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Development of experimental apparatus for in situ monitoring of the high-pressure natural gas dehydration process

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Abstract

The presence of water in natural gas (NG) is one of the major challenges to be solved by the petrochemical industry, as it can cause problems in the NG flow and storage stages, and does not comply with the standards of the National Agency of Petroleum, Natural Gas and Biofuels (ANP). Thus, the optimization of the NG dehydration process requires the study of materials that have a greater capacity to capture water and that withstand industrial conditions. In addition, there is a need to develop laboratory-scale experimental devices to evaluate the performance of these materials under high pressure conditions and to apply moisture monitoring techniques in NG with accurate and fast data collection. This work aimed to build an experimental device and develop a methodology to study the water capture of a model NG system through adsorption and monitor the gas moisture through a hygrometer based on a quartz crystal microbalance (QCM). The studies showed that the QCM was able to accurately analyze the moisture of gases at levels between 0.02 and 400 ppm with a response time of 30 s between each analysis, that the experimental apparatus was able to generate stable breakthrough curves that allowed calculating the water adsorptive capacity of a commercial adsorbent with an average of 249.36 mg/g at 100 bar and 50 ºC, as well as controlling all process variables such as pressure, temperature and flow.

Keywords: Natural gas; humidity; monitoring; quartz crystal microbalance.

1. Introduction

Natural gas (NG) has wide applications in several economic sectors, being responsible for generating 24.7% of the world's primary energy in 2019 and with prospects of continuous growth over the next 20 years [1]. To meet the growth in NG consumption, it is necessary to optimize its production, since the composition varies greatly for each reservoir, generating challenges. However, NG is mainly composed of methane (CH_4), in smaller fractions of ethane, propane, butane, C5+ (pentane and heavier hydrocarbons) and contaminants such as water, carbon dioxide, sulfur compounds, among others [2]. After NG processing, all these compounds can be separated, refined and destined for various commercial purposes[3].

One of the essential steps in NG processing is dehydration, where the removal of water prevents operational problems such as corrosion and erosion of equipment, formation of hydrates, among others. Hydrates, which are ice-like structures, are generated under high pressures and low temperatures when there is moisture in the NG, representing one of the major problems in the oil and gas industry [4].

There are several methodologies applied industrially and in the literature to dehydrate NG, such as absorption, adsorption, and condensation.

Among these, the removal of water by solid desiccants through adsorption is one of the methods that reduces moisture in NG to minimum values, making it compliant with ANP standards [4]. In addition, materials that present greater stability in more adsorption and desorption cycles, with high adsorptive capacity, and that withstand high pressure and temperature conditions have been developed to dehydrate NG [5].

The study of solid desiccants allows optimizing NG dehydration, reducing operating costs, and increasing the production capacity of the gas processing unit. However, proving the efficiency of these materials requires the development of robust devices capable of withstanding varied experimental conditions with precise monitoring techniques [6].

The American Society for Testing and Materials (ASTM) defines three model methods for measuring moisture in NG, which are: dew point detector (ASTM D1142), capacitance sensors (ASTM D5454), and tunable diode laser spectroscopy (ASTM D7904) [7]. Several studies in the literature analyze other methodologies such as Karl Fischer titration, quartz crystal microbalance (QCM), capacitance sensors, and optical methods [8] [9] [10] [11]. Among the options mentioned in the literature, the direct measurement by hygrometer based on QCM is an interesting option for monitoring humidity in gas streams, due to its high sensitivity in detecting water content in gases and data acquisition speed [8] [9]. Thus, the objective of this work was to develop an experimental apparatus that monitors in real time the humidity of a natural gas stream after adsorption dehydration under controlled temperature, stable flow rate, and high pressure through the use of QCM.

2. Material and methods

Materials

Nitrogen 99.99 and methane 99.5% (White Martins) where employed in the experiments. The adsorbent was a pelletized synthetic zeolite of the chabazite type (provided by Petrobras).

Experimental apparatus and procedures

The experimental apparatus developed is schematically presented in Figure 1. This unit allows gas saturation with water, adjustment of gas flow, temperature and adsorption pressure.

The experimental procedure begins by feeding the syringe pumps with the gas of interest (CH_4 or N_2). After this, all the accessories that make up the experimental unit (humidifier, column and MCQ) are connected and the system temperature is adjusted to 50 °C. Then, N_2 is injected right after the humidifier to purge the entire line of impurities present, mainly moisture. This procedure is carried out for a period of 10 to 14 h or until the MCQ detects a water content below 5 ppm in the output stream.

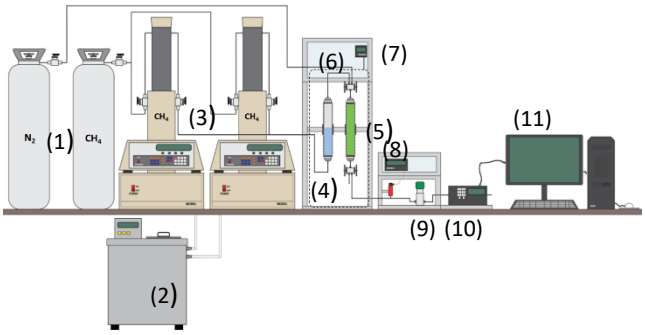

Fig. 1: Experimental apparatus developed. Where: (1) CH_4 and N_2 cylinders; (2) thermostatic bath; (3) syringe pumps; (4) gas humidifier; (5) adsorption column; (6) heating mantle; (7) temperature indicator and controller; (8) pressure indicator and transducer; (9) pressure regulating valve; (10) QCM; (11) computer.

Once conditioned, the system is pressurized with the gas of interest for the adsorption experiment, in this case CH_4. To do this, the syringe pumps are programmed to operate at a constant pressure of 100 bar and the flow rate is adjusted to approximately 3 mL/min with the aid of needle valves. The gas

displaced by the pumps passes through the humidifier and the adsorption column until it reaches the MCQ, where the humidity is monitored and the data that will be used to construct the rupture curves are acquired every 30 s to then calculate the adsorption capacity of the material. The experiment ends when it is observed that the water content in the gas stream after the adsorption column is equal to the initial water content, indicating its saturation.

Moisture analyzer by QCM

The moisture analyzer was based on the quartz crystal microbalance (QCM) hygrometer and has the capacity to detect water samples in a range of 0.1 to 2500 ppm (± 0.1 ppm deviation), with carbon dioxide concentrations of up to 60% of the gas molar fraction, at a pressure of 1.39 to 3.45 bar, maximum temperature of 70 °C and response time of 30 s. All collected data were saved on a computer using the AMETEK UHP software.

3. Results and discussion

With the experimental apparatus assembled, data acquisition was initiated to assess its functionality and sensitivity in relation to the water content of the gas streams. First, N_2 directly from the cylinder, without passing through the humidifier, and N_2 pumped through the QCM dryer (dry N_2) were used as samples. Good stability of the QCM measurements was observed over time, with the original N_2 presenting a moisture content of around 5 ppm, while the dehydrated N_2 presented moisture very close to zero (Table 1). This demonstrates the sensitivity of the equipment to differentiate water contents under conditions close to the equipment's lower detection limit.

After verifying that QMC responds to variations in water content in gas streams and that the experimental unit allows precise control of process variables such as flow, pressure and temperature, the high-pressure adsorption curves were collected. For these tests, different amounts of adsorbent material were evaluated, with a concentration of 0.5 g of zeolites being chosen as the best test condition.

Table 1: Mean, standard deviation and variation coeficient (VC) of original and N_2.

	Mean (ppm)	Standard deviation (ppm)	VC (%)
N_2	4.86	0.01	0.22
N_2 dry	0.02	0.01	6.77

In order for this amount of mass to form a column suitable for the process, the pellets were macerated and sieved to maintain grains with particle sizes between 32 and 60 mesh. The experiments were performed in duplicate and called AD(0.5g)n, where "n" is the experiment number, whose rupture curves are shown in Figure 2.

When analyzing Figure 2, it can be seen that the experiments with the fixed bed filled with approximately 0.5 g of zeolite present similar behaviors, including a similar experimental completion time for AD (0.5g)1 and AD (0.5g)2 at 270 min with average flow rates of 2.19 and 2.18 ml/min, respectively.

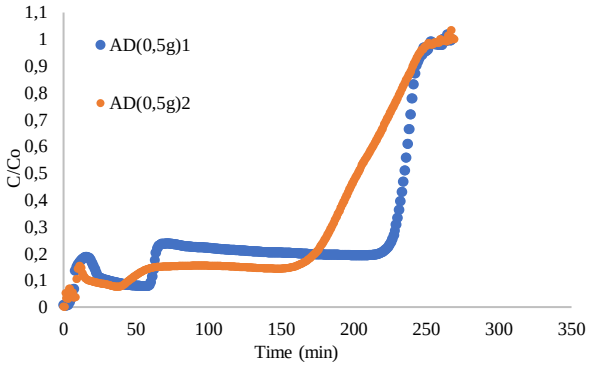

Fig. 2: Breakdown curves of the CH_4+H_2O system at a temperature of 50 °C, pressure of 100 bar and 0.5 g of adsorbent.

It is possible to observe a sudden increase in water content at the beginning of the experiment between 20 and 30 min for the curves, probably

caused by residual moisture in the system line. Subsequently, a significant reduction in moisture is seen until 60 min for AD (0.5g)1 and AD(0.5g)2, followed by an increase to a stable level of water content in the system for all curves. This second event occurs due to some preferential paths of the bed becoming saturated, however, there are still active adsorbents. The third stage of the rupture curve, where bed saturation begins, is seen from 220 min for AD (0.5g)1 and 150 min for AD (0.5g)2. In the last stage, the adsorbent exhaustion is seen at 270 min for AD (0.5g)1 and AD (0.5g)2.

4. Conclusions

The results obtained show that the experimental apparatus is functional, capable of monitoring moisture in N_2 in very low conditions below 0.2 ppm and CH_4 up to approximately 400 ppm. In addition, the experimental apparatus has operational versatility, allowing precise control of the gas flow and volume used with syringe pumps, thermal control up to 50 °C with heating blankets, adjustable pressure up to 100 bar through valves and the study of the water adsorption capacity of a commercial adsorbent in powder or pellet form.

An increase of more than 100% in the adsorption capacity of the zeolite at 100 bar and 50 °C was also determined, compared to the manufacturer's information. Therefore, it can be concluded that the experimental apparatus developed can be used to detect small amounts of water contained in natural gas streams, perform precise studies of the water capture capacity of an adsorbent, operate under controlled temperature and pressure and obtain results quickly and accurately.

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