Using a Rigorous Mathematical Model to Optimize a Natural Gas Dehydration Plant

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Abstract
Natural gas is a hydrocarbon gas mixture mainly composing of methane, and impurities such as water vapor, carbon dioxide, hydrogen sulfide and mercaptans. Water causes several problems like corrosion, condensation and decreasing natural gas energy content. In this study, a temperature swing adsorption (TSA) plant for dehydrating of natural gas is investigated. At first, a rigorous modeling methodology is introduced to calculate the breakthrough time of the target industrial TSA process using 3A molecular sieve, and then it is applied to study the cycle time of the adsorption process. Based on results obtained by the model, the cycle time for designed and actual conditions are about 12.3 h and 19.5 h, respectively, close enough to the observed values in the target dehydration plant. Then, to increase the cycle time, a special type 3A molecular sieve is proposed. Modeling results show that after replacing existing molecular sieve with the recommended one, breakthrough time increases about 20.8 h, higher enough than the desired value (20 h).

Keywords: Temperature swing adsorption; Rigorous mathematical model; Molecular sieve 3A; Natural gas dehydration

Introduction
The natural gas industry has recognized that dehydration is necessary to ensure smooth operation of gas transmission lines [1]. One of the methods to do such a task is adsorption process using a suitable zeolite molecular sieve. Zeolites are highly crystalline hydrated alumina silicates from the alkali metals and alkali earth metals groups [2].

There are two widely used approaches to estimate the breakthrough time of adsorption processes i.e., experimentation and mathematical modeling. The first method provides a direct and fast answer for a given system; but, it greatly depends upon the experimental conditions, such as ambient temperature and residence time [3]. In contrast, mathematical modeling is simple and easily understood with no experimental set-up required, and therefore, it has absorbed increasing interest in the industrial applications.

Up to now, many mathematical models have been presented to describe and calculate the breakthrough time of a column adsorption system in liquid or gaseous phase [4, 5]. The main objective of this work is to introduce a simple and accurate method to estimate the breakthrough time of an industrial temperature swing adsorption (TSA) process. According to the mathematical models, the breakthrough time of the target plant is calculated, and it is
compared with the actual value. Then, a new adsorbent is recommended for the target TSA plant, and the improvement of its efficiency is studied.

**Mathematical Modeling**

The following assumption is used to model the target TSA unit:

- The gas phase is ideal, and is only consisted of methane as the dominant component.
- The bed works in isothermal condition.
- The bed void is initially filled with methane.
- Only axial mass dispersion is assumed.
- Pressure gradient is related to superficial velocity based on Ergun equation.
- Mass transfer coefficients consist of film resistance and macro pore diffusion coefficient.

Above assumptions have been widely accepted by numerous adsorption studies [6-8]. Based on these assumptions, the general and particular equations are as follows.

**General Equation**

- Ergun’s equation is used as momentum balance [9].
- The mass balance in the gas phase depends on the effect of axial dispersion, convection term, gas phase accumulation and rate of fluid to the adsorbent [10, 11]:
  - The dispersion coefficient is calculated from correlations [6, 9]
  - Binary molecular diffusivity ($D_{AB}$) Fuller, Schettler and Giddings equation is used. This equation includes empirical constants and keeps the form of Chapman-Enskog kinetic theory [12].

**Particular Equations**

**Kinetic model.** Mass transfer driving force is assumed to be a linear function of solid phase loading with transport mechanism from fluid to solid.

**Isotherm model.** The relation between loading of molecular sieve and the partial pressure or concentration of adsorbate is known as isotherm curve. The Langmuir-type isotherm is the most relevant model for practical applications. In this research, the Langmuir isotherm for pure component adsorption is used. Details for estimating the isotherm parameters were described in the previous work [5].

**Numerical solution**

All of the mentioned general and particular equations are solved using the Matlab software (Mathworks, 2013a) with appropriate initial and boundary conditions to estimate the breakthrough time of the target TSA system.

**Results and Discussions**

Figure 1 (left picture) shows water content against time for the 1st sample connection (top) of drying vessel. As seen, water content has increased after 5 hours (300 minutes) gradually and breakthrough has been occurred. So, it can be concluded that this part of bed has fully been saturated. In this picture, the high water content of gas at the start of measurement is due to the initialization step of hygrometer sensor.

Furthermore, Fig.1 (right picture) demonstrates the water content vs. operation time for 2nd sample connection of vessel A (bottom). As shown in this figure, no breakthrough occurs in this sample connection after 12 h from start of operation. As seen, the water content has decreased gradually, and finally it is flattened. It means that breakthrough has not occurred yet during this cycle. It should be noted that the flowrate of the feed is about 40% less than the...
design value. So, a longer adsorption cycle can be expected. According to the requirement of the client, the dryer should operate at least for 20 h before facing any breakthrough conditions.

For the design case, it was assumed that the static water adsorption in 100% relative humidity was about 22wt%. Accordingly, it was found that the breakthrough time could be expected after 12.3 h. Then, the corresponding variables were calculated for the current operating conditions. As mentioned before, in this case, the flowrate of the feed is about 40% lower than the design case. Therefore, the considerable gap between the design (desired values) and the current case can be justified (see Table 1). Therefore, the validity of the model could be concluded. From these results, it was concluded that the target dehydration plant cannot operate more than 20h without facing breakthrough phenomenon, essentially required by the target gas refinery. Consequently, to improve the efficiency of the plant, a special type synthetic zeolite of A-type crystal structure in potassium-sodium form with a pore opening of 3 angstrom (0.3 nm) was suggested to replace with the current one.

In Table 1, the significant variables are recalculated for the proposed molecular sieve based on current operating conditions. It can be concluded that after replacing molecular sieve, breakthrough is happened after 20.8 h which is higher than the required value. But, to prevent any operating upsets, a shorter operating cycle about 20 h is suggested.

Table 1. Calculated parameters for the design case, current case and proposed Molecular Sieve

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Design case</th>
<th>Current case</th>
<th>Proposed Molecular Sieve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water loading</td>
<td>kg/h.m²</td>
<td>40.5</td>
<td>24.5</td>
<td>24.5</td>
</tr>
<tr>
<td>Superficial velocity</td>
<td>m/min</td>
<td>5.3</td>
<td>3.21</td>
<td>3.21</td>
</tr>
<tr>
<td>MTZ length</td>
<td>cm</td>
<td>185.5</td>
<td>164.5</td>
<td>164.5</td>
</tr>
<tr>
<td>Length of unused bed</td>
<td>m</td>
<td>0.151</td>
<td>1.35</td>
<td>1.95</td>
</tr>
<tr>
<td>Breakthrough time</td>
<td>h</td>
<td>12.3</td>
<td>19.5</td>
<td>20.8</td>
</tr>
</tbody>
</table>

Conclusions
To design and optimize temperature swing adsorber (TSA) plants, it is essential to develop a simple and accurate rigorous mathematical model. In this study, a method to estimate the breakthrough time of a commercial TSA process, designed to dehydrate natural gas, in consequence with decreasing the product dew point pure was presented.

At first, collected data from the top of the adsorbing vessel showed that water content was gradually increased after 5 hours, and breakthrough phenomenon was occurred. In contrast, observations from the bottom of vessel (water content vs. operation time) confirmed that no breakthrough occurs in this section after 12 h from the start of operation. Because the actual flowrate of the feed was about 40% lower than the nominal value, a longer adsorption cycle could be achievable. Based on the presented modeling approach, the expected cycle time for
nominal and actual conditions were about 12.3 h and 19.5 h, respectively. The former was about the same as the observed value (about 12 h), reported by the engineering department of the target plant; therefore, the difference between the nominal and actual cycle times can be justified, and the validity of the model was concluded.

To enhance the cycle time of the gas dehydration plant, and improve the operation, it was required to increase the cycle time to more than 20 h with enough safe margin. Consequently, a special type of 3A molecular sieve (a-type crystal structure in potassium-sodium) was proposed. Based on the results obtained by the introduced model, it was concluded that after loading proposed molecular sieve, breakthrough would happen after 20.8 h, confidently higher than the desired value. However, to have a confident operation, a shorter operating cycle (20 h) was suggested.

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References