Optimal thermobaric parameters determination of natural gas dehydration in LNG production

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Abstract. Gas dehydration is one of the main technological processes in natural gas treatment for pipeline transportation and LNG production. The main task of this research is to increase the efficiency of adsorption gas dehydration. This report presents the results of a comparative assessment and determination of the optimal thermobaric parameters of the process of natural gas dehydration with KSMG type of silica gel and NaA-BS type of zeolite-containing adsorbent. It has been shown that reducing the temperature of the natural gas before dehydration reduces the mass of loaded adsorbent, the mass of adsorber, the consumption of regeneration gas, cooling gases, and fuel gas for heating regeneration gas. Recommendations on the dehydration unit placement after pre-cooling stage in order to reduce capital and operating costs are given at the end of the article. The results are important in the design and modernization of technological processes of the LNG production.

1. Introduction

An adsorption gas dehydration plays an important role in the natural gas treatment for natural gas liquefaction [1, 2]. When liquefying natural gas, the important technological parameter is the moisture dew point temperature - the moisture content in natural gas before liquefaction must be less than $1 \times 10^{-6}$ m$^3$/nm$^3$. Gas dehydration is carried out to prevent the formation of hydrates in process piping and vessels when producing liquefied natural gas (LNG). Hydrate deposits inside piping and vessels reduce their inner size, increase the hydraulic resistance, which leads to additional energy consumption, and operational costs, and sometimes to emergency shutdowns [3].

In general, such adsorbents as silica gel and aluminum silicates of alkaline elements are used in industrial processes of natural gas adsorption drying. Adsorbents in the form of beads having a diameter of from 2 to 8 mm, and in the form of extrudates (thin cylinders) having a diameter of from 1 to 6 mm are used [3-6].

2. A comparative evaluation of silica gel and zeolite for natural gas dehydration

The purpose of this study is a comparative evaluation of silica gel KSMG type and zeolite NaA-BS type (4A type) adsorbents and determination of the optimal temperature and pressure of adsorption natural gas dehydration process in order to increase its effectiveness in the natural gas treatment for liquefaction. Properties of the adsorbents produced by the Salavat catalyst plant are presented in Tables 1 and 2.
Table 1. Physical and chemical properties of silica gel KSMG with diameter 4.5mm

| Specific surface (m²/g) | Pore volume (cm³/g) | Bulk density (g/cm³) |
|-------------------------|---------------------|----------------------|
| 720                     | 0.4                 | 0.85                 |

Table 2. Physical and chemical properties of granulated zeolite NaA-BS

| Size of the granules on the average diameter (mm) | Pore volume (cm³/g) | Bulk density (g/cm³) |
|--------------------------------------------------|---------------------|----------------------|
| 4.5 ± 0.5                                         | 0.38                | 0.82                 |

The dehydration process pressure doesn’t impact on an adsorption activity of adsorbents, so the pressure is determined by a liquefaction unit pressure. However, the adsorption process temperature has a significant effect on the process efficiency. A drying unit with inlet gas pressure of 4.5 MPa is considered for comparison of adsorbents properties. The temperature of the incoming gas stream is 20°C. At these therobaric conditions the moisture content in natural gas is 30.44 mg/m³.

An experiment was carried out to study the temperature influence on the equilibrium activity of the selected adsorbents. An adsorbent sample was placed in a U- tube, and the tube was installed in a thermostat. The temperature inside the thermostat was changed from plus 20 to minus 20 °C with the step of 5 °C. Air saturated with water vapor was passed through the adsorbent sample at each step of the temperature change. The tube with the adsorbent sample was weighed before the experiment and after getting the equilibrium. The adsorption activity of the sample was calculated by the equation

\[ a_t = \frac{(G_S - G_0)}{G_0} \cdot G_0^{-1} \]  \hspace{1cm} (1)

where \( a_t \) is an equilibrium adsorption activity of the sample at temperature \( t \); \( G_S \) is a weight of the sample at the equilibrium state (g); \( G_0 \) is a sample weight before passing saturated air through adsorbent (g).

The dependence of the adsorbents KSMG and NaA-BS equilibrium adsorption activity on temperature at a pressure of 4.5 MPa is shown in Figure 1. It can be noticed that, with a decreasing in temperature from 20°C to minus 20°C, silica gel activity increases from 4 to 6.7% mass, while zeolite activity increases from 16 to 27.8% mass.

The results obtained allow us to note that lowering the temperature of the adsorption gas dehydration process from 20°C to minus 20°C reduces the amount of adsorbent to provide the required quality of gas dehydration. For example, the calculations of adsorbent charge for two types of adsorbents were made, using a simplified equation [6]:

\[ G_a = \frac{\Delta W \cdot G_g \cdot \tau_c \cdot (A_t^{\infty})^{-1}}{} \]  \hspace{1cm} (2)

where \( G_a \) is the amount of adsorbent (kg); \( \Delta W \) is the amount of moisture that must be removed (kg/Nm³); \( G_g \) is installation capacity (Nm³/h); \( \tau_c \) is time of adsorption stage (h); \( A_t^{\infty} \) is the equilibrium activity of the adsorbent (% mass).

Taking the dehydration unit capacity - 300 t/h, the amount of moisture that must be removed – 30.44 mg/Nm³, time of adsorption stage – 24 h, results of adsorbent amount calculations are presented in Table 3.
Figure 1. Dependence of the adsorbent’s equilibrium adsorption activity on temperature at a pressure of 4.5 MPa.

Table 3. Adsorbent charge, t

| Temperature, C | 20     | 15     | 10     | 5      | 0      | -5     | -10    | -15    | -20    |
|---------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| KSMG          | 18.65  | 18.22  | 17.52  | 16.62  | 15.58  | 14.47  | 13.35  | 12.25  | 11.20  |
| NaA-BS        | 4.68   | 4.47   | 4.23   | 3.97   | 3.70   | 3.43   | 3.17   | 2.92   | 2.69   |

According to calculation results, at temperature of minus 20°C the amount of KSMG silica gel is 1.66 time less than at temperature of 20°C, the amount of NaA-BS zeolite is 1.74 time less for the same temperature change.

At the same time, the amount of NaA-BS zeolite in comparison with KSMG silica gel is approximately 4 times less. The reduction in the required mass of the adsorbent charge for a given degree of gas drying allows the size of the adsorbers and, consequently, the steel intensity and the cost of the adsorber to be reduced. It means that low-temperature adsorption process with zeolite could increase the efficiency of gas dehydration.

3. Research on low-temperature adsorption for LNG production and optimal thermobaric parameters determination

The low-temperature adsorption unit can be accomplished into the LNG train in different ways. For example, two of them are:

1) by cooling the gas stream entering the drying unit due to heat exchange with the boiloff gases from the end-flash process (Figure 2);
2) by placing the drying unit in the train at a pre-cooling stage of liquefaction unit (Figure 3).
Figure 2. Scheme of natural gas cooling with boiloff gas upstream the dehydration unit (option 1)
(I - Natural gas; II - boiloff gas; III - LNG; 1 - adsorption drying unit; 2 - pre-cooling unit; 3 – separator; 4 – liquefaction unit; 5 - recuperative heat exchanger; 6 - LNG storage tank)

Figure 3. Scheme of natural gas cooling upstream the dehydration unit (option 2)
(I - Natural gas; II - boiloff gas; III - LNG; 1 - adsorption drying unit; 2 - pre-cooling unit; 3 – separator; 4 – liquefaction unit; 6 - LNG storage tank)

Feed gas from the main gas pipeline corresponds to STO Gazprom 089-2010 (the temperature of the moisture dew point varies from minus 10 to minus 20 °C, depending on the season and the macroclimatic region). To prevent possible liquid formation from gas stream, which may include moisture and hydrocarbons, the temperature to which gas flow should be cooled at the inlet of dehydration unit, should not be below the moisture and hydrocarbons dew point.

Thermodynamic calculations of both options were carried out with the Aspen HYSYS. To simplify the calculations, the following assumptions were made:
− pure methane was taken as a feed stream;
− the hydraulic resistance of heat exchangers and heat exchange with the environment weren’t taken into account.

Calculation results of the first option (cooling gas stream with boiloff gas) showed an insignificant decrease in the temperature of natural gas stream: from 20 to 14°C (stream I downstream the heat
exchanger 5, Figure 2). This is due to small amount and low heat transfer coefficient of the boiloff gas. Thus, when natural gas flow is 300 t/h, the boil-off gas flow is 13 t/h. Downstream heat exchanger 5, the temperature of boiloff gas rises from minus 159.5 to 11°C.

Second technological option of low-temperature dehydration provides gas cooling in the pre-cooling refrigeration cycle (Figure 3) and has some features. Placing the dehydration unit between the pre-cooling cycle and liquefaction cycle in the train can cause the formation of hydrates, because the gas flow temperature at this stage might vary from minus 30°C (for example, for the APCI process C3MR) down to minus 80°C (for example, in winter for the Shell process DMR).

As a rule, pre-cooling cycles, regardless of refrigerant composition, are multi-stage, so that energy efficiency increases. In order to select the optimum temperature of the low-temperature adsorption process, it is possible to place the dehydration unit between separate stages of the pre-cooling cycle.

The effect of the low-temperature adsorption process with decreasing temperature is shown in Figure 4. The changes in the main parameters of the unit are presented as a function

\[ \varphi(t) = 1 - (A_t \cdot A_{20}^{-1}) \]  

where \( A_t \) is parameter value at temperature \( t \); \( A_{20} \) is parameter value at 20°C.

The following parameters were chosen as parameters of the dehydration unit:
- mass of loaded adsorbent;
- mass of an adsorber;
- regeneration gas flow rate;
- gas flow rate for adsorber cooling;
- fuel gas flow rate for regeneration gas heating in the furnace.

![Figure 4](image_url)  
**Figure 4.** Dependence of dehydration unit parameters on the temperature
Thus, reducing temperature of natural gas entering the adsorption drying unit allows to reduce mass of loaded adsorbent, mass of adsorber, regeneration gas flow rate and cooling gas flow rate, as well as to reduce fuel gas flow rate. Therefore, placing an adsorption drying unit between the stages of the pre-cooling cycle, without additional energy consumption for cooling the natural gas stream, both capital and operating costs for gas dehydration at LNG production can be significantly reduced.

4. Conclusions
The comparative evaluation of silica gel KSMG and zeolite NaA-BS adsorbents was carried out. It was shown that with a decrease in temperature, the activity of silica gel and zeolite increases, therefore, a decrease in temperature of the adsorption gas dehydration leads to an increase in the energy efficiency of the process. A comparison of two types of adsorbents has shown that adsorption activity of zeolite is sufficiently more than the one of silica gel at any temperature. The amount of NaA-BS zeolite for adsorber loading in comparison with KSMG silica gel is approximately 4 times less. The reduction in the required mass of the adsorbent charge for a given degree of gas drying allows the size of the adsorbers and, consequently, the steel intensity and the cost of the adsorber to be reduced. Two ways to reduce the temperature of the drying process were considered, it is more efficient to place the drying unit between the stages of the pre-cooling cycle at the liquefaction train. As a result, of calculations, the dependence of dehydration unit parameters on gas temperature was obtained: reducing the process temperature leads to decrease in both capital (adsorbent charge mass, adsorber steel intensity) and operating costs for gas dehydration (regeneration, cooling and fuel gas flow rates).

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