MODELING AND SIMULATION OF A TPSA SYSTEM FOR A VYNIL CLORIDE / NITROGEN SEPARATION FROM INDUSTRIAL STREAMS

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RESUME – Vinyl Chloride (VCM) is the main monomer used in the production of polyvinyl chloride. Classified as a toxic and carcinogenic agent, VCM must be thoroughly separated and recuperated from the resulting polymer. A literature review on adsorbent materials was performed and a temperature and pressure swing adsorption (TPSA) system was developed for the equilibrium adsorption separation of VCM and nitrogen (N₂). Using a 1-dimensional mathematical model, a 7-step, 2-column TPSA system was designed to treat an industrial scale 40:60% VCM/N₂ mixture and produce a 95% (v/v) VCM rich stream and a N₂ stream with a VCM content of 8 ppm (w/w). A process comparison and optimization was also performed to study the effects of the step configuration and duration on the system performance.

1. INTRODUCTION

PVC is produced from the free radical chain polymerization of VCM. As reported by Snell (1975), approximately 10-15% of VCM remains unreacted after the polymerization step, which requires the resulting polymer to be stripped in order to recover the unreacted monomer. In 1975, the U.S. Environmental Protection Agency (EPA 1982) classified VCM as a carcinogenic agent, after confirming the correlation between several cases of angiosarcoma of the liver with occupational exposure to VCM. From this incident, tighter regulations were established to control the levels of VCM in gaseous and liquid exhaust streams. Most of the unreacted VCM is recovered during the reactor purge, the slurry stripping step and other equipment purges, and is sent to one or more monomer recovery units. Here the purge stream is characterized by the high concentration of VCM, low volume and low temperature, which are the optimal conditions for the use of adsorption methods.

In this study, a literature review was performed on possible adsorbents for VCM with available, documented equilibrium adsorption isotherms. Based on the chosen adsorbent behavior, a 1-dimensional mathematical model was developed to simulate the cyclic behavior of a TPSA system for the separation and purification of a VCM rich stream. This process must be capable of producing a VCM rich stream with high enough purity to be recycled back into the reactor feed (95% (v/v)) and an inert stream with a VCM composition that complies with the regulated gas emission levels (8 ppm (w/w)).
2. ADSORBENT MATERIAL LITERATURE REVIEW

A collection of previous works was elaborated pertaining to the adsorption of VCM in different adsorbent materials. From the literature, although information regarding the use of adsorption for the treatment, capture or recovery of VCM were not uncommon, only 4 published examples of VCM equilibrium adsorption data were obtained, 3 studies reported the use of activated carbon (Raduly 1974, Scamehorn 1979, Chauveau et al. 2013), while one reported the use of a hybrid inorganic-organic material (Herdes et al. 2007). From the collected studies, the activated carbon Pittsburgh type PCB was selected for the present study. From Choi et al. (2003), equilibrium adsorption data for nitrogen using the same adsorption material was obtained within similar temperature ranges.

2.1. Comparison of the Non-Competitive VCM and \( N_2 \) Isotherms

From the obtained equilibrium adsorption data, it is possible to fit the Dual Site Langmuir adsorption model for both chemical species to the selected carbon adsorbent. The Dual Site Langmuir isotherm model can be written as shown in Equation (1).

\[
q_{eq} = \frac{q_{sat,1} b_1 P}{1 + b_1 P} + \frac{q_{sat,2} b_2 P}{1 + b_2 P} \quad \text{with} \quad b_i = b_0 i e^{-\Delta H_{ads,i}/RT}
\]

where \( q_{eq} \) is the equilibrium solid phase concentration, \( q_{sat} \) is the saturation solid phase concentration, \( b \) is the affinity parameter, \( P \) is the studied gas pressure, \( b_0 \) is the pre-exponential factor, \( -\Delta H_{ads} \) is the adsorption enthalpy, \( Rg \) is the ideal gas constant and \( T \) is the temperature. The model fitting is shown in Figure 1, while the resulting parameters in Table 1.

\[\text{Figure 1 – Adsorption isotherm fitting for VCM (a) at the temperatures of 294K ( ), 317K ( ), 339K ( ), and 368K ( ) and for } N_2 \text{ (b) at the temperatures of 293K ( ), 303K ( ), 313K ( ), and 318K ( ),}\]

\[\text{for the Pittsburgh type PCB activated carbon material.}\]

\[\text{Table 1 – Fitting Parameters for the Dual Site Langmuir Isotherm Models}\]

| Parameters | \( q_{sat,1} \) | \( q_{sat,2} \) | \( b_0 \) | \( -\Delta H_{ads,1} \) | \( -\Delta H_{ads,2} \) |
|------------|----------------|----------------|----------|----------------|----------------|
| VCM        | 3.30           | 8.15           | \( 3.49 \times 10^{-6} \) | \( 5.90 \times 10^{-6} \) | 53.90           | 37.09           |
| \( N_2 \)  | 1.88           | 1.88           | \( 1.15 \times 10^{-3} \) | \( 1.15 \times 10^{-3} \) | 16.13           | 16.13           |
3. PROCESS DESCRIPTION AND MODELLING

To simulate a multicomponent TPSA model, a set of mass, energy and momentum balances must be specified. Following a cylindrical geometry, the partial differential and algebraic equations are discretized along the axial direction, using the second order orthogonal collocation on finite elements method. The resulting ordinary differential equation with respect to time are solved using the DASOLV solver from gPROMS® Model Builder. Based on the framework established by Da Silva et al. (1999), the present mathematical model is built on the following assumptions:

1. The gas phase follows an ideal gas behavior;
2. The mass, temperature and momentum balances have no gradients in the radial direction;
3. The internal mass transfer resistance was expressed with the Linear Driving Force model;
4. The external mass and energy transfer resistances are expressed with the film model;
5. The column porosity, cross section and particle density are constant along the column;
6. The temperature profile is homogeneous inside the particle;
7. The Ergun equation is valid locally, only the pressure drop and the velocity change are considered in the momentum balance;
8. The jacketed heat exchanger is overdesigned as to maintain a constant temperature profile on the heat exchanger side for the duration of each step.

4. SIMULATION RESULTS

The proposed TPSA cycle consists of seven steps, which are represented in Figure 2.

![Figure 2 – Outline of the proposed TPSA cycle.](image)

The size of the column was determined based on the minimum fluidization velocity of the carbon adsorbent particles and the performance of the heat exchanger, resulting in a column length and diameter of 14.8 and 1 meters. For the estimated column dimensions, the following time steps were required to meet with the expected requirements. Sequentially, the feed last 24000s, the closed heating 2000s, the blowdown 7000s, the purge 1000s, the cooldown 7000s, the counter current pressurization 2000s and with an idle time of 5000s. These times allow the extension of this TPSA to a dual column unit that guarantees a continuous feed treatment and continuous production of VCM and nitrogen rich streams. Based on a feed flow rate of 195
Nm³/h and inlet velocity of 0.054 m/s, in order to accomplish the VCM purity requirements of 95%, a purge flow rate of 35 Nm³/h with an outlet velocity of 0.25 m/s was used. The temperature and pressure swing was designed to have a high and low temperature and pressure of, respectively, 463 and 293K, and, 100 and 50 kPa. Using these operating parameters, a product stream of nitrogen with a concentration of 7.8 ppm (w/w) of VCM was produced and a nitrogen recovery of 96.50% was achieved. The productivity of VCM was 0.46 mol/kg.h and 0.66 mol/kg.h for N₂. The system has an energy consumption of 3.62 MJ/kgVCM.

For a better understanding of the proposed conditions, a sensitivity study was performed to investigate the effects of the various step configurations and durations on the performance of the TPSA cycle. From this analysis, it was determined that the allocated cooling time is sufficient to maintain the system performance. The implemented closed heating step reveals a better performance than if the respective time would be allocated to the other VCM production steps, as the increased velocity profile is sufficient to stifle the deformation of the VCM front caused by molecular diffusion, over a long period of time. The maximum baseline for N₂ recovery in this particular system is determined by removing the purge step. The influence of the N₂ purge stream velocity is studied. A rinse step is introduced, and the its effects on the system performance are discussed relatively to the increased energy consumption.

5. NOMENCLATURE

\[ b_0 \] \quad \text{Pre-Exponential Factor (Pa}^{-1})
\[ b_i \] \quad \text{Affinity Parameter (Pa}^{-3})
\[ q_{eq} \] \quad \text{Equilibrium Solid Phase Concentration (mmol/g)}
\[ q_{sat} \] \quad \text{Saturation Solid Phase Concentration (mmol/g)}
\[-\Delta H_{ads}\] \quad \text{Adsorption Enthalpy (kJ/mol)}

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