PILOT PLANT PROCESS USING A TSA CONCEPT TO PROMOTE ADSORPTION STUDIES RELATED TO NATURAL GAS DEHYDRATION PHENOMENA

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Abstract

This abstract presents the new pilot plant (PP) created from a collaboration between Petrobras and the School of Chemistry/UFRJ. This PP aims to shed light on aging problems related to adsorbents responsible for dehydrating natural gas (NG) in pre-salt platforms. Its versatility was highlighted by presenting experimental results involving phase equilibrium (thermodynamics) and experimental results involving adsorption kinetics - rupture curves (dynamics) at high pressure. This versatility is possible thanks to the possibility of the PP forming a synthetic natural gas, including traces of heavy hydrocarbons and ethanol and water vapor near saturated conditions. Furthermore, the PP is equipped with two moisture analyzers: (1) TDLaS that uses IR to measure up to 2,500 ppm_V (before column) and (2) QCM balance that uses adsorption in quartz crystal frequency difference to measure from 20 ppb_V to 1 ppm_V (after column). The PP can be used with just a single column, which allows breakthrough curves and vapor/liquid equilibrium (VLE) in just one column per time. However, the PP can also be used with the four adsorption columns (all of them) operating cyclically, mimicking an actual adsorption process that uses the Thermal Swing Adsorption (TSA) concept, commonly used in offshore platforms.

Keywords: Thermal Swing Adsorption process; natural gas, zeolites, breakthrough curves; vapor/liquid equilibrium

1. INTRODUCTION

Oil and gas (O&G) are still the world's most critical non-renewable energy sources, and Brazil is one of the countries with big O&G reservoirs that need to be explored. It is not a coincidence that Brazil increased around 11,7% of its production in Barrel of Oil Equivalent (boe) in 2023 in comparison to 2022 [1]. Furthermore, the last oil and natural gas production national report [1] pointed out that Brazilian oil production coming from pre-salt reservoirs represented about 76% of the total production, totaling 1.585 billion boe, of which 0,343 billion is related to Natural Gas (NG). NG has advantages like (1) less carbon dioxide released during burning in comparison to oil and coal, (2) lower cost of transportation, storage, and distribution, (3) reduction of particulates, and the like.

Some challenges have appeared to produce NG from pre-salt layers, mainly made of methane (principal component), ethane, propane, and butane, but undesirable impurities can frequently be found. They are hydrogen sulfide (H_2S), nitrogen (N_2), carbon dioxide (CO_2), and water (H_2O) [2]. Water in a liquid or vapor state is always problematic because, once it is cooled, it can condense and create a corrosive atmosphere if associated with CO_2. Hydrates can also be formed in the presence of hydrocarbons, which could clog transportation pipelines [2].

Given the challenges and impurities associated with NG production, it is imperative that NG undergoes treatment to meet safety and quality standards before it is transported and used.

Adsorptive processes are one option, and conventionally, alumina, silica gel, or zeolites are common choices for dehydration in these processes [3-6].

Adsorption Processes

Adsorption processes are divided into two main categories: (1) cyclic batch or (2) continuous countercurrent contact between the adsorbent and the fluid phase. In the first one, the adsorbent bed is alternately saturated and regenerated cyclically, while the last involves a countercurrent contact between phases [7].

The adsorption process to be presented is in the first category. These types of adsorption processes differ mainly in how regeneration takes place. As adsorption is highly sensitive to pressure increase and temperature decrease, two common regeneration steps are promoted by lowering or increasing temperature. When using pressure to promote desorption, a Pressure Swing Adsorption (PSA) process is used, but when the temperature is used to promote desorption, a Temperature Swing Adsorption (TSA) is used. TSA process using molecular sieves is the only technology able to dehydrate NG under 1ppm$_V$, and this is required when Natural Gas Liquids (NGL - heavier hydrocarbons C_{2+}) or (Liquefied Natural Gas (LNG) are to be obtained. The latter is particularly important, when NG needs to be exported for other continents [8].

This work aims to present an TSA process to promote studies about adsorption dynamics, aiming to understand the reasons of zeolites aging problems. Furthermore, its versatility allows to characterize columns with breakthrough curves, providing valuable insights into the process dynamics.

2. PILOT PLANT CHARACTERISTICS

The conceptual and basic design of the pilot plant was developed in the ATOMS laboratory in collaboration with Petrobras. Prof. Amaro Gomes Barreto Jr. led it from the UFRJ/ School of Chemistry. The company AMETEK CHANDLER Engineering was responsible for developing the detailing and assembly project for the pilot plant, always following the guidelines given by the group.

The pilot plant has four adsorption columns, which are divided into four main sections: (1) in/out gas section, (2) gas saturation section, (3) adsorption/desorption section, and (4) analyses section.

The first section is responsible for proportionally promoting gas entrance to make specific gas mixtures. The gases available in the pilot plant are methane (CH_4), carbon dioxide (CO_2) and nitrogen (N_2). After mixing, the resulting mixture passes through two compressors, the first responsible for setting the working pressure and the second for establishing the nominal flow rate in the PP. The second section adds water vapor near the saturated condition and traces of ethanol and heavier hydrocarbons (C_{5+}). After these two sections, the synthetic natural gas is cyclically inserted into the columns, obeying the TSA concept (adsorption/desorption section). In order to characterize the synthetic NG before and after the adsorption process, there is the analyses section constituted by a Micro Gas Chromatography (MicroGC), a Tunable Diode Laser Spectrometer (TDLaS), and a Quartz Crystal Microbalance (QCM). The first one is responsible for monitoring the lighter gases and heavier hydrocarbons. In contrast, the last are moisture analyzers responsible for moisture monitoring before and after the adsorption columns, respectively.

The experiments (1) for water/nitrogen liquid-vapor equilibrium studies using the saturation tank and breakthrough curves for (2) CO_2/N_2 and (3) $H_2O_{(v)}/N_2$ using just one adsorption column and LTA 4A zeolite as adsorbent were carried out on the pilot plant. Breakthrough curve means the time required for an adsorption column to completely saturate with a given adsorbate.

3. EXPERIMENTAL METHODOLOGY

3.1. Saturation Dynamic

- Experiment

In these experiments, communication between the saturator and the PP *in/out section* occurs through the passage of part of the stream gas inside the saturator, while the 4 columns were by-passed. The only analyzer used in these experiments was the TDLaS, because it is able handle concentrations up to 2,500 ppm$_V$. Table 1 shows the conditions during these experiments.

Table 1. Experimental conditions - Saturation Dynamic

	Experiment 1	Experiment 2
Pressure (bar)	48	77
flow rate ($m^3.h^{-1}$)	0.5	
*Temperature (ºC)	31	

*Saturation tank temperature

- Simulation

The Vapor-Liquid Equilibrium (VLE) diagrams (Figure 1b and 2b) were obtained by root-finding algorithms that would lead to equal chemical potentials of the vapor and liquid phases for the $H_2O_{(v)}/N_2$ system. It calculated the water content in a water-saturated gas using the PC-SAFT equation of state provided by the FeOs package [9].

3.2 Breakthrough curves

- *With CO_2/N_2 content*

In these experiments, carbon dioxide was added using a mass flow meter in the pilot plant initially fulfilled with nitrogen, and after that this mixture went into one of the adsorption columns (the other ones remained closed). Prior the column entrance, the gas content was analyzed using a MicroGC in the pilot plant *analyzes section*.

- *With H_2O/N_2 content*

In these experiments, water vapor was added to the nitrogen gas stream by passing part of a nitrogen stream through a saturator. and after that into one of the adsorption columns (the other ones remained closed). Prior the column entrance, the gas humidity was analyzed using the TDLaS, and after the column the stream was analyzed with the QCM in the pilot plant *analyzes section*.

Table 2 shows the experimental conditions of these experiments.

Table 2. Experimental conditions - breakthrough curves

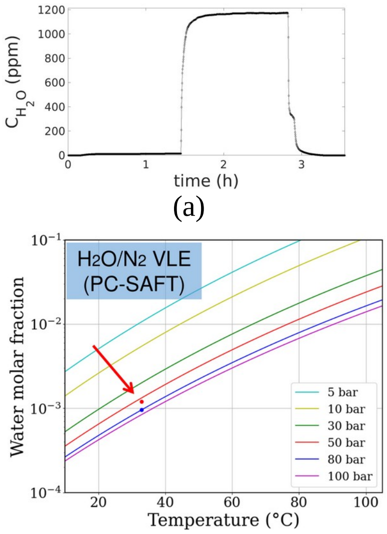
	Experiment with CO_2/N_2	Experiment with H_2O
*C_0 (mol.L^{-1})	0/400	35 * 10^{-6}
Pressure (bar)	48	
flow rate (m^3.h^{-1})	0.5	
T_{column} (ºC)	40	

* Initial concentration prior the experiment

4. RESULTS AND DISCUSSION

4.1. Saturation Dynamic

In the experiments at 48 bar, the upper level of water vapor concentration was approximately 1170±114 ppm$_V$; one of the experiments is illustrated in Figure 1a. In the experiments at 77 bar, the level reached was 902±20 ppm$_V$; one of the experiments is illustrated in Figure 2a.



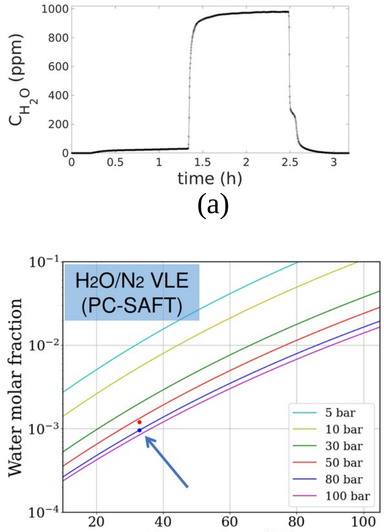
(a)

(b)

Fig 1. (a) Dynamics of the saturator at 48 bar with an upper level of 1170 ppm$_V$ of water vapor and (b) water dew point isobars for the $H_2O_{(v)}/N_2$ system. Markers represent experimental data and full lines represent water content calculation from the PC-SAFT EoS.

The phenomenon of decreasing water vapor concentration with increasing pressure is already expected since the saturation concentration is inversely proportional to the pressure to which the system is subjected.

Figures 1 and 2 displays a comparison between calculated and experimental data for this system. It is observed that the water content calculations for a nitrogen-rich gas phase yielded good results.



(a)

(b)

Fig. 2. (a) Saturator dynamics at 77 bar with an upper level of 960 ppm_V of water vapor and (B) water dew point isobars for the $H_2O_{(v)}/N_2$ system. Markers represent experimental data and full lines represent water content calculation from the PC-SAFT EoS.

Notably, the saturation dynamics proved more reproducible at higher water vapor concentrations in the gas stream. In general, it was found that the pilot plant was stable throughout its operation, and it can be used for ELV experiments of high-pressure mixtures with water vapor.

4.2 Breakthrough curves

Figure 3 shows a breakthrough curve obtained at 50 bar and 40ºC of a mixture of CO_2/N_2 with a saturation time of just 3 min.

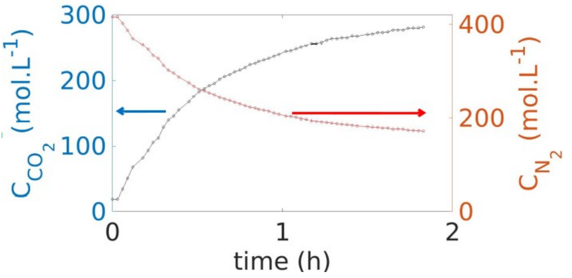


Fig. 3. Breakthrough curve of CO_2/N_2 at 50 bar and 40ºC using just one adsorption column of the PP.

Another critical parameter is the rupture time for water vapor (see Figure 4). Its rupture time was about 3 h and this curve was obtained at 50 bar and 40ºC, and an atmosphere of $H_2O_{(v)}/N_2$ was built using the PP (see details in Section 3).

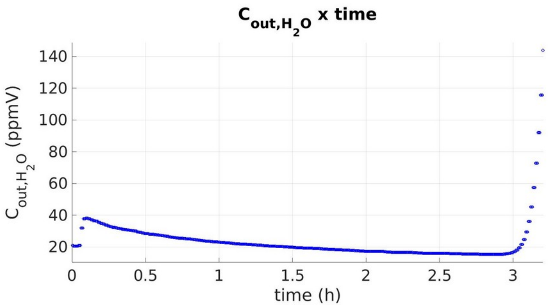


Fig 4. Breakthrough curve of H_2O/N_2 at 50 bar and 40ºC using just one PP adsorption column.

As the adsorbent has greater affinity to water molecules than carbon dioxide ones, evidenced by isotherms measurements. It can be seen from Figures 3 and 4, that the saturation time required to saturate the column was much greater with water, as water molecules found more adsorption sites than carbon dioxide ones.

5. CONCLUSIONS

Figures 1 to 4 show just part of the versatility of the built PP, which can be used to obtain experimental equilibrium at high pressure and breakthrough curves for different components. Furthermore, the TSA pilot plant can be used to find engineering process solutions regarding the real process used offshore.

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