



# ChemPor 2023

**14<sup>th</sup> International Chemical and Biological  
Engineering Conference**

**Book of Abstracts**

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This volume contains the extended abstracts presented at the 14<sup>th</sup> International Chemical and Biological Engineering Conference (CHEMPOR 2023), held in Bragança - Portugal, from the 12<sup>th</sup> to the 15<sup>th</sup> of September, 2023.

Instituto Politécnico de Bragança & Ordem dos Engenheiros

**14<sup>th</sup> International Chemical and Biological Engineering  
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(CHEMPOR-2023)**

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Edited by:

Ana Maria Alves Queiroz da Silva  
António Manuel Coelho Lino Peres  
António Manuel Esteves Ribeiro  
Maria Filomena Filipe Barreiro  
Maria Olga de Amorim e Sá Ferreira  
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**Title**

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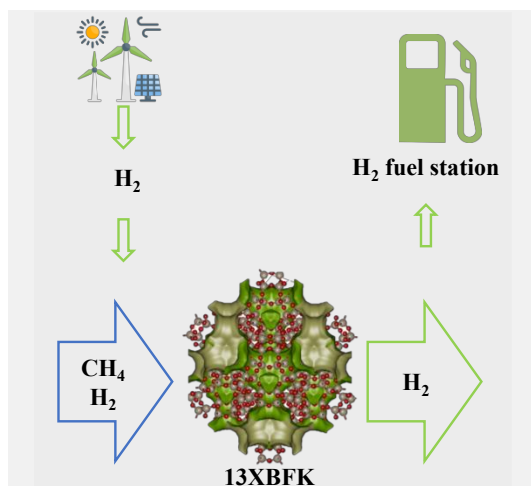


## Green hydrogen recovery from natural gas grids by adsorption process

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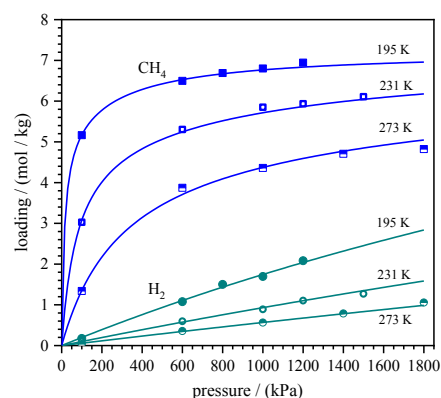
In this work, the binder-free zeolite 13X was tested to purify green hydrogen injected into natural gas grids. Green hydrogen can be a key factor in meeting global energy demand while contributing to climate goals. In this way, breakthrough curve experiments were performed to assess the equilibrium and kinetic adsorption for H<sub>2</sub> and CH<sub>4</sub> in binder-free zeolite 13X. This work covers the lack of adsorption data and multicomponent breakthrough curves of H<sub>2</sub>/CH<sub>4</sub> at low temperatures (until 195 K) which were not available in the literature. The equilibrium data were modeled by using the dual-site Langmuir isotherm model and the multicomponent breakthrough curves were simulated using a mathematical model implemented in MATLAB. Performance parameters based on equilibrium data were discussed. Overall, binder-free zeolite 13X has great potential to separate H<sub>2</sub> from CH<sub>4</sub> based on equilibrium (higher capacity for CH<sub>4</sub> with fast diffusion of both gases).

### Introduction

The Green Hydrogen (GH) produced by water electrolysis from renewable sources of energy (e.g., wind, solar, and hydroelectricity) is free of carbon emissions, which can be a key factor in achieving climate goals [1], since it can replace fossil fuel in the mobility sector, for example (see the Graphical Abstract). As the interest in GH grows, the development of its distribution network is a hot topic in the scientific community. One alternative is to inject GH into the existing natural gas (NG) pipelines, to avoid new infrastructure investments [2-4]. One problem concerning the extraction of GH from NG grids relies on the feed concentration that differs greatly from conventional H<sub>2</sub> purification processes (usually H<sub>2</sub> > 70%). In this case, the GH allowed to be injected into the NG grids is limited to 20%. Thus, to improve the conventional purification process, an adsorbent with an increased adsorption capacity towards CH<sub>4</sub> is needed, compared to the ones available.

### Methods

In this work, the commercial binder-free beads of zeolite 13X (13XBFK) evaluated were kindly provided by Chemiewerk Bad Köstritz GmbH (Germany). The beads of 13XBFK were manufactured through binder-free synthesis, in which the binder is itself transformed into zeolite matter during the hydrothermal reaction [5]. This procedure overcomes the loss in adsorption capacity associated with the binder composite. The adsorption equilibrium for H<sub>2</sub> and CH<sub>4</sub> were obtained through breakthrough curve experiments in a novel cryogenic fixed bed adsorption apparatus specially designed to screen materials at a wide range of temperatures (77 to 333 K) and pressures up to 4000 kPa [6]. The single and multicomponent breakthrough experiments were performed at 195, 231, and 273 K and pressure up to 1800 kPa. Figure 1 shows the equilibrium data for H<sub>2</sub> and CH<sub>4</sub> in 13XBFK and Table 1 summarized isotherm model parameters.

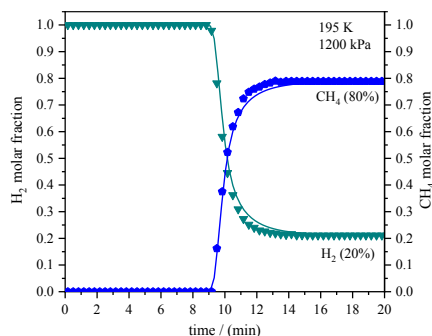


**Figure 1.** Adsorption equilibrium of H<sub>2</sub> and CH<sub>4</sub> on binder-free zeolite 13X. Symbol = experimental; Lines = model.

### Results

According to the adsorption isotherm in Figure 1, the adsorption capacity for CH<sub>4</sub> on 13XBFK is significantly higher than for H<sub>2</sub> at the entire experimental conditions. For example, at 195 K and 100 kPa, the loading obtained for CH<sub>4</sub> is 5.20 mol/kg in contrast with 0.17 mol/kg for H<sub>2</sub>, which results in a selectivity of 30 for CH<sub>4</sub> over H<sub>2</sub>. These results indicate that 13XBFK has excellent potential for the equilibrium separation of H<sub>2</sub> from H<sub>2</sub>/CH<sub>4</sub> by PSA. Lines in Figure 1 show the isotherm model that described very well the experimental data. The loadings of CH<sub>4</sub> were found to be 20% higher in the 13XBFK than the zeolite 13X manufactured by conventional pelletization using inert matter [7]. This result points out an opportunity to reduce the capital and operating costs of an industrial unit. Figure 2 shows the binary breakthrough curve for a mixture of H<sub>2</sub>/CH<sub>4</sub> (20/80%) in the 13XBFK at 195 K and 1200 kPa. This experiment starts with a saturated H<sub>2</sub> column. According to

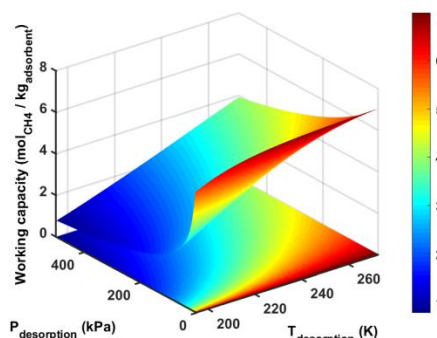
Figure 2, it is possible to obtain an H<sub>2</sub>-rich stream (~100 %) in the column outlet for approximately 9 min, when CH<sub>4</sub> starts to leave the column, confirming the separation performance of 13XBFK. The lines in Figure 2 show the mathematical model results that agree very well with the experimental data. The mathematical model was developed based on the mass and energy balances in a fixed-bed adsorption process and was validated in the previous work [6].



**Figure 2.** Binary breakthrough curve of CH<sub>4</sub>/H<sub>2</sub> on binder-free zeolite 13X at 195 K. Symbol = experimental; Lines = model.

Figure 3 shows the CH<sub>4</sub> working capacity (WC) surface plot estimated taking to account the competitiveness between CH<sub>4</sub> and H<sub>2</sub> to the sites of 13XBFK by the extended dual-site Langmuir isotherm model. The WC is simply the difference between the loading in the adsorption and desorption conditions [8]. For the adsorption condition, it was considered 4000 kPa and 195 K for the mixture ratio of CH<sub>4</sub>/H<sub>2</sub> (80/20%). In the case of desorption, it was considered a wide range of temperature (195 to 273 K) and pressure (5 to 500 kPa) for the same mixture ratio. Regarding the surface plot in Figure 3, the CH<sub>4</sub> WC increases as

desorption temperature increases and desorption pressure decreases, as expected.



**Figure 3.** CH<sub>4</sub> working capacity surface plot for binder-free zeolite 13X.

A maximum WC of 7.00 mol of CH<sub>4</sub> per kg 13XBFK is achieved with 5 kPa and 273 K. Note that the desorption pressure has a major impact on the WC since it changes exponentially the WC whereas the desorption temperature seems to affect the WC linearly. This observation points out that 13XBFK is suitable to be used in the pressure swing adsorption process which works cyclically by changing rapidly the pressure between adsorption and desorption steps to obtain high performance of production and regeneration.

### Conclusions

Overall, this work covers the lack of equilibrium data for CH<sub>4</sub> and H<sub>2</sub> at low temperatures (until 195 K) obtained through breakthrough curve experiments. Moreover, it was shown that the binder-free zeolite 13X has great potential to purify green hydrogen from natural gas pipelines. The data collected and the models developed are now being used to design a pressure swing adsorption process.

**Table 1.** Langmuir isotherm model parameters for CH<sub>4</sub> and H<sub>2</sub> on binder-free zeolite 13X.

Species	qm <sub>1</sub> (mol/kg)	qm <sub>2</sub> (mol/kg)	b <sub>1</sub> (kPa <sup>-1</sup> )	b <sub>2</sub> (kPa <sup>-1</sup> )	ΔH <sub>1</sub> (kJ/mol)	ΔH <sub>2</sub> (kJ/mol)
CH <sub>4</sub>	2.13	5.12	4.10x10 <sup>-3</sup>	8.04x10 <sup>-2</sup>	-16.1	-18.0
H <sub>2</sub>	12.65	-	1.60x10 <sup>-4</sup>	-	-7.00	-

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