thereof). Upon applying the model to the remainder of the simulation it was found that the shapes of the theoretical results were similar to the experimental results and this model was subsequently adopted.

**Adsorption Isotherm**

The validity of the adsorption isotherm was tested by modifying the model to produce results based on both the Langmuir isotherm and the Freundlich isotherm. There exists a number of other adsorption isotherm models, however because the Langmuir and Freundlich models are most frequently used, there is more data available in the literature allowing for more accurate estimation of constants (Do, 1998). It was observed that the changes in the results from using the Freundlich model in place of the Langmuir model are negligible. This was found to be the case for each of the four temperature and pressure combinations for which there are experimental results available. Because the use of the Langmuir isotherm is most common in other PSA studies, it was decided that this isotherm would be adopted into the final model (Yang, 1987).

**Mass Balance**

There are two alternatives presented above for the mass balance through each individual adsorbent particle and mathematical models were developed for each. Fick’s second law as approximated by a continuous equation was compared to the more rigorous mass balance. The two methods were compared by producing plots of the concentration profile through an adsorbant particle pore (for various different exposure times and surface concentrations). It was found that both methods gave similar predictions. However, due to the fact that the more rigorous mass balance was solved numerically, there was some degree of fluctuation observed in the corresponding results. These fluctuations were not observed in the simpler model. It was decided, based on this fact and the comparatively easier method of calculation, that Fick’s second law would be used in the simulation and the corresponding model was applied to the simulation.

**Equation of State**

The ideal gas law was modelled along with the Peng-Robinson equation of state. Both of these models were used in the simulation (whilst leaving the remainder of the simulation unchanged) and the results compared. It was found that there were only negligible differences between the two sets of results. As a result, the computationally less complicated ideal gas law was adopted and applied to the final simulation.

**Pressure Profile**

The Ergun equation was applied to the simulation and only a small pressure drop was calculated over the length of the reactor (2.1 Pa). Despite this apparent lack of any useful contribution to the simulation, the pressure drop in larger systems (that the
simulation may be applied to) may be more significant. It was therefore decided that the Ergun equation would still be included in the final model.

![Fig. 1. Plots showing experimental adsorption data with corresponding simulated curves superimposed. Plots differ by the conditions under which data was produced/simulated: (a) produced at 303K and 0 barg, (b) produced at 303K and 7 barg, (c) produced at 192K and 0 barg, (d) produced at 192K and 7 barg.]

Comparison of Model Output and Experimental Data

Given in Fig. 1 are each of the four curves produced in the course of the Centre for Energy’s experimentation with the results of the final simulation superimposed to allow for comparison. The results from the simulation have been produced by simulating under the same conditions as the practical experiments.

As there is experimental data available for four different temperature and pressure combinations, it is possible to gain an idea of the robustness of this model. There are two main observations to be made when comparing the lower pressure plots to the higher pressure plots in Fig. 1. The first is that the experimental results suggest that there is less mixing in the column at lower pressures. This is evidenced by the steeper climb in the mole fraction of methane and nitrogen in the outlet. This steeper gradient is observed in the results of the simulation and can be explained largely by the fact that there is less helium adsorbed on the adsorbent at lower pressures (due to its lower partial pressure) so the majority of the helium is removed from the column relatively early in the process (Perry & Green, 1997). The second observation is that there is less separation between the methane and nitrogen curves in the lower pressure plots. This indicates that at lower pressures, there is a decrease in selectivity between the two components. The Langmuir equation dictates that the amounts of each component adsorbed will converge as pressure decreases, explaining this observation (Do, 1998).

In addition, observations can be made when the lower temperature plots are compared to the higher temperature plots in Fig. 1. Once again, these observations are clear in both
the experimental and theoretical data. A greater degree of separation occurs between the two components at higher temperatures thereby indicating that the adsorbant is more selective under these conditions. This can be explained by the fact that as temperatures are increased, the diffusion and Langmuir constants for nitrogen and methane diverge (Do, 1998). In addition to this observation, it is also observed that there is a significantly larger number of moles of gas which are adsorbed at lower temperatures. This is expected as at lower temperatures, the Langmuir constants for each component are larger and there is therefore a greater equilibrium quantity adsorbed (Yang, 1987).

It is clear from the plots in Fig. 1 that the model does fit the data relatively well at cryogenic temperatures. Despite this observation and the above similarities between the models, it is obvious that there are some significant discrepancies between the experimental data and the model results (particularly at higher temperatures). It is clear that the main cause of these discrepancies is related to the separation of nitrogen and methane in the adsorption column. The model predicts that there is a much lower degree of separation than in the experimental results. In the model, the diffusivities and the Langmuir constants are the only properties which differentiate the components from another. As such, the problem could lie in this part of the simulation. The diffusion and Langmuir constants were all derived using measurements with temperatures at or above room temperature, there may be significant errors associated with extrapolating beyond this range (Ribeiro et al., 2008). In addition to this it is possible that the discrepancy between the data and the model is not limited to the diffusivity and Langmuir coefficient values and the adsorption isotherm that was used may not apply well at cryogenic conditions, or that minor programming errors still do exist in the simulation. A number of combinations of these effects could lead to there being a significant discrepancy between the model and the experimental data and a decrease in the robustness of the model.

CONCLUSIONS

There are a number of important conclusions that can be drawn from this project. Firstly it was found that the column was best modelled as a reactor with a mixture of PFR and CSTR flow patterns. It was also found that Fick’s second law could be used in place of a more rigorous mass balance without sacrificing accuracy to a large degree. Likewise, the ideal gas law can be used in place of the Peng-Robinson equation of state in order to reduce computation time without largely sacrificing the accuracy of the calculation.

The simulation does share some important similarities with the data (which are explained by the theory behind the model) and that the experimental data is relatively well modelled at low temperatures. However the accuracy with which the model represents the higher temperature experimental data is relatively low. In general, the model generally understates the degree of separation between the two components. There are several theories which offer possible explanations of these observed discrepancies.

REFERENCES


**BRIEF BIOGRAPHY OF PRESENTER**

Dane Renner has recently completed his final semester of study at the University of Auckland. He will soon be graduating with a Bachelor of Commerce/Bachelor of Engineering with first class honours majoring in Economics and Chemical and Materials Engineering. Dane is currently employed as a graduate process engineer at Woodside Energy and resides in Perth, Australia. In addition to the research presented herein, Dane has also published on energy and transportation economics issues in New Zealand. Outside of the academic world, Dane is a keen snowboarder and surfer and enjoys travelling.