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SEPARATION OF HEAVY SPECIES (C5+) FROM NATURAL GAS USING ABSORPTION

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ABSTRACT

The production of natural gas (NG) is increasing considerably, contributing to the energetic matrix of the world. New reserves of NG have been discovered and explored regularly. Despite the various applications of natural gas, which allow its use as a raw material for the production of synthesis gas (syngas), for instance, there are remote wells that demand treatment before use. In this work, a simplified approach to remove the heavy species of natural gas (C5+) is presented. The specification of the treated gas is based on the methane index to use the remote NG for fuel in the drive of engines of compressors and boilers. Thus, the present approach proposes the application of two simple operations, i.e., absorption followed by a flash, to regenerate the solvent. This approach may be applied in remote production fields. Based on process simulations and physicochemical properties, 1-octanol was selected as absorbent for this separation. New measurements of absorption in laboratory scale are reported using a synthetic NG and an on-line chromatography analysis. Soave-Redlich-Kwong equation of state (EoS) with Mathias-Copeman alpha function and MHV2 mixing rule with UNIFAC was applied to describe the required equilibrium data. In order to validate this model for the absorption calculations, predictions of vapor-liquid equilibrium of alkane and alcohol binary mixtures obtained from literature data were tested and evaluated. Based on the absorption measurements and SRK-MHV2 flash calculations, curves of operation and equilibrium were provided. Using n-heptane as key-component it was demonstrated that one or up to two theoretical stages are enough to proceed the separation. This work also presents a gas absorption pilot set-up up to 70 bars that is able to evaluate scale up and pressure effect. It is demonstrated, experimentally and computationally, that the proposed approach of C5+ species absorption from NG is simple and feasible to specify the methane index of the gas for remote combustion applications.

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1. INTRODUCTION

Chemical process design and unity operation are topics of high technological demand by the society. Chemical and petrochemical industries have the challenge of sustainability, that is, to be safe, efficient, and social. Remote petroleum fields present difficulties related to the direct use of the natural gas as fuel. This work seeks to introduce a simple absorption unit in order to become natural gas able to be used as a proper fuel for a compressor or boiler device.

In January 2014, the production of NG in Brazil came from 12 basins and 309 fields, resulting in 80.4 millions of cubic meters per day **(ANP, 2014)**. From this NG production, 65% was associated gas and 35% non-associated gas to petroleum. From this total amount, 23.6 millions of cubic meters per day were produced from onshore basins, summing 8213 wells. Approximately 64% of this gas production was directed to the market, 13% to the internal consumption of the company, and 17% re-injected. The utilization of NG has a wide spectrum. Therefore, it allows participation in the whole productive chain, providing energy in many forms and, therefore, income to various industries. Despite of its wide applications, NG production is not always optimal. For instance, specifications need to be matched in order to use NG as fuel **(Lieberman, 2008; Campbell, 1992)**.

The NG composition is directly associated directly to the detonation quality. Methane Index is the key parameter and is regulated by ISO 15403:2000(E). Firstly, Motor Octane Number (MON) may be calculated according to equation (1).

$$MON = -406.14 + [508.04 F(H/C)] - [173.55 F(H/C)^2] + [20.17 F(H/C)^3] \tag{1}$$

The signal of the coefficients indicates the contribution of each compound in relation to the Methane Index (*MN*). Methane, ethane, carbon dioxide, and nitrogen compositions increase *MN*. However, propane, butanes, and heavier fractions decrease *MN* and, thereby, must be separated from NG. This correlation is valid for H/C ratios higher than 2.5 and inert concentration less than 5%. Finally, *MN* is determined from *MON* according to equation (2).

$$MN = 1.624\,MON - 119.1 \tag{2}$$

The absorption process is an operation that can remove one or more species from a gas mixture by the introduction of a liquid solvent. It is a diffusional process at the interface of liquid and gas phases **(Coulson et al., 1991)**. Furthermore, absorption is widely used in industrial plants, both in the raw material preparation and product purification **(Leite et al., 2005)**. Various factors may affect the absorption, i.e., physical properties of the solvent, partial pressure of the gas, flow rates of the gas and of the solvent, and temperature **(Tan et al., 2012)**. Usually, lower temperatures increase gas absorption.

Netusil and Dilt (2011) have compared three processes of NG dehydration: absorption by triethylenoglycol, adsorption, and condensation. This comparison was based on the energetic demands in fixed conditions. Results show that absorption leads to lower energetic demands up to intermediate pressures (14 MPa). At pressures higher than 14 MPa the condensation route demonstrated to be more feasible and economic.

The absorption technique is exploited based on the demand to remove or to reduce the content of heavy components, usually hydrocarbons above pentanes (C5+), present in natural gas. The purpose of this removal is to specify the *MN* of the NG for fuel applications for compressors and boilers at the remote production fields. Figure 1 illustrates the proposed separation process, and the 1-octanol was selected as an absorbent for C5+ removal from NG.

2. EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

This work will be divided into two parts. The first one is concerned to the experimental measurements of absorption in laboratory and pilot scales. The other part is dedicated to the calculation of phase equilibrium and operational curves of the proposed absorption process.

2.1 Measurements of C5+ absorption from synthetic natural gas

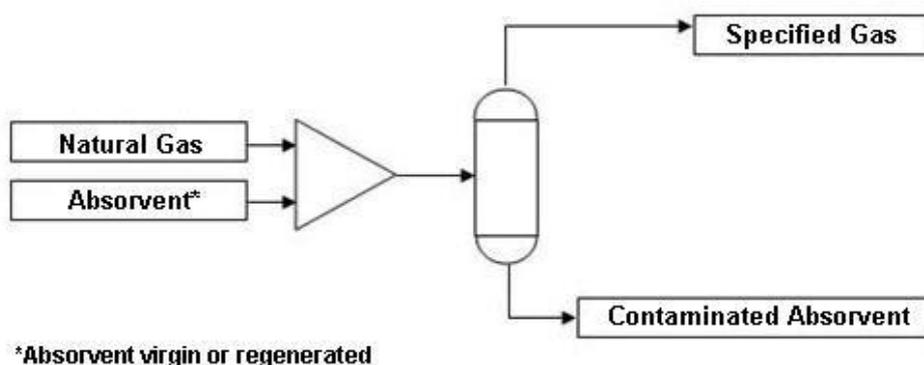The first step to carry out experiments of absorption was the preparation of the synthetic

*Absorvent virgin or regenerated

Figure 1. Flow sheet of the absorption unit for heavy (C5+) species removal of the natural gas.

natural gas. Heptane was chosen to be the heavy key component; methane was the main gas species and 1-octanol, the absorbent, or solvent. The selection of heptane was based on its reliability for analysis and adequate representation of C5+ fraction. A commercial heptane (from VETEC, for analysis, c.a. 99%) was used in the experiments and its impurities resulted in a series of isomers, and other hydrocarbons ranged from butane to decane. These compounds were determined quantitatively by gas chromatography and represented adequately natural gas composition. Previous simulations **(Gomes, 2007)** demonstrated that alcohols with carbon chain numbers between 6 and 10 may be applied as absorbent for the C5+ fraction. 1-octanol was selected as absorption solvent in this work both in laboratory experiments and calculations. Methane has a composition of 68.5 mol% in a typical associated natural gas, 81.8 mol% in non-associated gas, and 86.2 mol% in processed or treated gas. For this composition similarity, methane was used for the characterization of the gas species. Although natural gas can reach significant contents of C5+ species, in this work, the amount of the key component (heptane) was limited by the saturation point into methane, at pressure of 15 bar. Previous

dew point calculations allowed the determination of the amounts of heptane to be added to the cylinder in order to get the contamination of the methane without condensation or liquid phase formation. This calculation was also performed with the Soave-Redlich-Kwong (SRK) equation of state (EoS) with UNIFAC (Lyngby − 2 coefficients) mixing rule (MHV2). Table 1 lists the physicochemical properties of the pure species used for the characterization of the system of natural gas absorption with SRK EoS.

A schematic diagram of the absorption apparatus is shown in Figure 2. To study the absorption of the heptane in methane by the 1-octanol, an apparatus containing the absorption column was used. The apparatus consisted of a cylinder containing methane contaminated with heptane, a temperature-controlled bath with an uncertainty of ± 0.1 K, and a gas-washing bottle with an internal volume of 100 mL. The pressure of the system was measured with a manometer with an uncertainty of ± 0.01 MPa. The volume flow was measured with a flowmeter with an uncertainty of ± 0.1 mL/min. The apparatus also included a gas chromatography (GC) and an automated collector system that allowed data acquisition at 30 min

Table 1. Pure component parameters (critical properties and alpha function coefficients of Mathias-Copeman) and UNIFAC subgroups for the MHV2 mixing rule used in the thermodynamic modeling with SRK EoS.

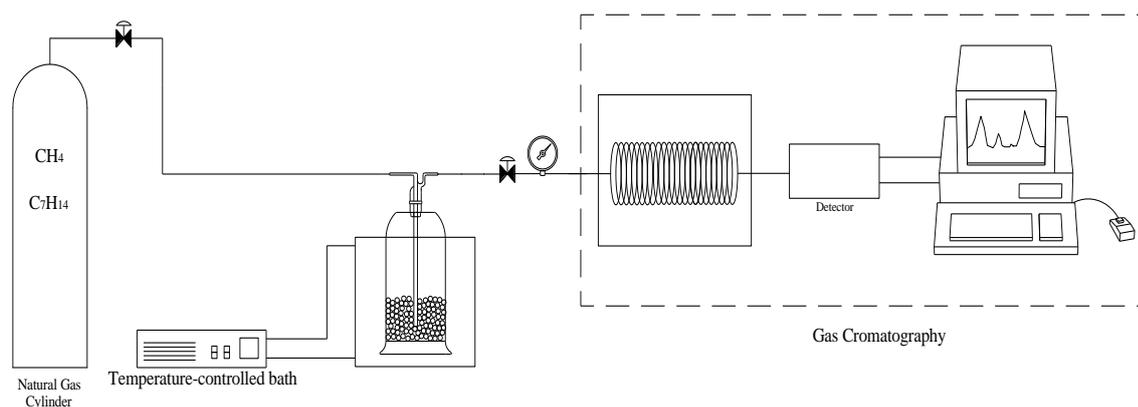| Species	T_c / K	P_c / bar	C_1	C_2	C_3	CH_4	CH_3	CH_2	CH	OH
Methane	190.58	45.44	0.5472	-0.3992	0.5751	1				
n-Butane	425.12	37.96	0.8487	-0.552	1.0774		2	2		
n-Heptane	540.20	27.40	1.0874	-0.7465	1.5765		2	5		
1-Butanol	563.05	44.23	1.1345	1.7856	-2.8325		1	3		1
1-Octanol	652.50	27.77	1.2858	0.1512	1.5920		1	7		1

Figure 2. Schematic diagram of the absorption apparatus used in this work in lab scale.
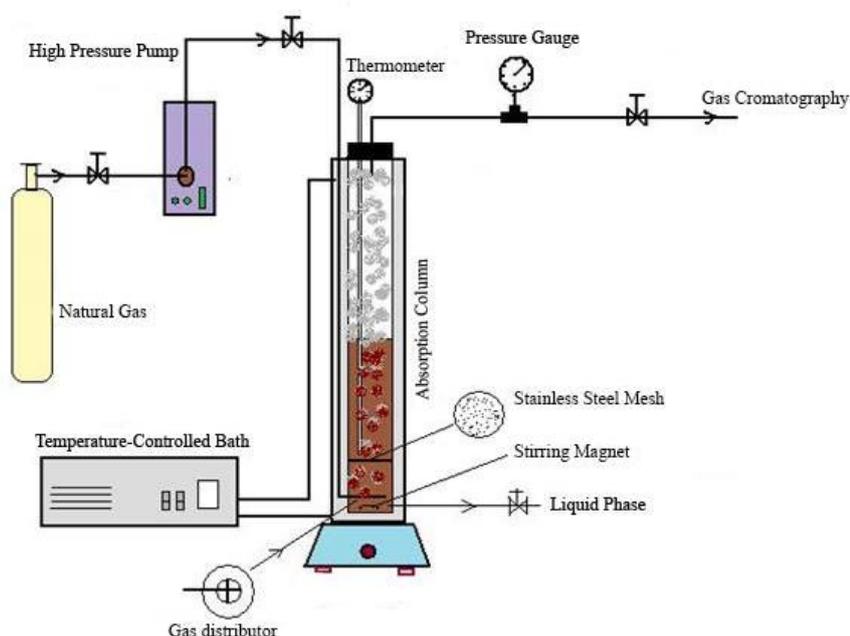

Figure 3. Flow sheet of the pilot unit of absorption of heavy (C5+) species from natural gas.

intervals of the absorption experiment. The GC was from Thermo Scientific with columns: Hayesep Q – 6 ft x 2 mm ID stainless, TR-1 – 60 m x 0.32 mm x 5.0 µm, and Mole Sieve 5A 80/100 – 6 ft x 2 mm ID stainless. The detectors used in the CG analysis were FID (Flame Ionization Detector) for the heavy species and TCD (Thermal Conductivity Detector) for the light and inert species of the gas.

Before beginning the experiments, the gas cylinder was purged. The lines, the absorption cell and the cylinder were cleaned, dried, and evacuated. Then, a pressure gauge and lines were provided to transfer methane into the cylinder. First, a known amount of contaminant, i.e.,

heptane, was charged into the cylinder. Then, a 15 bar of methane was injected into the cylinder. It was expected that the gauge would register the desired value and, then, shut the supply valve of the cylinder and evacuate the line. Next, a sufficient amount of 1-octanol was injected to the gas-washing bottle with small cylindrical inert particles, which were introduced to promote increased gas-liquid interaction. After that, the cell was set at constant-temperature with the aid of the bath and a line coming out of the gas cylinder passing under the gas-washing bottle to interact with the liquid, and, then, it left the gas-washing bottle to be analyzed in the chromatograph.

Samples for analysis were withdrawn, automatically, every 30 min.

Experiments of absorption with the developed pilot unity, see Figure 3, were also carried out. The pilot scale set-up presented a capacity of absorption that was somewhat enlarged and, for this reason, just preliminary experiments were carried out. These measurements checked the efficiency of the proposed system of C5+ removal.

2.2 Methods of calculation

SRK EoS was used with MHV2 mixing rule using UNIFAC-Lyngby model with 2 coefficients **(Dahl, 1991**; **Kontogeorgis and Folas, 2010)** with the aid of the thermodynamic package SPECS v.5.63 from the chemical engineering department of the Technical University of Denmark. In order to test this calculation approach, experimental data for vapor-liquid equilibrium have been collected from literature for the type of systems and conditions utilized in the absorption. This was alcohol + alkane systems at low pressure, the alcohol chain should have, approximately, eight carbons. After the validation of the phase diagrams, equilibrium curve was estimated with a two-phase flash calculation mode and considering all the main species presented in the system, i.e., C1 to C10, 1-octanol; and varying the feed of the key component, i.e., n-heptane content. To simulate the absorption process, the Aspen-Hysys 8.5 software was used. In the simulation environment, two streams were added: absorbent stream and contaminated gas stream. In the absorbent stream containing alcohol, parameters such as pressure, temperature, and volume were similar to those used in experimental conditions. The stream containing the contaminated gas had the same values of pressure and temperature of those used in experimental conditions; however, the fractions of the components present in this stream were considered as the first point at which the gas, after passing through the liquid absorbent, remained constant in the chromatographic evaluation. These two streams were mixed and sent to a separator vessel (Figure 1). Preliminary simulation results, in steady state mode, indicate the coherence of the proposed approach **(Gomes, 2007)**.

3. RESULTS AND DISCUSSIONS

This section is dedicated to the presentation of the results of heavy species (C5+) absorption with 1-octanol, using a lab scale absorber, or gas saturator, with the aid of an online analysis of the out-let gas (Figure 2). As mentioned, the pilot scale set-up is also considered as a result, and the preliminary experiments just served to confirm the efficiency of the approach. Simulations of the operational curve of absorption provided by a validated thermodynamic model using two-phase flash calculations are also presented.
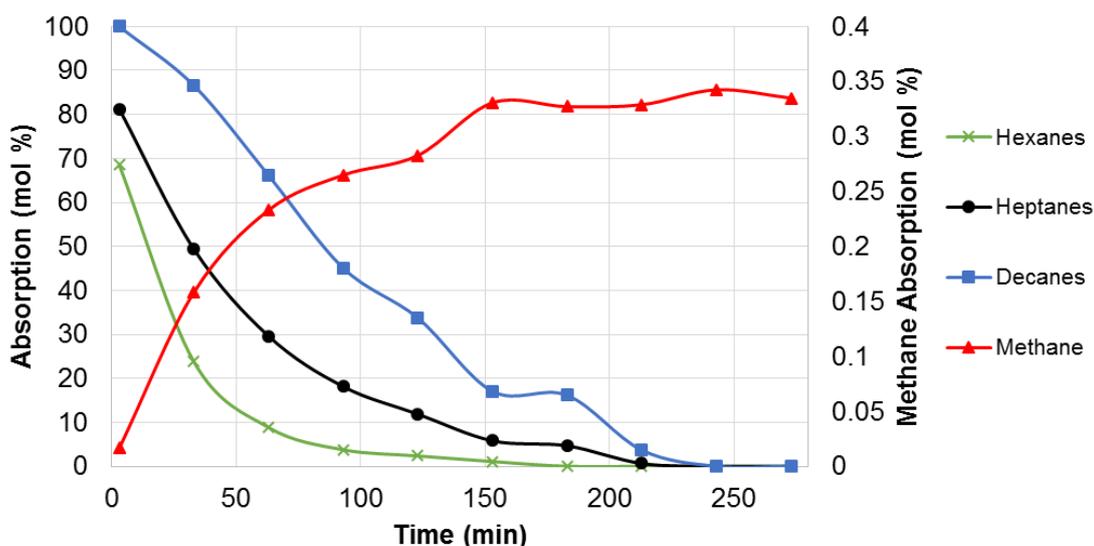

Figure 4. Measurements of absorption of the main species from natural gas at 313.15 K and 1.013 bar; flow rate of gas equal to 50 mL/min and volume of absorbent (1-octanol) of 15mL.

The experiments, carried out in the laboratory scale, allowed the determination of the quantities of each species absorbed along the time in a systematic form. Figure 4 reports the values of absorption of the main species present in the gas during the experiment. Samples were analyzed in-line by gas chromatography using a 30-minute interval. After 300 minutes of experiment, the value of the molar fraction of heptane became constant. Thus, it is concluded that, from that moment on, alcohol could no longer absorb the contaminant. To determine the amount of heptane absorbed into the alcohol, it was taken as a starting position, the point at which no further absorption (300 minutes). Up to 123 minutes, it can be observed a satisfactory absorption of the heavy species (C6, C7, and C10). At this period, it was also observed increasing methane absorption due to the chemical nature change of the solvent mixture. This is another indicative of the need of bed exchange. The factors of absorption and mass transfer coefficients may be determined from these measurements **(Ludwig, 1997; Edmister, 1957, 1943)**. It may be detected that the key solute presents the desirable behavior and, thereby, the content of the treated gas will not exceed the minimum limit of methane index for fuel applications.

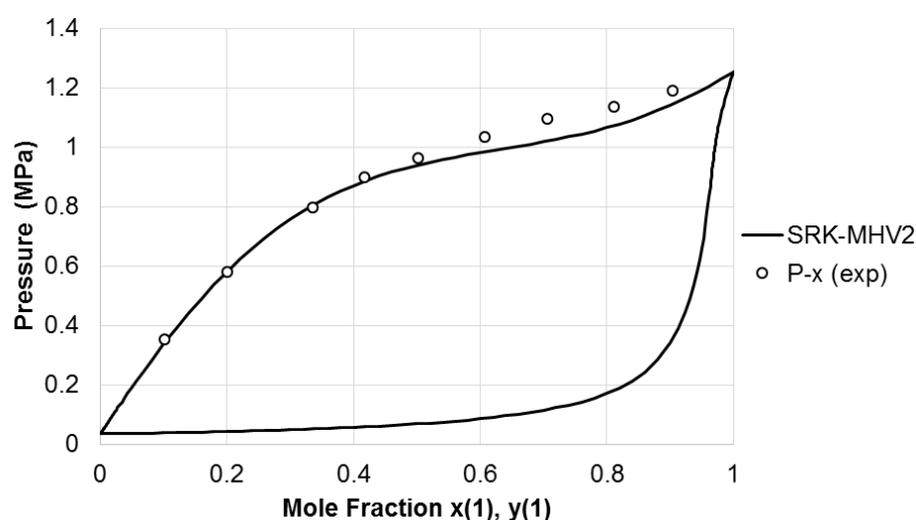Figures 5 and 6 have been prepared to

Figure 5. Diagram P-x,y for n-butane (1) + 1-butanol (2) at 363.15 K using SRK+MHV2 (UNIFAC); experimental data from **Deák et al. (1995)**.
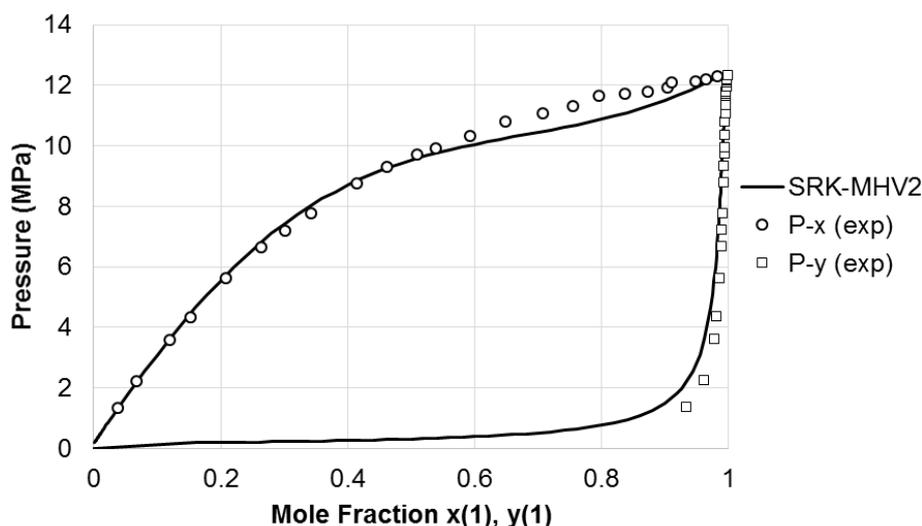

Figure 6. Diagram P-x,y for n-heptane (1) + 1-octanol (2) at 313.15 K using SRK+MHV2 (UNIFAC); experimental data from **Góral et al. (2002)**.
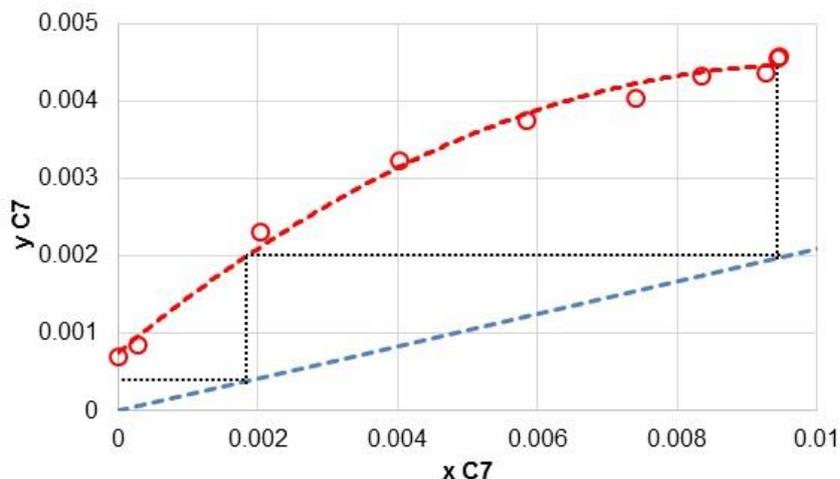
Figure 7. Operational (---) and equilibrium (---) curves for determination of the theoretical stage number in the absorption of n-heptane (key-component) present in a mixture of C1 to C10, using 1-octanol, as solvent at 313.15K and 1.013 bar.

demonstrate the predictability of the SRK+MHV2 EoS for the studied systems using alpha function of Mathias-Copeman **(Chiavone-Filho et al., 2001)** and UNIFAC-Lyngby.

Results of simulation are going to be restricted to the equilibrium curve presented in Figure 7. The operational curve is determined from Figure 4. These diagrams, together with the preliminary absorption measurements, with the pilot scale set-up can demonstrate the efficiency of the proposed approach of one column of absorption followed by a flash tank to regenerate the alcohol, or liquid absorbent. Thus, using n-heptane as key component, it is demonstrated that one or two theoretical stages are enough to proceed with the separation.

4. CONCLUSIONS

The proposed approach to remove C5+ fraction from the natural gas for fuel applications has demonstrated to be simple and efficient. The selection of the solvent, based on the previous simulations, was successful. For this particular system, other chemical species may also be applied and, thus, need this type of verification. The pilot set-up was built and tested. It may be used to describe the pressure effect and sizing evaluations. The measurements carried out in the lab allowed the determination of operational parameters and the feasibility analysis of the process. The

SRK+MHV2-UNIFAC EoS was adequate to describe the equilibrium data for the absorption system. The results of modeling and simulation are helpful for design and analysis of the absorption process of heavy species of natural gas for fuel applications. Equilibrium and operational curves provided a satisfactory estimation of the theoretical stage number required. For the composition range studied, the absorption column must have at least two stages to separate the heptane from the gas. In terms of process efficiency, it may be established between 50 and 75 minutes as an adequate ratio of time for the bed exchange of a single stage absorption column at the specified conditions.

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