

SEPARATION OF SPECIAL GASES BY PRESSURE SWING ADSORPTION

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Abstract

Over the last decades, Pressure Swing Adsorption (PSA) achieved important developments, presenting a reliable alternative to energy-intensive processes, such as cryogenic distillation. Although PSA is widespread in industry, there are still some challenges, namely on the development of adsorbent materials, process optimization, and accurate modeling.

Motivated by the significant increase in demand for high-purity hydrogen for fuel cells, particularly for small/middle-scale and decentralized applications, this thesis targets the enhancement of PSA technology in hydrogen purification. Though, the developments here presented are potentially promising for other types of separations, namely carbon monoxide purification.

A commercial activated carbon (Honeywell UOP 1.6-2.0 mm) was packed in a 4-column vacuum pressure swing adsorption (VPSA) unit for purifying a bioethanol reformat stream to fuel cell hydrogen grade. The adsorption equilibrium isotherms, on this adsorbent, indicate $H_2 \ll CO < CH_4 < CO_2$ adsorption capacities. From a feed mixture containing 70 % H_2 , 25 % CO_2 , 4 % CH_4 , and 1 % CO operating at 9.2 bar, a 99.999 % hydrogen stream was obtained, containing 10.1 ppm of CO and free of CO_2 and CH_4 , with a recovery of 73.2 %. At slightly lower recovery, 70.4 %, a 99.9996 % hydrogen stream was produced containing 4.4 ppm of CO also free of CO_2 and CH_4 . These results meet the requirements for feeding a stationary PEMFC according to ISO 14687-3 (Type I, Grade E), which requires a hydrogen stream containing no more than 10 ppm of CO.

Since CO is often the bottleneck in hydrogen purification, CO-selective adsorbents have the potential to increase hydrogen recovery and reduce CO to sub-ppm levels. Therefore, CO-selective π -complexation adsorbents were prepared from commercial activated carbon pellets (Kuraray 2GA-H2) by conventional wetness impregnation of $CuCl_2 \cdot 2H_2O$. Samples with different copper loadings were prepared and characterized concerning its adsorption behavior for CO, CO_2 , CH_4 , N_2 , and H_2 . The resulting Cu-AC adsorbents showed an enhanced

adsorption capacity for CO, also presenting fast kinetics, excellent reversibility, and high selectivity towards CO over the other gases under study. Cu-AC deactivates when exposed to oxidative atmospheres, but it can be easily reactivated under H₂ at 150 °C.

To attest the Cu-AC performance in hydrogen PSA, a Cu-AC sample with intermediate copper loading (2 mol_{Cu}/kg_{AC}) was selected. Fixed-bed experiments were conducted namely mono- and multi-component breakthroughs. Finally, the adsorbent was tested in a 4-column lab-scale PSA unit for purifying a synthetic reformat mixture of 70 % H₂, 25 % CO₂, 4 % CH₄, and 1 % CO. After optimization, hydrogen with a purity +99.97 % was obtained with a CO content of 0.17 ppm at a recovery of 76.2 %. The results meet the requirements for feeding an automotive PEMFC according to ISO 14687-2 (Type I, Grade D), which requires a hydrogen stream containing no more than 0.2 ppm of CO.

Finally, a PSA simulator with a built-in target-driven PSA optimization methodology was developed. The optimization is based on a self-adaptive cycle time strategy. Following a systematic heuristic, the method allows to simultaneously optimize the cycle time and purge-to-feed ratio. In the case study, a 4-column PSA unit fed with a mixture of 75.0 % H₂ and 25.0 % CO₂ was optimized for obtaining a product with a hydrogen purity above 99.5 %. The method was successfully implemented at different pressures (6 bar, 8 bar, 10 bar, 12 bar, 14 bar, and 16 bar), providing the optimal operating conditions for all the cases. The simulations were validated against experimental results showing always very good agreement. The highest recovery, $\rho_{\text{REC}} = 89.4 \%$, was obtained at the operating conditions of $P = 16 \text{ bar}$; $R_{\text{P/F}} = 0.051$; $t_{\text{AD}} = 612.0 \text{ s}$.

Sumário

Nas últimas décadas, a tecnologia de adsorção com modulação da pressão, comumente designada por PSA (do inglês *Pressure Swing Adsorption*), tem vindo a apresentar avanços significativos, apresentando-se como uma alternativa viável para processos com uma utilização intensiva de energia, como a destilação criogénica. No entanto, embora os processos de PSA sejam amplamente utilizados na indústria, ainda existem alguns desafios, nomeadamente no desenvolvimento de novos materiais adsorventes, estratégias de optimização e modulação.

Motivada pelo o aumento significativo da procura por hidrogénio de alta pureza para pilhas de combustível PEM, o presente trabalho visa o aprimoramento da tecnologia de PSA na purificação de hidrogénio, particularmente para aplicações descentralizadas e de pequena/média escala. Não obstante, os desenvolvimentos aqui apresentados são potencialmente promissores para outros tipos de separações, nomeadamente para a purificação de monóxido de carbono.

No trabalho inicial, uma unidade de VPSA foi empacotada com um carvão ativado comercial (Honeywell UOP 1.6-2.0 mm) com o objetivo de obter hidrogénio com um grau de pureza para pilhas de combustível PEM estacionárias, a partir de uma corrente de reformado de bioetanol. As isotermicas de adsorção neste adsorvente indicam que as capacidades seguem, por ordem crescente: $H_2 \ll CO < CH_4 < CO_2$. A partir de uma mistura composta por 70 % de H_2 , 25 % de CO_2 , 4 % de CH_4 e 1 % de CO, e operando a 9.2 bar, obteve-se hidrogénio com um grau de pureza de 99.999 % a uma recuperação de 73.2 %. A corrente apresentou ainda 10.1 ppm de CO, sendo que nem CO_2 nem CH_4 não foram detectados. A uma recuperação ligeiramente inferior, 70.4 %, foi produzida uma corrente de hidrogénio de 99.9996 %, também livre de CO_2 e CH_4 , mas contendo 4.4 ppm de CO. Os resultados obtidos cumprem os requisitos para alimentação de uma pilha de combustível PEM estacionária, de acordo com a ISO 14687-3 (Tipo I, Grau E), que requer uma corrente de hidrogenio contendo no máximo 10 ppm de CO.

Uma vez que o monóxido de carbono é tipicamente o componente que limita a purificação de hidrogénio, o desenvolvimento de adsorventes seletivos ao CO são de grande relevância. Assim, prepararam-se vários adsorventes de complexação- π seletivos para CO, impregnando *pellets* de carvão ativado comercial com $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. As amostras com diferentes cargas de cobre ($0.5\text{-}5 \text{ mol} \cdot \text{kg}^{-1}$) foram preparadas e caracterizadas quanto ao seu comportamento de adsorção para vários gases, nomeadamente CO, CO_2 , CH_4 , N_2 e H_2 . Os adsorventes resultantes, Cu-AC, mostraram uma capacidade de adsorção aprimorada para o CO, apresentando também uma cinética rápida, excelente reversibilidade e alta seletividade para o CO sobre os outros gases em estudo. Mostrou-se ainda que os adsorventes Cu-AC desativam quando expostos a atmosferas oxidativas, mas podem ser facilmente reativados sob H_2 a 150°C .

Para verificar o desempenho do Cu-AC em PSAs de hidrogénio, selecionou-se uma amostra de Cu-AC com uma concentração intermédia de cobre ($2 \text{ mol}_{\text{Cu}} / \text{kg}_{\text{AC}}$). Foram realizados ensaios de curvas de ruptura para mono- e multicomponente, tendo mostrado uma boa separação. Finalmente, o adsorvente foi testado numa unidade de PSA laboratorial composta por 4 colunas, que foi usada para purificar uma mistura de reformado sintético composta por 70 % H_2 , 25 % CO_2 , 4 % CH_4 e 1 % CO. Após otimização, foi obtido hidrogénio com uma pureza $>99,97\%$, com uma recuperação de 76.2 %, e apresentando um teor de CO de 0.17 ppm. Os resultados obtidos cumprem os requisitos para alimentação de uma pilha de combustível PEM estacionária, de acordo com a ISO 14687-2 (Tipo I, Grau D), que requer uma corrente de hidrogenio contendo no máximo 0.2 ppm de CO.

Finalmente, foi desenvolvido um simulador de PSA com uma metodologia de otimização PSA embutida. A otimização é baseada numa estratégia de tempo de ciclo auto-adaptativo. Seguindo uma heurística, o método permite otimizar simultaneamente o tempo de ciclo e a quantidade de purga. Para validar a estratégia, a unidade de PSA laboratorial de 4 colunas foi utilizada como caso de estudo. Neste caso, considerou-se a alimentação de uma mistura de 75.0 % H_2 e 25.0 % CO_2 , e optimizou-se a unidade para obter hidrogénio com uma pureza $>99.5\%$ a diferentes pressões, nomeadamente 6 bar, 8 bar, 10 bar, 12 bar, 14 bar e 16 bar. Para todos os casos, o método encontrou eficazmente os

melhores parâmetros de operação. As simulações foram validadas contra resultados experimentais mostrando sempre uma excelente concordância. A maior recuperação, $\rho_{\text{REC}} = 89.4 \%$, foi obtida para condições de funcionamento de $P_{\text{H}} = 16 \text{ bar}$; $R_{\text{P/F}} = 0.051$ e $t_{\text{AD}} = 612.0 \text{ s}$.

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Chapter 1. Introduction

1.1. Relevance & Motivation

Hydrogen demand for fuel cell applications has been increasing over the last decade. According to the U.S. Department of Energy, the number of fuel cell systems shipped worldwide per year increased from 10 000 to more than 60 000 units, from 2008 to 2016 [1]. Moreover, the European Commission refers to the hydrogen and fuel cells combination as a reliable strategy for the transition to a sustainable and competitive energy system and has increased the funding for hydrogen applications [2]. Among the fuel cell technologies, hydrogen-fed polymer electrolyte membrane fuel cells (PEMFC) are one of the most promising technologies. Due to their fast start-up time, power-to-weight ratio, and low operation temperature (typically ca. 80 °C), PEMFC are suitable for a wide range of applications, including portable power, distribution generation, and transportation [3]. However, the platinum catalyst used in PEMFC is very sensitive to carbon monoxide poisoning, even at very low concentrations such as 10 ppm, hence the need of using high purity hydrogen [4, 5]. Besides, fuel quality specified by ISO 14687-2 for road vehicles states a hydrogen fuel index of 99.97 %, where the total of hydrocarbons should not exceed 2 ppm and CO should not exceed 0.2 ppm.

Currently, hydrogen is mainly produced from steam methane reforming (SMR) followed by water-gas-shift, producing a stream containing hydrogen, carbon dioxide, methane, and carbon monoxide. Pressure swing adsorption (PSA) is used afterward to achieve the desired hydrogen grade [7]. Although fossil fuels are still the most viable option in the near term, currently representing more than 90 % of the total H₂ production worldwide, great efforts are being made towards the development of alternative sources. Accordingly, hydrogen from zero carbon-emitting sources is expected to play a significant role in mitigating global warming and reducing GHG emissions in the energy sector. This

includes water electrolysis and the use of biomass through biological or thermochemical methods [8]. Additionally, growing research on *in situ* hydrogen production from bio-based hydrocarbons has been observed, including methanol and ethanol steam reforming [9, 10].

Due to the low density of hydrogen, its storage and transportation are long-standing challenges, thus limiting the adoption of hydrogen-based technologies. Different solutions have been put forward for this challenge, including liquefying hydrogen for transportation; injecting hydrogen in the natural gas grid network; or storing hydrogen in liquid organic carriers (LOHC) [11, 12]. Among these, LOHC allows transporting larger quantities of H₂ in trucks and ships, besides enabling long-term storage at reduced costs, which is particularly important in backup and off-grid power applications. In this context, locally produced LOHC such as bioethanol can be also part of the solution, particularly because it can be produced by local communities from waste, including agricultural residues and lignocellulosic biomass, thus promoting circular economy [13].

Apart from hydrolysis, all the processes include the production of a hydrogen stream followed by purification. The typical concentration before purification, either from ethanol, methanol, or methane reforming, after water-gas-shift is 70–80 % H₂, 15–25 % CO₂, 3–6 % CH₄, 1–3 % CO, and trace N₂ (depending on the source) [9, 14, 15]. Hydrogen purification can be performed by different technologies, including cryogenic distillation, amine-based absorption, membrane technology, and pressure swing adsorption[16]. The first two are very energy-intensive and therefore only suitable in very large-scale applications, while membranes and PSA appear as suitable approaches. Membranes have been widely studied over the last decades [17, 18]. For instance, dense palladium membranes and their alloys, such as Pd-Ag, display very high permeabilities and selectivities, allowing to produce high purity hydrogen with recoveries up to 99 % [19]. However, the high price of Pd is an obvious drawback, turning dense Pd-based membranes into an infeasible solution in applications where capital costs play a major role [20]. To address this challenge, many authors started depositing very thin films of Pd-based alloys onto porous ceramic substrates and researching other types of membranes such as carbon molecular sieve membranes, polymeric and polymer-ionic liquid membranes, and also electrochemical hydrogen

pumping [16, 21-23]. Although very promising, further developments are needed to make these membranes reliable cost-competitive for hydrogen purification. Pressure swing adsorption (PSA), on the other hand, is a well-established technology, widely used in industry and consisting of a set of columns packed with an adsorbent and running a well-defined pressure swing cycle. Separation occurs based on the affinity of the gases to the adsorbent material and its molecular sieve characteristics, which are enhanced by the pressure increase; hence the adsorption step is carried out at high pressure while regeneration occurs at atmospheric or vacuum pressure. Thus, if the upstream process operates at high pressure, the PSA unit needs then only a minimal amount of energy to deliver the purified hydrogen at atmospheric pressure. Because only hydrogen impurities are adsorbed, PSA has a clear advantage over other processes, since the size of the adsorption columns is mostly determined by the flow rate of impurities [24].

Although commercial utilization of PSA is widespread, several challenges are still present, namely on the development of materials, process optimization, and accurate modeling. The focus of this thesis is on PSA technology for small-scale hydrogen production, where 4-column units are typically used. Though, the findings of this thesis are also of relevance for other PSA applications, including carbon monoxide separation. A greater emphasis on CO separation is given in Chapter 3. For a better understanding of PSA technology, a brief overview of the fundamentals of adsorption is given in the next section.

1.2. Fundamentals of adsorption

Adsorption is the phenomenon in which the molecules of a fluid (adsorbate), adhere to a solid surface (adsorbent). It occurs when the potential energy of adsorbate-adsorbent interactions equals the work required to bring the adsorbate molecule into the adsorbed state [25]. Depending on the type of interactions, adsorption can be classified as chemisorption or physisorption. Chemisorption involves the formation of chemical bonds between the solid and the adsorbate at specific sites. Thus, it is restricted to the first surface layer of adsorbent and the isosteric heat of adsorption is typically 2-3 times higher than the

latent heat of evaporation [26]. In turn, in physisorption, adsorbate-adsorbent interactions occur through van der Waals and electrostatic interactions, such as polarization, dipole, and quadrupole [24, 27]. Because these types of interactions are weak, physisorption has a low heat of adsorption, 2-3 times lower than the latent heat of evaporation [26]. Physisorption is a fast phenomenon, non-activated and reversible, which make it the desired mechanism in PSA processes, allowing adsorbent-adsorbate interactions to be broken during the pressure swing, and thus avoiding external energy during the regeneration step [24].

Since the adsorption mechanism is strictly related to the adsorbate-adsorbent interactions, it is therefore possible to separate different components of a mixture based on the preferred surface interaction for a particular adsorbate. Accordingly, selecting the proper adsorbent is crucial for an effective separation, where the following aspects should be taken into account:

- Selective adsorption capacity towards the component(s) to be adsorbed;
- Adsorption kinetics;
- The method of adsorbent regeneration – temperature swing, vacuum, pressure swing, or “stripping”;
- Physical and chemical resistance of the adsorbent;
- Moderate cost.

In the end, the role of an adsorbent is to provide the surface area for selective adsorption to take place, hence the use of highly porous materials such as zeolites, carbon molecular sieves, activated carbon, alumina, and silica gel. Most recently, metal-organic-frameworks (MOFs) have shown promising results in a wide range of applications, though applicability toward industrial production still needs a suitable scale-up [28]. Examples of commercial adsorption processes and the corresponding adsorbents are described in Table 1.1. An overview of adsorbents and their applications is given by Yang [29] and Táscon [30].

Table 1.1 – Examples of adsorbents and their current major industrial applications.

Separation	Adsorbent
<i>Gas Bulk Separations</i>	
Normal paraffins/isoparaffins, aromatics	Zeolite
N ₂ /O ₂	Zeolite
O ₂ /N ₂	Carbon molecular sieve
CO, CH ₄ , CO ₂ , N ₂ , Ar, NH ₃ /H ₂	Activated carbon followed by zeolite
NH ₃ /H ₂	Activated carbon, activated alumina [31]
Hydrocarbons/vent streams	Activated carbon
H ₂ O/Ethanol	Zeolite 3A
Chromatographic analytical separations	Wide range of inorganic and polymer resin agents
<i>Gas Purification</i>	
Air drying	Activated alumina, silica gel, zeolite and polymeric adsorbents [32]
CO ₂ /C ₂ H ₄ , natural gas, etc.	Zeolite, carbon molecular sieve
Sulfur compounds/natural gas, H ₂ , liquified petroleum gas, etc.	Zeolite, activated alumina
Indoor air pollutants – VOCs	Activated carbon, silicalite, resins
Hg/chlor-alkali cell gas effluent	Zeolite
<i>Liquid Bulk Separations</i>	
Normal paraffins/isoparaffins, aromatics	Zeolite
<i>p</i> -xylene/ <i>o</i> -xylene, <i>m</i> -xylene	Zeolite
Detergent-range olefins/paraffins	Zeolite
Fructose/glucose	Zeolite
Chromatographic analytical separations	Wide range of inorganic, polymer, and affinity agents

Liquid Purifications

H ₂ /organics, oxygenated organics, halogenated organics, etc., dehydration	Silica, alumina, zeolite, corn grits
Water purification	Activated carbon, silicalite, resins
Sulfur compounds/organics	Zeolite, alumina, others
Decolorizing petroleum fractions, syrups, vegetable oils, etc.	Activated carbon
Drug detoxification in the body	Activated carbon

Adapted from Yang (2003) with minor modifications [29].

1.3. Adsorption equilibrium

Adsorption equilibrium is governed by the principles of thermodynamics and is attained when the rate of adsorption equals the rate of desorption. Adsorption equilibrium is typically presented in the form of the so-called adsorption isotherms – a relationship between the pressure and the amount of adsorbed gas by unit of adsorbent, at a fixed temperature.

The first mathematical model for quantifying adsorption was proposed by Herbert Freundlich, in 1907 [33]. In its study, Freundlich found that the adsorption variation of several adsorbate-adsorbent pairs could be described according to eq.(1.1):

$$q = kP^{\frac{1}{n}} \quad (1.1)$$

where q is the amount of adsorbed fluid mole per unit mass of adsorbent and k and n are empirical constants specific for each adsorbate-adsorbent pair and are temperature dependent. The amount of adsorbed molecules is a function of the partial pressure, which in the case of pure-component adsorption is equivalent to the total pressure, P . The magnitude of the exponent n indicates how favorable the adsorption is. It is generally stated that $n > 1$ represents good adsorption characteristics, while poor adsorption occurs

for $n < 1$ [34]. Although the Freundlich isotherm is widely used given its simplicity and broad applicability, it fails in describing adsorption under high-pressure conditions and does not converge for Henry's Law at very low pressure. Accordingly, the Freundlich isotherm is not thermodynamically consistent [29].

Years later, in 1916, Irving Langmuir proposed a thermodynamically consistent adsorption model based on a kinetic approach. The assumptions were that adsorption is the result of gas condensation and evaporation on a homogeneous solid surface with a limited number of sites so that the maximum adsorption capacity corresponds to the complete coverage of the active sites. A higher adsorbed concentration can only be achieved with additional adsorbed layers; in this case, however, the acting forces are much smaller than those between the solid surface and the adsorbed gas. As a result, a much faster evaporation rate is observed and the adsorbed concentration in the second layer becomes negligible [35]. The Langmuir-type isotherm remains the most widely used for practical applications and is written according to eq. (1.2):

$$q = \frac{q_{\max} bP}{1 + bP} \quad (1.2)$$

where $q_{\max}$ is the maximum concentration in the adsorbed phase corresponding to the complete monolayer coverage, and b is called Langmuir constant calculated according to eq. (1.3):

$$b = b_{\infty} e^{\frac{-\Delta H}{\Re T}} \quad (1.3)$$

where ΔH_i is the isosteric heat of adsorption, $\Re$ is the ideal gas constant, and b_{∞} is the pre-exponential factor of the affinity constant, which is related to the sticking probability and the rate constant of desorption [29]. Contrarily to the Freundlich equation, the Langmuir model approaches Henry's Law for the low-pressure region and the saturation limit at high-pressure. Yet the model does not consider adsorbate-adsorbate interactions, which may affect the accuracy of Langmuir isotherm in some specific cases [36].

To address the heterogeneity of adsorbents, it can be considered that two different sites are available, in which the Langmuir model is valid. This model is known as the Dual-Site Langmuir model, described as follows [35]:

$$q = \frac{q_{\max,1} b_1 P}{1 + b_1 P} + \frac{q_{\max,2} b_2 P}{1 + b_2 P} \quad (1.4)$$

Alternatively, Sips proposed a model combining both Langmuir and Freundlich equations and it is given the following expression:

$$q = \frac{q_{\max} \left(b P^{\frac{1}{n}} \right)}{1 + \left(b P^{\frac{1}{n}} \right)} \quad (1.5)$$

The model circumvents the unlimited rise in adsorption with the pressure increasing associated with the Freundlich model and approaches the monolayer capacity at high pressure. Despite the improvement in accuracy for a wider range of conditions, Sips does not follow Henry's Law due to the reduction to the Freundlich model at very low pressure [36]. To overcome the thermodynamic inconsistency, Toth developed an empirical model that converges against Henry's Law at low pressures, though the similarities with the Sips' equation:

$$q = \frac{q_{\max} b P}{\left[1 + \left(b P^{\frac{1}{n}} \right) \right]^{\frac{1}{n}}} \quad (1.6)$$

It is easy to understand that the Toth equation reduces to the Langmuir equation when $n = 1$. Thus, adsorbent heterogeneity is generally related to values of $n \neq 1$ [37].

The above-mentioned isotherms can be extended for an n -component mixture to address multi-component adsorption. For example, extended Langmuir isotherm can be derived from pure component adsorption according to eq. (1.7):

$$q_i = \frac{q_{i,\max} b_i P_i}{1 + \sum_{i=1}^{nc} b_i P_i} \quad (1.7)$$

where total pressure is now replaced by the partial pressure of the i th component. However, the extended Langmuir model assumes that the area covered by a molecule is not influenced by the presence of other species, and therefore the monolayer amounts are not equal [29]. Although this is not thermodynamically consistent, the model can be widely used for modeling purposes since many adsorption systems, such as PSA, operate under low loading conditions, $q/q_{\max} < 1$.

For predicting multicomponent adsorption equilibrium, one of the most reliable and often-used methods for predicting gas mixture adsorption equilibrium is using the ideal adsorption theory (IAST). Introduced by Myers and Praunsnitz in 1965, IAST uses a classical surface thermodynamic approach assuming an ideal adsorbed solution phase, giving rise to an expression analogous to Raoult's law for vapor-liquid equilibria. To meet the ideal requirement, the spreading pressure at a given temperature must be equal for the different components and no adsorbate-adsorbate interactions can occur. The drawback of the IAST model is the need of solving an implicit equation, only possible to solve numerically. Yet, combining IAST with molecular simulations provides a useful approach to screening the potential of different porous materials for adsorption applications [38].

1.4. Adsorption kinetics

Although equilibrium plays an important role in all adsorption-based processes, separation can be also achieved by other means, namely by steric and kinetic mechanisms. The first one is associated with the sieving concept, where the gas molecules are separated according to their molecular size within the pore structure of a highly porous solid. In this case, only small molecules are accommodated in the adsorbent while larger molecules are completely excluded. In turn, kinetic separation is based on the different diffusion rates of the molecules inside the adsorbent, in which the steric effect is also involved. Thus, the

faster diffusing species can be preferentially removed by controlling the adsorption time [24]. Knowledge in diffusion mechanisms is therefore of great importance, not only in the preparation and characterization of adsorbents but also to select the proper adsorbent for a given separation.

The mass transfer of an adsorbate molecule onto an adsorbent can be divided into 4 stages:

1. External diffusion, corresponding to the diffusion of the adsorbate through the fluid film to the entrance of the pores;
2. Internal diffusion, in which the molecules diffuse throughout the pores;
3. Surface diffusion, corresponding to the mobility of the adsorbate molecules on the surface due to their interaction with the surface;
4. Adsorption/desorption, corresponding to the bonding of the adsorbate in the active sites of the surface.

Under practical conditions, the external film resistance and adsorption are very fast steps when compared to diffusion in the pores. Thus, the rate of adsorption is generally controlled by diffusion limitations, which in turn may be sub-divided in four mechanisms: molecular diffusion; Knudsen diffusion; viscous flow (or Poiseuille flow); and surface diffusion [36]. The combination of the four mechanisms can be interpreted as series of parallel resistances, as shown in Figure 1.1 [39].

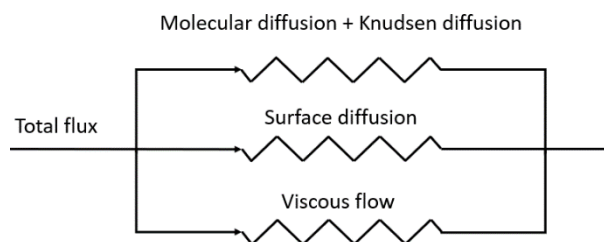


Figure 1.1 – Schematic representation of the four diffusion mechanisms as an analogous circuit of parallel resistances.

The flux resulting from the contribution of the four mechanisms is, therefore:

$$N_{i,\text{Total}} = N_{i,m} + N_{i,K} + N_{i,v} + N_{i,s} \quad (1.8)$$

where $N_{i,m}$ is the flux resulting from molecular diffusion, $N_{i,K}$ is the flux resulting from Knudsen mechanism, $N_{i,v}$ results from viscous flow, and $N_{i,s}$ regards the flux corresponding to surface diffusion. For each mechanism, the flux can be described by Fick's law, which for a spherical particle can be generally described as follows:

$$N_i = -D \frac{\partial C_i}{\partial r} \quad (1.9)$$

where D is the diffusion coefficient and is specific to each mass transfer mechanism.

In pores with substantially larger diameters than the mean free path of the molecules, molecular diffusion is the prevailing mechanism, as sketched in Figure 1.2 [36].

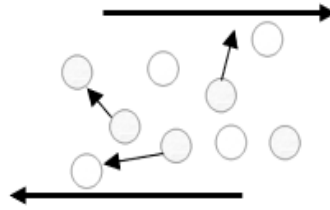


Figure 1.2 – Schematic representation of the molecular diffusion mechanism.

The exerting resistance is resulting from the collisions among molecules of different species, which can be estimated by the Chapman-Enskog correlation:

$$D_{m,i,j} = \frac{0.00158 T^{3/2} \sqrt{(1/M_i + 1/M_j)}}{P \sigma_{i,j}^2 \Omega_{D,ij}} \quad (1.10)$$

where $D_{m,i,j}$ is the binary diffusion coefficient between species i and j expressed in $\text{m}^2 \cdot \text{s}^{-1}$; M is the molecular weight of each species in $\text{g} \cdot \text{mol}^{-1}$; and $\sigma_{i,j}$ is the collision diameter expressed in Angstrom. $\Omega_{D,ij}$ is the collision integral and is a function of ε/KT , where ε is the molecular interaction energy; and K is the Boltzmann constant ($1.38 \times 10^{-23} \text{ m}^2 \cdot \text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1}$) [36].

As the pore diameter decreases, Knudsen diffusion becomes dominant. The collisions of the gas molecules with the pore walls occur at higher frequencies, being instantly adsorbed and re-emitted in a random direction unrelated to the original flow direction, as schematically shown in Figure 1.3 [36].

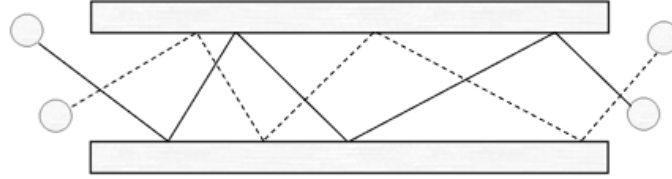


Figure 1.3 – Schematic representation of the Knudsen diffusion mechanism.

The driving force of this mechanism is the concentration gradient and is characterized by the Knudsen diffusion coefficient, D_K , calculated as follows:

$$D_{K,i} = 3.068 \frac{r}{\tau_K} \sqrt{\frac{T}{M_i}} \quad (1.11)$$

where r is the pore radius in m; and τ_K is the pore tortuosity.

In addition to the molecular and Knudsen diffusion, Poiseuille flow may contribute to the adsorbate diffusion. In this case, the driving force is the total pressure inside the pore rather than the concentration gradient (Figure 1.4) [36]. Accordingly, no separation of the species occurs by Poiseuille flow.

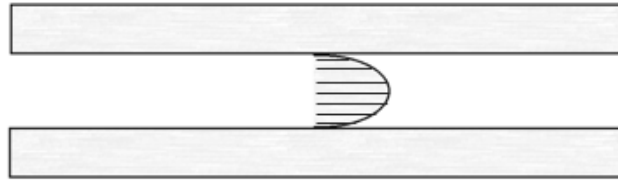


Figure 1.4 – Schematic representation of the viscous flow mechanism.

The equivalent Poiseuille diffusivity is given by eq. (1.12):

$$D_v = \frac{B_0 P}{\mu_{\text{mix}}} \quad (1.12)$$

where μ_{mix} is the viscosity of the mixture; and B_0 is the parameter that characterizes the viscous flow, defined as $B_0 = r^2 / 8$. Following eq. (1.12), it is evident that for larger pores and higher pressures, the viscous flow becomes significant and the flow results from a combination of the Knudsen and viscous flow mechanisms. In PSA systems this mechanism can be particularly important during the pressurization step [40].

Finally, surface diffusion is an activated process where the gas molecules at each site must attain enough energy to hop to the next site (Figure 1.5) [36].

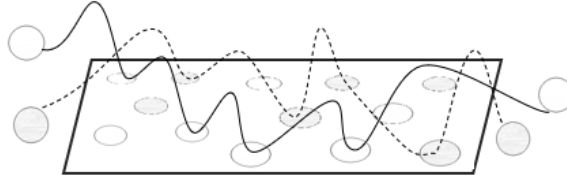


Figure 1.5 – Schematic representation of the surface diffusion mechanism.

The surface diffusivity is then given by the hopping mechanism as follows:

$$D_s = \frac{\delta^2}{4\tau} \quad (1.13)$$

where δ is the distance between adjacent sites. Factor 4 is used for 2-D systems, while for 3-D systems the factor is 6. The average time that a site is occupied is given by τ and is temperature-dependent, according to (1.14):

$$\tau = \tau_0 \exp\left(\frac{E_a}{\mathcal{R}T}\right) \quad (1.14)$$

where E_a is the activation energy needed for the hop. The process resembles micropore diffusion, in which the diffusion of the adsorbate never escapes the force field of the pore wall. However, in micropore diffusion, other factors come into play, namely the steric restrictions, the polarity of both adsorbate and adsorbent, temperature, concentration, etc. [41].

LDF simplification

Whatever the dominant mechanism in the intraparticle mass transfer, the mathematical formulation of the mass transport introduces a differential equation with associated boundary conditions. In the dynamic modeling of an adsorption bed, this must be coupled with the momentum balance and with heat and mass balance equations, thus increasing the complexity of calculations and consequently the computing time. However, for many different boundary conditions, diffusion-controlled kinetics can be simplified using the linear driving force (LDF) approximation, proposed by Glueckauf and Coates [42]. In LDF approximation, the partial differential equation related to diffusion is replaced by an ordinary differential equation, whose mathematical solution is considerably simpler. The original mathematical formulation was derived by Glueckauf from the analytical solution of the diffusion equation [43]. If the change of the surface concentration q_s proceeds as a continuous change (rather than in a step) the average adsorbed concentration is given by:

$$\bar{q} = q_s - \frac{6}{\pi^2} \int_{\theta=0}^{\theta=t} \left(\frac{dq_s}{dt} \right)_{\theta} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left[-n^2 \pi^2 D t / r^2 (t - \theta) \right] d\theta \quad (1.15)$$

and

$$\frac{d\bar{q}}{dt} = 6 \int_{\theta=0}^{\theta=t} \left(\frac{dq_s}{dt} \right)_{\theta} \sum_{n=1}^{\infty} \exp \left[-n^2 \pi^2 D t / r^2 (t - \theta) \right] d\theta \quad (1.16)$$

After adequate integration, the resulting LDF equation can be written as:

$$\frac{d\bar{q}}{dt} = \frac{15D_e}{r_p^2} (q^* - \bar{q}) \quad (1.17)$$

where $\bar{q}$ is the average concentration on the adsorbed phase and q^* is the equilibrium concentration of the adsorbed phase at given pressure and temperature. The LDF approximation provides a reasonable prediction over a wide range of conditions and is commonly used in PSA modeling.

1.5. PSA overview

Pressure swing adsorption is the state of the art for several gas separations. The working principle is the selective adsorption of one or more components of a gas mixture on an adsorbent material packed in two or more beds. PSA involves two main steps: adsorption and desorption. Because adsorption is enhanced by the pressure, the adsorption step is carried out at high pressure. The desorption step is performed afterward by depressurizing the bed. Therefore, the working capacity is given by the difference in loading, q , between two points of the adsorption isotherm, corresponding to the high operating pressure, P_H (adsorption step) and low pressure, P_L (desorption step). The concept of “pressure swing” is sketched in Figure 1.6 [24].

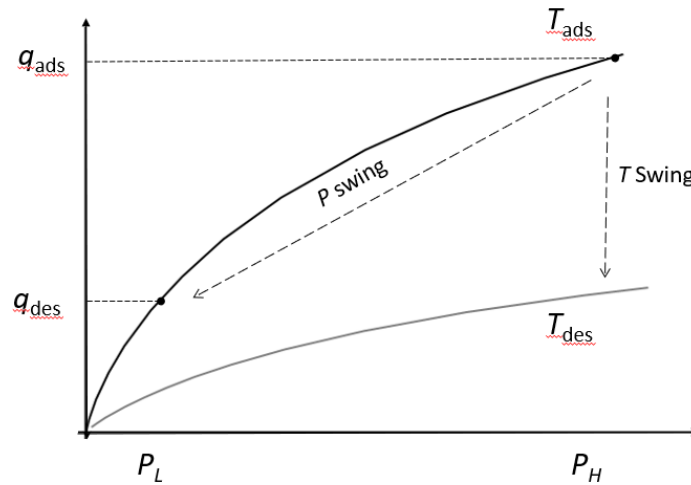


Figure 1.6 – Schematic representation of the pressure and temperature swing concepts in two generic adsorption equilibrium isotherms.

Alternatively, regeneration can be attained by increasing the temperature, where the working capacity results from the different adsorption capacities at different temperatures. In this case, the process is referred to as Temperature Swing Adsorption. Other regenerating methods includes reducing the partial pressure with a purge gas (stripping); through vacuum; or using a combination of those methods [24].

The first use of industrial PSAs was proposed by Charles W. Skarstrom in 1958, in a patent assigned to Esso [44]. The unit consisted of two packed adsorbent beds, as shown schematically in Figure 1.7.

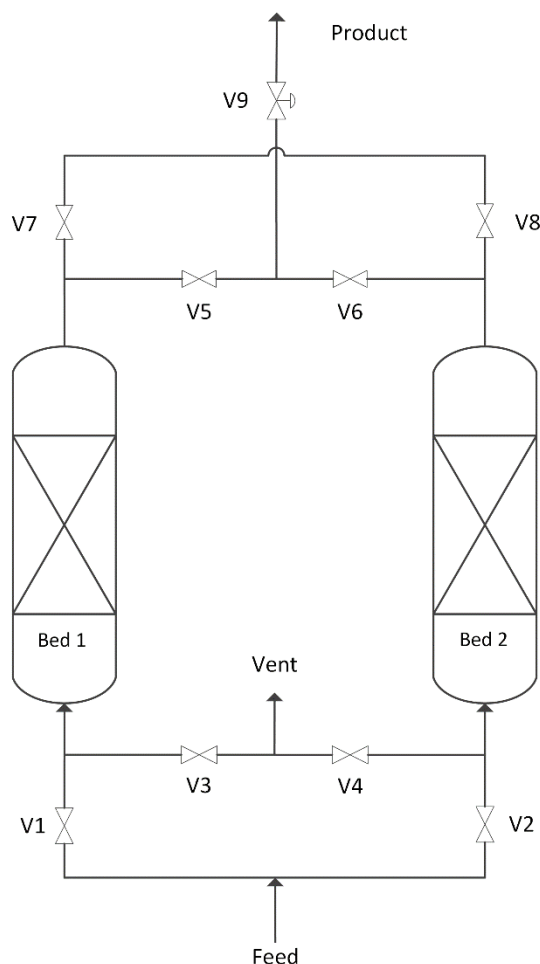


Figure 1.7 – Scheme of the PSA unit patented by Charles W. Skarstrom

During operation, the Skarstrom PSA runs a well-defined pressure swing cycle comprising four steps, namely: pressurization, adsorption, countercurrent blowdown, and countercurrent purge. Both beds undergo throughout the same sequence but are symmetrically phased. Following the operation in bed 1, a PSA undergoes the steps:

1. Pressurization - The mixture is fed to bed 1 through valve V1 and the pressure is elevated to the operating pressure, P_H . During this step, the remaining valves are kept closed.
2. Adsorption - Once the P_H is reached, the product valve V5 opens and the gas flows through bed 1. The more strongly adsorbed species are retained in the adsorbent and the product is enriched in the less adsorbed component. Before the bed is fully saturated (the undesired component reaches the top end of the column), the step is interrupted, thus avoiding the breakthrough of the undesired species;
3. Countercurrent blowdown - Adsorbent regeneration is introduced in this step. The feed and production valves, V1 and V5, are closed and the off-gas valve V3 opens. The working pressure decreases to the low pressure, P_L , (typically ambient pressure), and the off-gas is enriched in the preferred adsorbed component.
4. Countercurrent purge - A fraction of the product stream from bed 2 is used to purge bed 1, completing the regeneration procedure. Valves V7, V8, and V3 are opened and the gas flows from the top of bed 2 to the top of bed 1 and flows counter currently to the bottom end of bed 1. Since the product (from bed 2) is rich in the light component, the partial pressure of the heavier components is reduced, enhancing the adsorbent regeneration.

The Skarstrom cycle was initially designed for air separation and air drying and is still widely used. In the original arrangement, the beds were packed with silica gel, allowing reducing water content from 3800 ppm to < 1 ppm with a recovery of 73 % [44]. This cycle has also proved successful for other separations, including biogas upgrading oxygen enrichment and biogas upgrading [45].

Soon after Skarstrom, Guerin de Mongareuil and Domine, in a patent assigned to Air Liquide, introduced a vacuum step for regenerating the adsorbent, thus referring to the process as vacuum pressure swing adsorption or VPSA [46]. The additional mechanical

energy required for the vacuum pump was compensated by a significant gain in recovery. Using this cycle, oxygen with a purity of 98 % was produced at 51 % recovery vs. 90 % pure oxygen at 10 % recovery in the original Skarstrom cycle [24].

The introduction of a pressure equalization step was proposed by Marsh et al, where the off-gas was stored in a third column instead of blowing down the high-pressure gas during the blowdown step [47]. The objective was to store part of the compressed gas from the saturated bed and use it afterward to purge the same. Since the product purge was partially replaced with off-gas, higher recoveries could be achieved. Years later, Berlin proposed a similar approach, but instead of using the third column, the equalization step was performed connecting the product end of both columns [48]. Besides increasing the recovery, Berlin's modification allowed decreasing the energy consumption of the PSA, since the quantity of compressed gas used to partially pressurize the low-pressure bed was reduced. Figure 1.8 compares the pressure history along the cycle in the original Skarstrom cycle and the modification proposed by Berlin.

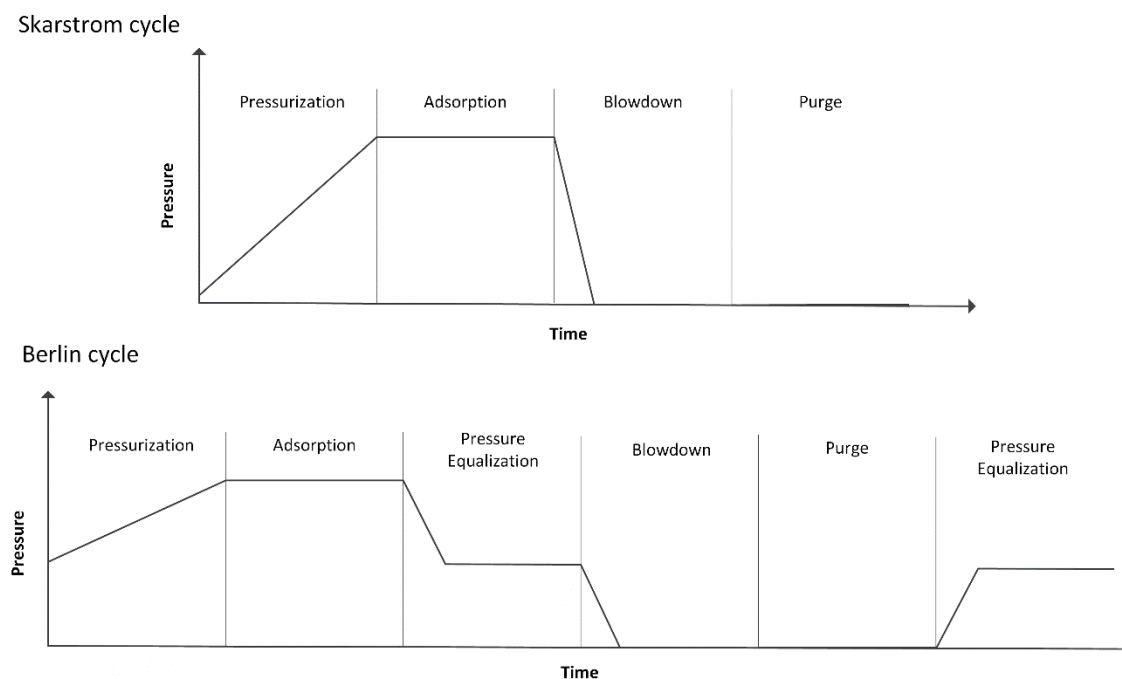


Figure 1.8 - Pressure history along the PSA cycle using Skarstrom cycle and Berlin cycle.

Three different configurations have been proposed to perform the equalization step, namely top-to-top; top-to-bottom, and bottom-to-bottom. However, apart from some cases, it has been experimentally demonstrated that the PSA performs better using a top-to-top configuration [24]. A schematic representation of each arrangement is given in Figure 1.9.

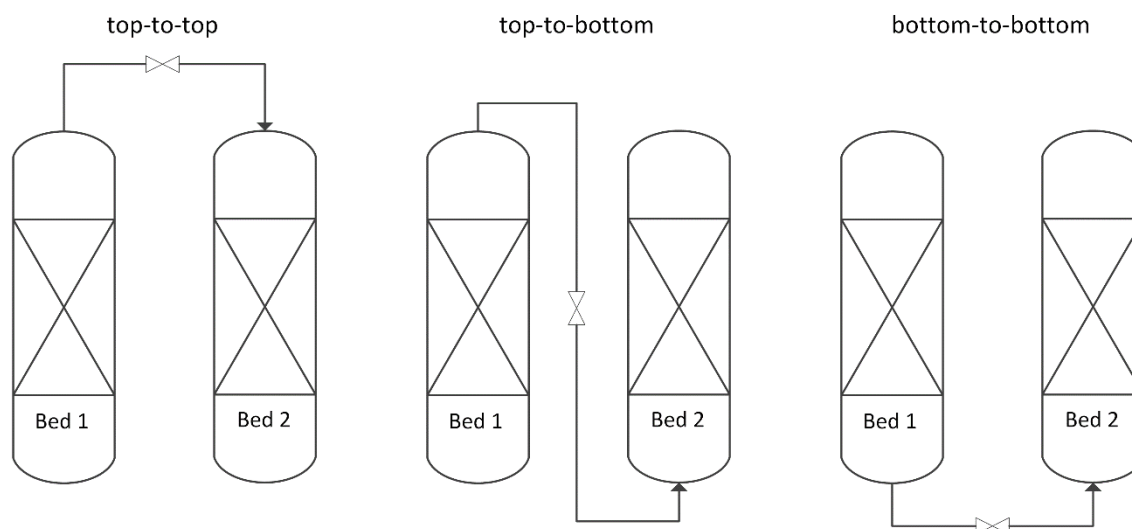


Figure 1.9 – Different configurations proposed for the pressure equalization step: top-to-top, top-to-bottom, and bottom-to-bottom.

In a PSA designed for hydrogen purification, Skarstrom introduced a different approach for bed pressurization: the backfill step [49]. This step involves feeding the column counter-currently using part of the purified gas, thus leading to high product purity and improving the recovery. In addition, the backfill step allows the next producing column to be repressurized before the other bed is dumped, also ensuring continuity in the product pressure and flow. Later on, the backfill step became used in other separations for achieving high purities [50].

Thanks to the growth in research and development, further improvements in PSA technology have been proposed, namely through the design and deployment of new adsorbents, improved cycles, process control, and integrated flow schemes, etc. A quick search in the portal of the World Intellectual Property Organization reveals that more than

4500 families of patents have been published from 1971 up to date [51]. Overall, the objective is to increase the process reliability and performance, while keeping the costs as low as possible.

1.5.1. PSA for hydrogen purification

After the patent from Skarstrom for the recovery of hydrogen from hydrocarbon streams, John L. Wagner proposed a PSA composed of at least four beds for similar applications[52]. Each bed was packed with two layers of adsorbent: the first of activated carbon for selective removal of water and CO₂; and the second of calcium exchanged zeolite A for removing CO and CH₄. The bed arrangement, comprising a valve-skid interconnecting all the columns through separate pipelines, allowed simultaneous interactions between the beds. Blowdown losses were minimized by using the residual gas from the equalization step for purging. From a feed gas containing 77.10 % H₂, 22.50 % CO₂, 0.35 % CO and 0.013 % CH₄, saturated in water, Wagner's PSA was able to deliver hydrogen with a purity higher than 99.9999 %, at a recovery rate of 76.5 %. The process was known as Hysiv PSA and it is the origin of the well-known Polybed™ PSA, from UOP.

With the increasing demand for hydrogen, larger-scale PSAs have been developed. However, since it is not always feasible to enlarge adsorption beds, an increase in the PSA production capacity has mainly been achieved by increasing the number of beds. Nevertheless, thanks to the development of new adsorbents, improved simulation tools, and innovative engineering hardware (e.g. valves), it is now possible to increase the production capacity using the same number of columns, thus decreasing the complexity and reducing the capital costs of the PSA systems. A timeline of the development of PSA technology and hydrogen capacity is given in Figure 1.10. A typical arrangement of today's hydrogen PSAs is illustrated in Figure 1.11. The top of each column is connected to at least 3 pipelines, one for the produced stream, one for pressure equalization, and the other for backfilling. In some configurations, a fourth line can be used, giving the system more

flexibility. At the bottom side, each column is connected to the feed and the offgas lines. Top-to-top is the preferred configuration for pressure equalization.

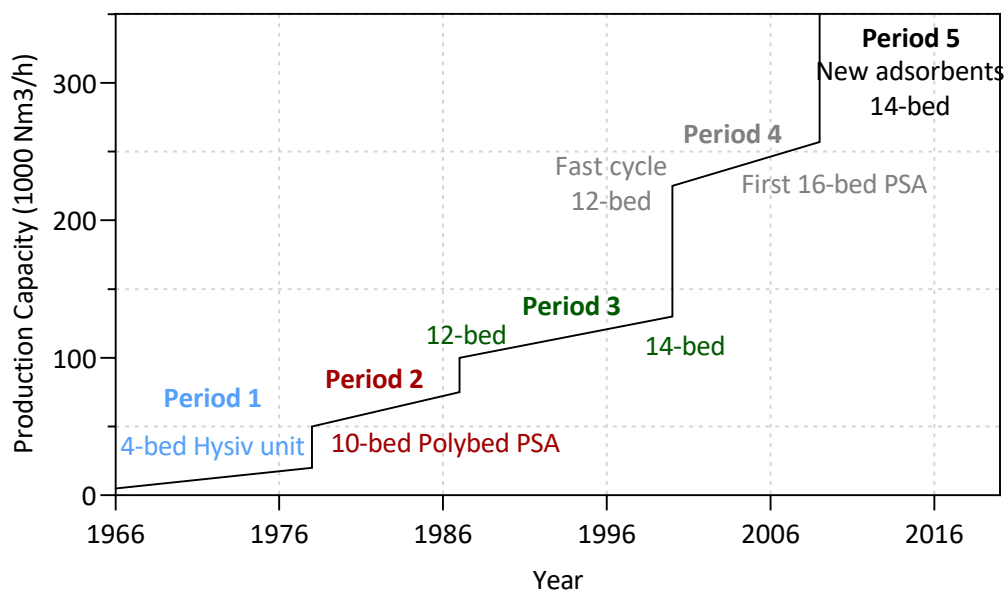


Figure 1.10 – Historical evolution of PSA technology from UOP.

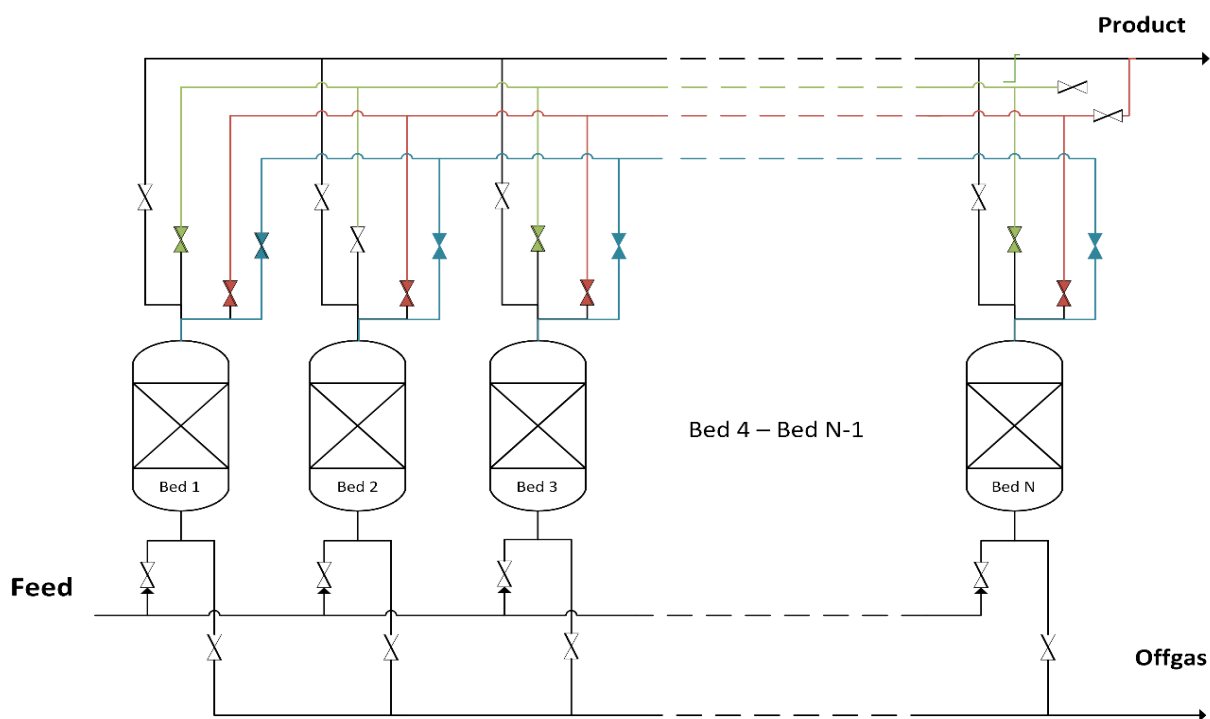


Figure 1.11 – PSA process diagram of an N-bed system.

Despite the additional investment associated with the increased number of beds, additional columns enable extra pressure equalization steps, thereby enhancing the overall recovery due to the lower blowdown losses. An interesting work by Luberti et. al compares different PSA configurations for H₂ production from integrated gasification combined cycle power plants (88.75 % H₂, 2.12 % CO₂, 2.66 % CO, 5.44 % N₂, 1.03 % Ar at 34 bar). Figure 1.12 (adapted from the article) shows a comparison of H₂ purity and recovery at various Polybed PSA systems using a different number of columns and different step configurations [53].

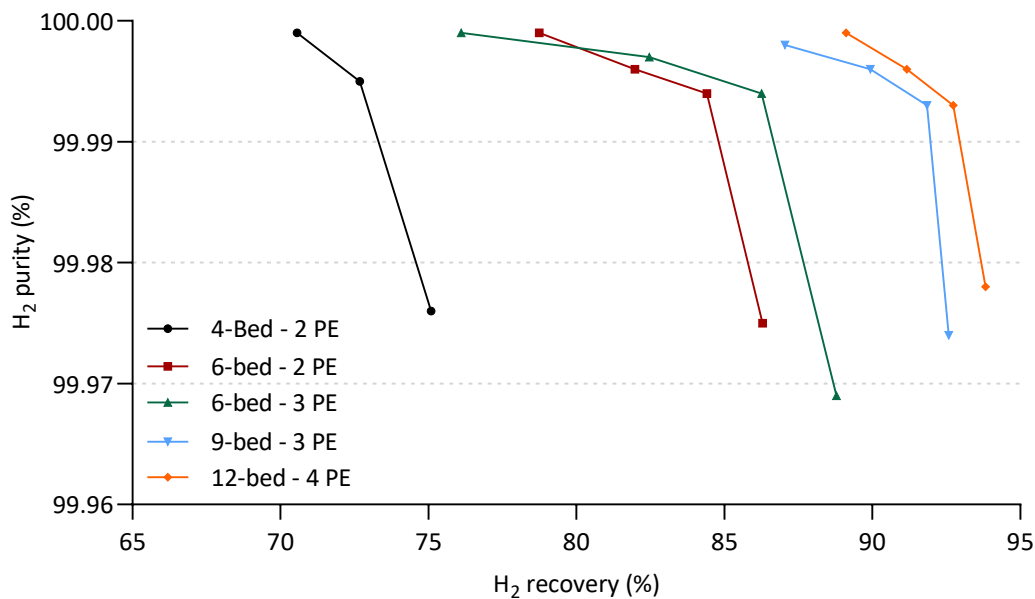


Figure 1.12 – Comparison of hydrogen purity of various PSA systems with a different number of beds and different PE step configurations.

As it can be observed, high-purity hydrogen of 99.999 % with a recovery of 93 % can be achieved. However, when changing from the nine to the twelve-bed system, only a marginal hydrogen recovery is achieved at the expense of a significant increase in the unit costs. Accordingly, selecting the right layout of the PSA system is a compromise between the unit capacity, CAPEX, and hydrogen recovery. This question has been gaining more relevance with the increased interest in decentralized hydrogen production, where the acquisition costs associated with the hydrogen purification system are relevant for the process economics [54].

1.5.2. Hydrogen PSA in small-scale applications

With the implementation of the decentralized “hydrogen economy”, namely for the PEMFCs market, one of the challenges is the scale-down of the PSA units. Four adsorption bed PSA systems are normally used to reduce the capital cost; however, the lower operating pressure and the reduced number of columns give less flexibility for cycle optimization and thus lower recovery values are found, ca. < 70 % [55]. Since this is a fairly new market and PSA is a well-established technology at a large scale, experimental data of small-scale units are scarce. Yet, in recent years, some research-based mainly on simulations has been carried out.

Se-II Yang et al. reported a 4-column PSA unit operating at 8 bar and achieving 99.999 % H₂ with 66 % recovery [56]. Ribeiro et al. reported a dual-layer PSA, with the first one of activated carbon followed by zeolite layer, producing a stream with 99.9958 % H₂ with recovery up to 52.11 %, operating at 7 bar [57]. Delgado et al. reported simulation results using an activated carbon layer combined with zeolite 13X operating at 16 bar, achieving 99.993 % H₂ and 90.3 % recovery; nonetheless, a CO concentration of 63 ppm in the product stream was predicted, which is still far from the PEMFC hydrogen grade [58]. Using the same feed conditions, Agueda et al. simulated a PSA packed with the metal-organic framework UTSA-16, reaching a H₂ purity of 99.999 % H₂ and a recovery of 93 %; however, the commercial supply of MOFs still needs further developments [59]. Golmakani et al. evaluated different methods for purifying hydrogen produced by SMR [60]. To achieve the automotive-grade hydrogen, the highest recovery obtained was 47.5 %, for a H₂ purity of 99.99 % and a CO content of 0.19 ppm. This result was obtained by simulation using a vacuum pressure swing unit operated at 22 bar feed. In a study evaluating the performance of ion-exchanged 13X zeolites, Brea et al. simulated a PSA operating a 9-bed cycle with pressure equalization steps, achieving >99 % hydrogen at a recovery of 69.6 % from a mixture of 76 H₂, 17 % CO₂, 4 % CH₄ and 3 % CO [61].

More recently, some works have expanded the use of PSA to purify industrial off-gases including industrial hydrogen tail-gas PSA and waste hydrogen from ammonia plants. Divekar et al. implemented a 2-bed VSA operating at 2 bar – adsorption pressure; and 0.1

bar – regeneration pressure, enriching H_2 from 25 % to 99 mol %, at a recovery of 80 %, from a mixture of 25 % H_2 , 65 % CO_2 , and balance CH_4 [62]. From a lean hydrogen mixture of 19.9 % H_2 , 0.1 % CO , 44.6 % N_2 , and 35.4 % CO_2 , Park et al. showed that a series of three- and four-bed PSA operating at 10 bar could produce H_2 with >99 % purity and a recovery of 62.5 % and 82.6 %, respectively [63]. However, when only a single stage is used, H_2 purity is limited to 94.6–98.3 %, mostly due to the presence of N_2 . In turn, Yáñez et al. were able to purify hydrogen from ammonia purge gas up to 99.25 % and 99.97 % of H_2 , with a recovery of 75.3 % and 55.5 %, respectively [64]. This work was performed using the same unit used in this thesis and had a great contribution from the author.

As it can be observed from the above-mentioned studies, small-scale H_2 PSAs are not able to attain very high recoveries, particularly when the objective is to produce fuel cell grade hydrogen. Typically, carbon monoxide is the component that limits higher recoveries, though nitrogen is also difficult to remove. Moreover, most of the studies are based on simulation only, lacking experimental validation. In addition, further challenges in PSA technology regards reliable simulation and optimization strategies, which will be deeper analyzed in Chapter 5.

1.6. Objectives and outline

The main purpose of this work is to improve hydrogen PSAs for small/middle-scale applications. Such units have gained particular interest with the increase of new decentralized systems where hydrogen is produced from alternative sources including biomass, solid-waste residues, ammonia decomposition, biogas, etc. The trigger point was the author's involvement in the EU Project "PEMBeyond", where a small-scale PSA was needed to purify hydrogen from an ethanol reformer to deliver fuel cell grade hydrogen for backup and off-grid applications.

The work was mainly developed at LEPABE, a research unit of the Faculty of Engineering of the University of Porto.

Chapter 1 framed the basics of adsorption and gives a historical review of PSA technology.

In Chapter 2, a commercial 4-bed hydrogen PSA prototype was adapted to operate in VPSA mode, aiming to produce stationary fuel cell grade hydrogen (ISO 14687-3: Type I, Grade E) from an ethanol reformat stream containing 70 % H₂, 25 % CO₂, 4 % CH₄, and 1 % CO. The PSA/VPSA was optimized following an experimental design of experiments approach. The experiments were performed at VTT Technical Research Centre of Finland, under the scope of the PEMBeyond project.

Chapter 3 addresses the development of a series of CO-selective adsorbents, Cu-AC, prepared by wetness impregnation of CuCl₂·H₂O onto commercial activated carbon pellets. Different samples with different loadings were prepared and the resulting adsorbents were characterized concerning their adsorption behavior for CO, CO₂, CH₄, N₂, and H₂, namely through adsorption equilibrium isotherms and adsorption kinetics. In addition, a deactivation study under oxidative atmospheres was also performed to evaluate the adsorbents' deactivation and regenerability.

In Chapter 4, a Cu-AC was packed in a 4-bed lab-scale hydrogen PSA to assess its performance under practical conditions. The unit was optimized following a design of experiments approach, targeting the automotive PEM fuel cells (ISO 14687-2: Type I, Grade D).

Chapter 5 describes a target-driven PSA optimization strategy built-in a simulator developed for the purpose. A stream composed of 75 % H₂ and 25 % CO₂ was used as a case study and the simulation results were experimentally validated using the 4-bed lab-scale PSA unit.

Finally, Chapter 6 summarizes the main conclusions of this work and provides suggestions for future work.

1.7. References

1. Efficiency, U.S.D.o.E.O.o.E., et al., *Fuel Cell Technologies Market Report 2016*. 2016: United States. Department of Energy. Office of Energy Efficiency and Renewable Energy.
2. Melideo, D., R. Ortiz-Cebolla, and E. Weidner, *Life Cycle Assessment of Hydrogen and Fuel Cell Technologies*. JCR Joint Research Centre: Brussels, Belgium, 2020.
3. Wang, S. and S.P. Jiang, *Prospects of fuel cell technologies*. National Science Review, 2017. **4**(2): p. 163-166.
4. Stolten, D., R.C. Samsun, and N. Garland, *Fuel Cells: Data, Facts, and Figures*. 2016: John Wiley & Sons. 22 - 29.
5. Kunusch, C., P. Puleston, and M. Mayosky, *Sliding-Mode control of PEM fuel cells*. 2012: Springer Science & Business Media.
6. Standardization, I.O.f., *Hydrogen fuel–product specification–Part 2: proton exchange membrane (PEM) fuel cell applications for road vehicles*. ISO/TS, 2012: p. 14687-2.
7. Hosseini, S.E. and M.A. Wahid, *Hydrogen production from renewable and sustainable energy resources: Promising green energy carrier for clean development*. Renewable and Sustainable Energy Reviews, 2016. **57**: p. 850-866.
8. Nikolaidis, P. and A. Poullikkas, *A comparative overview of hydrogen production processes*. Renewable and sustainable energy reviews, 2017. **67**: p. 597-611.
9. Iulianelli, A., et al., *Methanol steam reforming for hydrogen generation via conventional and membrane reactors: A review*. Renewable and Sustainable Energy Reviews, 2014. **29**: p. 355-368.
10. Contreras, J., et al., *Catalysts for H₂ production using the ethanol steam reforming (a review)*. International journal of hydrogen energy, 2014. **39**(33): p. 18835-18853.
11. Niermann, M., et al., *Liquid Organic Hydrogen Carriers and alternatives for international transport of renewable hydrogen*. Renewable and Sustainable Energy Reviews, 2021. **135**: p. 110171.

12. Modisha, P.M., et al., *The prospect of hydrogen storage using liquid organic hydrogen carriers*. Energy & fuels, 2019. **33**(4): p. 2778-2796.
13. Liguori, R. and V. Faraco, *Biological processes for advancing lignocellulosic waste biorefinery by advocating circular economy*. Bioresource technology, 2016. **215**: p. 13-20.
14. Chen, C.-C., et al., *Hydrogen production and carbon dioxide enrichment from ethanol steam reforming followed by water gas shift reaction*. Journal of Cleaner Production, 2017. **162**: p. 1430-1441.
15. Sircar, S. and T. Golden, *Purification of hydrogen by pressure swing adsorption*. Separation Science and Technology, 2000. **35**(5): p. 667-687.
16. Bernardo, G., et al., *Recent advances in membrane technologies for hydrogen purification*. International Journal of Hydrogen Energy, 2020. **45**(12): p. 7313-7338.
17. Ritter, J.A. and A.D. Ebner, *State-of-the-art adsorption and membrane separation processes for hydrogen production in the chemical and petrochemical industries*. Separation Science and Technology, 2007. **42**(6): p. 1123-1193.
18. Cardoso, S.P., et al., *Inorganic membranes for hydrogen separation*. Separation & Purification Reviews, 2018. **47**(3): p. 229-266.
19. Grashoff, G., C. Pilkington, and C. Corti, *The purification of hydrogen*. Platinum Metals Review, 1983. **27**(4): p. 157-169.
20. Al-Mufachi, N., N. Rees, and R. Steinberger-Wilkens, *Hydrogen selective membranes: A review of palladium-based dense metal membranes*. Renewable and Sustainable Energy Reviews, 2015. **47**: p. 540-551.
21. Fasolin, S., et al., *Hydrogen separation by thin vanadium-based multi-layered membranes*. International Journal of Hydrogen Energy, 2018. **43**(6): p. 3235-3243.
22. Fernandez, E., et al., *Preparation and characterization of metallic supported thin Pd–Ag membranes for hydrogen separation*. Chemical Engineering Journal, 2016. **305**: p. 182-190.

23. Zarca, G., et al., *Synthesis and gas separation properties of poly (ionic liquid)-ionic liquid composite membranes containing a copper salt*. Journal of Membrane Science, 2016. **515**: p. 109-114.
24. Ruthven, D.M. and F. Pressure, *Pressure Swing Adsorption*. New York: VCH Publishers. Vol. 1. 1994. 352.
25. Yang, R.T., *Adsorbents: fundamentals and applications*. 2003, John Wiley & Sons. Chap. 2 - Fundamental factors for designing adsorbent.
26. Ruthven, D.M., *Principles of adsorption and adsorption processes*. 1984, John Wiley & Sons. Chap. 11. p. 338.
27. Ruthven, D.M. and F. Pressure, *Pressure Swing Adsorption*, in *Pressure Swing Adsorption*. 1994. Chap. 2 - Fundamentals of Adsorption.
28. Firmino, A.D., et al., *Synthesis of MOFs at the Industrial Scale*. Metal-Organic Frameworks: Applications in Separations and Catalysis, 2018: p. 57-80.
29. Yang, R.T., *Adsorbents: fundamentals and applications*. 2003: John Wiley & Sons. 191-230.
30. Tascón, J.M., *Novel carbon adsorbents*. 2012: Elsevier.
31. CHO, S.-H., K.-T. CHUE, and J.-N. KIM, *A two stage PSA for argon and hydrogen recovery from ammonia purge gas*. Chemical Engineering Communications, 1998. **163**(1): p. 97-109.
32. Knaebel, K.S. *Adsorbent selection*. 2002. **6**.
33. Freundlich, H., *Über die adsorption in lösungen*. Zeitschrift für physikalische Chemie, 1907. **57**(1): p. 385-470.
34. Húmpola, P., et al., *Thermodynamic analysis of adsorption models of phenol in liquid phase on different activated carbons*. Journal of the Chilean Chemical Society, 2013. **58**(1): p. 1541-1544.
35. Swenson, H. and N.P. Stadie, *Langmuir's theory of adsorption: A centennial review*. Langmuir, 2019. **35**(16): p. 5409-5426.
36. Do, D.D., *Adsorption analysis: equilibria and kinetics*. Vol. 2. 1998: Imperial college press London.

37. Al-Ghouti, M.A. and D.A. Da'ana, *Guidelines for the use and interpretation of adsorption isotherm models: A review*. Journal of hazardous materials, 2020. **393**: p. 122383.
38. Walton, K.S. and D.S. Sholl, *Predicting multicomponent adsorption: 50 years of the ideal adsorbed solution theory*. AIChE Journal, 2015. **61**(9): p. 2757-2762.
39. Phattaranawik, J., R. Jiratananon, and A. Fane, *Effect of pore size distribution and air flux on mass transport in direct contact membrane distillation*. Journal of Membrane Science, 2003. **215**(1-2): p. 75-85.
40. Ruthven, D.M. and F. Pressure, *Pressure Swing Adsorption*. New York: VCH Publishers. Vol. 1. 1994. 235.
41. Yang, R.T., *Gas separation by adsorption processes*. Vol. 1. 1997: World Scientific.
42. Glueckauf, E. and J. Coates, *241. Theory of chromatography. Part IV. The influence of incomplete equilibrium on the front boundary of chromatograms and on the effectiveness of separation*. Journal of the Chemical Society (Resumed), 1947: p. 1315-1321.
43. Glueckauf, E., *Theory of chromatography. Part 10. —Formulæ for diffusion into spheres and their application to chromatography*. Transactions of the Faraday Society, 1955. **51**: p. 1540-1551.
44. Skarstrom, C.W., *Method and apparatus for fractionating gaseous mixtures by adsorption*. 1960, Esso Research and Engineering Co: USA.
45. Grande, C.A., *Biogas upgrading by pressure swing adsorption*. Biofuel's engineering process technology, 2011: p. 65-84.
46. De, M.P.G. and D. Daniel, *Process for separating a binary gaseous mixture by adsorption*. 1964, US3155468A, Air Liquid SA.
47. Marsh, W.D., et al., *Pressure equalization depressuring in heatless adsorption*. 1964, Esso Research and Engineering Co: USA.
48. Berlin, N.H., *Method for providing an oxygen-enriched environment*. 1966, US3280536A, ExxonMobil Research and Engineering Co.
49. Skarstrom, C.W., *Process for the recovery of hydrogen from hydrocarbon gas streams*. 1963, Esso Research and Engineering Co: USA.

50. Liow, J.L. and C. Kenney, *The backfill cycle of the pressure swing adsorption process*. AIChE journal, 1990. **36**(1): p. 53-65.
51. Organization, W.I.P. 05-07-2021 [cited 2021 02-07-2021]; Available from: <https://patentscope.wipo.int/search/en/result.jsf? vid=P22-KQPV2E-49019>.
52. Wagner, J.L., *Selective adsorption process*. 1969, Union Carbide Corporation: USA.
53. Luberti, M., et al., *Design of a H₂ PSA for cogeneration of ultrapure hydrogen and power at an advanced integrated gasification combined cycle with pre-combustion capture*. Adsorption, 2014. **20**(2-3): p. 511-524.
54. Taibi, E., et al., *Hydrogen from renewable power: Technology outlook for the energy transition*. 2018.
55. Hellas, F.f.R.a.T., *Final Report Summary - HY2SEPS-2 (Hybrid Membrane–Pressure Swing Adsorption (PSA) Hydrogen Purification Systems)*. 2015.
56. Yang, S.-I., et al., *Hydrogen separation by multi-bed pressure swing adsorption of synthesis gas*. Adsorption, 2008. **14**(4-5): p. 583-590.
57. Ribeiro, A.M., et al., *A parametric study of layered bed PSA for hydrogen purification*. Chemical Engineering Science, 2008. **63**(21): p. 5258-5273.
58. Delgado, J.A., et al., *Adsorption and diffusion of H₂, CO, CH₄, and CO₂ in BPL activated carbon and 13X zeolite: evaluation of performance in pressure swing adsorption hydrogen purification by simulation*. Industrial & Engineering Chemistry Research, 2014. **53**(40): p. 15414-15426.
59. Agueda, V.I., et al., *Adsorption and diffusion of H₂, N₂, CO, CH₄ and CO₂ in UTSA-16 metal-organic framework extrudates*. Chemical Engineering Science, 2015. **124**: p. 159-169.
60. Golmakani, A., S. Fatemi, and J. Tamnanloo, *Investigating PSA, VSA, and TSA methods in SMR unit of refineries for hydrogen production with fuel cell specification*. Separation and Purification Technology, 2017. **176**: p. 73-91.
61. Brea, P., et al., *Multicomponent adsorption of H₂, CH₄, CO and CO₂ in zeolites NaX, CaX and MgX. Evaluation of performance in PSA cycles for hydrogen purification*. Microporous and Mesoporous Materials, 2019. **286**: p. 187-198.

62. Divekar, S., et al., *Recovery of hydrogen and carbon dioxide from hydrogen PSA tail gas by vacuum swing adsorption*. Separation and Purification Technology, 2021. **254**: p. 117113.
63. Park, Y., et al., *Parallel and series multi-bed pressure swing adsorption processes for H₂ recovery from a lean hydrogen mixture*. Chemical Engineering Journal, 2021. **408**: p. 127299.
64. Yáñez, M., et al., *PSA purification of waste hydrogen from ammonia plants to fuel cell grade*. Separation and Purification Technology, 2020. **240**: p. 116334.

Chapter 2. Hydrogen Purification by PSA and VPSA from a bioethanol reformat stream

2.1. Introduction

Backup and off-grid power generation holds a very promising market for hydrogen fuel cells. In comparison to the commonly used diesel generators, fuel cells can provide power at lower maintenance costs, lower total cost of ownership, and operate almost silently, which represents a clear benefit in areas where low level of noise is required [1, 2]. Fuel cells must be fed with high purity hydrogen, particularly in the case of PEMFC, whose platinum catalyst is very susceptible to poisoning in the presence of trace levels of carbon monoxide, ammonia, hydrogen sulphide, among others.

Apart from electrolysis, hydrogen is produced from hydrocarbons, where the produced stream typically contains 70–80 % H₂, 15–25 % CO₂, 3–6 % CH₄, 1–3 % CO, and trace N₂ (depending on the source). Therefore, a purification step is always necessary, commonly using PSA.

In large-scale applications, PSA units with up to 16 columns are commonly used achieving a purity up to 99.999 % with more than 90 % of recovery [3]. On the other hand, in decentralized systems and for small-scale applications, hydrogen recovery is lower owing to the lower feed pressure (ca. < 10 bar) and the smaller number of adsorption columns, typically four.[4] Furthermore, when the objective is to produce automotive-grade hydrogen (ISO 14687-2)[5], the recovery of these units can decrease down to 50-76 %[6], mainly due to the low capacity of commercially available adsorbents to carbon monoxide, which must be removed down to 0.2 ppm. A common strategy to increase the recovery of

PSA systems is to install a vacuum pump on the off-gas side [7-10]. Several studies showed that vacuum regeneration helps to improve the adsorbent productivity, increasing both product recovery and purity [11-15]. Golmankani et al. compared the performance of VPSA, PSA, and temperature swing adsorption (TSA) systems for hydrogen purification from methane steam reforming off-gas stream and obtained a recovery of 16.2 % and 47.5 % respectively for the PSA and VPSA units; the TSA reached a recovery of 46.5 % but displayed higher energy consumption and the low productivity [11]. The same conclusions were drawn by Marcoberardino et al. who obtained a recovery of 39 %, using a PSA unit, and of 61 % using a VPSA [12]. Although higher recoveries are found in literature for similar separations, these two works prove the great potential of VPSA to increase the hydrogen recovery [16-18]. Yet there is a lack of comparative studies between these two approaches in a real context.

The present work deals with the purification of an ethanol fuel processor off-gas containing 70 % H₂, 25 % CO₂, 4 % CH₄, and 1 % CO by PSA and VPSA, to produce fuel cell grade hydrogen. Depending on the reformer feedstock traces of N₂ can be found in the reformat stream but are not likely to occur in this specific case (bioethanol reforming) [19]. Thus, a PSA unit packed with a commercial activated carbon was optimized to obtain fuel cell grade hydrogen based on an ethanol reformat stream. The PSA was operated in VPSA mode, and the performance was evaluated in terms of hydrogen recovery and carbon monoxide content. According to ISO 14687-3 (Type I, Grade E), which sets the hydrogen requirements for stationary applications, the maximum allowable CO content was defined as 10 ppm.

2.2. Experimental

2.2.1. Adsorbent characterization

The adsorption isotherms of H₂, CO₂, CH₄, and CO on activated carbon (AC, Honeywell UOP) at 30, 40, and 50 °C and up to 7 bar were obtained. The isotherms were obtained using a volumetric method setup described elsewhere and shown in Appendix B.1.1 [20]. The

parameters of the dual-site Langmuir model, given by Eq. (1), were fitted to the experimental data.

$$q_i = \frac{q_{\max,1} b_1 P_i}{1 + b_1 P_i} + \frac{q_{\max,2} b_2 P_i}{1 + b_2 P_i} \quad (2.1)$$

where q_i is the adsorption concentration of component i at partial pressure P_i , $q_{\max}$ is the saturated adsorption concentration and b is the affinity constant. The heat of adsorption of each site, ΔH_1 and ΔH_2 , were calculated according to eqs. (2) and (3), respectively, where b_∞ is the pre-exponential factor of the affinity constant.

$$b_1 = b_{\infty,1} e^{-\Delta H_1 / RT} \quad (2.2)$$

$$b_2 = b_{\infty,2} e^{-\Delta H_2 / RT} \quad (2.3)$$

Before adsorption measurements, the structural density of the AC was assessed by helium pycnometry using the same setup.

2.2.2. PSA experiments

A 4-column PSA prototype packed with a commercial activated carbon (AC) from UOP (1.6-2.0 mm) was operated following either a PSA or VPSA cycles. Each column has a length of 50 cm with an inner diameter of 7 cm and a Programmable Logic Controller (PLC) controls a set of 19 solenoid valves according to the PSA cycle (Table 2.1). At the top end of each column two valves are placed, a proportional valve in the product line and an on-off valve in the equalization line, both using a solenoid actuator. Additionally, a valve in the product line (common to all columns) controls the product flow rate according to the pressure setpoint. At the bottom end, each column is connected to two on-off valves, one for feeding the column and one for the off-gas. A 30 W vacuum pump GD Thomas 118ZC20/24 was installed in the off-gas outlet in parallel with a 69 mbar check valve (Swagelok SS-6C-1) allowing to operate also in VPSA mode. A 20-liter tank was placed in the feed line to minimize pressure fluctuations, while a synthetic reformat gas mixture of hydrogen (70 %),

carbon dioxide (25 %), methane (4 %) and carbon monoxide (1 %) was prepared using Bronkhorst mass flow controllers (series F201 and F202) to feed the PSA unit. The feed composition was based on the outlet composition of the bioethanol fuel processor used in the PEMBeyond project [19]. The feed gas was analyzed using a gas chromatograph Agilent 490 Micro GC, while a Hewlett Packard 5890 equipped with a methanizer and a FID detector was used to analyze the product composition. A sketch of the entire system is given in Figure 2.1.

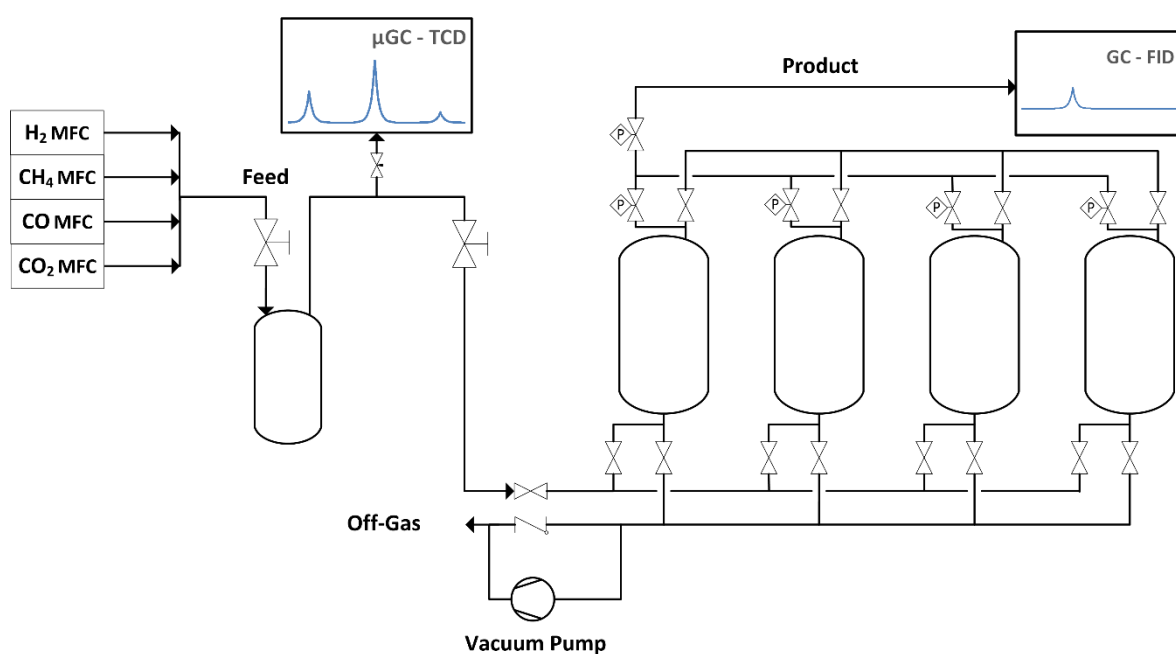


Figure 2.1 – Schematic representation of the PSA unit and auxiliary equipment.

During the PSA cycle, each column undergoes 8 steps, in the following order:

- adsorption (AD) at high pressure, P_H ;
- adsorption/providing backfill (AD/BF), where part of the produced gas is split into two streams: one for product tank and one for repressurizing another column (backfilling);
- co-current depressurization pressure equalization (DPE);

- providing purge (PP), where the remaining gas of the column, at mid-range pressure, is used for purging. The step ends when the P decreases down to the setpoint, P_{PP} ;
- blowdown (BD), where the column depressurizes to atmospheric pressure
- purge (PG), where the gas from PP column flow counter-current to displace the contaminants;
- counter-current pressurization pressure equalization (PPE);
- backfill (BF), or pressurization, using part of the purified H_2 ;

When operating in VPSA mode, an evacuation step (EV) takes place after the blowdown with $P_L = 0.4$ bar for improving the regeneration of the adsorbent. A typical pressure history along the cycle for both PSA and VPSA operating modes is presented in Figure 2.2. The cycle sequence is given in Table 2.1.

Table 2.1 – Sequence of the PSA/VPSA cycle and step duration.

Step	1	2	3	4	5	6	7	8	9	10	11	12
t / s	2	11**	29-41	2	11**	29-41	2	11**	29-41	2	11**	29-41
Col I	AD	AD/BF	AD/BF	DPE	PP	BD	BD	PG*	IDLE*	PPE		BF
Col II	PPE		BF	AD	AD/BF	AD/BF	DPE	PP	BD	BD	PG*	IDLE*
Col III	BD	PG*	IDLE*	PPE		BF	AD	AD/BF	AD/BF	DPE	PP	BD
Col IV	DPE	PP	BD	BD	PG*	IDLE*	PPE		BF	AD	AD/BF	AD/BF

* + EV in VPSA operating mode; **Used as a factor in the VPSA experimental design.

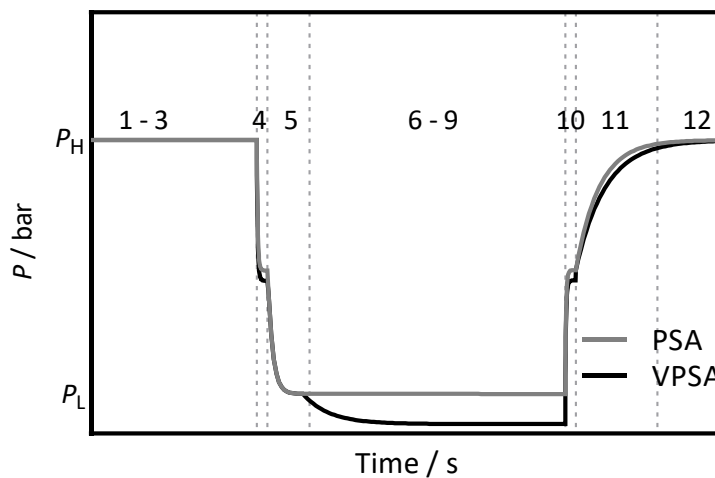


Figure 2.2 – Typical pressure history along the PSA cycle. Black line – PSA operating mode;
Grey line – VPSA operating mode

The performance indicators, recovery, purity, and productivity were obtained as follows (eqs. (4) to (6)):

$$y_{H_2} = \frac{\int_0^{t_{AD}} y_{prod,H_2} Q_{prod} dt}{\sum_{i=1}^n \int_0^{t_{AD}} y_{prod,i} Q_{prod} dt} \times 100 \quad (2.4)$$

$$\rho_{REC} = \frac{\int_0^{t_{AD}} y_{prod,H_2} Q_{prod} dt}{\int_0^{t_{AD}} y_{feed,H_2} Q_{feed} dt} \times 100 \quad (2.5)$$

$$\rho_{PROD} = \frac{\int_0^{t_{AD}} y_{prod,H_2} Q_{prod} dt}{t_{cycle} m_{AC}} \times 100 \quad (2.6)$$

where y_{H_2} is the hydrogen molar fraction, ρ_{REC} denotes hydrogen recovery, ρ_{PROD} is the adsorbent productivity, Q_{feed} and Q_{prod} are the feed and product flow rates at standard pressure and temperature conditions, respectively, t_{cycle} is the total time of one cycle and m_{AC} is the mass of activated carbon. Based on standard ISO 14687-3 for stationary hydrogen, the purity of the hydrogen product stream was set to:

$$y_{H_2} = >99.9; y_{CO} < 10 \text{ ppm.}$$

2.2.3. Design of experiments and data analysis

Two experimental designs were set, one for each operating mode (PSA and VPSA), aiming to assess the influence of the different operating variables (factors) on hydrogen recovery and purity. A response surface methodology with a central composite design was chosen for conducting systematically the experimentation program. The experimental values were fitted to a quadratic polynomial, which allowed to plot response surfaces for recovery and purity [21].

For the PSA operating mode high pressure, P_H , and adsorption time, t_{AD} (which includes the time of the elementary steps AD and AD/BF) were selected as factors with three levels

each. The P_{PP} setpoint was fixed at 1.6 bar, giving a purge time, t_{PG} , of ≈ 11 s (steps 2, 5, 8, and 11 of Table 2.1). In VPSA operating mode, it is possible to increase the evacuation time by partially replacing the purge step. Therefore, t_{PG} was also used as factor, where P_{PP} was used and manipulated variable to obtain the desired purge time. The information of the DoE factor and levels is summarized in Table 2.2.

Table 2.2 – DoE factors and corresponding lower and upper levels.

DoE factors	Lower level (-1)	Upper level (+1)
P_H (bar)	9 (PSA); 8 (VPSA)	10
t_{AD} (s)	42	54
t_{PG} (s) - Fixed at 11 s in PSA	0	11

All the experiments were carried out at room temperature (*ca.* 25 °C) feeding a mixture of 70 % H₂, 25 % CO₂, 4 % CH₄ and 1 % CO at a feed flow rate of 50 L_N min⁻¹. During the PSA screening experiments (not reported here) it was found that carbon monoxide is the limiting species for obtaining fuel cell grade hydrogen and both CO₂ and CH₄ concentrations were lower than CO. At this order of magnitude (few ppm), the impact of CH₄ in the fuel cell performance is insignificant[22], while CO₂ can form CO on the catalyst surface but with an impact much smaller than CO at the same concentration level[23]. Accordingly, the presence of CH₄ and CO₂ were neglected, and hydrogen quality was assessed solely based on the carbon monoxide content, y_{CO} . For the construction of the response surfaces, the experimental values were fitted to a second-order polynomial equation – eq. (7). Since the PSA has one operating variable less than the VPSA operating mode, coefficients β_3 , β_5 , β_6 and $\beta_9 = 0$. This equation applies for obtaining the recovery and purity and the fitting was performed using the statistical software JMP®.

$$\hat{y}_{VPSA}(\rho_{REC}; y_{CO}) = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_1 X_2 + \beta_5 X_1 X_3 + \beta_6 X_2 X_3 + \beta_7 X_1^2 + \beta_8 X_2^2 + \beta_9 X_3^2 \quad (2.7)$$

where $\hat{y}$ is the process response (recovery or purity) and β are the coefficients of the model. X_1 , X_2 and X_3 are the dimensionless factors, which can be defined as follows:

$$X_1 = \frac{P_H - \bar{P}_H}{\left(\frac{P_{H+1} - P_{H-1}}{2}\right)}; X_2 = \frac{t_{AD} - \bar{t}_{AD}}{\left(\frac{t_{AD+1} - t_{AD-1}}{2}\right)}; X_3 = \frac{t_{PG} - \bar{t}_{PG}}{\left(\frac{t_{PG+1} - t_{PG-1}}{2}\right)} \quad (2.8)$$

where +1 and -1 denotes the higher and lower level, as shown in Table 2.2.

The significance of the parameters was assessed based on the p-value, while the lack-of-fit test and the coefficient of determination (R^2) were used to measure the model accuracy. The operating conditions of the PSA/VPSA tests as well as the DoE parameters are summarized in Table 2.3.

Table 2.3 – Column characteristics and operating conditions of the PSA/VPSA runs.

Fixed operating conditions	
Q_{feed} (L _N min ⁻¹)	50
T (°C)	25
t_{EQ} (s)	2
P_L (bar)	1 (PSA); 0.4 (VPSA)
Feed molar ratio H ₂ :CO ₂ :CH ₄ :CO	70:25:5:1
Minimum number of cycles	60
Column characteristics	
L (cm)	50.0
d_{in} (cm)	7.0

2.3. Results and Discussion

2.3.1. Adsorbent characterization

Adsorption equilibrium isotherms of H₂, CO₂, CH₄, and CO on activated carbon (AC) were obtained at 30 °C, 40 °C, and 50 °C, and the results are presented in Figure 2.3a-d. Carbon dioxide displays the highest adsorption capacity followed by methane, carbon monoxide, and hydrogen. This last species displays particularly low adsorption on the activated carbon; hence indicating the AC as a suitable material for hydrogen separation. As it can be observed in the same figure, the experimental data is well represented by the dual-site Langmuir equation (dotted-lines), whose parameters are listed in

Table 2.4. Helium pycnometry of the activated carbon revealed a true density of $1.95 \text{ g}\cdot\text{cm}^{-3}$, which is in agreement with values reported for similar adsorbents [24, 25].

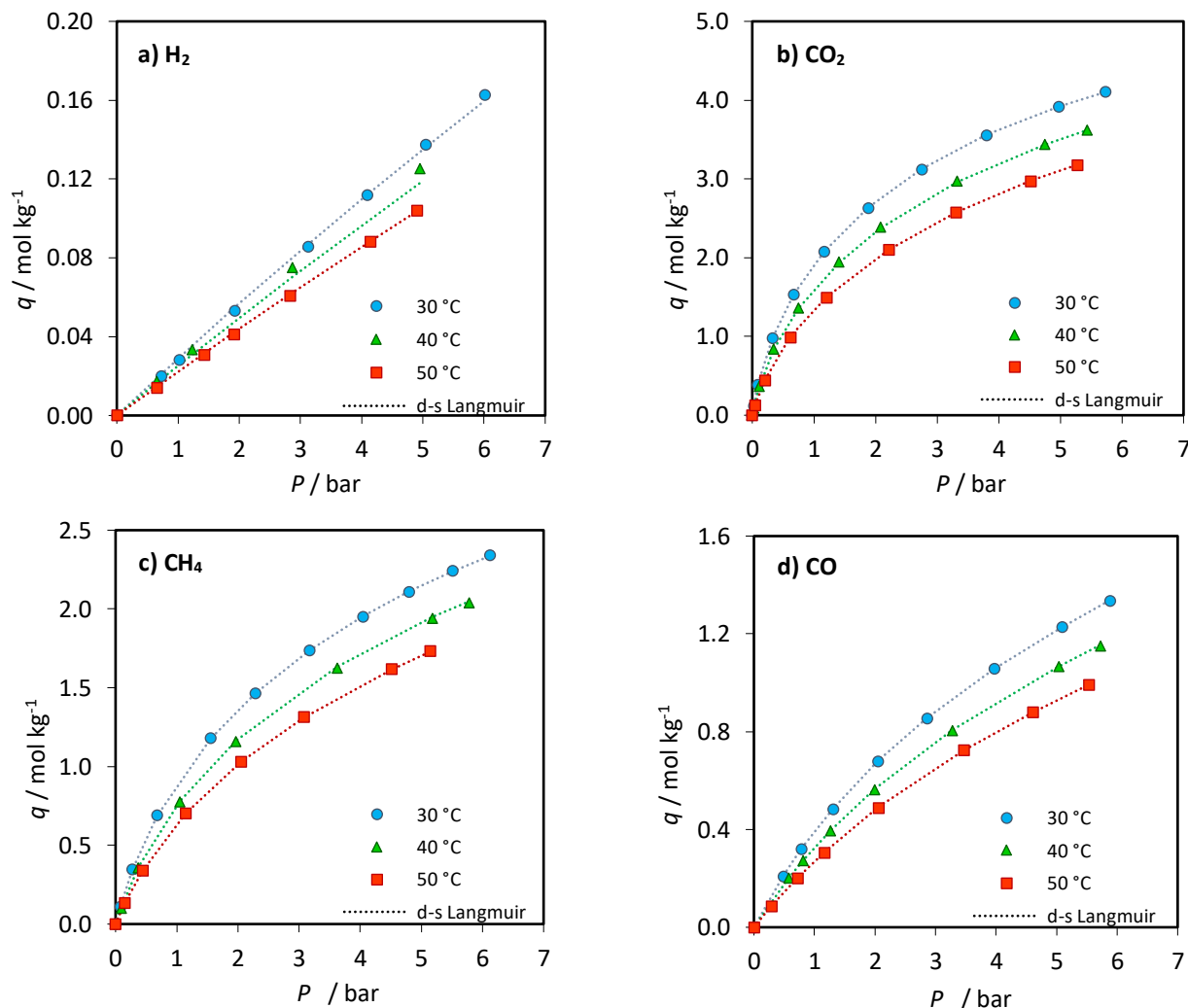


Figure 2.3 – Experimental adsorption isotherms on activated carbon at 30 °C, 40 °C and 50 °C. Dotted-lines were obtained fitting the experimental data to dual-site Langmuir model. (a) H_2 ; (b) CO_2 ; (c) CH_4 ; (d) CO .

Table 2.4 – Dual-site Langmuir equation parameters of H_2 , CO_2 , CH_4 , and CO on UOP activated carbon and its true density.

Parameter	H_2	CO_2	CH_4	CO
$q_{\max,1} \text{ (mol kg}^{-1}\text{)}$	0.059	5.089	3.433	4.163
$b_{\infty,1} \times 10^4 \text{ (bar}^{-1}\text{)}$	1.536	0.333	0.552	0.417
$\Delta H_1 \text{ (kJ mol}^{-1}\text{)}$	14.41	24.97	20.09	16.76

$q_{\max,2}$ (mol kg ⁻¹)	1.764	1.074	0.711	0.994
$b_{\infty,2} \times 10^4$ (bar ⁻¹)	2.348	1.638	4.410	1.985
ΔH_2 (kJ mol ⁻¹)	10.50	25.13	20.40	18.92
True density (g cm ⁻³)	1.95			

2.3.2. PSA experiments

A synthetic reformat gas mixture composed of 70 % H₂, 25 % CO₂, 4 % CH₄, and 1 % CO was fed to the PSA unit at a feed flow rate of 50 L_N min⁻¹ aiming to produce hydrogen for stationary PEMFC systems (Type I, Grade E - max. CO = 10 ppm – standard ISO 14687-3). The experimental PSA unit was operated following either a PSA or VPSA cycles. Considering the selected factors and levels of Design of Experiments, 10 operating conditions were defined for the PSA cycle, while 15 operating conditions were defined for the VPSA cycle, as in Table 2.5. This table also reports the CO₂, CH₄, and CO average product concentrations as well as the productivity and hydrogen recovery. For the same t_{AD} , it can be observed that as the feed pressure increases the hydrogen purity increases, while the recovery and productivity decrease; the opposite trend is observed as the cycle time is made to increase.

Table 2.5 – DoE of PSA runs - Experimental conditions and experimental results.

Run No. #	P_H (bar)	t_{AD} (s)	H ₂ (%)	y_{CO_2} (ppm)	y_{CH_4} (ppm)	y_{CO} (ppm)	ρ_{REC} (%)	ρ_{REC} (L _N kg _{ads} ⁻¹ min ⁻¹)
1	9.5	42	99.999	5.3	0.0	4.2	67.9	15.0
2	9.0	48	99.994	6.5	4.3	52.4	76.0	19.1
3	9.5	48	99.997	0.0	1.6	26.4	73.7	18.6
4	10.0	54	99.995	0.0	4.0	49.8	74.4	21.1
5	10.0	48	99.999	0.0	0.0	7.54	69.5	17.5
6	9.0	54	99.966	10.5	49.4	282	79.1	22.4
7	9.5	48	99.997	0.0	1.5	26.6	73.6	18.5
8	9.0	42	99.999	6.1	0.0	6.8	66.7	14.7
9	9.5	54	99.992	0.0	6.8	75.6	77.8	22.0
10	10.0	42	99.999	0.0	0.0	0.7	63.8	14.1

Table 2.6 presents the operating conditions and experimental results for the VPSA operating mode. The effect of pressure and cycle time on recovery, productivity and CO content is similar to that observed for the PSA operating mode. However, concerning the purge time (which was fixed in PSA) a more detailed analysis is needed to assess its influence. For example, comparing runs #2, #4 and #15 (same high pressure and cycle time), an increase t_{PG} led to a higher recovery, while CO concentration exhibited a minimum for an intermediate purge time. However, comparing runs #9 and #16, the highest recovery was obtained when t_{PG} was minimum. These results suggest an interaction between factors P_H and t_{AD} .

Table 2.6 – DoE of VPSA runs - Experimental conditions and results.

Run No. #	P_H (bar)	t_{AD} (s)	t_{PG} (s)	H ₂ (%)	y _{CO2} (ppm)	y _{CH4} (ppm)	y _{CO} (ppm)	ρ_{REC} (%)	ρ_{REC} (L _N kg _{ads} ⁻¹ min ⁻¹)
1	10.0	48	5.4	99.9999	0.0	0.0	0.6	63.9	16.0
2	9.0	48	0.7	99.9949	18.6	2.4	30.3	70.9	17.6
3	8.0	42	8.9	99.9992	0.0	0.0	8.4	69.9	15.2
4	9.0	48	5.1	99.9991	3.3	0.0	6.2	71.4	17.7
5	10.0	42	0.6	99.9999	0.0	0.0	0.9	63.4	13.5
6	8.0	54	0.7	99.9133	32.7	172	662	82.4	22.4
7	8.0	54	9.4	99.9702	29.7	36.4	232	78.1	23.0
8	9.0	48	5.1	99.9991	3.3	0.0	6.0	71.3	17.7
9	10.0	54	11.2	99.9993	0.0	0.0	7.3	70.5	20.1
10	8.0	48	4.8	99.9947	7.9	3.8	41.0	74.8	18.7
11	8.0	42	0.7	99.9969	0.0	2.3	28.6	72.4	15.5
12	10.0	42	10.9	100.000	0.0	0.0	0.0	56.9	13.2
13	9.0	42	4.7	99.9996	2.8	0.0	1.01	64.4	14.3
14	9.0	54	5.1	99.9961	6.3	2.0	30.3	72.6	21.2
15	9.0	48	10.0	99.9992	0.0	0.0	8.4	72.3	17.7
16	10.0	54	0.6	99.9960	2.4	3.4	34.4	72.7	19.8

From the experimental results in Table 2.5 and Table 2.6, it was possible to fit the four polynomial empirical models. The coefficients of these polynomials and ANOVA

analysis are given in Table 2.7 and were obtained using the software JMP®. Model 1 and 2 relate to the CO average product content and hydrogen recovery of the PSA unit operated in PSA mode, while models 3 and 4 relate to CO average product content and hydrogen recovery of the PSA unit operated in VPSA mode. Because the CO content in the product stream of run #6 – PSA operating mode and runs #6 and #7 – VPSA operating mode, are far from the region of interest, they were excluded from the empiric model for improving the accuracy in the targeted region ($y_{CO} < 10$ ppm). The four fitting models proved to be statistically significant with a p -value < 0.05 . Besides, the low root mean square error (RMSE) values – between 1.0490 and 4.9379 – and the determination coefficient R^2 – between 0.9656 and 0.9918 – indicate that the empirical models fit quite well the experimental results.

Table 2.7 – Regression parameters and ANOVA of the empirical models.

	PSA				VPSA			
	Model 1 - CO		Model 2 - Recovery		Model 3 - CO		Model 4 - Recovery	
	Estimate	p -value	Estimate	p -value	Estimate	p -value	Estimate	p -value
β_0	26.454	0.0016	73.81	0.0000	8.1999	0.0280	70.142	0.0000
β_1	-19.664	0.0027	-2.6127	0.0203	-17.8088	0.0033	-5.0183	0.0015
β_2	38.420	0.0004	5.7461	0.0022	16.981	0.0028	4.8953	0.0012
β_3					-11.941	0.0134	-0.4526	0.5226
β_4	-15.231	0.0135	-0.8441	0.3606	-8.0004	0.0624	0.2078	0.7856
β_5					4.8010	0.2043	0.4908	0.5357
β_6					-7.3919	0.0546	0.6715	0.3455
β_7	3.5618	0.2964	-1.2176	0.2089	8.0878	0.0680	-0.8311	0.3274
β_8	13.492	0.0174	-1.1176	0.2393	2.7689	0.4438	0.0438	0.9560
β_9					12.665	0.0681	1.1263	0.3896
R^2	0.9918		0.9813		0.9656		0.9824	
RMSE	3.8812		1.0490		4.9379		1.1201	
p -value	0.0025		0.0085		0.0135		0.0037	
Lack-of-fit (p -value)	0.0210		0.0389		0.0182		0.0398	

The response surfaces of models 1 and 2 (PSA operating mode) are presented in Figure 2.4.a and Figure 2.4.b, respectively, where the experimental values are located close to the model surfaces. For the CO concentration, there is an outlier value for run #6 ($t_{AD} = 52$ s; $P_H = 9$ bar) as it can be observed in Figure 2.4.a. As previously mentioned, this value was

not used in the fitting model, since otherwise the CO concentration in the region of interest would be poorly predicted. Therefore, particular care should be taken when using the fitting model in that region (low P_H and high t_{AD}), since the predicted CO concentration may display a higher error.

The response surfaces of models 3 and 4 (VPSA operating mode) are plotted in Figure 2.5a and Figure 2.5b. The response surfaces for feed pressure values 8 bar (red), 9 bar (green), 10 bar (blue) are shown in these figures. The shape of the response surfaces for each feed pressure is similar but shifted in the y axis, showing that increasing the feed pressure improves the product purity (lowers the CO content) and the recovery. On the other hand, increasing the adsorption time benefits the recovery but deteriorates the product purity. Increasing the purge time both y_{CO} and ρ_{REC} increase, but the effect is more pronounced in y_{CO} . The experimental values are located close to the model surfaces, attesting the accuracy of the model. The exception are outliers for CO concentration of runs #6 ($t_{AD} = 54$ s, $P_H = 8$ bar, $t_{PG} = 0.73$ s) and #7 ($t_{AD} = 54$ s; $P_H = 8$ bar; $t_{PG} = 9.36$ s), which were not used for building the empiric model.

Analyzing Figure 2.4a and Figure 2.4b, it can be concluded that to meet the CO concentration target (max. 10 ppm) operating in PSA mode, recoveries lower than 70 % are likely to occur under the conditions under study. On the other hand, operating in VPSA mode, hydrogen recoveries > 73 % are achievable (Figure 2.5a and Figure 2.5b).

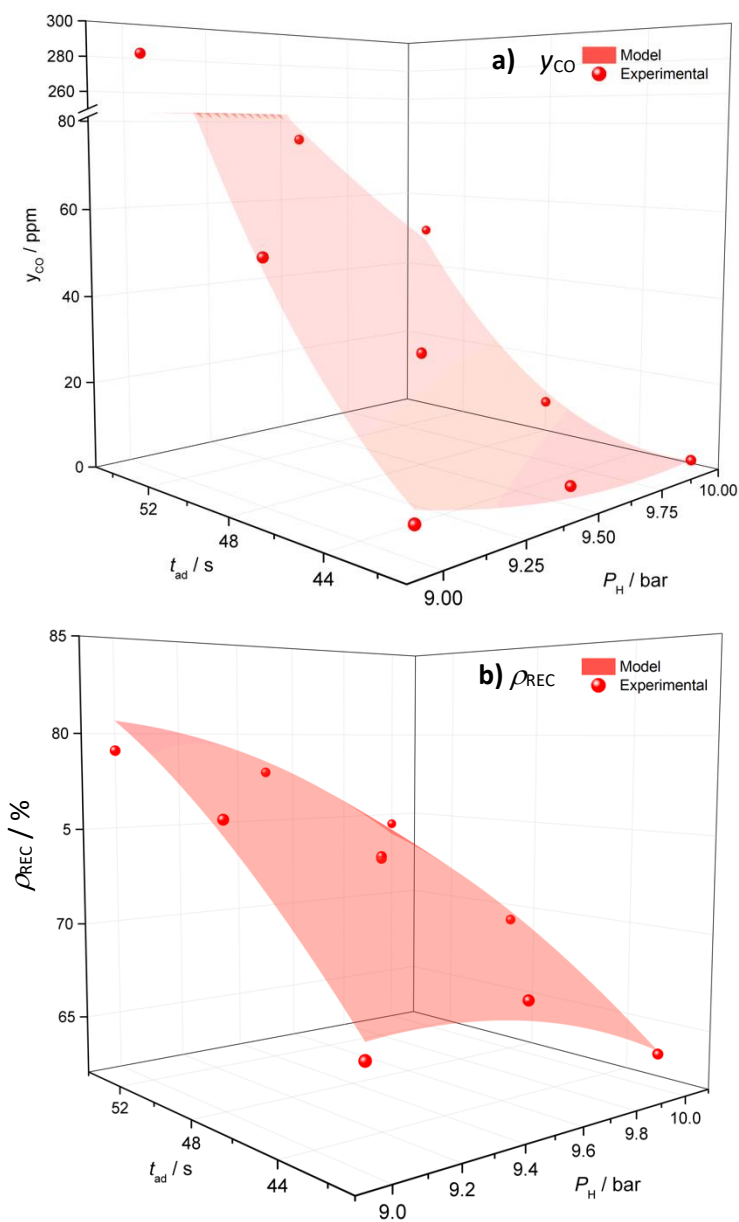


Figure 2.4 – PSA response surface. a) carbon monoxide content (y_{CO}); b) recovery (ρ_{REC}).

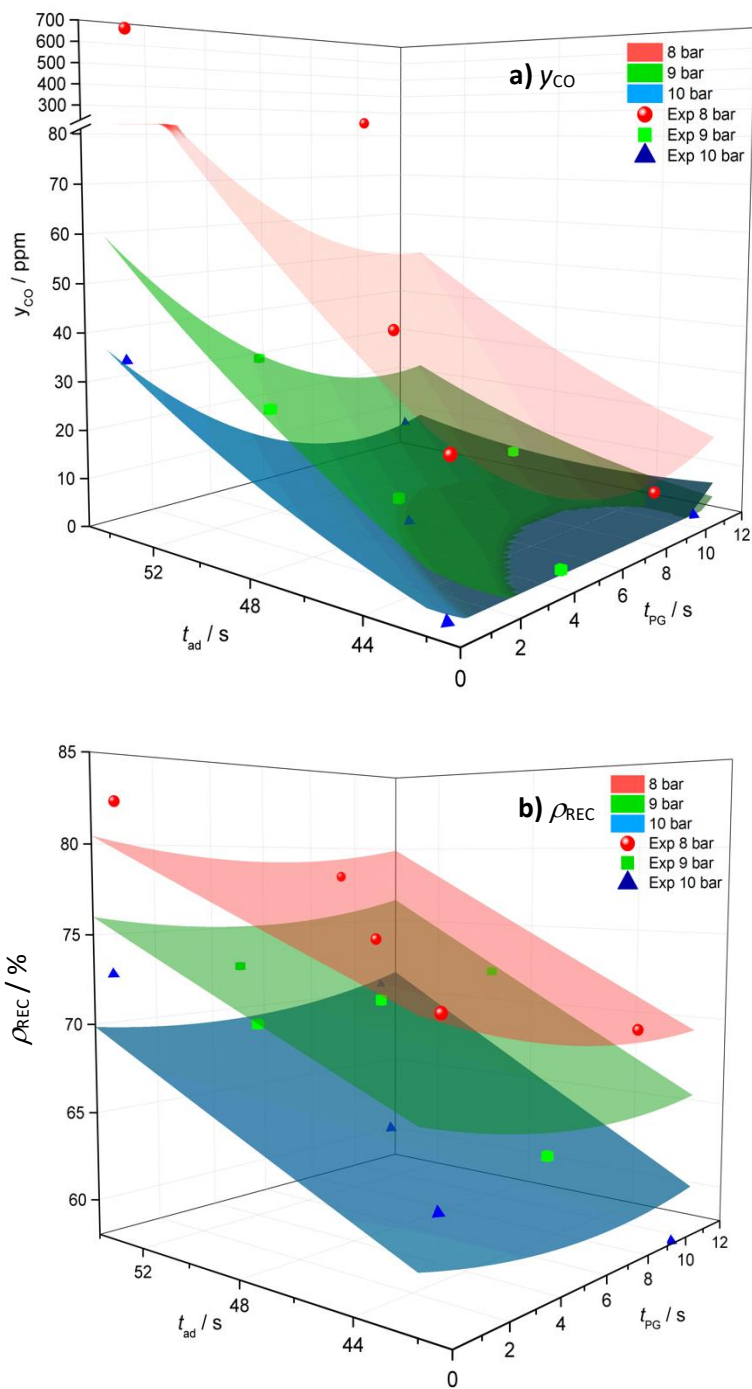


Figure 2.5 – VPSA response surface for a) carbon monoxide content (y_{CO}) and b) recovery (ρ_{REC}) at 8 bar (red); 9 bar (green) and 10 bar (blue).

2.3.3. PSA/VPSA optimization

Using the obtained fitting models, the operating conditions were optimized for PSA and VPSA operating modes. The objective was maximizing the recovery for two targeted CO concentrations: Opt # 1 - $y_{CO} = 10$ ppm - the CO maximum concentration complying with standard ISO 14687-3; Opt # 2 - $y_{CO} = 5$ ppm - a more conservative approach to accommodate possible fluctuations in the feed conditions. For the purpose, the desirability function of JMP software was used for coding the optimal conditions.

Table 2.8 displays the predicted and experimental recoveries and hydrogen product purity for the forecasted optimal operating conditions. Accordingly, the PSA unit operating in VPSA mode can produce fuel cell grade hydrogen when operated at $P_H = 9.2$ bar and $P_L = 0.4$ bar with an adsorption time of 51 s and a purge time of 10.4 s – Opt #1-1. For these operating conditions, 10.1 ppm of CO (vs. 10 ppm predicted) and 73.2 % of recovery (vs. 72.4 % predicted) are obtained and the computed experimental productivity is $19.6 \text{ L}_N \text{ kg}_{ads}^{-1} \text{ min}^{-1}$ (vs. $19.4 \text{ L}_N \text{ kg}_{ads}^{-1} \text{ min}^{-1}$ predicted). To obtain the same hydrogen grade operating in PSA mode, Opt #1-2, the recovery decreases to 69.8 %. This is related to the decrease of the adsorption time, from 51 s to 45.8 s, and the increase of the operating pressure from 9.2 bar to 9.6 bar. On the other hand, operating the unit in VPSA mode at $P_H = 9.1$ bar and $P_L = 0.4$ with an adsorption time of 47 s and a purge time of 9.7 s the experimental CO product concentration is 4.4 ppm (vs. 5.0 ppm predicted) with a recovery of 70.4 % (vs. 69.7 % predicted) and productivity of $17.4 \text{ L}_N \text{ kg}_{ads}^{-1} \text{ min}^{-1}$ (vs. $17.2 \text{ L}_N \text{ kg}_{ads}^{-1} \text{ min}^{-1}$ predicted) – Opt #2-1. Operating in PSA mode, Opt #2-2, the pressure should increase to 9.7 bar, while the adsorption time should be 44.6 s. Under such conditions, the experimental CO product concentration is 4.4 ppm (vs. 5 ppm predicted) with a recovery of 68.3 % (vs. 67.9 % predicted) and productivity of $16.0 \text{ L}_N \text{ kg}_{ads}^{-1} \text{ min}^{-1}$ (vs. $15.9 \text{ L}_N \text{ kg}_{ads}^{-1} \text{ min}^{-1}$ predicted) – Opt #2-2. It is worth mentioning that CO_2 was detected in none of the experiments, while 3.2 ppm of CH_4 was obtained only for Opt #1-2.

Table 2.8 – Optimal operating conditions and corresponding predicted and experimental results for PSA and VPSA operating modes.

Run #	Operating conditions				Predicted/Experimental Results					
		P_H (bar)	t_{AD} (s)	t_{PG} (s)	H_2 (%)	y_{CO_2} (ppm)	y_{CH_4} (ppm)	y_{CO} (ppm)	ρ_{REC} (%)	ρ_{PROD} ($L_N \text{ kg}_{ads}^{-1} \text{ min}^{-1}$)
Opt # 1-1	VPSA	9.2	51.0	10.4	99.9990	0 / 0	0 / 0	10 / 10.1	72.4 / 73.2	19.4 / 19.6
Opt # 1-2	PSA	9.6	45.8	11.0	99.9987	0 / 0	0 / 3.2	10 / 10.0	70.6 / 69.8	17.0 / 16.7
Opt # 2-1	VPSA	9.1	47.0	9.7	99.9996	0 / 0	0	5 / 4.4	69.7 / 70.4	17.2 / 17.4
Opt # 2-2	PSA	9.7	44.6	11.0	99.9995	0 / 0	0	5 / 4.6	67.9 / 68.3	15.9 / 16.0

2.4. Conclusions

Locally produced bioethanol is a promising feedstock for decentralized hydrogen production. Steam reforming of bioethanol followed by a water gas shift reaction produces a hydrogen-rich stream that can be used to produce fuel cell grade hydrogen after purification by PSA/VPSA. In this work, a 4-bed PSA packed with activated carbon was used to separate and purify hydrogen from a synthetic reformat gas mixture containing 70 % H_2 , 25 % CO_2 , 4 % CH_4 , and 1 % CO .

The adsorption equilibrium isotherms of H_2 , CO_2 , CH_4 and CO on the activated carbon were obtained at 30 °C, 40 °C, and 50 °C. It was concluded that the activated carbon presents a very low hydrogen adsorption capacity. The optimization of the operating conditions of the PSA unit, operating in PSA and in VPSA model, was accomplished following a design of experiments approach. The desirability function was set to maximize the recovery for target average product CO concentration of 5 ppm and 10 ppm, this latter value complying with standard ISO 14687-3 for stationary hydrogen PEMFC units. In PSA operating mode it was possible to reach the required CO concentration of 10 ppm with 69.8 % of recovery and a productivity $16.7 L_N \text{ kg}_{ads}^{-1} \text{ min}^{-1}$ – [$P_H = 9.6 \text{ bar}$; $t_{AD} = 45.8 \text{ s}$], where the design of experiments display a quite good fit with the experimental results; requiring a lower CO concentration of 5 ppm, the unit produced a maximum recovery of 68.3 %. In VPSA mode it was possible to reach a CO concentration of 10.1 ppm (experimental hydrogen concentration of 99.9990 %) with a recovery of 73.2 % and a productivity of

$19.6 \text{ L}_N \text{ kg}_{\text{ads}}^{-1} \text{ min}^{-1}$ – [$P_H = 9.2 \text{ bar}$; $P_L = 0.4 \text{ bar}$ $t_{\text{AD}} = 51.0 \text{ s}$]; requiring a lower CO concentration of 5 ppm, the unit produced a maximum recovery of 70.4 % and the experimental hydrogen purity was of >99.9996 %.

This work shows that it is possible to separate and purify reformat hydrogen using a single 4-column PSA unit, loaded with activated carbon, and working in both PSA and VPSA operating models with quite higher recoveries. It also shows that as the required hydrogen purity increases, the VPSA operating mode becomes more attractive. Finally, the removal of CO proved to be the limiting specification of the PSA unit; the use of an adsorbent displaying higher adsorption CO capacity and or higher vacuum would allow for smaller size PSA units.

2.5. Acknowledgments

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2.6. Nomenclature

Parameters	Description	Units
b_{∞}	Langmuir affinity constant at infinite temperature	bar^{-1}
b	Langmuir affinity constant	bar^{-1}
d	Diameter	cm
L	Length	cm
L	Length	cm
m	Mass	kg
P	Pressure	bar
$\bar{P}$	Average pressure	bar
Q	Volumetric flow rate	$\text{L}_N \text{ min}^{-1}$
q	Isotherm parameter, maximum adsorption capacity	mol kg^{-1}
$\mathcal{R}$	Ideal gas constant	$\text{J mol}^{-1} \text{ K}^{-1}$
R^2	Coefficient of determination	mol kg^{-1}
t	time variable	s
T	Temperature	$^{\circ}\text{C}$
$\bar{t}$	Average time	s
X	DoE dimensionless process factors	
y	Gas-phase mole fraction	
Greek Symbol	Description	Units
β	Empiric model equation parameter	mol kg^{-1}
ΔH	Heat of adsorption	J mol^{-1}
ρ_{REC}	Recovery	%
ρ_{PROD}	Productivity	$\text{L}_N \text{ kg}^{-1} \text{ min}^{-1}$
Acronym	Description	
AD	Adsorption	
AC	Activated carbon	
BD	Blowdown	
BF	Backfill	
DoE	Design of experiments	
DPE	Depressurization pressure equalization	
LOHC	Liquid organic hydrogen carrier	
MFC	Mass flow controller	
PEM	Polymer electrolyte membrane	
PEP	Pressurization pressure equalization with product	
PG	Purge	
PP	Providing Purge	

PPE	Pressurization pressure equalization
RMSE	Root mean square error
RSM	Response surface methodology
Subscripts	Description
-1	Lower level of the DoE factor
1	Upper level of the DoE factor
EQ	Equalization
H	Refers to high pressure
<i>i</i>	Component
in	Inside
L	Refers to low pressure
Prod	Product
PROD	Productivity

2.7. References

1. Energy, U.D.o., *Fuel Cell Technologies Office Multi-Year Research, Development and Demonstration Plan*. 2012, US Department of Energy Washington, DC.
2. Ruth, M.F., B.S. Pivovar, and J.D. Eichman, *Hydrogen's Expanding Role in the Energy System*. Chemical Engineering Progress, 2019. **115**(NREL/JA-6A20-73511).
3. Wim Elseviers, P.F.H., Jean-Louis Navarre, and Michael Whysall. *50 Years of PSA Technology for H₂ Purification*. 2015 [cited 2019 24-10-2019]; Available from: <https://www.uop.com/?document=psa-50-paper&download=1>.
4. Hellas, F.f.R.a.T., *Final Report Summary - HY2SEPS-2 (Hybrid Membrane–Pressure Swing Adsorption (PSA) Hydrogen Purification Systems)*. 2015.
5. Standardization, I.O.f., *Hydrogen fuel–product specification–Part 2: proton exchange membrane (PEM) fuel cell applications for road vehicles*. ISO/TS, 2012: p. 14687-2.
6. Yang, S.-I.; Choi, D.-Y.; Jang, S.-C.; Kim, S.-H.; Choi, D.-K., Hydrogen separation by multi-bed pressure swing adsorption of synthesis gas. *Adsorption* 2008, 14, (4-5), 583-590.
7. Sircar, S., *Separation of multicomponent gas mixtures*. 1979, Patent no. US4171206A, Air Products and Chemicals Inc.

8. Riboldi, L. and O. Bolland, *Overview on pressure swing adsorption (PSA) as CO₂ capture technology: state-of-the-art, limits and potentials*. Energy Procedia, 2017. **114**: p. 2390-2400.
9. Shi, W., et al., *Two-stage PSA/VSA to produce H₂ with CO₂ capture via steam methane reforming (SMR)*. International Journal of Hydrogen Energy, 2018. **43**(41): p. 19057-19074.
10. Streb, A., et al., *Novel Adsorption Process for Co-Production of Hydrogen and CO₂ from a Multicomponent Stream*. Industrial & Engineering Chemistry Research, 2019. **58**(37): p. 17489-17506.
11. Golmakani, A., S. Fatemi, and J. Tamnanloo, *Investigating PSA, VSA, and TSA methods in SMR unit of refineries for hydrogen production with fuel cell specification*. Separation and Purification Technology, 2017. **176**: p. 73-91.
12. Marcoberardino, G., et al., *Green hydrogen production from raw biogas: A techno-economic investigation of conventional processes using pressure swing adsorption unit*. Processes, 2018. **6**(3): p. 19.
13. Wang, Y., et al., *Integrated VPSA Processes for Air Separation Based on Dual Reflux Configuration*. Industrial & Engineering Chemistry Research, 2019.
14. Ferreira, D., et al., *Two-stage vacuum pressure swing adsorption using AgLiLSX zeolite for producing 99.5+% oxygen from air*. Industrial & Engineering Chemistry Research, 2016. **55**(3): p. 722-736.
15. Divekar, S., et al., *Recovery of hydrogen and carbon dioxide from hydrogen PSA tail gas by vacuum swing adsorption*. Separation and Purification Technology, 2020: p. 117113.
16. Relvas, F., et al., *Single-stage pressure swing adsorption for producing fuel cell grade hydrogen*. Industrial & Engineering Chemistry Research, 2018. **57**(14): p. 5106-5118.
17. Xiao, J., et al., *Parametric study of pressure swing adsorption cycle for hydrogen purification using Cu-BTC*. International Journal of Hydrogen Energy, 2018. **43**(30): p. 13962-13974.
18. Delgado, J.A., et al., *Adsorption and diffusion of H₂, CO, CH₄, and CO₂ in BPL activated carbon and 13X zeolite: evaluation of performance in pressure swing adsorption*

- hydrogen purification by simulation*. Industrial & Engineering Chemistry Research, 2014. **53**(40): p. 15414-15426.
19. Koski, P., et al. *Development of reformed ethanol fuel cell system for backup and off-grid applications—system design and integration*. in *2016 IEEE International Telecommunications Energy Conference (INTELEC)*. 2016. IEEE.
 20. Santos, J., F. Magalhaes, and A. Mendes, *Contamination of zeolites used in oxygen production by PSA: effects of water and carbon dioxide*. Industrial & engineering chemistry research, 2008. **47**(16): p. 6197-6203.
 21. Proust, M. and A. Imp, *Design of experiments guide*. SAS Institute: Cary, NC, USA, 2007.
 22. Ohi, J., et al., *Hydrogen fuel quality specifications for polymer electrolyte fuel cells in road vehicles*. Office of Energy Efficiency and Renewable Energy: Washington, DC, USA, 2016.
 23. Erbach, S., et al., *CO₂ Enrichment in Anode Loop and Correlation with CO Poisoning of Low Pt Anodes in PEM Fuel Cells*. Fuel Cells, 2018. **18**(5): p. 613-618.
 24. Moon, D.-K., D.-G. Lee, and C.-H. Lee, *H₂ pressure swing adsorption for high pressure syngas from an integrated gasification combined cycle with a carbon capture process*. Applied Energy, 2016. **183**: p. 760-774.
 25. Lopes, F.V., et al., *Adsorption of H₂, CO₂, CH₄, CO, N₂ and H₂O in activated carbon and zeolite for hydrogen production*. Separation Science and Technology, 2009. **44**(5): p. 1045-1073.

Chapter 3. CO-selective π -complexation adsorbent based on a commercial activated carbon for carbon monoxide separation

3.1. Introduction

Carbon monoxide is an important feedstock in a wide range of industrial sectors [1-4]. It is commonly produced from steam reforming of light hydrocarbons, coal gasification, and partial oxidation[5], in which mixtures containing 30-85 % of CO are obtained, commonly balanced with carbon dioxide, hydrogen, methane, and nitrogen, hence the need for further purification [5, 6]. In this regard, cryogenic distillation is the most widely used process[7], but due to the similar boiling points of CO and N₂, distillation is not suitable for producing high purity CO in the presence of N₂-rich mixtures. The conventional alternatives are the chemical absorption-based processes COSORB™ and COPURE™, where an aromatic-Cu salt complex, usually toluene-CuAlCl₄, selectively removes carbon monoxide by complexation/decomplexation, achieving a recovery of 98 %, with 99 % of purity[8]. However, a pre-purification process is required to remove traces of water and sulfur compounds, which otherwise would poison the copper complex[9]. More recently, a great interest has been paid to (vacuum) pressure swing adsorption, (V)PSA, owing to its simpler operation, cost-effectiveness, and lower environmental impact. PSA allows reducing the payback period by >50 % compared with the commercial COSORB™ process [10], thanks to the recent developments of CO-selective π -complexation adsorbents [6, 11]. These materials are also of particular interest in hydrogen purification, where CO is commonly the limiting species and must be removed down to sub-ppm levels. In π -complexation, CO

bonds with a transition metal (d block) based on two-electron interactions: the first refers to the σ -type bonding, in which CO donates a pair of electrons to the empty metal d orbital; the second is the back-donation, a π -type bond in which the flow of electrons occurs in the reverse direction[12]. Since these type of interactions are stronger than the usual van der Waals and electrostatic interactions, π -complexation adsorbents are highly selective for CO over the other gases present in syngas. Yet, the bonds are weak enough to be broken by pressure swing, thus avoiding adsorbent thermal regeneration. In addition to CO separation, π -complexation adsorbents are especially suitable for other challenging separation processes, such as olefin-paraffin separation, aromatics-aliphatics, desulfurization, etc. [13-15].

The preparation of π -complexation adsorbents involves dispersing a transition metal cation on high-surface-area substrates, typically activated carbons (ACs), zeolites, activated alumina, and metal-organic frameworks (MOFs) [7, 16-18]. In this regard, two different approaches are commonly used: solid-state thermal monolayer dispersion and incipient wetness impregnation, though ion exchange is used in some cases, e.g. for zeolites. The solid-state thermal monolayer technique involves the use of fine powders, which are thoroughly mixed with the desired salt and further activated at ca. 200-300 °C[19]. It has the advantage of allowing dispersing insoluble salts but requires further pelletization of the resulting powder. In its turn, in incipient wetness impregnation, the substrate is soaked into a metal salt solution, allowing it to access the pore structure. Then, the sample is heated to remove the solvent and the activation procedure is carried out for obtaining the desired metal oxidation state. A different approach considers the use of MOFs, where the organic linkers self-assemble with metal ions to form 3-periodic structures. In this class of adsorbents, the CO-metal binding usually leads to other interactions, which may reinforce or weaken the bonding, therefore a more careful breakdown is needed [7]. Despite the great potential of MOFs, their applicability in industrial processes still needs further developments [20].

Among the transition metals used in the preparation of π -complexation adsorbents, copper has been the most used due to its abundance, low cost, and great performance.

Typically, CuCl and CuCl₂ are the preferred salts, though CuAlCl₄ and Cu(NH₃)₂Cl are also suitable, but not desired since the presence of another salt limits the copper loading [19]. J. Ma et al. [21] successfully prepared two different types of adsorbents, the first via solid-state dispersion of CuCl and the second by conventional impregnation using CuCl₂ salt. For both adsorbents, the CO adsorption capacity was 10 fold higher compared to the original AC, 2.3 mmol·g⁻¹ vs. 0.2 mmol·g⁻¹ at 1 bar and 25 °C. In the same study, a Y-type zeolite was modified via impregnation of CuCl₂; this adsorbent displayed the same high CO capacity but also quasi-irreversible adsorption under mild conditions. Similar conclusions were taken by Gao et al. [16] where wooden activated carbon and CuCl₂·2H₂O were mixed and ground thoroughly for obtaining a solid-state dispersion. These authors studied the influence of different copper loadings, achieving a maximum CO adsorption capacity of 3.6 mmol·g⁻¹ for copper loadings of 7 mmol·g⁻¹; CO adsorption did not increase for higher copper loadings. The obtained adsorption ratios at 1 bar and 30 °C were 6.28, 16.39, and 42.14, for the gas pairs CO/CO₂, CO/CH₄, and CO/N₂, respectively. In a more recent study, the same authors [22] used a VPSA numerical simulator for assessing the CuCl (@ 7 mmol·g⁻¹) impregnated AC, obtaining a product stream with a CO concentration of 98.1 % and a recovery of 92.9 %, from a syngas mixture containing 32.3 % CO, 1.0 % CO₂, 2.4 % CH₄, 18.3 % N₂ and 46.0 % H₂. Similar work has also been pursued by other authors using different types of adsorbents, namely Cho et al. [23], who successfully impregnated CuCl into high-purity synthetic bayerite via a thermal monolayer dispersion. For an overview of adsorption-based CO removal, the reader is referred to the review work by Feyzbar et al. [24].

Though the potential of π -complexation adsorbents, all of the existing studies developed powder adsorbents, not suitable for use in a PSA process. In addition, deactivation studies and kinetic data were not addressed or were poorly addressed. The exception the previous work by the authors [25] in which a copper modified adsorbent was prepared and used in a lab-scale PSA for hydrogen purification from CO-containing mixtures. This work studies fully characterizes the previously reported Cu-loaded AC pellets, reporting the adsorption equilibrium, kinetics, deactivation, and reactivation, and this for a brother set of gases – CO, CO₂, CH₄, H₂, and N₂.

3.2. Experimental

3.2.1. Materials

The activated carbon pellets (AC) were provided by Kuraray CO., Ltd, displaying a particle size of 1.6-2.0 mm. Hydrogen, nitrogen, and helium were supplied with a purity of 99.999 % by Praxair, while carbon monoxide and methane were supplied with a purity of 99.9 % and 99.995 %, respectively, also by Praxair. Both copper(II) chloride dehydrate and ammonium citrate (reagent grade) were purchased from Sigma-Aldrich.

3.2.2. Samples preparation

Firstly, the AC was heated in air at 250 °C to enhance the surface hydrophilicity. After, it was soaked into an aqueous copper solution and left for 1 h at room temperature and then dried in the oven at 120 °C for 2 h. The copper solution was prepared according to the desired copper loading ($0.5\text{--}6\text{ mol}_{\text{Cu}}/\text{kg}_{\text{AC}}$), using a solution volume equal to the porosity volume of the activated carbon sample employed. Ammonium citrate was used with a weight ratio of 0.07 ($(\text{NH}_4)_2\text{C}_6\text{H}_6\text{O}_7/\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) for improving the copper dispersion. Finally, the adsorbent was activated overnight under a hydrogen atmosphere at 150 °C, inside a tubular horizontal Termolab TH furnace, with a flow rate of 150 mL min^{-1} ; this treatment should reduce the loaded copper to Cu^+ . The activation temperature was selected to maximize the Cu^+ dispersion on the AC surface [26]. The modified samples were denoted as Cu-AC-X, where X indicates the targeted copper loading in mol/kg, while the pristine sample was denoted as AC.

3.2.3. Adsorbent characterization

Physicochemical characterization

The specific surface area, S_{BET} , of the samples was determined from nitrogen adsorption/desorption equilibrium isotherms measured at $-196\text{ }^\circ\text{C}$ (Quantachrome Autosorb AS-1 instrument) using multi-point Brunauer-Emmett-Teller (BET) method. Before

the analysis, the samples were outgassed in vacuum at 300 °C for 6 h. The morphology and elemental distribution of the AC and Cu-AC were obtained by scanning electron microscopy with energy dispersive spectroscopy analysis (Phenom XL Desktop SEM). The amount of copper in the Cu-AC was assessed by flame atomic absorption spectrophotometry (AAS - Unicam 939).

Adsorption measurements

Before obtaining the adsorption equilibrium isotherms, helium pycnometry was performed to determine the structural volume of the sample. The adsorption equilibrium isotherms of CO, CO₂, CH₄, N₂, and H₂ were obtained using an in-house built volumetric method setup, described elsewhere and shown in Appendix B.1.1 [27]. Briefly, the setup comprises two tanks (A and B) with accurately known volumes, connected through an on-off valve. A given mass of the Cu-AC was introduced in tank B, while tank A was left empty. After evacuating the entire system (Alcatel 1004A rotary vacuum pump), the valve was closed and tank A was pressurized using the gas under study. The connecting valve was opened and the pressure history was recorded until reaching the new equilibrium pressure (Drück pressure transducer PMP 4000 series, 0-7 bar). The adsorbed concentration was determined from the pressure decrease assuming ideal gas behavior. To guarantee isothermal operation, the tanks were placed in a thermostatic bath (Huber, K12-cc-NR). The experimental adsorption equilibrium isotherms were fitted to the dual-site Langmuir model, according to eq. (3.1):

$$q = \frac{q_{\max,1} b_1 P}{1 + b_1 P} + \frac{q_{\max,2} b_2 P}{1 + b_2 P} \quad (3.1)$$

where q is the molar concentration in the adsorbed phase, $q_{\max,1}$ and $q_{\max,2}$ are the maximum concentration in the adsorbed phase on sites 1 and 2, respectively, corresponding to the complete monolayer coverage, b_i is the adsorption affinity parameter and P is the total pressure [28]. For obtaining the temperature dependence in the Langmuir isotherm, b_i can be calculated according to eq. (3.2):

$$b = b_{\infty} e^{\frac{-\Delta H}{RT}} \quad (3.2)$$

The adsorption ratio of carbon monoxide over other gases under study, at 1 bar and 30 °C was obtained from eq. (3):

$$\eta_{CO/Y} = \frac{q_{CO}}{q_Y} \quad (3.3)$$

where Y represents any other gas than CO.

Adsorption kinetics

The adsorption kinetics was obtained from the experimental adsorbed concentration history (uptake curves) for each adsorption equilibrium value, where the mass transport is assumed to be described by Fick's law. Accordingly, the analytical solution for describing simultaneous mass and heat transfer under variable pressure conditions was used for obtaining the inverse of apparent diffusion time constant, $D \cdot r^2$, and is given by eq. (3.4):

$$F = 1 - \sum_{n=1}^{\infty} \frac{9(1 + \alpha^*) \left[Y_n / (-p_n^2) \right]^2 e^{(-p_n^2 \tau)}}{\frac{1}{\beta_n^*} + \frac{3}{2} \frac{\beta}{\beta_n^*} \left[p_n \cot q_n \left(\frac{Y_n}{p_n^2} \right) + 1 \right] + \frac{3}{2} \frac{\alpha^*}{p_n^4} \frac{\beta_n}{\beta_n^*}} \quad (3.4)$$

where F is the fractional adsorption uptake, p_n are the series of poles of the Laplace transform. The inverse dimensionless time variable is given by $\tau = \frac{D \cdot t}{r_o^2}$ and B_n and Y_n are given by eq. (3.5) and (3.6), respectively:

$$B_n = Y_n \left[(p_n^2 - \alpha) p_n \cot p_n - 2\alpha \right] + p_n^2 (p_n^2 - \alpha) \quad (3.5)$$

$$Y_n = p_n \cot p_n - 1 \quad (3.6)$$

where β and α are parameters related to the non-isothermal adsorption and are given by eqs. (3.7) and (3.8), respectively:

$$\beta = \frac{\Delta H}{C_p} \left(\frac{\partial q}{\partial T} \right)_{P_0, T_0} \quad (3.7)$$

$$\alpha = \frac{h a}{\rho_{\text{ads}} C_p} \frac{r^2}{D} \quad (3.8)$$

The experimental uptake curves were fitted to this mathematical model using a nonlinear optimization algorithm, where β , α and $D \cdot r^2$ were used as fitting variables. α^* is an experimental parameter related to the pressure difference before and after the experiment and is calculated as follows:

$$\alpha^* = \frac{P(0_+) - P(\infty)}{P(\infty) - P(0_-)} \quad (3.9)$$

More details about the mathematical formulation can be found in relevant literature [29, 30].

Deactivation and regenerability studies

For assessing the deactivation under oxidative atmosphere, two tests were performed: one comprising exposing the Cu-AC samples to atmospheric air for two weeks, and the other exposing the samples to pure O₂ overnight. The samples were then regenerated under vacuum conditions and new CO and CO₂ isotherms were determined. The deactivation was assessed by comparing the adsorption isotherms with the “fresh sample”. After the deactivation tests, the Cu-AC samples were re-activated overnight, at 150 °C and under hydrogen flow, and new CO and CO₂ isotherms were obtained for comparison.

3.3. Results and discussion

3.3.1. Physicochemical analysis of the pristine and modified adsorbent

In the present study, five samples of Cu-AC were prepared with different nominal copper loadings, namely 0.5, 2.0, 3.0, 4.0, and 5.0 mol_{Cu}/kg_{AC}. The experimental Cu content

determined by AAS and the BET surface area were obtained and are given in Table 3.1. The AAS analysis revealed a good agreement between the measured and nominal Cu content, with a maximum deviation of 12 %, observed for sample Cu-AC-3. A possible source for these deviations is the volume of solution used for preparing the samples, which may have been overestimated due to the intraparticle volume of the carbon pellets. It should be noted that when using the incipient wetness impregnation method, the copper solution volume added should be equal to the intraparticle pore volume of the activated carbon sample [31]. This may also explain why the deviations are higher for higher copper loadings. Nevertheless, the deviations are quite acceptable and are in the same order of magnitude as reported in the literature [16, 17, 32]. As expected, as the copper loading increases, the specific intraparticle surface area decreases following a negative linear correlation, $R^2= 0.9816$.

Table 3.1 – Copper content and BET surface area of the pristine AC and Cu-AC samples.

	Nominal Cu content (wt %)	Measured Cu content (wt %)	Deviation (%)	S_{BET} m^2/g
AC	0	0	0	1280
Cu-AC-0.5	3.0	2.9	3.8	994
Cu-AC-2	10.6	10.1	4.7	686
Cu-AC-3	14.7	13.0	11.8	603
Cu-AC-4	18.2	16.6	9.0	421
Cu-AC-5	21.2	19.2	9.2	230

Representative SEM images of the AC and Cu-AC-5 samples are shown in Figure 3.1.a and Figure 3.1.b, respectively. No significant differences can be observed between the pristine and the modified samples. The absence of CuCl_2 particles in Cu-AC-5 is a clear indicator of a good Cu dispersion on the surface during the activation, which is supported by the Cu and Cl elemental mapping displayed in Figure 3.1.c and Figure 3.1.d. Moreover, the elemental quantification showed that copper is present with a weight concentration of 20.56 %, which is in agreement with the nominal and measured Cu contents presented in Table 3.1[†]. These results are in agreement with other SEM/EDS reported results [32, 33].

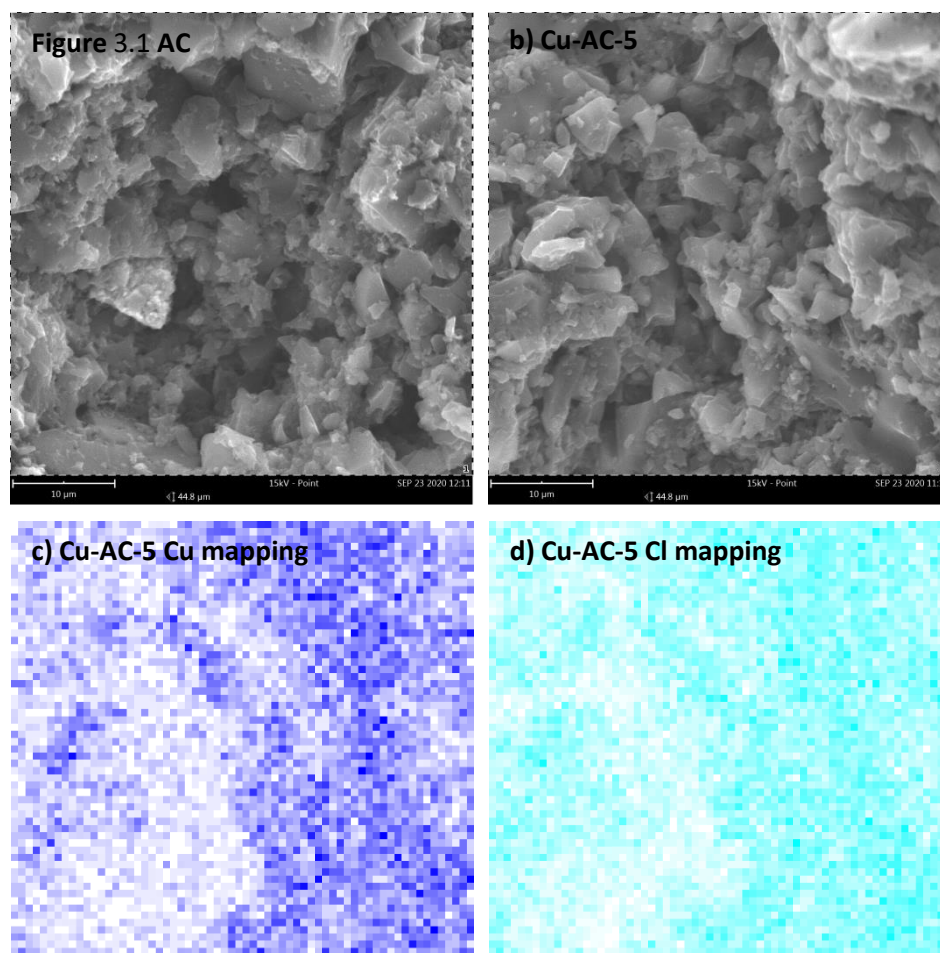
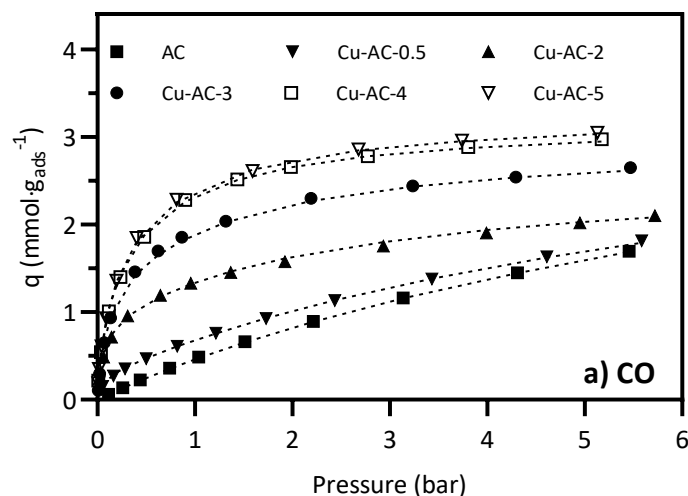


Figure 3.1 – SEM images and element analysis mapping obtained from EDS. a) AC SEM image; b) Cu-AC-5 SEM image; c) Cu mapping of the Cu-AC-5 sample; d) Cl mapping of the Cu-AC-5 sample.

3.3.2. Adsorption measurements

Figure 3.2 depicts the adsorption equilibrium isotherms of CO and CO₂ for the pristine AC and Cu-AC adsorbents at 30 °C. All the experimental data, including for other gases is given in Appendix A. Figure 3.2.a shows an increase of CO adsorption with the copper loading, which was assigned to the π -complexation bonds between the CO and Cu⁺, where the CO adsorption enhancement is mainly observed at low pressures (ca. < 1 bar), which is typical for chemisorption isotherms. Yet, cyclic adsorption/desorption tests were

performed at 30 °C and no hysteresis was observed. In contrast, for $P > 1$ bar, dq_{CO}/dP decreases significantly, indicating the saturation of the copper sites; CO onsets adsorbing in carbon sites based on van der Waals interactions. When the copper loading increases from 4 to 5 mol/kg, the CO adsorption increases only slightly. This phenomenon was assigned to the decrease in the surface area, from 421 to 230 m²/g, and to the onset of multilayer copper deposition, as reported by Wang et al. [34] and Gao et al. [16]. In the case of CO₂, an opposite behavior was observed, as the adsorption decreased with the copper loading (Figure 3.2.b). In this case, the copper sites have no particular adsorption affinity for CO₂ and the adsorption concentration decreases with the copper loading and with the specific surface area (*cf.* Table 3.1). For both gases, the Dual-site Langmuir equation was able to describe quite accurately the adsorption behavior, as indicated in Table 3.2. The same conclusions drawn for CO₂ are valid for the remaining gases under study, namely CH₄, N₂, and H₂, whose experimental data and dual-site Langmuir parameters can be found in Appendix A.2.



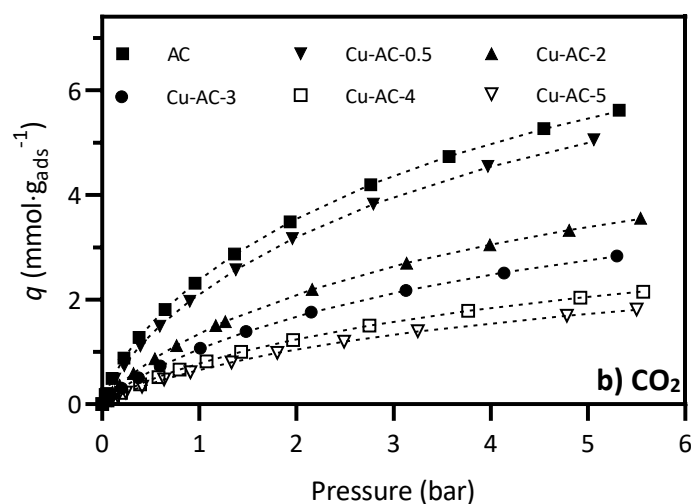


Figure 3.2 – Experimental adsorption equilibrium isotherms on AC and Cu-AC at 30 °C for a) CO and for b) CO₂. Dashed lines refer to the Dual-site Langmuir fitting.

Table 3.2 – Dual-Site Langmuir equation parameters for adsorption of CO and CO₂ on pristine AC and Cu-AC samples.

Parameters	AC		Cu-AC-0.5		Cu-AC-2		Cu-AC-3		Cu-AC-4		Cu-AC-5	
	CO	CO ₂	CO	CO ₂	CO	CO ₂	CO	CO ₂	CO	CO ₂	CO	CO ₂
$q_{\max,1}$ (mol kg ⁻¹)	3.91	8.42	0.29	7.95	1.25	5.79	1.55	4.89	2.19	3.70	2.22	3.11
$b_{\infty,1} \times 10^4$ (bar ⁻¹)	3.61	1.68	5.78×10^{-3}	1.74	9.29×10^{-3}	1.44	3.72×10^{-3}	1.51	1.26×10^{-3}	1.87	1.08×10^{-3}	1.91
ΔH_1 (kJ mol ⁻¹)	20.7	24.0	49.2	23.8	43.0	23.8	43.4	23.6	47.4	23.3	47.4	23.2
$q_{\max,2}$ (mol kg ⁻¹)	0.25	1.04	3.70	0.87	0.98	0.70	1.21	0.52	0.98	0.25	1.10	0.22
$b_{\infty,2} \times 10^4$ (bar ⁻¹)	2.63	5.21	12.40	5.21	5.06	5.06	1.92	25.02	3.78	5.32	3.78	5.32
ΔH_2 (kJ mol ⁻¹)	2.0	28.2	17.4	27.8	26.6	26.6	33.4	22.2	32.8	27.2	32.8	27.0

In this study, the adsorbed concentration ratio at 30 °C, η , as a function of the pressure, was used as an indicator for assessing the adsorption selectivity to CO. Figure 3.3 shows η as a function of the partial pressure in an equimolar mixture of CO and CO₂, for the prepared adsorbent samples.

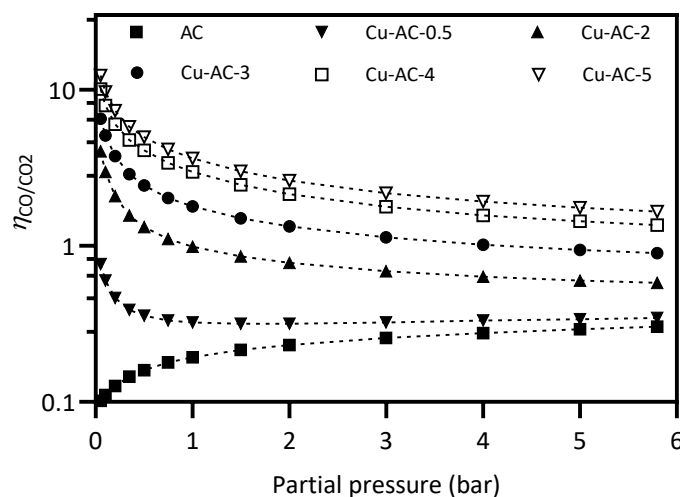


Figure 3.3 – Adsorbed concentration ratio of CO over CO₂ for the same partial pressure at 30 °C on AC and Cu-AC.

As it can be observed, the presence of copper sites in the adsorbent surface leads to an inversion in the adsorption selectivity ($\eta > 1$), favoring the CO adsorption over the CO₂, for the adsorbents with ≥ 2 mol/kg of copper loading. Figure 3.4 plots the adsorption concentration ratio of CO over the remaining gases on Cu-AC-5; the adsorption concentration ratio for the different gases is as follows: $\eta_{\text{CO}/\text{H}_2} > \eta_{\text{CO}/\text{N}_2} > \eta_{\text{CO}/\text{CH}_4} > \eta_{\text{CO}/\text{CO}_2}$.

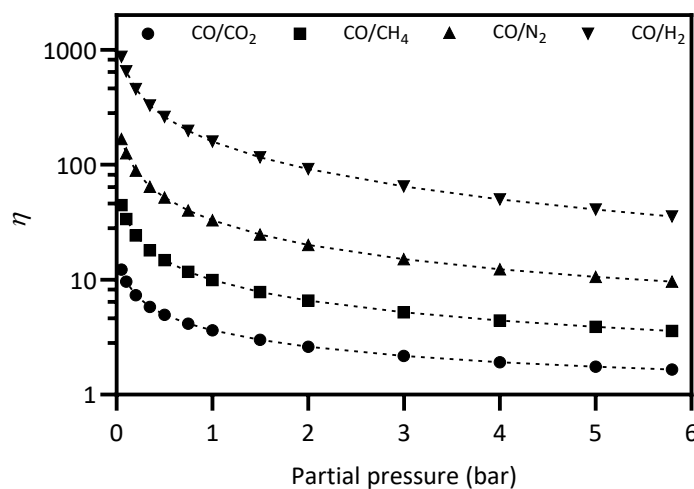


Figure 3.4 – Adsorbed concentration ratio of CO over CO₂; CH₄; N₂ and H₂ at 30 °C on Cu-AC-5.

3.3.3. Adsorption kinetics

Experimental uptake curves were determined for each experimental value of the adsorption isotherms. The data was fitted to the kinetic model based on intraparticle diffusion previously described by eq. (3.4), which allows obtaining the inversed apparent diffusion time constant, $D \cdot r^2$. The parameters for the pristine AC and Cu-AC-5 samples, obtained at 1 bar and 30 °C, are summarized in Table 3.3.

Table 3.3 – Kinetic model parameters obtained at 1 bar and 30 °C for the pristine AC and Cu-AC-5 for CO, CO₂, CH₄, and N₂.

	$D \cdot r^2$ (s ⁻¹)		α		β		α^*		$ha/\rho C_P$	
	AC	Cu-AC-5	AC	Cu-AC-5	AC	Cu-AC-5	AC	Cu-AC-5	AC	Cu-AC-5
CO	0.114	0.022	0.208	0.521	0.119	0.779	0.003	0.011	0.014	0.011
CO₂	0.028	0.027	0.539	0.372	0.492	0.195	0.007	0.006	0.015	0.010
CH₄	0.095	0.082	0.100	0.261	0.170	0.138	0.028	0.004	0.024	0.021
N₂	0.136	0.116	0.138	0.116	0.085	0.063	0.003	0.003	0.019	0.013

Regarding the intraparticle diffusion, all gases display a high $D \cdot r^2$, indicating that both adsorbents are suitable for equilibrium-controlled separation processes. The hydrogen uptake was too fast, and it was not possible to obtain experimentally the inversed apparent diffusion time constant. Apart from CO, the kinetic parameters of the remaining gases in AC and Cu-AC samples are similar, suggesting that the impregnation with copper salt of the AC does not affect the intraparticle gas diffusion kinetics. Nitrogen shows the fastest adsorption kinetics, with a $D \cdot r^2$ of 0.136 s⁻¹ in pristine AC, while Cu-AC-5 displays a $D \cdot r^2$ of 0.116 s⁻¹; similar values of ca. 0.103 s⁻¹ can be found in relevant literature [35]. CO₂ presents the slowest kinetics in the pristine AC, with a $D \cdot r^2$ of 0.028 s⁻¹, very close to the value obtained for sample Cu-AC-5, 0.027 s⁻¹; these results are in agreement with the CO₂ kinetics reported by Delgado et al. [36]. The same study reports a $D \cdot r^2$ of 0.067 s⁻¹ for methane, which is close to the values determined in this study, 0.095 s⁻¹ and 0.082 s⁻¹, for AC and Cu-AC-5 respectively. CO uptake is quite different on pristine AC and sample Cu-AC-5, respectively $D \cdot r^2 = 0.114$ s⁻¹ and $D \cdot r^2 = 0.022$ s⁻¹. The must slower CO uptake on sample Cu-AC-5 was assigned to fast chemisorption at the π -complexation sites, which hiders the

surface diffusion. Though the slower diffusion of CO in the copper-modified AC, the mass transport is fast enough for use in equilibrium-based PSA processes, $D \cdot r^{-2} \geq 0.02 \text{ s}^{-1}$ [25].

3.3.4. Deactivation and regenerability studies

To study the deactivation of copper-modified AC under oxidative atmospheres, a sample of Cu-AC-5 was exposed to ambient air for two weeks and another was exposed to pure oxygen overnight. After that, adsorption measurements were repeated for all the gases. In the case of CO₂, CH₄, N₂, and H₂, no differences in adsorption equilibrium or kinetics were observed. On the other hand, CO displayed a very slow adsorption uptake, as illustrated in Figure 3.5. After evacuating these two samples and repeating the measurements, a significant increase in CO adsorption capacity was observed, indicating that a certain degree of reactivation occurred. This reactivation was assigned to the partial reduction of Cu²⁺ to Cu⁺ after having contacted with CO, a slow process when conducted at low temperature. Accordingly, the slow adsorption uptakes should be assigned to the reduction of copper and consequent CO oxidation to CO₂.

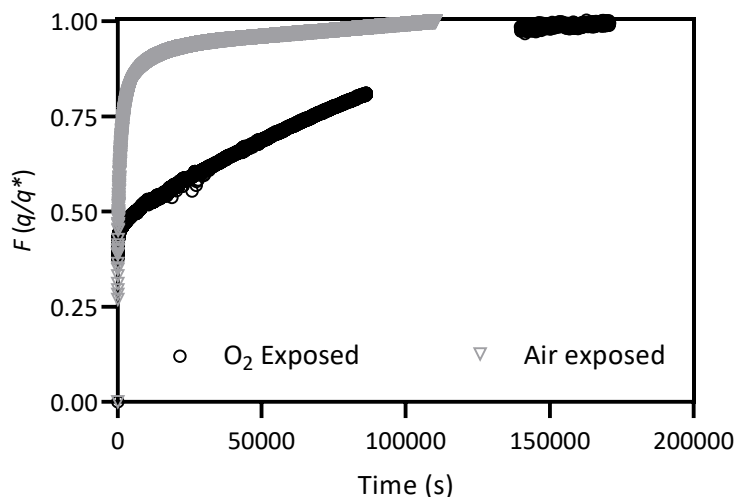


Figure 3.5 – Adsorption uptake of CO on Cu-AC sample exposed to air and pure oxygen. Missing data in the O₂ exposed sample is related to limitations in the data acquisition system.

Since it was not possible to obtain the true CO adsorption isotherms on air/O₂-exposed samples, the degree of deactivation was then evaluated based on “pseudo-adsorption isotherms”. The CO pseudo-adsorption isotherms were calculated based on the adsorbed concentration at instant 1000 s – Figure 3.6. As it can be observed, the deactivation is much more significant in the O₂-exposed sample.

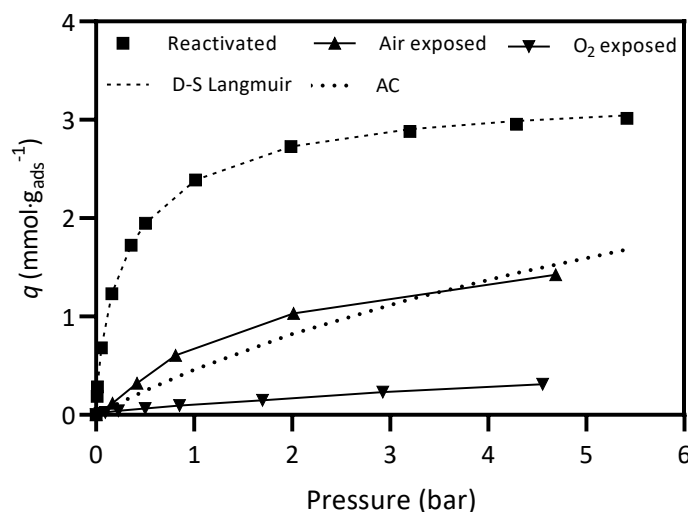


Figure 3.6 – Experimental adsorption equilibrium isotherms on O₂-exposed Cu-AC-5, air-exposed Cu-AC-5, and reactivated Cu-AC-5 at 30 °C. Dashed lines represent the dual-site Langmuir model of Cu-AC-5 before deactivation; dotted lines represent CO adsorption on pristine AC. Solid lines were added to improve readability.

After the deactivation tests, both samples were reactivated overnight under H₂ at 150 °C. As displayed in Figure 3.6, the reactivated Cu-AC-5 presents the same CO adsorption isotherm as before the deactivation tests, regardless of its deactivation state. These findings give important insights for the handling and storage of the samples since no particular care seems to be necessary, provided that an adequate activation is performed before using these copper-modified activated carbons.

3.4. Conclusions

The preparation of π -complexation adsorbents from a commercial activated carbon by wetness impregnation of copper chloride was investigated. The results indicate that the copper loading have a positive effect on carbon monoxide adsorption, but it is limited by the monolayer dispersion capacity. The opposite was observed for the other gases under study, whose adsorption capacity decrease is attributed to the decrease of specific surface area. Despite the slower CO kinetics in Cu-AC samples, the apparent diffusion is still high enough for equilibrium-based separation.

Finally, the deactivation studies suggest that Cu-AC suffers from deactivation when exposed to oxidative atmospheres, leading to CO adsorption decrease. However, the samples can be reactivated without losing their initial features.

The present findings may help to solve practical aspects related to adsorbent preparation, handling, storage, and in-site reactivation.

3.5. Acknowledgements

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3.6. Nomenclature

Parameters	Description	Units
a	External surface area per unit volume of adsorbent sample	cm^{-1}
b	Langmuir affinity constant	bar^{-1}
d	Diameter	cm
C_p	Effective heat capacity of adsorbent sample	$\text{J g}^{-1} \text{K}^{-1}$
D	Diffusivity	$\text{cm}^2 \text{s}^{-1}$
F	Fractional adsorbed quantity	
h	Heat transfer coefficient	$\text{W cm}^{-2} \text{K}^{-1}$
P	Pressure	bar^{-1}
q	Molar concentration in the adsorbed phase	mmol g^{-1}
R	Ideal gas constant	$\text{J K}^{-1} \text{mmol}^{-1}$
T	Temperature	K
t	Time	s
Greek Symbol	Description	Units
α	Adjusting parameter	
β	Adjusting parameter	
ΔH	Heat of adsorption	J mmol^{-1}
ρ	Density of the adsorbent sample	J cm^{-3}
η	Adsorbed concentration ratio	
Subscripts	Description	
ads	Adsorbent	
i	Component j	
j	Component j	
max	Maximum	
mix	Mixture	
nc	Number of components	

*Unless explicitly stated otherwise.

3.7. References

1. Chakraborty, S., et al., *Enrichment of a solventogenic anaerobic sludge converting carbon monoxide and syngas into acids and alcohols*. Bioresource technology, 2019. **272**: p. 130-136.
2. Patel, D.M., P. Kodgire, and A.H. Dwivedi, *Low temperature oxidation of carbon monoxide for heat recuperation: A green approach for energy production and a catalytic review*. Journal of Cleaner Production, 2020. **245**: p. 118838.
3. Gomes, K.K., et al., *Designer Dirac fermions and topological phases in molecular graphene*. Nature, 2012. **483**(7389): p. 306-310.
4. Johnson, T.R., et al., *Metal carbonyls: a new class of pharmaceuticals?* Angewandte Chemie International Edition, 2003. **42**(32): p. 3722-3729.
5. Bierhals, J., *Carbon monoxide*. Ullmann's encyclopedia of industrial chemistry, 2000.
6. Medrano-García, J., R. Ruiz-Femenia, and J. Caballero, *Optimal carbon dioxide and hydrogen utilization in carbon monoxide production*. Journal of CO₂ Utilization, 2019. **34**: p. 215-230.
7. Evans, A., R. Luebke, and C. Petit, *The use of metal–organic frameworks for CO purification*. Journal of Materials Chemistry A, 2018. **6**(23): p. 10570-10594.
8. Ramírez-Santos, Á.A., C. Castel, and E. Favre, *A review of gas separation technologies within emission reduction programs in the iron and steel sector: Current application and development perspectives*. Separation and Purification Technology, 2018. **194**: p. 425-442.
9. Dutta, N. and G. Patil, *Developments in CO separation*. Gas separation & purification, 1995. **9**(4): p. 277-283.
10. Lim, Y.-I., et al., *Techno-economic comparison of absorption and adsorption processes for carbon monoxide (CO) separation from Linde-Donawitz gas (LDG)*. Korean Chemical Engineering Research, 2016. **54**(3): p. 320-331.

11. Vo, T.K., et al., *Cost-effective and eco-friendly synthesis of MIL-101 (Cr) from waste hexavalent chromium and its application for carbon monoxide separation*. Journal of Industrial and Engineering Chemistry, 2019. **80**: p. 345-351.
12. Bistoni, G., et al., *How π back-donation quantitatively controls the CO stretching response in classical and non-classical metal carbonyl complexes*. Chemical science, 2016. **7**(2): p. 1174-1184.
13. Grande, C.A., et al., *New π -complexation adsorbents for propane– propylene separation*. Langmuir, 2004. **20**(13): p. 5291-5297.
14. Khan, N.A. and S.H. Jhung, *Adsorptive removal and separation of chemicals with metal-organic frameworks: contribution of π -complexation*. Journal of hazardous materials, 2017. **325**: p. 198-213.
15. Cao, Y., et al., *Adsorption desulfurization via π -complexation with Ag⁺-exchanged anionic metal–organic framework*. Industrial & Engineering Chemistry Research, 2019. **58**(16): p. 6704-6711.
16. Gao, F., et al., *Selective CO adsorbent CuCl/AC prepared using CuCl₂ as a precursor by a facile method*. RSC Advances, 2016. **6**(41): p. 34439-34446.
17. Gao, F., Y. Wang, and S. Wang, *Selective adsorption of CO on CuCl/Y adsorbent prepared using CuCl₂ as precursor: Equilibrium and thermodynamics*. Chemical Engineering Journal, 2016. **290**: p. 418-427.
18. Yeom, C. and Y. Kim, *Mesoporous alumina with high capacity for carbon monoxide adsorption*. Korean Journal of Chemical Engineering, 2018. **35**(2): p. 587-593.
19. Yang, R.T., *π -Complexation Sorbents and Applications*, in *Adsorbents: Fundamentals and Applications*. 2003. p. 191-230.
20. Firmino, A.D.G., et al., *Synthesis of MOFs at the Industrial Scale*, in *Metal-Organic Frameworks*. 2018. p. 57-80.
21. Ma, J., et al., *CO adsorption on activated carbon-supported Cu-based adsorbent prepared by a facile route*. Separation and purification technology, 2010. **76**(1): p. 89-93.

22. Gao, F., et al., *Adsorption separation of CO from syngas with CuCl@ AC adsorbent by a VPSA process*. RSC advances, 2018. **8**(69): p. 39362-39370.
23. Cho, K., et al., *High CO adsorption capacity, and CO selectivity to CO₂, N₂, H₂, and CH₄ of CuCl/bayerite adsorbent*. Microporous and Mesoporous Materials, 2019. **277**: p. 142-148.
24. Feyzbar-Khalkhali-Nejad, F., et al., *Adsorption-based CO removal: principles and materials*. Journal of Environmental Chemical Engineering, 2021: p. 105317.
25. Relvas, F., et al., *Single-stage pressure swing adsorption for producing fuel cell grade hydrogen*. Industrial & Engineering Chemistry Research, 2018. **57**(14): p. 5106-5118.
26. Golden, T.C., W.C. Kratz, and F.C. Wilhelm, *Highly dispersed cuprous compositions*. 1992, US5126310A, Air Products and Chemicals Inc.
27. Andrade, M., F. Relvas, and A. Mendes, *Highly propylene equilibrium selective carbon molecular sieve adsorbent*. Separation and Purification Technology, 2020: p. 116853.
28. Do, D.D., *Adsorption analysis: equilibria and kinetics*. Vol. 2. 1998: Imperial college press London.
29. Kočirík, M., P. Struve, and M. Bülow, *Analytical solution of simultaneous mass and heat transfer in zeolite crystals under constant-volume/variable-pressure conditions*. Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 1984. **80**(8): p. 2167-2174.
30. Ruthven, D. and L.K. Lee, *Kinetics of nonisothermal sorption: Systems with bed diffusion control*. AIChE Journal, 1981. **27**(4): p. 654-663.
31. Deraz, N., *The comparative jurisprudence of catalysts preparation methods: I. Precipitation and impregnation methods*. J. Ind. Environ. Chem, 2018. **2**(1): p. 19-21.
32. Xue, C., et al., *CO Adsorption Performance of CuCl/Activated Carbon by Simultaneous Reduction–Dispersion of Mixed Cu (II) Salts*. Materials, 2019. **12**(10): p. 1605.
33. Cho, K., et al., *Synthesis of CuCl/Boehmite adsorbents that exhibit high CO selectivity in CO/CO₂ separation*. Journal of hazardous materials, 2018. **344**: p. 857-864.

34. Wang, Y.-C., et al., *Unusual Copper Oxide Dispersion Achieved by Combining the Confinement Effect and Guest–Host Interaction Modulation*. Industrial & Engineering Chemistry Research, 2020. **59**(37): p. 16296-16304.
35. Shen, C., et al., *Adsorption equilibria and kinetics of CO₂ and N₂ on activated carbon beads*. Chemical Engineering Journal, 2010. **160**(2): p. 398-407.
36. Delgado, J.A., et al., *Adsorption and diffusion of H₂, CO, CH₄, and CO₂ in BPL activated carbon and 13X zeolite: evaluation of performance in pressure swing adsorption hydrogen purification by simulation*. Industrial & Engineering Chemistry Research, 2014. **53**(40): p. 15414-15426.

Chapter 4. Single-stage pressure swing adsorption for producing fuel cell hydrogen grade

4.1. Introduction

PSAs designed for hydrogen from reformat streams typically use zeolites, activated carbons (ACs), and more recently, metal-organic-frameworks (MOFs) [1-5]. However, commercially available adsorbents display highly favorable CO₂ adsorption, partially inhibiting CO removal. For this reason, improvements in CO separation are of particular interest. Great attention has been paid to π -complexation adsorbents. The stronger π -complex interaction between transition metal ions and CO molecules leads to a higher CO adsorption affinity, thus increasing its selectivity [6]. Several authors successfully prepared π -complexation adsorbents from different types of samples including zeolites, MOFs, and ACs [6-11]. For instance, the US patent 4.470.829 disclosed by Hirai *et al.* (Nippon Steel Corporation) describes a water-resistant adsorbent comprising one copper halide and activated carbon, where no changes in carbon monoxide adsorption are observed after contacting with 4420 ppm of humidity [9]. Among the π -complexation adsorbents, activated carbons are the cheapest option and can be easily regenerated during the PSA operation. S.H. Cho *et al.* disclosed a 4-beds vacuum pressure swing adsorption (VPSA) unit, each bed containing a plurality of adsorbent layers, including CuCl-impregnated alumina adsorbent combined with activated carbon, zeolite 13X, and zeolite 5A [12]. The claimed unit can produce hydrogen containing 210 ppm of CH₄ and 1 ppm of CO, at a recovery of 93 %, from a feed stream containing 73.5 % H₂, 18.2 % CO₂, 3.8 % CH₄ and 4.5 % CO. However, the need for a vacuum source increases the capital and operation costs of the VPSA unit and increases the operation complexity.

In the present work, a commercial activated carbon was used to prepare π -complexation adsorbents by wet impregnation of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with different copper loadings. The best performing adsorbent was fully characterized and tested in a lab-scale PSA unit. The PSA unit was supplied with an ethanol steam reforming synthetic stream, containing 70 % of H_2 , 25 % of CO_2 , 4 % of CH_4 , 1 % of CO , and no nitrogen, aiming to produce a purified stream of hydrogen +99.97 % and containing < 0.2 ppm of CO and displaying a recovery > 75 %.

4.2. Experimental

4.2.1. Adsorbent preparation

A sample of commercial activated carbon (AC), Kuraray 2GA-H2 (Kuraray CO., LTD.), was modified by wet impregnation according to the method described by U.S Patent 5.175.137, disclosed by Golden et al. [13] (Air Products and Chemicals Inc.). The AC was heated at 250 °C overnight under air atmosphere. The aim was to increase the hydrophilicity of the surface and thus enhancing the copper dispersion. After the heat treatment, the sample was cooled down to 120 °C and soaked into an aqueous copper solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, originally at room temperature, whose concentration depends on the desired copper loading. Ammonium citrate with a weight ratio of 0.07 ($w_{(\text{NH}_4)_2\text{C}_6\text{H}_6\text{O}_7} / w_{\text{CuCl}_2 \cdot 2\text{H}_2\text{O}}$), was used as dispersing agent. The AC was activated under hydrogen atmosphere at 150 °C during 16 h, for reducing copper to its monovalent state. The modified adsorbents were named as Cu-AC-X, where X denotes the copper loading in $\text{mmol g}_{\text{ads}}^{-1}$.

4.2.2. Adsorbent characterization

To study the copper loading effect, adsorption equilibrium isotherms of CO_2 , CO , CH_4 , and H_2 were obtained at 40 °C for all samples, using the volumetric method described by Santos *et al.* (2008) [14]. The sample with a copper loading of 2 $\text{mmol g}_{\text{ads}}^{-1}$, Cu-AC-2, was fully characterized concerning its adsorption capacity towards the gases under study at

30 °C, 40 °C, and 50 °C. The criteria for the sample selection will be discussed further below. In the present work, the experimental adsorption equilibrium isotherms were fitted to dual-site Langmuir model, according to eq. (4.1) [15].

$$q_i = \frac{q_{\max,1} b_1 P_i}{1 + b_1 P_i} + \frac{q_{\max,2} b_2 P_i}{1 + b_2 P_i} \quad (4.1)$$

where q_i is the molar concentration in the adsorbed phase in mole per unit of mass, $q_{\max}$ is the maximum adsorbed concentration, corresponding to a complete monolayer coverage according to Langmuir theory, b is the affinity constant, and the subscript i denotes the gas under study. Obtaining the adsorption isotherms at different temperatures allows determining the heat of adsorption, ΔH_1 , according to eq. (4.2) and (4.3), where b_{∞} is the pre-exponential factor of the affinity constant [16].

$$b_1 = b_{\infty,1} e^{-\Delta H_1 / RT} \quad (4.2)$$

$$b_2 = b_{\infty,2} e^{-\Delta H_2 / RT} \quad (4.3)$$

The identification of the copper states in the selected sample was done by XPS.

4.2.3. Breakthrough experiments

The study of effluent composition vs. time during adsorption and desorption steps is essential for modelling and analysis. A set of breakthrough experiments were carried out to assess the adsorption column dynamics. The assays were conducted in an in-house built setup, described elsewhere and shown in Appendix B.1.2 [17], comprising a packed column placed in a thermostatic chamber. The column is feed through a mass flow controller and the product flow rate determined using a mass flow meter. Two thermocouples and pressure transducers were placed at the entrance and at the column's exit and the pressure was manipulated using a backpressure regulator. The outlet compositions were measured by mass spectrometer, Pfeifer GSD 301 O2.

The experiments were conducted at 1 bar and 2 bar, varying the feed flow rate between $0.5 \text{ L}_N \cdot \text{min}^{-1}$ and $1.0 \text{ L}_N \cdot \text{min}^{-1}$. The temperature of the thermostatic chamber was kept at 40°C for all experiments. Monocomponent and multicomponent breakthroughs were performed using a mixture of the gas balanced with helium, while desorption measurements were carried out passing helium through the column after each adsorption experiment. The characteristics of the column and the experimental conditions are detailed in Table 4.1.

Table 4.1 – Characteristics of the column and experimental conditions used in breakthrough experiments.

Column characteristics		
L / cm		34.0
$d_{\text{in}} / \text{cm}$		3.2
d_{o} / cm		3.5
Thermocouple distance from the column ends / cm		2.5 cm
$m_{\text{Cu-AC-2}} / \text{kg}$		0.161
Feed conditions		
Feed molar ratio / dimensionless	He:CO ₂	75:25
	He:CO	95:5
	He:CH ₄	90:10
	He:H ₂	80:20
	He:CO ₂ : H ₂ :CH ₄	49:25:20:4:1
$Q_{\text{feed}} / \text{L}_N \cdot \text{min}^{-1}$		0.5 - 1
$T / ^\circ\text{C}$		40
P / bar		1 - 2

4.2.4. Lab-scale PSA

An in-house lab-scale PSA unit was built, loaded with the selected adsorbent and fed with a synthetic reformat mixture of 70 % H₂, 25 % CO₂, 4 % CH₄ and 1 % CO, based on the outlet composition of a bioethanol fuel processor (reformer followed by a water gas shift reactor) [18]. The unit comprises four columns packed with the adsorbent and a fifth column used to store part of the product. Each column, made of stainless steel, has length of 34.5 cm and inner and outer diameters and of 2.7 cm and 3.0 cm, respectively. The feed and purge flow rates are measured by mass flow meters (Bronkhorst High-tech, El Flow F-

112AC, 0 - 20 L_N min⁻¹ and F-111C, 0 - 2 L_N min⁻¹, respectively). The product flow rate is controlled using a mass flow controller (Bronkhorst, El-Flow F-201CV, 0 - 10 L_N min⁻¹). The purge and backfill flow rates are adjustable using a needle valve. Four pressure transducers (Druck, PMP 4010, 0 – 10 bar) placed at the bottom of each column are used to obtain the pressure history inside adsorption beds during operation. A set of solenoid valves (SCG325B036 by ASCO) and check valves (Swagelok, SS-2C-1/3) are used to direct the flow according to the adsorption cycle. Before starting operating the PSA unit, the columns were purged with pure H₂ and then pressurized to the operation pressure. The system was controlled using a LabView interface and a Visual Basic routine for controlling the opening/closing of the valves, with a maximum frequency of 10 Hz, according to the PSA cycle. A sketch of the system is shown in Figure 4.1.

The analysis of the outlet concentration was carried out by gas chromatography (Dani GC 1000 equipped with a TCD detector), a CO₂ analyzer (Thermo Scientific 410i), and a CO analyzer (Signal Instruments 7000FM, equipped with a low range cell (0-40 ppm)). The PSA performance was assessed according to H₂ purity, contaminants concentration as well as productivity and recovery. Productivity, ρ_{PROD} was calculated in terms of produced hydrogen per adsorbent mass per cycle time, according to eq. (4.4); eq. (4.5) was used to calculate the recovery, ρ_{REC} [19].

$$\rho_{\text{PROD}} = \frac{\int_0^{t_{\text{AD}}} y_{\text{prod}, \text{H}_2} \cdot Q_{\text{prod}} dt}{t_{\text{cycle}} \cdot m_{\text{AC}}} \cdot 100 \quad (4.4)$$

$$\rho_{\text{REC}} = \frac{\int_0^{t_{\text{AD}}} y_{\text{prod}, \text{H}_2} \cdot Q_{\text{prod}} dt}{\int_0^{t_{\text{AD}}} y_{\text{feed}, \text{H}_2} \cdot Q_{\text{feed}} dt} \cdot 100 \quad (4.5)$$

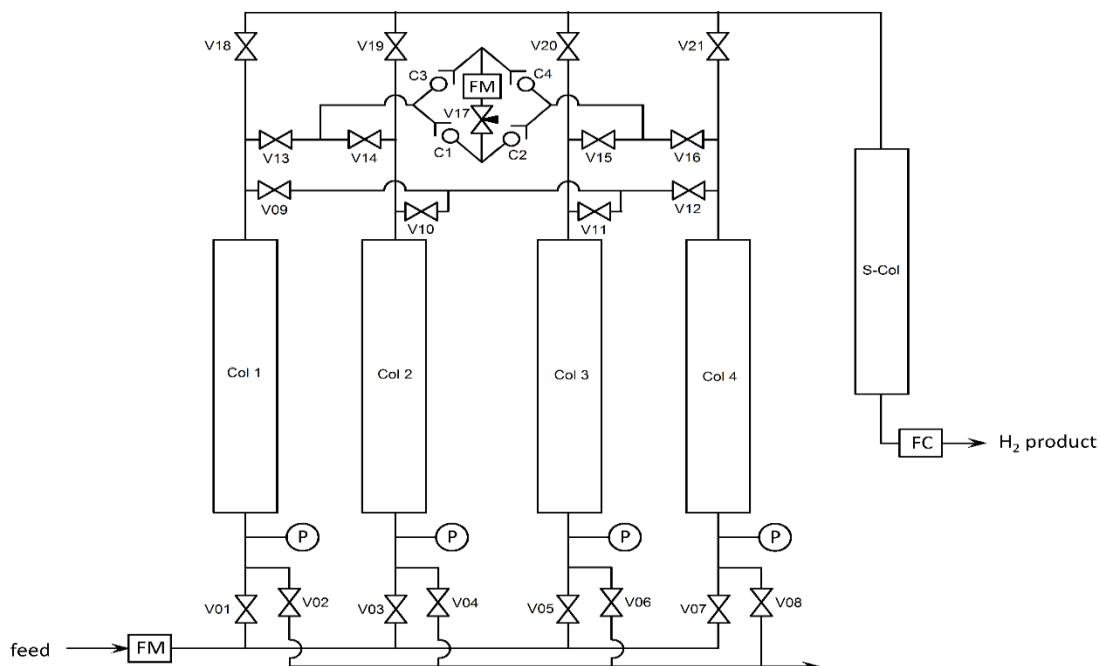


Figure 4.1 – Schematic representation of the lab PSA unit. FM – Flow meter; FC – Flow controller; V – On-off valve; C – Check valve.

During the PSA cycle, each column runs through 8 elementary steps, sketched in Figure 4.2. However, when considering the 4-columns, the steps do not completely align in the PSA cycle due to their different durations, resulting in a 12-events cycle. The full cycle sequence is given in Table 4.2, which can be described as follows (following Bed 1):

- Step 1 and 2 – Adsorption (AD): Col I is fed through an on/off valve placed in the feed line, while the product flow rate is controlled through a mass flow controller placed after the storage column;
- Step 3 – Adsorption/providing backfill (AD/PBF): The produced stream is split in two parts, one part continuously flowing to the storage column and the other is used to pressurize (backfill) the next producing column, col IV. The needle valve placed in the backfilling line (identified as V17 in Figure 4.1) was adjusted so no pressure variation occurs in col I: exiting flow rate, made of product flow rate and backfilling flow rate, should be close to the feed flow rate;

- Step 4 – Depressurization Pressure Equalization (DPE): After the producing phase, col I equalizes pressure with col II. The time of equalization step was fixed at 2 s, the time needed to achieve pressure equilibrium;
- Step 5 – Providing Purge (PP): The gas remaining in col I is used to purge Col III. The purging is performed through the top end of both columns. The step time was adjusted so the pressure in the col I decreases to 2 bar, P_{BD} .
- Step 6 and 7 – Blowdown (PP): Col I is depressurized from the bottom end of the column;
- Step 8 – Purge (PG): Col I is purged receiving the purging gas from the top end of the column. This step improves the regeneration of the adsorbent;
- Step 9 and 11 – Idle: In this step, all the valves connected to the column are closed;
- Step 10 – Pressurization Pressure Equalization (PPE): Col I equalizes pressure with col II;
- Step 12 – Backfill (BF): Col I is backfilled with purified hydrogen from the producing column, col III. In the end of the step, the pressure of the backfilled column (col I) should be the maximum operating pressure. This allows that when col I moves towards from step 12 to step 1, respectively elementary steps 8 and 1, the feed flow rate stills constant, since the entering pressure does not suffer any change.

A typical pressure history in the PSA columns along the cycle is given in Figure 4.3.

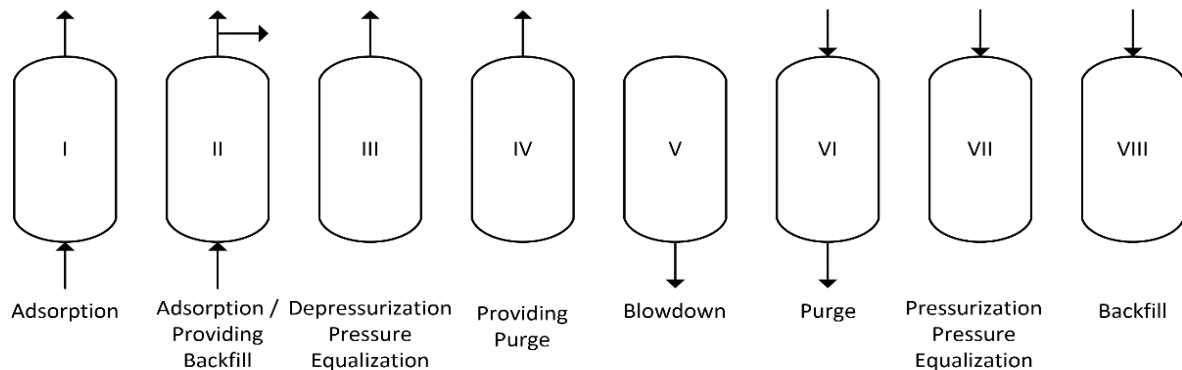


Figure 4.2 – Elementary steps of the PSA cycle.

Table 4.2 – Sequence of the 12-step PSA cycle. AD – Adsorption; PBF – Providing backfill;
DPE – Depressurization pressure equalization; PP – Providing purge; BD – Blowdown; PG – Purge;
PPE – Pressurization pressure equalization; BF – Backfill.

Step	1	2	3	4	5	6	7	8	9	10	11	12
Time / s	2	40-90	40-90	2	40-60	40-90	2	40-60	40-90	2	40-60	40-90
Col I	AD		AD/PBF	DPE	PP	BD		PG	IDLE	PPE	IDLE	BF
Col II	BD	PG	IDLE	PPE	IDLE	BF	AD		AD/PBF	DPE	PP	BD
Col III	DPE	PP	BD		PG	IDLE	PPE	IDLE	BF		AD	AD/PBF
Col IV	PPE	IDLE	BF	AD		AD/PBF	DPE	PP	BD		PG	IDLE

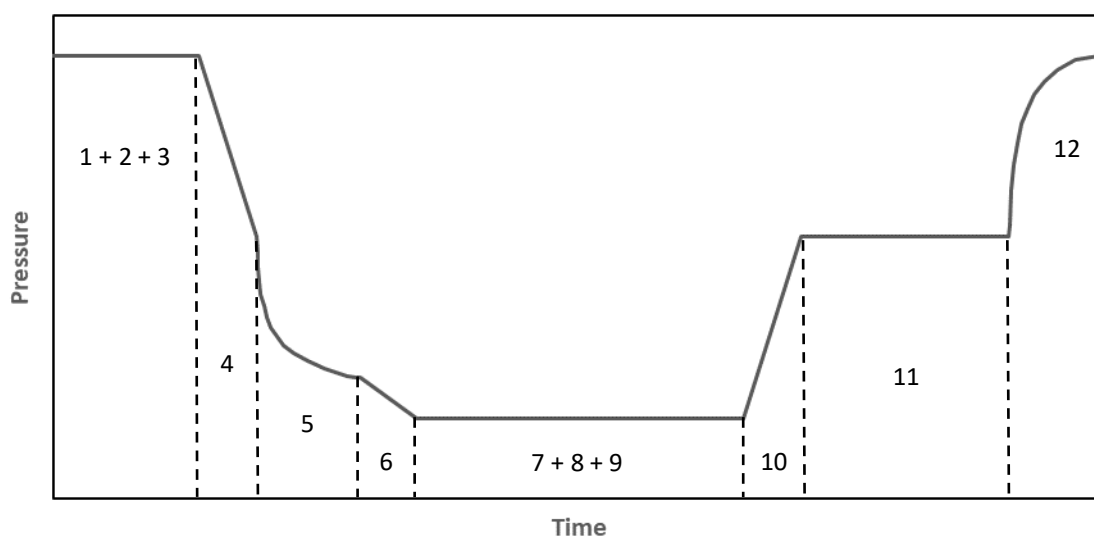


Figure 4.3 – Typical pressure history in the adsorption columns along the PSA cycle.

4.2.5. Design of Experiments

The operating conditions of the PSA unit were systematically optimized following a Design of Experiments (DoE). Response Surface Methodology (RSM) is part of the DoE toolbox, which uses multiple regression analysis as a tool to relate process responses with the factors under study. Within the experimental designs, central composite design (CCD) is one of the most commonly used, combining two-level factorial points with center points at the midrange value [20]. An empirical second-order polynomial model can be obtained and the interaction amongst the factors accessed by fitting the regression parameters to the experimental values [21]. In the case of PSA operation, process responses such as purity

and recovery are influenced by several factors, namely operating pressure, temperature, cycle sequence, product flow rate, etc.

In the present study, pressure, P_H , product flow rate, Q_{prod} , and production time, which includes the time of elementary steps I and II, $t_{\text{AD}} = t_1 + t_{11}$, were selected as factors with three levels each as suggested elsewhere [22]. The selected response variables were CO content, y_{CO} , and recovery, ρ_{REC} , and the objective functions consider maximizing the hydrogen recovery keeping y_{CO} below 0.2 ppm.

Considering the response variable $\hat{y}$ (y_{CO} or ρ_{REC}), the response equation may be written as follows:

$$\begin{aligned} \hat{y} = & \beta_0 + \beta_1 \left(\frac{P - \bar{P}}{P_{+1} - P_{-1}} \right) + \beta_2 \left(\frac{t_{\text{AD}} - \bar{t}_{\text{AD}}}{t_{\text{AD},+1} - t_{\text{AD},-1}} \right) + \beta_3 \left(\frac{Q_{\text{prod}} - \bar{Q}_{\text{prod}}}{Q_{\text{prod},+1} - Q_{\text{prod},-1}} \right) \\ & + \beta_4 \left(\frac{P - \bar{P}}{P_{+1} - P_{-1}} \right) \left(\frac{t_{\text{AD}} - \bar{t}_{\text{AD}}}{t_{\text{AD},+1} - t_{\text{AD},-1}} \right) + \beta_5 \left(\frac{P - \bar{P}}{P_{+1} - P_{-1}} \right) \left(\frac{Q_{\text{prod}} - \bar{Q}_{\text{prod}}}{Q_{\text{prod},+1} - Q_{\text{prod},-1}} \right) \\ & + \beta_6 \left(\frac{Q_{\text{prod}} - \bar{Q}_{\text{prod}}}{Q_{\text{prod},+1} - Q_{\text{prod},-1}} \right) \left(\frac{t_{\text{AD}} - \bar{t}_{\text{AD}}}{t_{\text{AD},+1} - t_{\text{AD},-1}} \right) + \beta_7 \left(\frac{P - \bar{P}}{P_{+1} - P_{-1}} \right)^2 + \beta_8 \left(\frac{t_{\text{AD}} - \bar{t}_{\text{AD}}}{t_{\text{AD},+1} - t_{\text{AD},-1}} \right)^2 + \beta_9 \left(\frac{Q_{\text{prod}} - \bar{Q}_{\text{prod}}}{Q_{\text{prod},+1} - Q_{\text{prod},-1}} \right)^2 \end{aligned} \quad (4.6)$$

where β_0 is the average response obtained experimentally and β_1 , β_2 and β_3 are the regression coefficients associated with P , t_{AD} and Q_{prod} , respectively. Coefficients β_4 , β_5 , and β_6 are related to the cross effects, while β_7 , β_8 and β_9 are the coefficients of quadratic effects. The subscripts +1 and -1 denote the upper and lower levels of factors.

The operating conditions, as well as the factors used in the PSA runs, are shown in Table 4.3. The fitness of the model was assessed by applying the analysis of variance (ANOVA). The parameters' significance was characterized by the p-value, while the coefficient of determination (R^2), the root mean square error (RMSE), and lack of fit test were used to assess the model fitness and accuracy.

Table 4.3 – Operating conditions of the PSA runs.

Feed molar ratio / dimensionless	H ₂ :CO ₂ :CH ₄ :CO - 70:25:4:1	
$Q_{\text{feed}} / \text{L}_\text{N} \text{ min}^{-1}$	1.48 - 2.07	
$T / ^\circ\text{C}$	ca. 25	
t_{eq} / s	2	
$P_{\text{BD}} / \text{bar}$	2	
Minimum number of PSA cycles ($4 \times t_{\text{AD}}$)	60	
$m_{\text{Cu-AC-2}} / \text{kg}$	0.121	
L / cm	35	
$d_{\text{in}} / \text{cm}$	2.2	
d_0 / cm	2.7	
DoE factors	Lower level (-1)	Upper level (+1)
$P_{\text{H}} / \text{bar}$	7.5	9
t_{AD} / s	92	152
$Q_{\text{prod}} / \text{L}_\text{N} \text{ min}^{-1}$	0.8	1.0

4.3. Results and Discussion

4.3.1. Adsorbent characterization

Adsorption isotherms of CO₂, CO, CH₄, and H₂ at 40 °C on the commercial and modified samples are shown in Figure 4.4. CO displays an enhanced adsorption capacity with the increase of copper loading; the opposite trend is observed for the other gases. In the commercial sample, CO₂ shows the highest adsorption capacity for the entire range of pressures studied. On the contrary, with the increase of the copper loading on the modified samples, CO becomes the most adsorbed species, in particular for the low-pressure range. Thus, as depicted in Figure 4.5, the adsorbed concentration ratio of carbon monoxide to carbon dioxide for the same partial pressure increases. Comparing the pristine AC sample and Cu-AC-2, the ratio increased from 0.12 to 3.26 at 0.1 bar and from 0.19 to 1.20 at 1 bar. The increase is even more noticeable at higher copper loadings, such as 5 mmol g_{ads}⁻¹, with an increase to 10.4 at 0.1 bar and 4.50 at 1 bar. Similar conclusions were drawn elsewhere [6, 8, 11]. As carbon monoxide is usually present in low quantities in reformat off-gases,

the high adsorption selectivity at low partial pressures plays an important role in effective CO removal. The increase in CO adsorption is attributed to the π -complexation interactions between CO and the monovalent copper, which occurs when CO molecule approaches the copper and an electron is transferred from the π orbital of CO to the valence s orbital of Cu^+ ; simultaneously, Cu^+ d orbitals back-donate electrons to the antibonding π -orbitals of CO [23]. In turn, the load of the AC internal surface by CuCl_2 and consequent reduction of pore volume and surface leads to lower CO_2 , CH_4 , and H_2 adsorption [7].

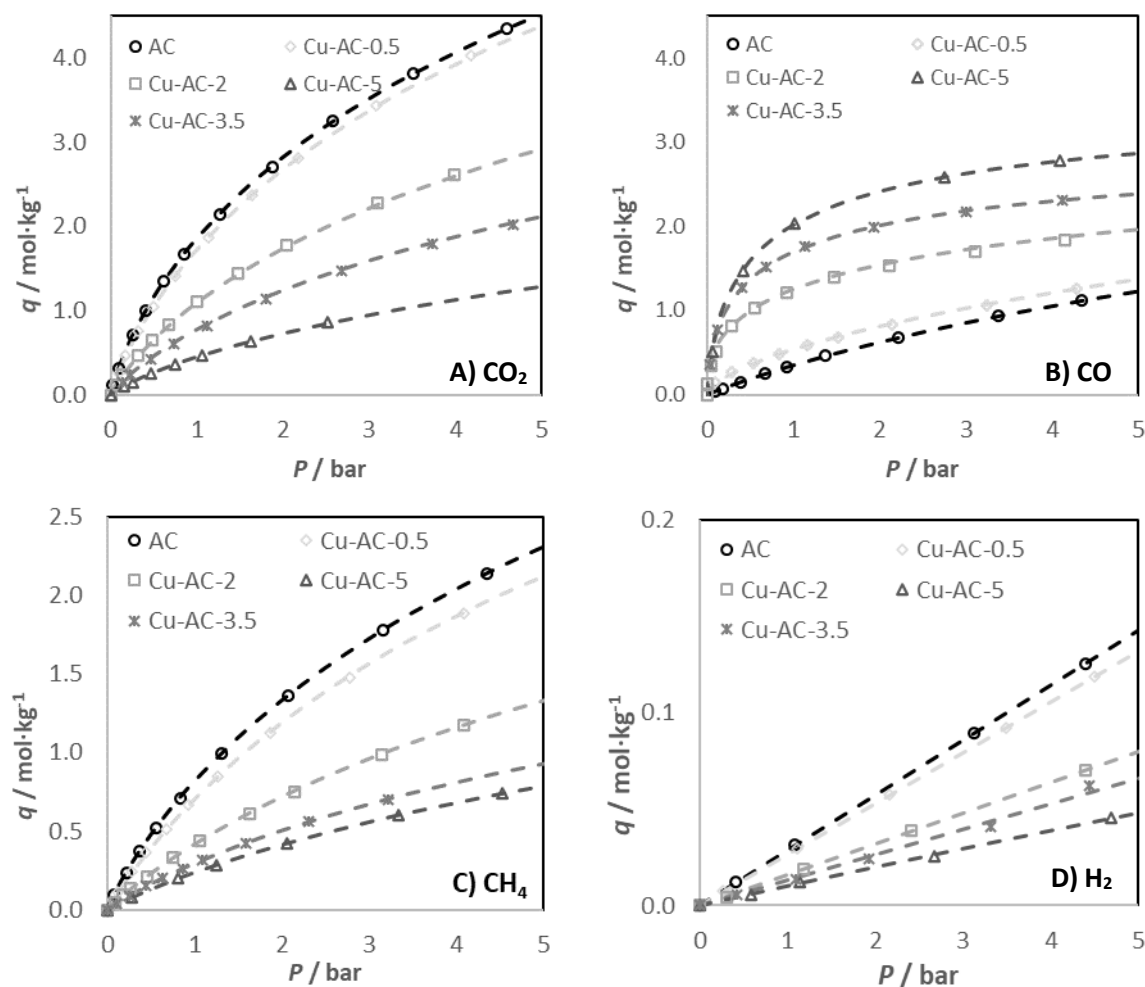


Figure 4.4 – Experimental adsorption isotherms in commercial and modified adsorbents at 40 °C. Dashed lines were obtained with dual-site Langmuir model; a) carbon dioxide; b) carbon monoxide; c) methane; d) hydrogen.

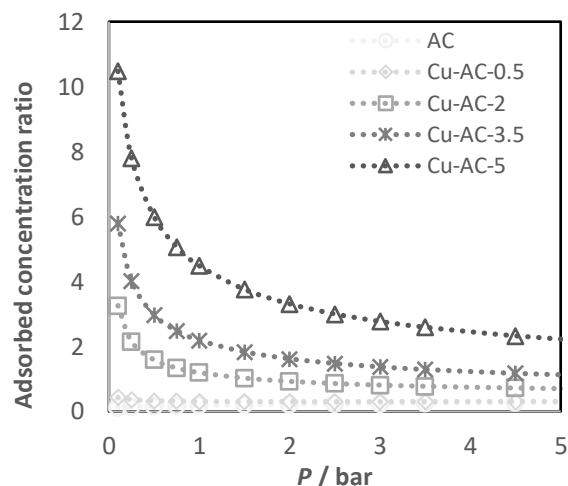


Figure 4.5 – Adsorbed concentration ratio of CO to CO₂ for the same partial pressure.

Curves were obtained based on dual-site Langmuir model.

Within the gases under study, carbon monoxide is the most problematic contaminant for fuel cell catalyst. However, to produce high purity hydrogen, removing other contaminants is also of great importance. As steam-reforming off-gases contain high amounts of carbon dioxide, the adsorption capacity to this species should be also high enough to guarantee its effective removal. Thus, based on CO and CO₂ adsorption isotherms, a copper loading of 2 mmol g_{ads}⁻¹ was selected for breakthrough and PSA testing. For this adsorbent, CO selectivity is high enough for an effective CO removal and CO₂ still presents a reasonable adsorption capacity.

Figure 4.6 depicts the adsorption equilibrium isotherms of H₂, CO₂, CH₄ and CO on Cu-AC-2 obtained at 30 °C, 40 °C, and 50 °C. The results were fitted using the dual-site Langmuir isotherm and are well predicted by the model. Isotherm parameters are presented in Table 4.4. Despite the lower $q_{\max}$ for CO in comparison to CO₂ and CH₄, the higher selectivity at low partial pressures has a greater contribution, namely at operating pressures in the range of 10 to 25 bar. It can be seen that carbon monoxide displays the highest heat of adsorption, ΔH_2 of 45.5 kJ mol⁻¹, which is close to the heat of adsorption on pure CuCl, 42.7 kJ mol⁻¹ [7, 23], and thus attributed to the bonding between CO and the copper salt. However, on the first set of sites, ΔH_1 is low as 18.5 kJ mol⁻¹. This value is most likely related to the adsorption on activated carbon, as it is very close to the value obtained by Brea *et al.* [24] on BPL

activated carbon, 18.7 kJ mol^{-1} . The parameters obtained for both sets of sites for the other gases under study are also in agreement with those reported in the same reference for BPL activated carbon.

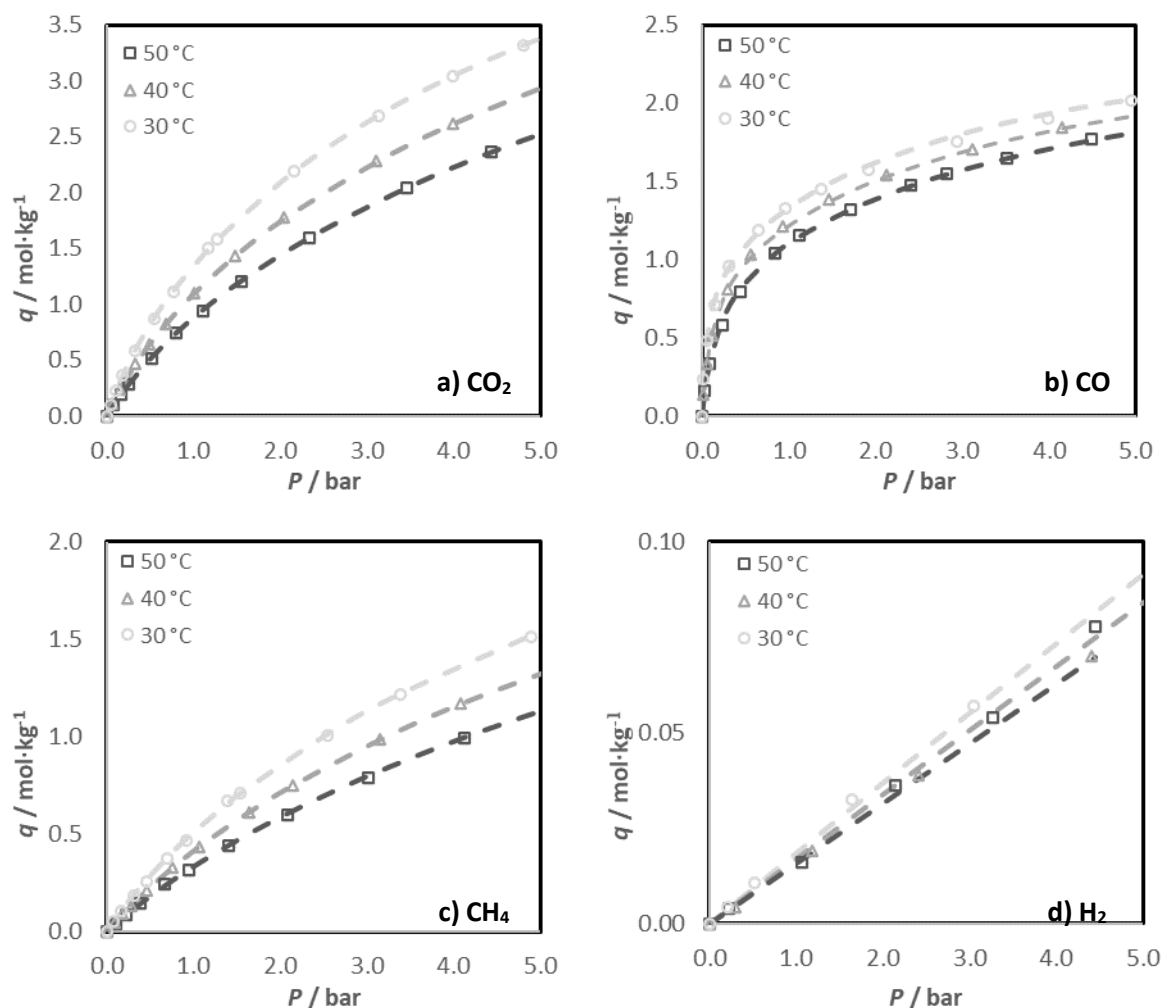


Figure 4.6 – Experimental adsorption isotherms in Cu-AC-2 at 30 °C, 40 °C, and 50 °C. Dashed lines were obtained with dual-site Langmuir model. a) CO₂; b) CO; c) CH₄; d) H₂.

Table 4.4 – Dual-site Langmuir equation parameters of CO₂, CO, CH₄ and H₂ adsorption isotherms on Cu-AC-2.

Parameter	CO ₂	CO	CH ₄	H ₂
$q_{\max,1} / \text{mol kg}^{-1}$	5.795	1.743	3.474	0.0275
$b_{\infty,1} \times 10^{-4} / \text{bar}^{-1}$	0.145	2.263	0.382	4.528
$\Delta H_1 \times 10^3 / \text{kJ mol}^{-1}$	23.74	18.513	20.35	6.857

$q_{\max,2} / \text{mol kg}^{-1}$	0.721	0.932	0.257	6.846
$b_{\infty,2} \times 10^{-4} / \text{bar}^{-1}$	0.474	0.0025	0.745	1.769
$\Delta H_2 \times 10^3 / \text{kJ mol}^{-1}$	26.74	45.45	24.02	6.876

4.3.2. XPS analysis

To determine the copper state in the selected modified adsorbent, two samples were subjected to x-ray photoelectron spectroscopy (XPS) analysis, one before and another after activation, Cu-AC-2-NA, and Cu-AC-2, respectively. The results are depicted in

Figure 4.7a and show the Cu 2p spectra for both samples. The activated sample, Cu-AC-2, presents two peaks at 932.2 eV and 952.0 eV, attributed to the binding energies of $\text{Cu}^+ 2p_{3/2}$ and $\text{Cu}^+ 2p_{1/2}$, respectively [25]. The non-activated sample Cu-AC-2-NA, in addition to the Cu^+ peaks, also presents the peaks attributed to Cu^{2+} at 934.7 and 954.7 eV and the Cu^{2+} satellite peak from 940 to 947 eV, indicating the presence of both copper species Cu^{2+} and Cu^+ [26]. The absence of peaks assigned to Cu^{2+} in Cu-AC-2 indicates a successful reduction of the copper during the activation procedure.

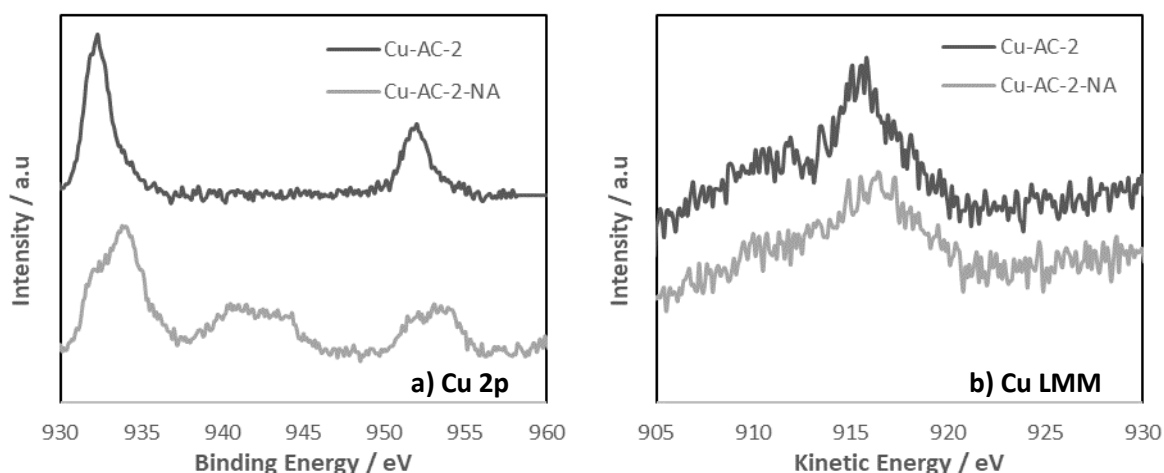


Figure 4.7 – XPS spectra of modified adsorbent before and after activation, Cu-AC-2-NA and Cu-AC-2. a) Cu 2p spectra; b) Cu Auger LMM spectra.

Due to the similarity of Cu 2p spectra of Cu^+ and Cu^0 , the Cu Auger LMM spectra was also analyzed, as depicted in

.b. It is observed an overlap of the peaks of the two samples near 916 eV, while the characteristic peak of Cu^0 was not observed, 919 eV [27]. Accordingly, it can be concluded that none of the samples contains Cu^0 .

4.3.3. Mono/multicomponent breakthrough experiments

Breakthrough experiments were performed to study the column dynamics at different conditions.

Figure 4.8 presents the concentration history of the monocomponent breakthroughs of CO_2 , CO , CH_4 , and H_2 . The results exhibit a sharp concentration profile at the column exit, which is characteristic of favorable isotherms. The runs performed at higher flow rates display sharper fronts; in turn, the assays performed at higher pressure (*i.e.* 2 bar) display higher dispersion. Such fact is related to the higher partial pressure in the feed stream, which increases the heat generated during the adsorption; as adsorption is negatively affected with the increase of temperature, the dispersion increases. The same conclusions were reported by Bastos-Neto *et al.* (2010) on zeolite 5A and activated carbon [28]. In the particular case of the carbon monoxide, the concentration profile exhibits a larger degree of dispersion for all assays in comparison to other gases. However, carbon monoxide profiles do not present the same degree of dispersion along the entire breakthrough curve, it shows a bi-modal behavior; the concentration increases sharply in the first instant, exhibiting a larger degree of dispersion as the outlet concentration moves towards the feed composition. This was assigned to the contribution of both physisorption on the surface of the activated carbon and the formation of π -complex between CO and the copper salt. In the first moment, both phenomena are contributing to the CO adsorption, leading to a fast kinetics region. After the occupation of the active sites in the activated carbon where physisorption takes place, only π -complex formation occurs, which is a slower process and blurs the concentration front. Additionally, the higher heat of adsorption of CO , and consequent higher heat effects, may also contribute to the degree of dispersion increasing. Nonetheless, further research is needed to clarify this behaviour.

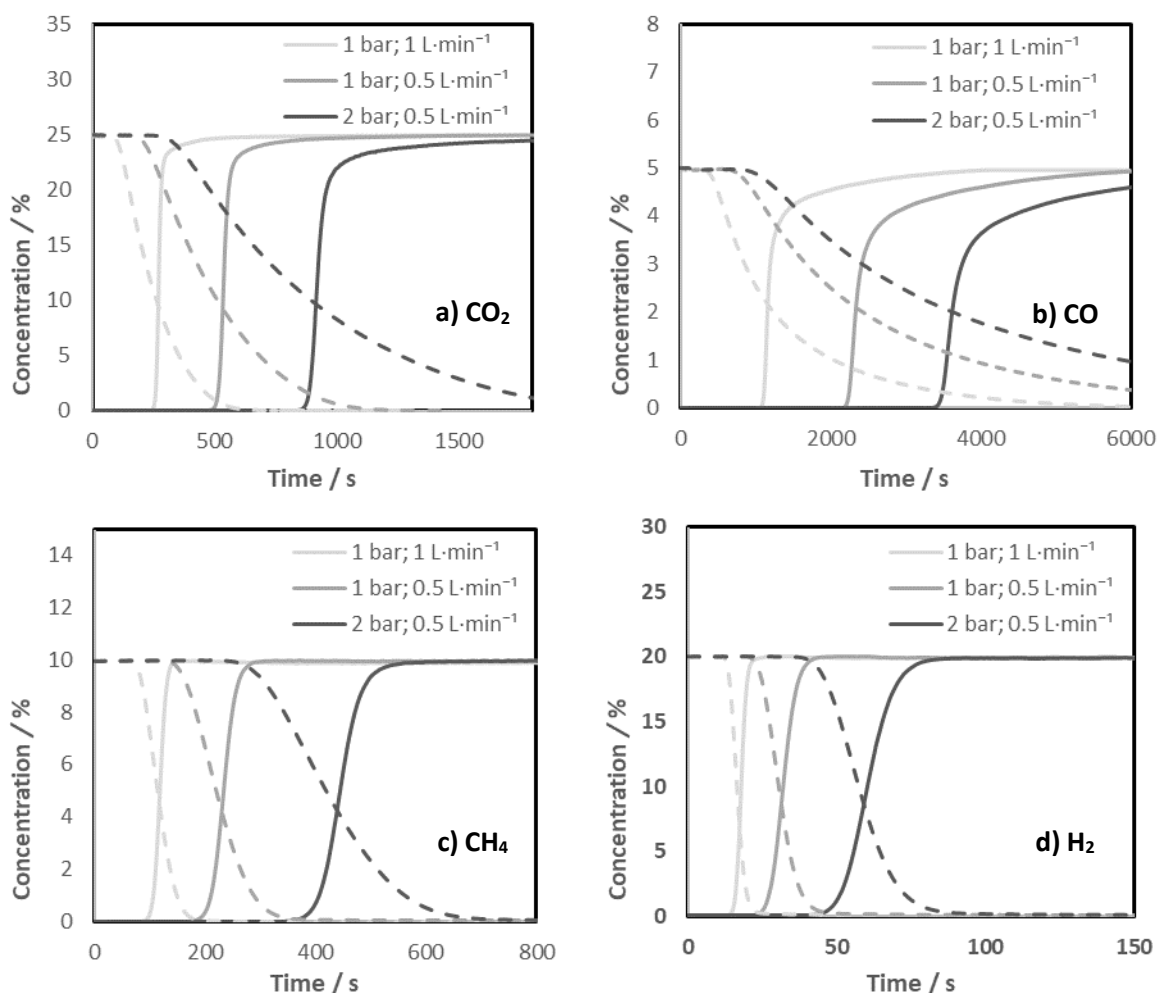


Figure 4.8 – Experimental monocomponent adsorption and desorption breakthroughs of a) CO_2 ; b) CO ; c) CH_4 ; d) H_2 . Solid lines denote the adsorption data; dashed-lines denotes desorption data.

Figure 4.9 shows the temperature histories of the monocomponent breakthroughs at 1 bar with a feed flow rate of $0.5 \text{ L}_\text{N} \text{ min}^{-1}$. Due to the exothermic nature of adsorption phenomena, a sharp temperature increase is observed at the bottom of the column during the first seconds of the experiments. Likewise, as the time draws near the breakthrough time, the temperature increases at the top of the column. A decrease in temperature is observed afterward. However, due to the heat transfer resistances through the column wall, the decrease in temperature displays a smoother profile. Comparing the temperatures reached in the different experiments, a higher temperature peak was observed in CO monocomponent breakthrough. This detail is related to the formation of the π -

complexation bonds between the CO and the copper, which is stronger than the Van der Waals interactions between the activated carbon and the other gases under study. This fact also confirms the higher heat of adsorption predicted by the dual-site Langmuir model in Table 4.4 and may explain the higher degree of dispersion observed in the breakthrough front for CO, illustrated in

Figure 4.8. In the case of the H₂ breakthrough, no changes in temperature were observed, reinforcing the idea that hydrogen is practically not adsorbed.

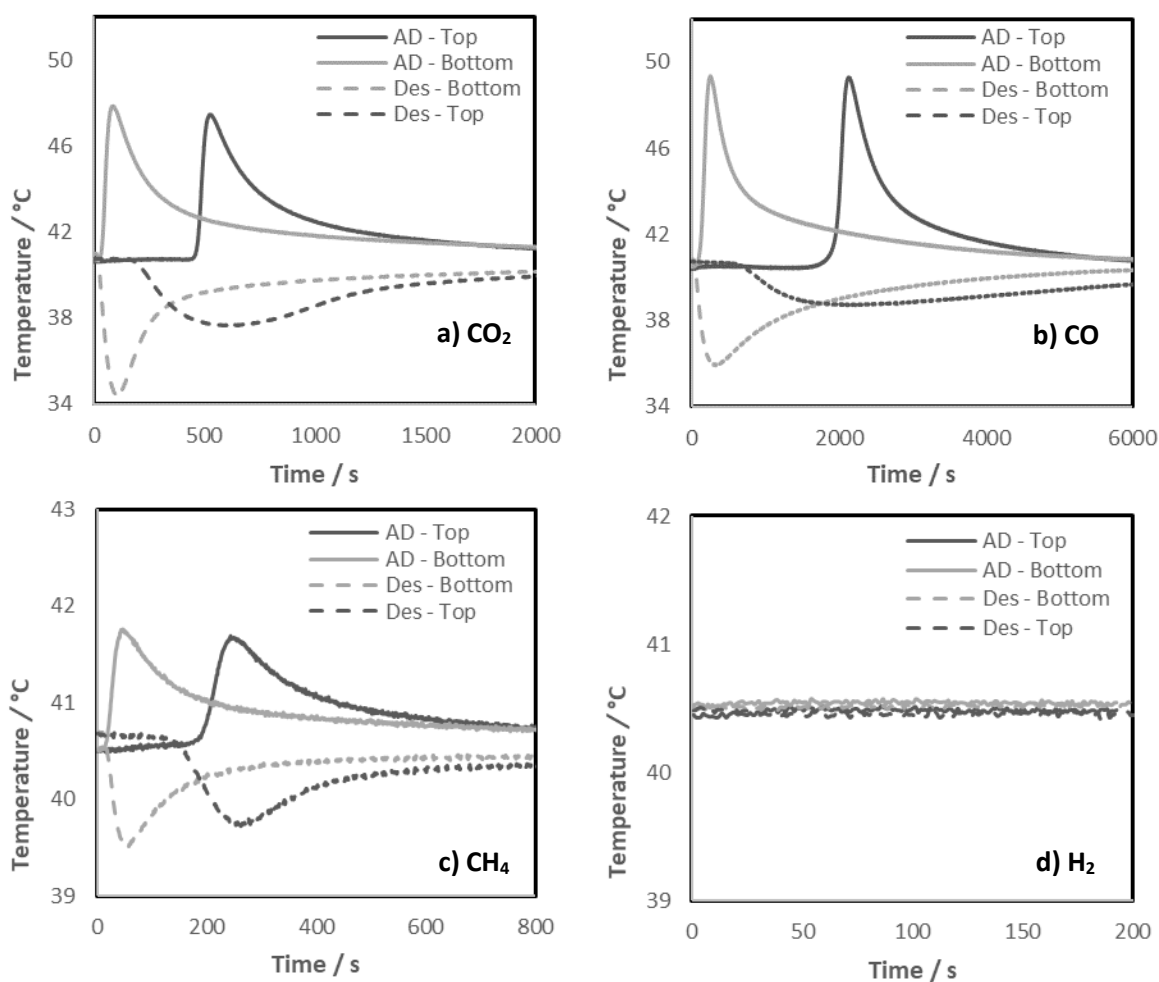


Figure 4.9 – Temperature profiles of the monocomponent breakthroughs of: a) CO₂; b) CO; c) CH₄; d) H₂. Feed flow rate 0.5 L_N·min⁻¹; 1 bar and 40 °C. Solid lines – adsorption; dashed lines – desorption.

To assess the adsorbent performance with a real mixture, multicomponent breakthroughs were performed using a mixture of 20 % H₂, 25 % CO₂, 5 % CH₄, and 1 % CO. Because the

available mass spectrometer cannot operate with hydrogen concentration above 20 %, the mixture was balanced with He, 49 %. Figure 4.10 depicts the result obtained with a feed flow rate of $0.5 \text{ L}_N \text{ min}^{-1}$, 1 bar, and 40°C . As expected from the monocomponent breakthroughs, the first component to break is hydrogen, followed by methane, carbon dioxide and carbon monoxide, respectively. Accordingly, the species move along the column at different rates resulting in distinct temperature peaks, observed in the temperature profile depicted in Figure 4.10 b. The different plateaus observed for H_2 , CH_4 and CO_2 are related to their intermediate adsorption capacities.

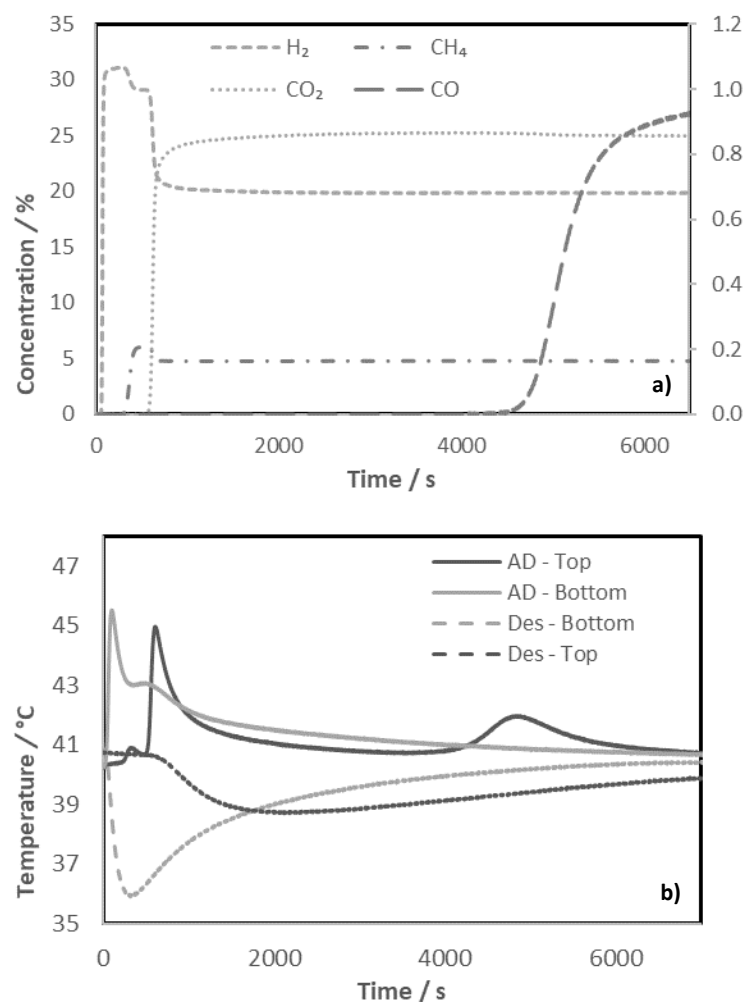


Figure 4.10 – Multicomponent breakthrough of H_2 , CO_2 , CH_4 and CO at 1 bar; $0.5 \text{ L}_N \text{ min}^{-1}$.

a) concentration history - Primary axis: H_2 , CO_2 and CH_4 ; Secondary axis: CO ; b) temperature history. Thermostatic chamber was kept at 40°C .

4.3.4. PSA tests and DoE optimization

The in-house assembled lab-scale PSA was used for purifying hydrogen from a synthetic reformat stream. A detailed description of the experiments performed is given in Table 4.5. For each experiment, hydrogen purity, contaminants concentration, recovery and productivity were determined and introduced in the table as well as the predicted results by the polynomial model. The 16 runs of the DoE show very low CO concentrations with high hydrogen recoveries, particularly if compared with the results available in the literature for the feed pressure range considered [15, 17 18]. Apart from experiments #15 and #16, both CO₂ and CH₄ concentrations were lower than the detection limit (150 ppm) of the used analyzers; the CO concentration values of these two runs were considered outliers (based on the residual analysis) and not used for fitting the model. When not detected, CO₂ and CH₄ concentrations were assumed to be < 150 ppm each, thus giving a H₂ purity better than 99.97 %. This means that the DoE had no sensitivity for the impact of operating conditions on overall purity and consequently the study was based on the final CO content. It can be also observed that the increase of the higher pressure leads to lower CO concentrations, while the recovery and productivity decrease; the opposite trend is observed increasing t_{AD} and Q_{prod} . Finally, an extra experiment, Run #17, was performed for assessing the PSA performance at the intermediate feed pressure, 8.25 bar, in a region of the design domain with fewer experimental values.

Table 4.5 – DoE parameters, experimental and RSM predicted results of the PSA.

DoE Factors				Experimental results						RSM pred.	
Run #	P_H bar	t_{AD} s	Q_{prod} L _N ·min ⁻¹	y_{H_2} %	$Y_{CO_2}^*$ ppm	$Y_{CH_4}^*$ ppm	y_{CO} ppm	ρ_{REC} %	ρ_{PROD} L _N kg _{ads} ⁻¹ cycle ⁻¹	y_{CO} ppm	ρ_{REC} %
#1	9.00	152	0.90	+99.97	< 150	< 150	0.75	77.92	18.86	0.81	77.45
#2	8.25	152	0.80	+99.97	< 150	< 150	0.68	76.19	16.76	0.71	76.41
#3	9.00	122	0.80	+99.97	< 150	< 150	0.02	69.26	13.45	0.02	69.17
#4	8.25	122	0.90	+99.97	< 150	< 150	0.20	73.47	15.14	0.18	73.80
#5	8.25	92	0.80	+99.97	< 150	< 150	0.07	64.57	10.15	0.15	64.48
#6	9.00	92	1.00	+99.97	< 150	< 150	0.00	68.68	12.68	-0.03	68.46

#7	7.50	92	1.00	+99.97	< 150	< 150	1.04	73.26	12.68	1.03	73.43
#8	8.25	122	1.00	+99.97	< 150	< 150	0.35	76.39	16.82	0.47	76.19
#9	9.00	152	1.00	+99.97	< 150	< 150	1.18	79.81	20.95	1.14	80.31
#10	8.25	122	0.80	+99.97	< 150	< 150	0.15	71.43	13.45	0.04	71.79
#11	8.25	122	0.80	+99.97	< 150	< 150	0.10	71.88	13.45	0.03	71.57
#12	7.50	92	0.90	+99.97	< 150	< 150	0.62	71.03	11.41	0.58	70.90
#13	7.50	122	0.80	+99.97	< 150	< 150	0.23	75.19	13.45	0.30	75.09
#14	9.00	92	0.90	+99.97	< 150	< 150	0.00	64.61	11.41	0.00	64.88
#15	7.50	152	0.90	99.93	163	500	28.25	81.89	18.86	1.48	80.53
#16	7.50	152	1.00	99.66	715	2725	> 32.00	83.54	20.95	2.21	82.14
#17	8.25	152	1.00	+99.97	< 150	< 150	1.54	80.71	20.95	1.49	80.46

*limit detection of 150 ppm.

The results were fitted with second-order polynomial models, previously described by Eq. (6), using the statistical software JMP[®] (SAS Institute Inc.). Two empiric models were obtained, model 1 for describing y_{CO} and model 2 for describing ρ_{REC} ; regression parameters are presented in Table 4.6 along with ANOVA analysis. Both models were considered statistically significant, p-value 0.0006 and p-value <0.0001, respectively for models 1 and 2.

The response surfaces by the models are displayed in Figure 4.11 and Figure 4.12 along with the experimental data - Figure 4.11 presents y_{CO} response and Figure 4.12 depicts the ρ_{REC} behavior. Three response surfaces are presented in each graph, depicting the model at 7.50 bar (red), 8.25 bar (green), and 9.00 bar (blue). The 3D plots display a similar surface shape for the three feed pressures positioned at sequential levels along the y_{CO} / ρ_{REC} axes. The positioning of the experimental points on the response surface confirms the model agreement towards the experimental data, for both recovery and CO content. The exception is given to the experimental y_{CO} points of runs #15 and #16 performed at 7.50 bar. As previously mentioned, these points were not considered in the model, resulting in a misleading response of y_{CO} at 7.50 bar. The surface was kept in the figure to demonstrate this discrepancy.

Table 4.6 – Regression parameters of the polynomial empiric model (Eq. (6)).

Parameter	Model 1		Model 2	
	Estimate	<i>p</i> -value	Estimate	<i>p</i> -value
β_0	0.1668	0.0823	73.6138	<0.0001
β_1	-0.3349	0.0021	-2.4365	0.0002
β_2	0.4366	0.0005	5.9434	<0.0001
β_3	0.2150	0.0018	2.3199	<0.0001
β_4	-0.0517	0.5726	0.6609	0.1285
β_5	-0.1730	0.0300	0.9284	0.0126
β_6	0.1758	0.0198	-0.295	0.2392
β_7	0.1620	0.1188	0.8347	0.0712
β_8	0.4217	0.0017	-1.1972	0.0092
β_9	0.0721	0.3145	0.0735	0.7988
Lack of fit (<i>p</i> -value)	0.2225		0.4531	
R^2	0.9838		0.9972	
RMSE	0.1034		0.4384	
<i>p</i> -value	0.0006		<0.0001	

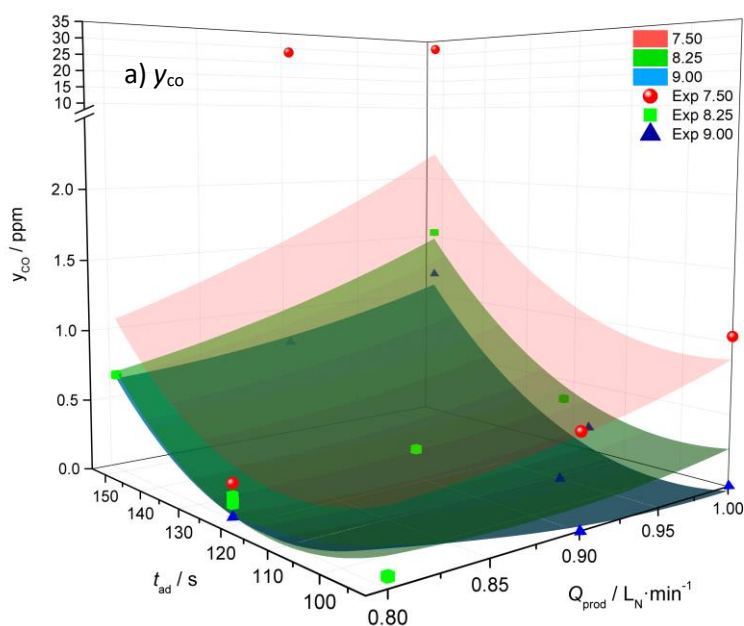


Figure 4.11 – Response surface for CO (y_{CO}) content as function of the independent variables t_{AD} and Q_{PROD} at 7.50 bar - ●; 8.25 bar – ■ and 9.00 bar - ▲. a) y_{CO} ; b) ρ_{REC} .

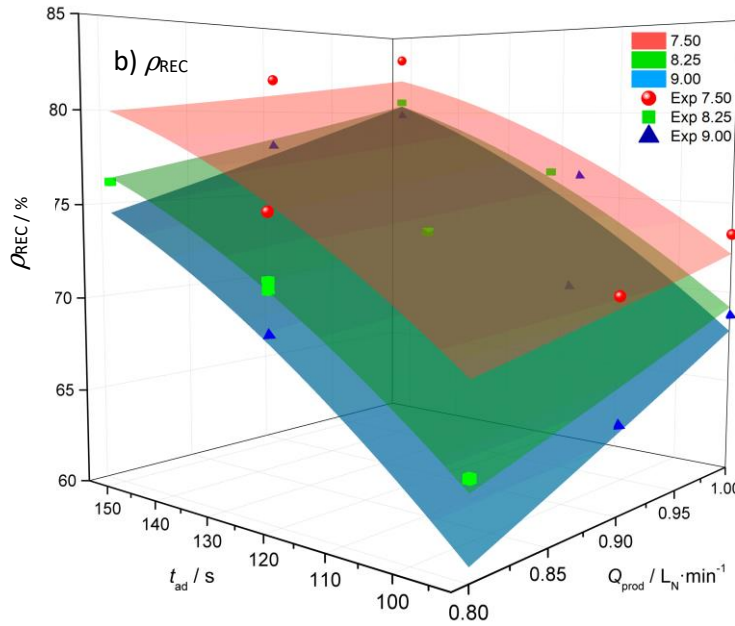


Figure 4.12 – Response surface for recovery (ρ_{REC}) as function of the independent variables t_{AD} and Q_{prod} at 7.50 bar - ●; 8.25 bar – ■ and 9.00 bar - ▲. a) y_{CO} ; b) ρ_{REC} .

Models 1 and 2 were then used to find the operating conditions that maximize the recovery and minimize the CO concentration. Two different conditions were considered:

- Opt #1 – Maximizes the recovery and sets the CO concentration to 0.20 ppm;
- Opt #2 – Maximizes the recovery and sets the CO concentration to 0.00 ppm.

Table 4.7 depicts the obtained experimental and model results. A good agreement between experimental and predicted results is observed. The first objective function, Opt #1, indicates a model recovery of $\rho_{\text{REC}} = 75.5\%$ and a CO concentration of 0.13 ppm of CO, which agrees with the experimental values, respectively $\rho_{\text{REC}} = 76.2\%$ and $y_{\text{CO}} = 0.17$ ppm. The second objective function, Opt #2, indicates a model recovery of $\rho_{\text{REC}} = 71.0\%$ and a CO concentration of 0.00 ppm of CO, which agrees with the experimental values, respectively $\rho_{\text{REC}} = 70.3\%$ and $y_{\text{CO}} = 0.00$ ppm.

The hydrogen produced by the developed PSA unit loaded with modified activated carbon meets the requirements for the automotive industry concerning CO content and

shows quite high recovery values, even for a system with only 4 adsorption columns fed at relatively low pressures ≤ 9 bar. Moreover, the PSA unit was operated continuously for more than 1 month for producing the reported results; this points out the great stability of the adsorbent since no signs of deactivation were observed.

Table 4.7 – Optimal DoE parameters, experimental and RSM predicted results of the PSA.

Operating conditions				Experimental results						RSM pred.	
Run #	P_H bar	t_{AD} s	Q_{prod} $L_N \text{ min}^{-1}$	y_{H_2} %	$y_{CO_2}^*$ ppm	$y_{CH_4}^*$ ppm	y_{CO} ppm	ρ_{REC} %	ρ_{PROD} $L_N \text{ kg}_{ads}^{-1} \text{ cycle}^{-1}$	y_{CO} ppm	ρ_{REC} %
Opt #1	9.00	122	1.00	+99.97	N.D	N.D	0.17	76.19	16.82	0.13	75.54
Opt #2	9.00	109	0.95	+99.97	N.D	N.D	0.00	70.32	14.27	0.00	70.98

4.4. Conclusions

A commercial sample of activated carbon, Kuraray 2GA-H2, was modified by wet impregnation of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. After activation under hydrogen atmosphere, the copper was successfully reduced to its monovalent state, while before activation, XPS analysis revealed the presence of both Cu^{2+} and Cu^+ . An increase in carbon monoxide adsorption capacity was observed with the increase of copper loading; the opposite effect was observed for the other gases under study, resulting in an increase in the carbon monoxide selectivity, namely over carbon dioxide. The effect is particularly evident at low partial pressures.

To assess the adsorbent performance for hydrogen purification from a synthetic ethanol reformat mixture, a sample with a copper loading of $2 \text{ mmol g}_{ads}^{-1}$, Cu-AC-2, was selected. The PSA experiments were conducted in an in-house built unit comprising four adsorption beds. A 12-steps cycle, comprising 8 elementary steps, was implemented, including backfill and equalization steps. A design of experiments was conducted for determining the influence of pressure, product flow rate, and cycle time in PSA performance. A polynomial second-order empirical model was established by fitting to the experimental values, and the experimental unit was optimized based on the developed models. A product stream with +99.97 % hydrogen was obtained, with 76.19 % recovery and a carbon monoxide concentration of 0.17 ppm. A thorough literature survey found no

experimental results displaying such low carbon monoxide concentration using small-scale PSA units, particularly when considering the applied range of feed pressures (< 10 bar) and the number of adsorption columns. The produced stream meets the requirements for the automotive industry regarding CO impurities (< 0.2 ppm of CO), presenting an important outcome in PSA utilization for hydrogen purification. The developed PSA opens the doors for cheaper production of automotive-grade hydrogen from reformat streams.

4.5. Acknowledgements

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4.6. Nomenclature

Parameters	Description	Units
b_{∞}	Langmuir affinity constant at infinite temperature	bar ⁻¹
b	Langmuir affinity constant	bar ⁻¹
d	Diameter	cm
L	Length	cm
L	Length	cm
m	Mass	kg
P	Pressure	bar
$\bar{P}$	Average pressure	bar
Q	Volumetric flow rate	L _N min ⁻¹
q	Isotherm parameter, maximum adsorption capacity	mol kg ⁻¹
$\mathcal{R}$	Ideal gas constant	J mol ⁻¹ K ⁻¹
R^2	Coefficient of determination	mol kg ⁻¹
t	time variable	s
T	Temperature	°C
$\bar{t}$	Average time	s
X	DoE dimensionless process factors	
y	Gas-phase mole fraction	
Greek Symbol	Description	Units
β	Empiric model equation parameter	mol kg ⁻¹
ΔH	Heat of adsorption	J mol ⁻¹
ρ_{REC}	Recovery	%
ρ_{PROD}	Productivity	L _N kg ⁻¹ min ⁻¹
Acronym	Description	
AD	Adsorption	
AC	Activated carbon	
BD	Blowdown	
BF	Backfill	
DoE	Design of experiments	
DPE	Depressurization pressure equalization	
MFC	Mass flow controller	
PBF	Providing backfill	
PEM	Polymer electrolyte membrane	
PEP	Pressurization pressure equalization with product	

PG	Purge
PP	Providing Purge
PPE	Pressurization pressure equalization
RMSE	Root mean square error
RSM	Response surface methodology
WGS	Water gas shift
Subscripts	Description
-1	Lower level of the DoE factor
1	Upper level of the DoE factor
EQ	Equalization
H	Refers to high pressure
<i>i</i>	Component
in	Inside
L	Refers to low pressure
Prod	Product
PROD	Productivity

4.7. References

1. Agueda, V.I., et al., *Adsorption and diffusion of H₂, N₂, CO, CH₄ and CO₂ in UTSA-16 metal-organic framework extrudates*. Chemical Engineering Science, 2015. **124**: p. 159-169.
2. Ahn, S., et al., *Layered two-and four-bed PSA processes for H₂ recovery from coal gas*. Chemical engineering science, 2012. **68**(1): p. 413-423.
3. Delgado, J.A., et al., *Adsorption and diffusion of H₂, CO, CH₄, and CO₂ in BPL activated carbon and 13X zeolite: evaluation of performance in pressure swing adsorption hydrogen purification by simulation*. Industrial & Engineering Chemistry Research, 2014. **53**(40): p. 15414-15426.
4. Golmakani, A., S. Fatemi, and J. Tamnanloo, *Investigating PSA, VSA, and TSA methods in SMR unit of refineries for hydrogen production with fuel cell specification*. Separation and Purification Technology, 2017. **176**: p. 73-91.

5. Majlan, E.H., et al., *Hydrogen purification using compact pressure swing adsorption system for fuel cell*. International Journal of Hydrogen Energy, 2009. **34**(6): p. 2771-2777.
6. Tamon, H., K. Kitamura, and M. Okazaki, *Adsorption of carbon monoxide on activated carbon impregnated with metal halide*. AIChE Journal, 1996. **42**(2): p. 422-430.
7. Gao, F., Y. Wang, and S. Wang, *Selective adsorption of CO on CuCl/Y adsorbent prepared using CuCl₂ as precursor: equilibrium and thermodynamics*. Chemical Engineering Journal, 2016. **290**: p. 418-427.
8. Gao, F., et al., *Selective CO adsorbent CuCl/AC prepared using CuCl₂ as a precursor by a facile method*. RSC Advances, 2016. **6**(41): p. 34439-34446.
9. Hirai, H., K. Wada, and M. Komiyama, *Active carbon-supported aluminium copper (I) chloride as solid carbon monoxide adsorbent*. Bulletin of the Chemical Society of Japan, 1986. **59**(4): p. 1043-1049.
10. Peng, J., et al., *A supported Cu (I)@ MIL-100 (Fe) adsorbent with high CO adsorption capacity and CO/N₂ selectivity*. Chemical Engineering Journal, 2015. **270**: p. 282-289.
11. Ma, J., et al., *CO adsorption on activated carbon-supported Cu-based adsorbent prepared by a facile route*. Separation and Purification Technology, 2010. **76**(1): p. 89-93.
12. Cho, S.H., et al., *Pressure swing adsorption apparatus and method for hydrogen purification using the same*. 2012, Korean Institute Of Energy Research.
13. Golden, T.C., et al., *Highly dispersed cuprous compositions*. 1992, Air Products and Chemicals, Inc., Allentown, Pa.: United States.
14. Santos, J., F. Magalhaes, and A. Mendes, *Contamination of zeolites used in oxygen production by PSA: effects of water and carbon dioxide*. Industrial & engineering chemistry research, 2008. **47**(16): p. 6197-6203.
15. Mathias, P.M., et al., *Correlation of multicomponent gas adsorption by the dual-site Langmuir model. Application to nitrogen/oxygen adsorption on 5A-zeolite*. Industrial & engineering chemistry research, 1996. **35**(7): p. 2477-2483.

16. Do, D.D., *Adsorption Analysis: Equilibria and Kinetics: (With CD Containing Computer Matlab Programs)*. Vol. 2. 1998: World Scientific.
17. Ferreira, D., et al., *Effective adsorption equilibrium isotherms and breakthroughs of water vapor and carbon dioxide on different adsorbents*. Industrial & Engineering Chemistry Research, 2011. **50**(17): p. 10201-10210.
18. Karimäki, T.K.H., *System and subsystem specification report*. 2014, VTT Technical Research Centre of Finland. p. 9.
19. Waldron, W.E. and S. Sircar, *Parametric Study of a Pressure Swing Adsorption Process*. Adsorption, 2000. **6**(2): p. 179-188.
20. Institute, S., *JMP Design of Experiments, Release 6*. 2005.
21. Myers, R.H., D.C. Montgomery, and C.M. Anderson-Cook, *Response surface methodology: process and product optimization using designed experiments*. 2016: John Wiley & Sons.
22. Cruz, P., et al., *Cyclic adsorption separation processes: analysis strategy and optimization procedure*. Chemical Engineering Science, 2003. **58**(14): p. 3143-3158.
23. Huang, H.Y., J. Padin, and R.T. Yang, *Comparison of π -complexations of ethylene and carbon monoxide with Cu^+ and Ag^+* . Industrial & engineering chemistry research, 1999. **38**(7): p. 2720-2725.
24. Brea, P., et al., *Modeling of breakthrough curves of N_2 , CH_4 , CO , CO_2 and a SMR type off-gas mixture on a fixed bed of BPL activated carbon*. Separation and Purification Technology, 2017. **179**: p. 61-71.
25. Vasquez, R.P., *CuCl by XPS*. Surface Science Spectra, 1993. **2**(2): p. 138-143.
26. Vasquez, R.P., *CuCl_2 by XPS*. Surface Science Spectra, 1993. **2**(2): p. 160-164.
27. Yin, A., et al., *The nature of active copper species in Cu-HMS catalyst for hydrogenation of dimethyl oxalate to ethylene glycol: new insights on the synergetic effect between CuO and Cu^+* . The Journal of Physical Chemistry C, 2009. **113**(25): p. 11003-11013.

28. Bastos-Neto, M., et al., *Dynamic bed measurements of CO adsorption on microporous adsorbents at high pressures for hydrogen purification processes*. Separation and purification technology, 2011. **77**(2): p. 251-260.

Chapter 5. Optimization procedure for maximizing raffinate recovery in Pressure Swing Adsorption processes

5.1. Introduction

To determine PSA efficiency, it is required to run the PSA until the bed conditions in consecutive cycles are identical, the so-called cyclic steady state (CSS). This makes simulation a fundamental tool in PSA design and optimization since it allows replacing time-consuming and costly pilot plant studies [1]. Due to the process dynamics and the sharp temperature and concentration profiles, PSA modelling involves solving a set of complex partial derivative equations (PDEs) in time and space, whose solution must be found numerically. Two strategies are commonly used, the complete discretization and the method of lines. The first consists of discretizing the PDEs both in space and time and further solving the algebraic system of non-linear equations. Despite being an efficient approach for simple models, error accumulation are likely to occur, leading to convergence failure [2]. On the other hand, the method of lines uses a two-step approach, where the PDEs are discretized in space and then integrated over time using an suitable integrator [2].

For obtaining the CSS, the method of lines calculates the conditions for $t = t + \delta t$ based on the conditions for $t = t$ [2]. However, depending on the system complexity, simulating a full PSA operation can be as or more time-consuming than experimental studies, hindering the computer-based optimization process. Accordingly, different methods have been purposed for accelerating the convergence rate towards CSS, including reduced-order modeling[3], successive node refinement[4], Newton-based methods[5, 6], model switching[7]. These acceleration strategies can be further coupled with optimization

procedures such as black or grey-box based methods and simultaneous tailored methods [8-11]. Even though, optimization procedures with computing times >700 h can be found in literature [12]. More recently, PSA simulation studies are exploiting the benefits of parallel computing, obtaining the optimization results in 5-29 h [8, 13]. Also, machine learning algorithms[14] and artificial neural networks are being developed to study the influence of several parameters in a reasonable computing time [15].

Product purity and recovery are the typical performance indicators of the PSA units. These parameters evolve in the opposite direction, so the maximum recovery is obtained at the point of minimum acceptable purity, which is usually defined by the customer [16]. However, due to the influence of different operating conditions, several local maxima can be obtained. Therefore, an optimization procedure should focus on finding these maxima and compare them to the global maximum.

In the present study, the authors suggest a very effective optimization strategy of the operating conditions: cycle time, and purge-to-feed ratio, based on a self-adaptive cycle-time strategy. This is a suitable approach for processes where the less adsorbed gas is the component of interest. Instead of fixing the duration of the adsorption time, it is made to increase, while the product concentration at the top of the production column is controlled. Whenever the top product concentration reaches the target concentration, the production step time for iteration j is established and used to define the next steps of the cycle, namely the purge and backfill. This process is repeated until converging to CSS. A low purge-to-feed ratio is initially used and its optimization is obtained by increasing it after reaching each CSS, until finding the optimum. This methodology was named by the authors as “self-adaptive cycle time”.

A similar procedure can be implemented for adjusting the operating conditions to new feed or product specifications. This is optimization procedure avoids overshooting having demonstrated to be suitable for online optimization [17]. The effectiveness of this optimization strategy is here demonstrated for the purification of a hydrogen/carbon dioxide gas mixture, where hydrogen is the desirable product.

5.2. Modelling and Experimental Methods

Due to the large number of operating conditions and non-linear behavior concerning maximizing the product purity and recovery, optimizing a PSA process requires a reliable dynamic simulator capable to describe the process during each step of the PSA cycle. In the present work, a phenomenological dynamic PSA model was implemented in FORTRAN, using an in-house built numerical package [18], where the space derivatives were computed using the finite difference method to obtain the grid point values and the time integration was completed using the LSODA package [19].

5.2.1. PSA model

The complete mathematical model was based on the model proposed by Cruz *et. al* [20], where the following assumptions were considered:

- Ideal gas behavior.
- Isotropic and homogenous adsorbent properties.
- Pressure drop described by Blake-Kozeny equation.
- The fluid flow was assumed to be laminar and Newtonian.
- Non-isothermal and non-adiabatic conditions with negligible heat of adsorbed phase and negligible heat transfer by gas conduction.
- Negligible radial concentration and temperature gradients.
- Competitive adsorption behavior is described by the extended Langmuir isotherm.

Accordingly, the mass balance and energy balance can be written in the dimensionless form as follows:

Partial and total mass balance equations for the column

Total mass balance

$$\frac{\partial P_T^*}{\partial \theta} = \frac{P_T^*}{T^*} \left(\frac{\partial T^*}{\partial \theta} + u^* \frac{\partial T^*}{\partial x} \right) - \left(\frac{\partial u^* P_T^*}{\partial x} \right) - T^* \sum_{i=1}^{nc} N_i^* \quad (5.1)$$

Partial mass balance

$$\frac{\partial y_i}{\partial \theta} = \frac{1}{Pe} \frac{\partial y_i}{\partial x} \left(\frac{1}{P^*} \frac{\partial P^*}{\partial x} - \frac{1}{T^*} \frac{\partial T^*}{\partial x} \right) + \frac{1}{Pe} \frac{\partial^2 y_i}{\partial x^2} - u^* \frac{\partial y_i}{\partial x} + \frac{T^*}{P^*} \left(y_i \sum_{j=1}^{nc} N_j^* - N_i^* \right) \quad (5.2)$$

where θ is the dimensionless time, $\theta = t / \tau$; τ is time bed constant, $\tau = L / u_{ref}$; x denotes the dimensionless axial coordinate, $x = z / L$; and Pe is the Peclet number, $Pe = u_{ref} L / D_{ax}$. The superscript $*$ denotes the dimensionless form of the variable, therefore P^* , T^* , u^* are the dimensionless pressure, temperature and velocity, respectively as $P^* = P / P_{ref}$, $T^* = T / T_{ref}$ and $u^* = u / u_{ref}$. N_i^* is dimensionless molar flux of the component i , and is given by eq.(5.3), where it is assumed that the accumulation in the intraparticle gas phase is negligible.

$$N_i = \zeta_a \sum_{i=1}^{nc} \frac{\partial \bar{q}_i^*}{\partial \theta} \quad (5.3)$$

Where ζ_a is the capacity factor of the adsorbed phase, given by eq.(5.4) and $\bar{q}_i^*$ is the average intraparticle molar concentration.

$$\zeta_a = \frac{(1 - \varepsilon_b)}{\varepsilon_b} \rho_{ads} \frac{q_{ref}}{c_{ref}} \quad (5.4)$$

Pressure drop in the column

The pressure drop was assumed to be described by the Blake-Kozeny equation, as follows:

$$\frac{\partial P_T^*}{\partial x} = - \frac{150 \mu_{mix}^* (1 - \varepsilon_b)^2 L}{\varepsilon_b^3 d_p^{*2} P_{ref}} u^* \quad (5.5)$$

where L is the bed length, ε_b is the bed voidage, d_p is the particle diameter and μ_{mix} is the gas mixture viscosity.

Particle's mass balance

In the present work, the accumulation in intraparticle gas phase is assumed to be negligible. Therefore, the mass transfer to the particle is based on the linear driving force model according to eq. (5.6):

$$\frac{\partial \bar{q}_i^*}{\partial \theta} = \varphi \alpha_i^M (q_i^* - \bar{q}_i^*) \quad (5.6)$$

Where $\varphi = \tau_b k_{\text{ref}} = 15 \tau_b D_{\text{ref}} / r_p^2$ and $\alpha_i^M = D_{M,i}^e / D_{\text{ref}} = k_i / k_{\text{ref}}$ and where k is the LDF coefficient of the component i . The dimensionless q_i^* is calculated from the reference conditions as $q_i^* = q_i / q_{\text{ref}}$. For the calculation of q_i , the competitive adsorption behavior was taken into account according to the extend Langmuir isotherm as follows:

$$q_i = \frac{q_{i,\text{max}} b_i P_i}{1 + \sum_{i=1}^{\text{nc}} b_i P_i} \quad (5.7)$$

where $q_{i,\text{max}}$ is the maximum adsorption capacity, b_i is the adsorption affinity parameter and P_i is the partial pressure of the i th component. For obtaining the temperature dependence in the Langmuir isotherm, b_i can be calculated according to eq. (5.8).

$$b_i = b_{\infty,i} e^{\frac{\Delta H_i}{RT}} \quad (5.8)$$

Energy balance

Taking into account the non-isothermal behaviour of the PSA process, the energy balance can be written in the dimensionless form as follows:

$$\frac{\partial T^*}{\partial \theta} = \frac{\frac{1}{Pe_T} \frac{\partial^2 T^*}{\partial z^2} - u^* \frac{P^*}{T^*} \sum_{i=1}^{\text{nc}} y_i C_{p,i}^* \frac{\partial T^*}{\partial x} + \sum_{i=1}^{\text{nc}} R_{g,i}^a \frac{\partial \bar{q}_i^*}{\partial \theta} - R_g^h (T_g^* - T_\infty^*)}{(1 + \zeta_p) \frac{P^*}{T^*} \sum_{i=1}^{\text{nc}} y_i C_{p,i}^* + \zeta_a \sum_{i=1}^{\text{nc}} \bar{q}_i^* C_{p,i}^* + R_g^s} \quad (5.9)$$

where different dimensionless groups $R_{g,i}^a$, R_g^s , R_g^h , ζ_p and thermal Peclet number Pe_T can be calculated according to eq. (5.10)-(5.14), where the variables are defined in the nomenclature section.

$$R_{g,i}^a = \zeta_a \frac{(-\Delta H_i)}{T_{ref} C_{P,ref}} \quad (5.10) \quad R_g^s = \frac{(1 - \varepsilon_b)}{\varepsilon_b} \frac{\rho_{ads} C_{P,ads}}{c_{ref} C_{P,ref}} \quad (5.11) \quad R_g^h = \frac{4h_w \tau_b}{\varepsilon_b d_o c_{ref} C_{P,ref}} \quad (5.12)$$

$$Pe_T = \frac{\rho_{ref} C_{P,ref} u_{ref} L}{k_g} \quad (5.13) \quad \zeta_p = \frac{(1 - \varepsilon_b)}{\varepsilon_b} \varepsilon_p \quad (5.14)$$

PSA cycle and boundary conditions

This work considers a PSA unit for hydrogen purification, where hydrogen is the less adsorbing specie in the feed mixture. In this sense, a typical 6-step PSA cycle was implemented, as follows:

- Adsorption (AD) – where the gas mixture is fed to the PSA, the contaminants are trapped in the adsorption bed and the purified product is collected in the top of the column;
- Depressurization Pressure Equalization (DPE) – where the high pressure column (after adsorption) equalizes its pressure with another column;
- Blowdown (BD) – where the remaining gas, after equalization, is released through the off gas valve in the bottom (to atmospheric pressure);
- Purge (PG) – where part of the purified gas flows counter-current to regenerate the bed;
- Pressurization Pressure Equalization (PPE) – where the regenerated bed is pre-pressurized by receiving the gas from the DPE column;
- Backfill (BF) – where part of purified gas is used to pressurize the column to the operating pressure.

A schematic representation of each step is present in Figure 5.1. Depending on the working pressure and number of columns, additional equalization steps are often considered, but

for the sake of simplicity were not taken into account in the present work. For modelling the different steps, the boundary conditions were defined according to Table 5.1.

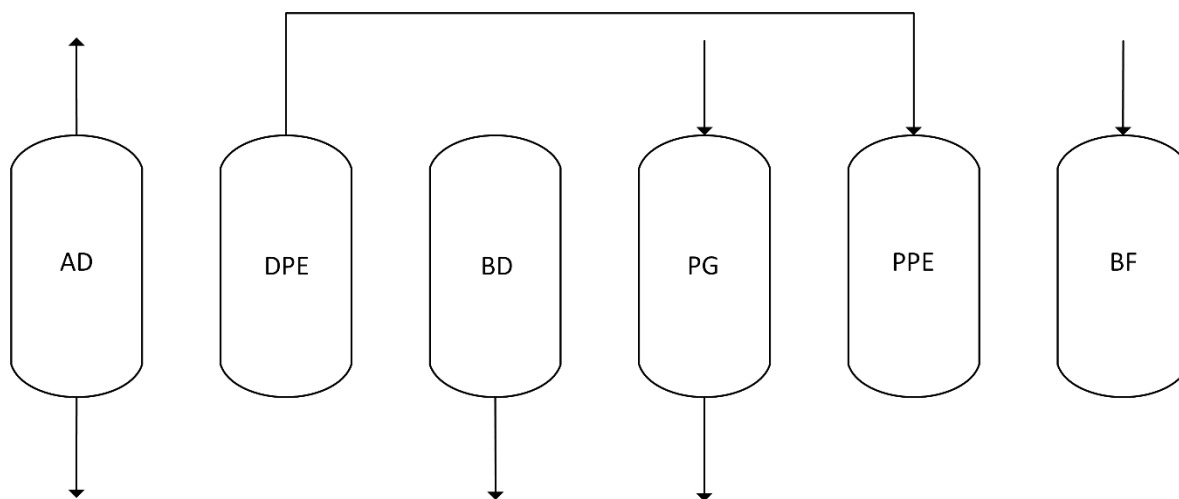


Figure 5.1 – Elementary steps of the PSA. AD - adsorption; DPE - depressurization pressure equalization; BD - blowdown; PG - purge; PPE - pressurization pressure equalization; BF - backfill.

Table 5.1 – Boundary conditions for the different steps of the PSA cycle.

<u>Adsorption Step</u>			
	Temperature	Composition	Pressure/velocity
$x = 0$	$T^* = T_{in}^*$	$\frac{1}{Pe} \frac{\partial y_i}{\partial x} = u_{in}^* (y_i - y_{in,i})$	$\frac{\partial P^*}{\partial x} = -\alpha u_{i,in}^*$
$x = 1$	$\frac{\partial T^*}{\partial x} = 0$	$\frac{\partial y_i}{\partial x} = 0$	$P^* = P_H^*$
<u>Depressurization pressure equalization (DPE)</u>			
	Temperature	Composition	Pressure/velocity
$x = 0$	$\frac{\partial T^*}{\partial x} = 0$	$\frac{\partial y_i}{\partial x} = 0$	$\frac{\partial P^*}{\partial x} = 0$
$x = 1$	$\frac{\partial T^*}{\partial x} = 0$	$\frac{\partial y_i}{\partial x} = 0$	Flux given by the valve equation[21]: $u^* P^* = \begin{cases} -1.179 K_{V, EQ} \sqrt{P_{DPE}^{*2} - P_{PPE}^{*2}} & \text{if } P_{PPE}^* > 0.528 P_{DPE}^* \\ K_{V, EQ} P_{DPE}^* & \text{if } P_{PPE}^* \leq 0.528 P_{DPE}^* \end{cases}$

Blowdown

	Temperature	Composition	Pressure
$x = 0$	$\frac{\partial T^*}{\partial x} = 0$	$\frac{\partial y_i}{\partial x} = 0$	$P^* = P_{\text{low}}^* + (P _{\theta_c=0}^* - P_{\text{low}}^*) \exp(-\theta_c K_{V,BD})$
$x = 1$	$\frac{\partial T^*}{\partial x} = 0$	$\frac{\partial y_i}{\partial x} = 0$	$\frac{\partial P^*}{\partial x} = 0$

Purge

	Temperature	Composition	Pressure
$x = 0$	$\frac{\partial T^*}{\partial x} = 0$	$\frac{\partial y_i}{\partial x} = 0$	$P^* = P_{\text{low}}^*$
$x = 1$	$\frac{\partial T^*}{\partial x} = T_{\text{PG}}^*$	$\frac{1}{Pe} \frac{\partial y_i}{\partial x} = u_{\text{PG}}^* (y_i - y_{\text{PG},i})$	$\frac{\partial P}{\partial x} = -\alpha u_{\text{PG}}^*$

Pressurization pressure equalization (PPE)

	Temperature	Composition**	Pressure
$x = 0$	$\frac{\partial T^*}{\partial x} = 0$	$\frac{\partial y_i}{\partial x} = 0$	$\frac{\partial P^*}{\partial x} = 0$
$x = 1$	$T^* = T_{\text{DPE}, x=1}^*$	$\frac{1}{Pe} \frac{\partial y_i}{\partial x} = u_{\text{PPE}}^* (y_i - y_{\text{PPE}})$	Flux given by the valve equation: $u^* P^* = \begin{cases} -1.179 K_{V,EQ} \sqrt{P_{\text{DPE}}^{*2} - P_{\text{PPE}}^{*2}} & \text{if } P_{\text{PPE}}^* > 0.528 P_{\text{DPE}}^* \\ K_{V,EQ} P_{\text{DPE}}^* & \text{if } P_{\text{PPE}}^* \leq 0.528 P_{\text{DPE}}^* \end{cases}$

** y_{PPE} corresponds to the outlet composition of DPE column ($x = 1$).

Backfill

	Temperature	Composition	Pressure
$x = 0$	$\frac{\partial T^*}{\partial x} = 0$	$\frac{\partial y_i}{\partial x} = 0$	$\frac{\partial P^*}{\partial x} = 0$
$x = 1$	$T^* = T_{\text{BF}}^*$	$\frac{1}{Pe} \frac{\partial y_i}{\partial x} = u_{\text{BF}}^* (y_i - y_{\text{Prod}})$	$P^* = P_{\text{high}}^* - (P_{\text{high}}^* - P _{\theta_c=0}^*) \exp(-\theta_c K_{V,BF})$

5.2.2. Optimization methodology

When designing a PSA process the product purity and some design or operating conditions are defined *a priori*, either due to the upstream/downstream process requirements, a standard, or according to the customer constraints. These conditions

usually include the operating temperature, feed or product flow rate, and maximum pressure. Thus, the optimization procedure aims at to establish the optimal operating conditions and cycle parameters that maximize the product recovery, while keeping the purity above the design specification while meeting the design or operating constraints. In this study, a strategy was implemented to optimize a typical 6-step cycle, previously described, based on the factors with the highest impact in the process performance: the operating pressure, the adsorption time, t_{AD} , and the purge-to-feed ratio, $R_{P/F}$ [22, 23]. Considering the component of interest A , recovery and purity are defined according to eqs. (5.15) and (5.16), respectively, while the purge-to-feed ratio, is calculated using eq. (5.17):

$$\rho_{REC,A} = \frac{\int_t^{t+t_{AD}} F_{prod} y_A dt - \int_t^{t+t_{PG}} F_{PG} y_{A,PG} dt - \int_t^{t+t_{BF}} F_{BF} y_{A,BF} dt}{\int_t^{t+t_{AD}} F_{Feed} y_{A,feed} dt} \times 100 \quad (5.15)$$

$$y_A = \frac{\int_t^{t+t_{AD}} F_{prod,A} dt}{\int_t^{t+t_{AD}} F_{prod,total} dt} \quad (5.16)$$

$$R_{P/F} = \frac{\int_t^{t+t_{PG}} F_{PG} y_A dt}{\int_t^{t+t_{AD}} F_{Feed} y_A dt} \quad (5.17)$$

Self-adaptive cycle time

The cycle time optimization follows the previously mentioned “self-adaptive cycle time” methodology. This strategy implies a continuous measurement of the product composition, at the column top, so when the concentration of the product of interest reaches a given threshold, the adsorption step ends and the cycle advances one step. To apply this strategy, the following assumptions should be taken into account:

- All the columns are equal and start from the same initial bed conditions (free of contaminants).

- After a certain number of cycles, the adsorption time converges for a constant value t_{AD} .
- The CSS is independent of the initial conditions.
- If a purge step is considered, its duration depends on the duration of the adsorption step, which must be the same. Because the adsorption and purge steps change at the same rate, the purge-to-feed ratio is kept constant.
- The duration of the backfill step is equal to the adsorption step duration.
- The duration of the pressure equalization steps is fixed (boundary condition).
- The duration of a complete PSA cycle should be $4 \times t_{AD}$.

The assumptions described above are, in general, applicable to most common cycles.

Purge-to-feed ratio

Assuming that the purging gas is vented to waste and is not adsorbed, the recovery of a gas of interest A will be at most:

$$\rho_{REC,A,max} = 1 - R_{P/F} \quad (5.18)$$

Likewise, if the recovery is known for a given operating conditions, then the maximum purge-to-feed ratio can be constraint according to eq.(5.19).

$$R_{P/F,max} = 1 - \rho_{REC,A} \quad (5.19)$$

Following the proposed strategy $R_{P/F,max}$ is updated after each CSS is attained. An important feature of this method methodology is that the recovery for the following $R_{P/F,max}$ will be higher than the previous, until reaching a global maximum. This way, both cycle time and purge-to-feed ratio are optimized simultaneously. Figure 5.2 summarizes the flowchart of the proposed methodology for a given process pressure, where the subscript N J denotes the iteration numbers. This process can be repeated for different pressures to get the best overall operating conditions.

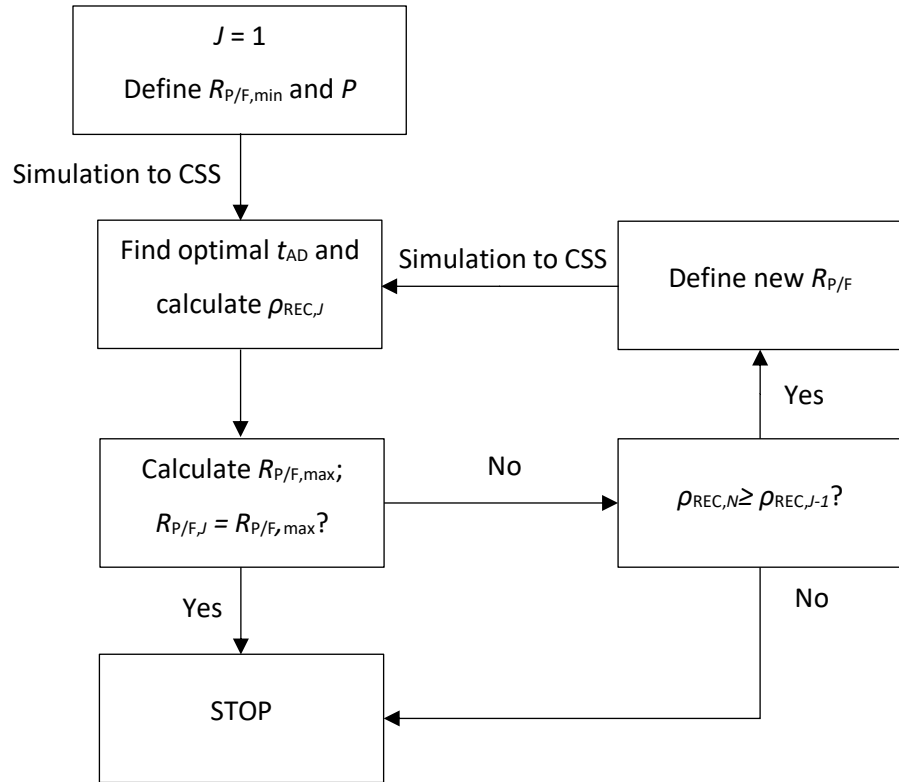


Figure 5.2 – Flowchart of the proposed optimization methodology. Subscript J denotes the number of iterations.

CSS convergence criteria

Unlike other separation methods, cyclic adsorption processes do not have a “true” steady state. Yet, a cyclic steady state can be defined, which is established when the dependent variables do not change in two consecutive cycles more than an accepted error. In this study, the CSS was assumed to reach CSS when the variation of a variable of interest φ is

$$\frac{|\varphi_N - \varphi_{N-1}|}{\varphi_{N-1}} \leq 0.001.$$

Three control variables were considered: t_{AD} , y_A and ρ_{REC} . Regardless of the CSS criterium, a minimum of 35 cycles has been imposed for each operating condition.

5.2.3. Experimental Validation

The simulated performance of the PSA unit was compared with the experimental results obtained in a lab-scale PSA unit. The feed conditions were 75.0 % H_2 and 25.0 % CO_2

at 9 bar and ambient temperature, and the required product minimum purity was 99.5 % H_2 . The lab-scale unit, is described elsewhere in literature and is shown in Appendix B.1.3 [22, 23]. Briefly, it comprises 4 columns connected through a set of solenoid and check valves to direct the flow according to the PSA cycle. The 4 columns were packed with a commercial activated carbon Kuraray 2GA- H_2 , whose single-component adsorption equilibrium isotherms were obtained using the volumetric method [24]. The experimental results of the adsorption data are detailed in Appendix A.1.1. A feed mixture was controlled using two Bronkhorst mass flow controllers (series F-201C) while the operating pressure was regulated using a Bronkhorst pressure controller (series P-702CV, 0–10 bar) placed at the PSA outlet to regulate. The product (outlet) and purge flow rates were measured using Bronkhorst mass flow meters (series F-111C). A fifth column was used for storing the produced gas. The column characteristics and the isotherm parameters are summarized in Table 5.2.

Table 5.2 – Characteristics of the lab-PSA columns and isotherm parameters of H_2 and CO_2 for Kuraray 2GA- H_2 .

Column Characteristics		
Length, L (cm)	34.0	
Outside diameter, d_o (cm)	3.0	
Inside diameter, d_{in} (cm)	2.7	
Mass of adsorbent per column, m_{ads} (g)	109.5	
Isotherm parameters	H_2	CO_2
q_{max} (mol kg^{-1})	4.23	7.08
b_{∞} (bar $^{-1}$)	1.37×10^{-4}	1.84×10^{-5}
ΔH (kJ mol^{-1})	10.23	25.64
k_{LDF} (s $^{-1}$)	1.50	1.36

The PLC (programmable logic controller) unit was programmed with the 6-step PSA cycle, according to the sequence given in Table 5.3. As it can be observed, the duration of blowdown, backfill and purge steps depends on the adsorption time; the duration of the equalization steps was fixed to 2 s.

Table 5.3 – PSA cycle sequence.

Time	2 s	$t_{AD} - 2$	2 s	$t_{AD} - 2$	2 s	$t_{AD} - 2$	2 s	$t_{AD} - 2$
Bed 1	AD		DPE	BD		PG	PPE	BF
Bed 2	PPE	BF	AD		DPE	BD		PG
Bed 3	BD	PG	PPE	BF	AD		DPE	BD
Bed 4	DPE	BD		PG	PPE	BF	AD	

5.3. Results and Discussion

To assess the devised optimization strategy, the lab-PSA was optimized following depicted methodology in Figure 5.2. The 4-beds were assumed to be initially free of CO_2 and pressurized with pure H_2 , operating under room temperature, $T_\infty = 25^\circ\text{C}$. The feed flowrate was set to 2.5 L min^{-1} and an initial $R_{P/F}$ was set to 0.01. After reaching the CSS, the $R_{P/F}$ was incremented by 10 % at a time and new CSS were calculated.

The optimization procedure was run for 6 working pressure, namely 6 bar; 8 bar; 10 bar; 12 bar; 14 bar and 16 bar; and the optimized operating conditions and the corresponding optimized PSA performing parameters obtained and compared with the experimental ones.

5.3.1. Simulation

5.3.1.1. Optimal adsorption time and purge-to-feed ratio

The simulated optimization steps of the lab-PSA are depicted in Table 5.4, along with the optimized operating conditions and PSA optimized performing parameters; the purge-to-feed-ratio was stopped when the set maximum value was reached, as indicated by eqs. (5.18) and (5.19).

The minimum recovery obtained was 66.3 %, for an operating pressure of 6 bar and a $R_{P/F} = 0.01$. For these conditions, the optimal t_{AD} is 37.0 s. On the other hand, the maximum recovery, $\rho_{\text{REC}} = 89.41\%$ was estimated for an operating pressure of 16 bar, with a corresponding optimal t_{AD} of 612.0 s and a $R_{P/F} = 0.051$. Furthermore, the simulated optimized hydrogen concentration meets always the required specification of $y_{\text{H}_2} > 0.9950$, which was known *a priori* since the instant purity was used as a trigger for stopping the

adsorption step in the optimization algorithm. If the constraint was on the average purity, higher recoveries could have been obtained. However, such approach would lead to the breakthrough of CO₂ up to higher concentration, thus propagating the contamination to other columns during the interaction steps (backfill, purge and equalization). In fact, preliminary studies (results not shown) indicated that using the average concentration leads to oscillations, failing to converge for a fixed t_{AD} . Moreover, from the practical point of view, it is important to keep the purity always above design specification, particularly if the hydrogen is to be used in a downstream process without intermediate storing and mixing.

Table 5.4 – Lab-PSA optimization results using the “self-adaptive cycle time” methodology.

NC denotes “not calculated”.

6 bar				8 bar			10 bar		
P	t_{AD} (s)	ρ_{REC} (%)	y_{H_2}	t_{AD} (s)	ρ_{REC} (%)	y_{H_2}	t_{AD} (s)	ρ_{REC} (%)	y_{H_2}
$R_{P/F}$									
0.010	37.0	66.30	0.996	71.0	75.39	0.996	109.5	79.25	0.996
0.012	49.0	71.70	0.996	73.5	76.02	0.996	107.5	78.71	0.996
0.014	46.0	72.70	0.996	77.0	76.92	0.996	111.0	79.04	0.996
0.017	48.5	73.83	0.996	79.0	77.21	0.996	116.0	79.66	0.996
0.021	49.5	73.95	0.996	82.5	77.75	0.996	122.0	80.34	0.996
0.025	51.5	74.48	0.996	86.5	78.36	0.996	130.0	81.08	0.996
0.030	53.0	74.76	0.996	91.5	78.92	0.996	141.5	82.00	0.996
0.036	56.0	75.41	0.996	99.0	79.77	0.996	156.5	82.94	0.996
0.043	59.5	76.00	0.996	108.5	80.63	0.996	178.5	83.97	0.997
0.051	64.0	76.59	0.996	122.5	81.60	0.997	212.5	85.17	0.997
0.062	71.0	77.43	0.996	144.0	82.62	0.997	266.5	86.29	0.997
0.074	81.0	78.28	0.997	179.5	83.82	0.997	352.5	87.10	0.998
0.089	96.5	79.29	0.997	241.0	84.78	0.997	465.0	87.08	0.998
0.107	124.0	80.31	0.997	345.5	85.15	0.998	570.5	86.22	0.998
0.128	178.0	81.12	0.998	466.0	84.26	0.998	685.0	84.74	0.998
0.154	282.5	81.05	0.998	NC			NC		
12 bar				14 bar			16 bar		
P	t_{AD} (s)	ρ_{REC} (%)	y_{H_2}	t_{AD} (s)	ρ_{REC} (%)	y_{H_2}	t_{AD} (s)	ρ_{REC} (%)	y_{H_2}
$R_{P/F}$									
0.010	139.5	79.76	0.996	174.0	80.40	0.996	216.0	81.35	0.996
0.012	143.0	80.10	0.996	183.5	81.27	0.996	227.5	82.16	0.996
0.014	149.5	80.67	0.996	194.0	82.05	0.996	242.5	83.03	0.996
0.017	158.0	81.46	0.996	206.5	82.83	0.996	261.5	83.97	0.996
0.021	169.5	82.29	0.996	224.0	83.79	0.996	287.0	85.02	0.996
0.025	184.0	83.24	0.996	248.0	84.87	0.996	322.5	86.14	0.997
0.030	204.0	84.20	0.996	281.0	86.00	0.997	371.5	87.34	0.997
0.036	233.0	85.37	0.997	329.0	87.18	0.997	438.5	88.42	0.997

0.043	276.0	86.52	0.997	397.5	88.24	0.997	522.0	89.14	0.997
0.051	345	87.60	0.997	486.5	88.96	0.997	612.0	89.41	0.998
0.062	433.0	88.33	0.998	584.0	89.08	0.998	699.5	89.20	0.998
0.074	538.5	88.35	0.998	675.5	88.59	0.998	808.0	88.75	0.998
0.089	635.5	87.63	0.998	802.5	87.88	0.998	900-0	87.49	0.997
0.107	761.0	86.66	0.998						
0.128		NC			NC			NC	
0.154									

Figure 5.3 shows the hydrogen recovery as function of the PF for the studied pressures. The most important conclusion is that a single maximum is obtained for all cases. The recovery increases with pressure, but not at the same rate. This phenomenon was assigned to the shape of the CO_2 adsorption isotherm, which approaches to the Henry's law for low partial pressure. At higher pressure, the CO_2 isotherm tends to an asymptotic behavior and therefore, the "pressure swing" becomes less effective. On the other hand, at higher pressures, the maximum is obtained at lower $R_{P/F}$. For example, while at 16 bar the maximum recovery was obtained for a $R_{P/F} = 0.051$, the maximum at 6 bar was obtained for a $R_{P/F} = 0.128$.

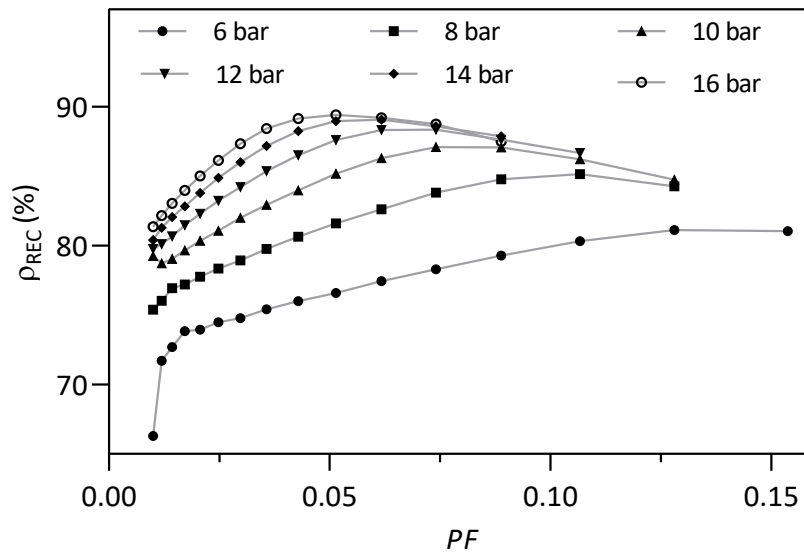


Figure 5.3 – Recovery at optimal t_{AD} as function of $R_{P/F}$; ● - 6 bar ; ■ - 8 bar ▲ - 10 bar ; ▼ - 12 bar; ◆ - 14 bar; ○ – 16 bar. Dashed-lines were added to improve readability.

At the first sight, it seems that lower purging is needed for higher working pressures. However, higher pressures are also associated to longer adsorption steps (see Table 5.4), which results into greater amounts of purging gas for the same $R_{P/F}$. Accordingly, it is worth to analyze the data also in terms of purging gas volume rather than $R_{P/F}$, as shown in Figure 5.4. From this figure, it can be concluded that optimal purging gas volume is roughly the same for all cases, corresponding approximately to 5 times the volume of one adsorption column. Besides, the plateaus observed for each pressure, reinforce the conclusion that a maximum recovery can be met when using the proposed optimization strategy.

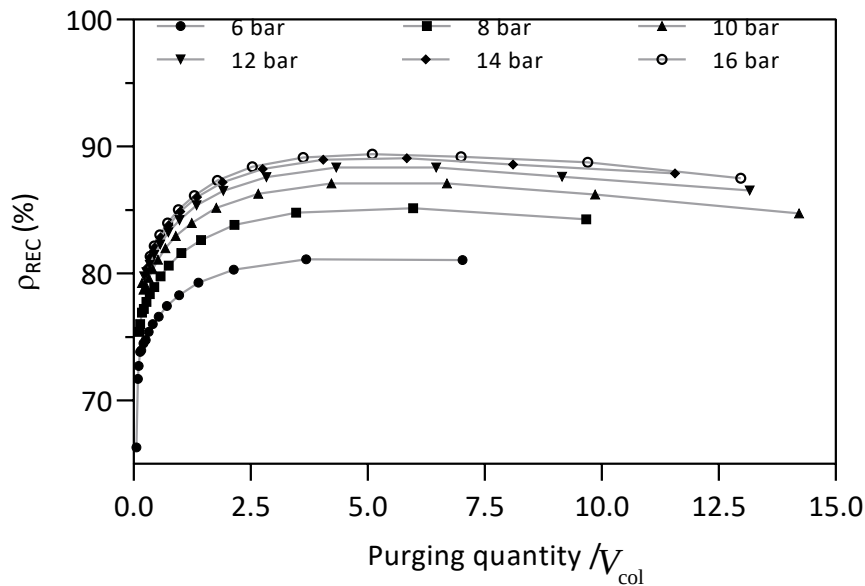


Figure 5.4 – Recovery at optimal t_{AD} as function of purging quantity (column volume equivalent) at different pressures; ● - 6 bar ; ■ - 8 bar ▲ - 10 bar ; ▼ – 12 bar; ◆ - 14 bar; ○ – 16 bar. Dashed-lines were added to improve readability.

For a better understanding of how the adsorption time is adjusted using the proposed methodology, Figure 5.5 shows the simulated t_{AD} history along the optimization procedure of the lab-PSA running at 8 bar. As previously mentioned, the adsorption time converges for a constant value using the self-adaptive cycle time strategy, hence the plateaus attained for each $R_{P/F}$. These plateaus correspond to the CSS conditions. Apart from the first cycle, as the $R_{P/F}$ increases, longer adsorption steps are observed, which was attributed to a more

effective bed regeneration. However, the highest adsorption time, $t_{AD} = 755.5$ s, is observed in the first cycle at $R_{p/F} = 0.01$, and is followed by a minimum in the second cycle, $t_{AD} = 25.0$ s. This behavior is related to axial the spreading of the concentration front, as shown in Figure 5.6. Because the bed was initially “cleaned”, the highest quantity adsorbed was attained in the first adsorption step. At this stage, the CO_2 concentration front spreads only due to the dispersive phenomena inherent to the adsorption step. Then, desorption in takes place (pressure equalization and blowdown) and a dispersive concentration wave is formed due to thermodynamic and kinetic effects. Due to the higher quantity adsorbed in the first adsorption step, the front dispersion is more pronounced in the first cycle. Consequently, the next adsorption step (2nd cycle) starts with more dispersed front and a minimum t_{AD} is observed. As the cyclic operation continues, the profile becomes more stable and reaching the CSS, at $t_{AD} = 71.0$ s.

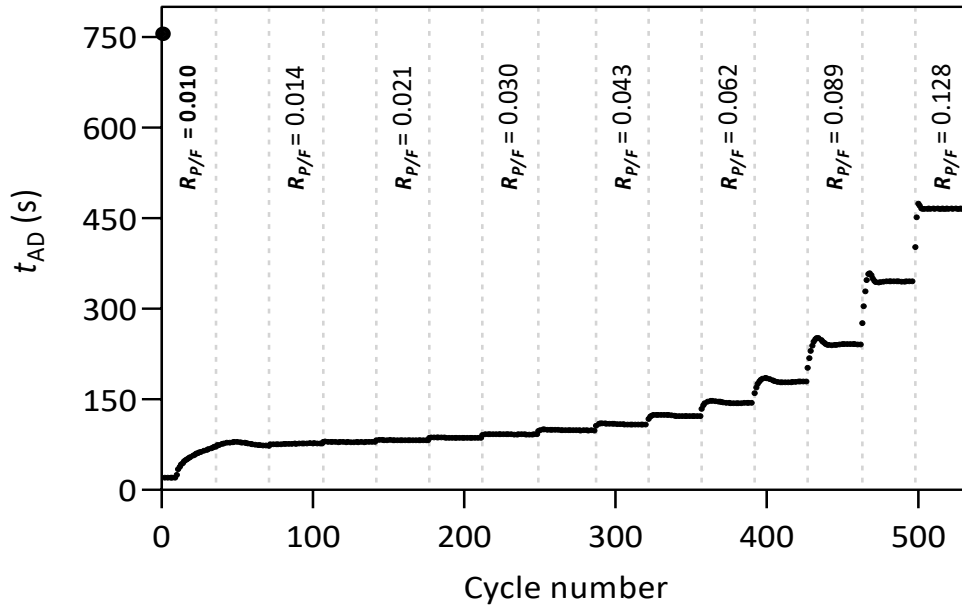


Figure 5.5 – Adsorption time history along the optimization procedure; $P = 8$ bar.

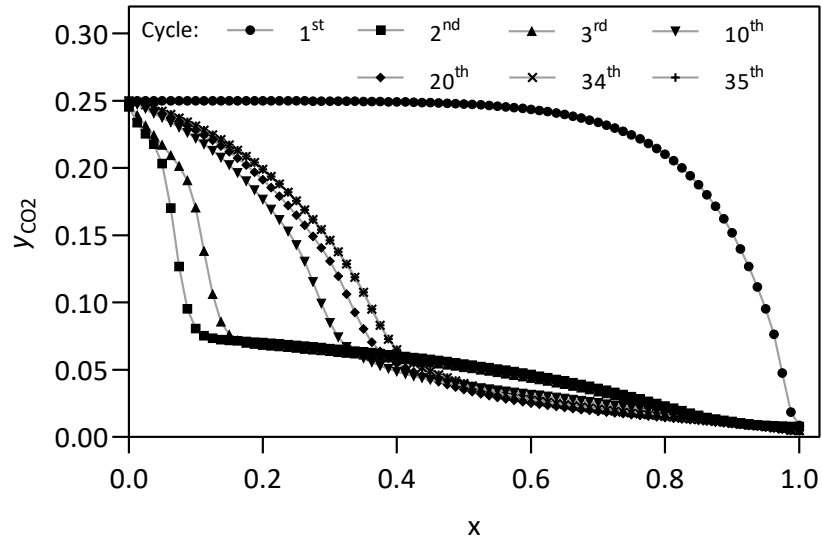


Figure 5.6 – CO₂ profile in the gas-phase at the end of the adsorption step as a function of dimensionless bed length for different cycles; $P = 8$ bar; $R_{P/F} = 0.01$.

5.3.1.2. Computation time

In typical optimization studies, the influence of the different variables is assessed separately. Then, the data is analyzed and empirical correlations are drawn to obtain the optimal operating conditions[25]. This strategy requires simulating each operating condition until the CSS is reached, which can be very time-consuming, particularly if rigorous modeling is needed. Following the proposed self-adaptive cycle time strategy, the computation time can be significantly reduced. Firstly, while conventional strategies need several simulations (1 simulation per condition) to obtain the data for *a posteriori* optimization, here, cycle time is optimized in only one simulation. Moreover, the CSS converges faster. For example, while the first CSS attained in Figure 5.5 ($t_{AD} = 71.0$ s; $R_{P/F} = 0.01$ and $P = 8$ bar) was reached after only 34 cycles and a computation time of 2456 seconds, fixing the adsorption time requires 114 cycles and a computation time of 5138 s to obtain the same CSS. Moreover, the strategy of using the previous CSS as initial conditions for the next simulation allows for an even greater reduction in computation time. For instance, it took only 5 cycles to find the last CSS ($t_{AD} = 466.0$ s; $R_{P/F} = 0.128$; $P = 8$ bar)

and a computing time of 382 s, while using a fixed cycle time operation takes 16 cycles and a computing time of 1644 s. Overall, the optimization procedure for operating at 8 bar took 531 cycles and a computation time of 38367 s, a very reasonable time compared to the fixed cycle time operation. Besides, it should be noted that a minimum of 35 cycles was imposed for each operating condition, although most of the cases reached the CSS much sooner. Also, there is certainly room for improvement, namely using parallelization strategies but it falls outside the scope of this paper.

5.3.2. Experimental

To validate the simulations, a set of six experiments based on the previous analysis were carried out in the lab-PSA unit. Because the laboratory gas grid is limited to 8 bar, three runs were performed at 6 bar and another three were performed at 8 bar. The PSA was operated for at least 40 cycles until the product concentration history remained constant. Table 5.5 summarizes the operating conditions and compares the experimental and simulation results. A good agreement between the data is observed for both purity and recovery. As in the simulation, when operating at 6 bar, the highest recovery was obtained for a $R_{P/F} = 0.128$ and a $t_{AD} = 178.0$ s (Run # 2). At these conditions, a recovery of 80.5 % was obtained (vs. 81.1 % predicted) for $y_{H_2} = 0.9976$ (vs. 0.9976 predicted). For a $P = 8$ bar, the highest recovery is also in agreement, corresponding to a $R_{P/F} = 0.107$ and a $t_{AD} = 345.5$ s (Run # 5). In this case, $\rho_{REC} = 84.4$ % (vs. 85.1 % predicted) and $y_{H_2} = 0.9978$ (vs. 0.9980 predicted). On the other hand, while the simulation predicts an increase in purity with $R_{P/F}$, experimentally this was not observed in runs # 2 ($R_{P/F} = 0.128$, $y_{H_2} = 0.9976$) and # 3 ($R_{P/F} = 0.154$, $y_{H_2} = 0.9975$).

Table 5.5 – Operating conditions of the lab-PSA experiments and corresponding experimental and simulation results.

Run #	Operating conditions			Simulation / Experimental results					
	P	$R_{P/F}$	t_{AD}	y_{H_2}		y_{CO_2}		$\rho_{REC} (\%)$	
1	6	0.107	124.0	0.9971	0.9961	0.0029	0.0039	80.3	79.8
2	6	0.128	178.0	0.9976	0.9976	0.0024	0.0024	81.1	80.5
3	6	0.154	282.5	0.9982	0.9975	0.0018	0.0025	81.1	80.0
4	8	0.089	241.0	0.9974	0.9971	0.0026	0.0029	84.8	82.9
5	8	0.107	345.5	0.9980	0.9978	0.0020	0.0022	85.1	84.4
6	8	0.128	466.0	0.9985	0.9981	0.0015	0.0019	84.3	83.5

5.4. Conclusions

In this article, a PSA simulator was developed and an efficient optimization procedure has been proposed for PSA processes where the less adsorbing species is the component of interest. The procedure was based on a self-adaptive cycle time strategy. A lab-scale PSA unit used for hydrogen purification was used as case study, where a typical 6-step cycle was implemented. The unit was optimized by simulation aiming to obtain 99.5 % H_2 from a mixture containing 75.0 % H_2 and 25.0 % CO_2 .

The results obtained indicate that the proposed self-adaptive cycle time strategy is a reliable approach, not only to obtain the optimum cycle time, but also to accelerate the CSS convergence. Comparing to fixed time simulations, the self-adaptive can be more than 3 times faster. Parallelization strategies are currently being implemented to accelerate the convergence, but it falls outside the scope of this paper.

The developed strategy to optimize the purge-to-feed ratio proved to be efficient and allowed reducing the number of simulated conditions. On average, the maximum hydrogen recovery is obtained when the purge-to-feed ratio corresponds to approximately 5 times the volume of one adsorption column. It was concluded that the hydrogen recovery is improved by the pressure increase, till a certain point, and the highest recovery, $\rho_{REC} = 89.4 \%$, was obtained at the best operating conditions, $P = 16$ bar; $R_{P/F} = 0.051$; $t_{AD} = 612.0$ s, with a corresponding $y_{H_2} = 0.998$.

Although this study does not consider all the variables of a real process, the proposed strategy can significantly reduce computational efforts, given that optimum operating conditions were determined using a reduced number of simulations. Moreover, the given heuristic can be combined with other CSS acceleration techniques and machine learning algorithms, giving researchers a very powerful tool for PSA optimization.

5.5. Acknowledgments

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5.6. Nomenclature

Symbol	Description	Units
b	Langmuir affinity constant	Pa^{-1}
C_p	Specific heat capacity	$\text{J kg}^{-1} \text{K}^{-1}$
d	Diameter	m
F	Molar flow rate	mol s^{-1}
k	Thermal conductivity	$\text{W m}^{-1} \text{K}^{-1}$
K_v	Valve constant	
L	Length	m
m	Mass	kg
P	Pressure	Pa
Pe	Peclet number	

$R_{P/F}$	Purge-to-feed ratio	
q	Molecular concentration in the adsorbed phase	mol kg ⁻¹
$\mathfrak{R}$	Ideal gas constant	J mol ⁻¹ K ⁻¹
R_g^a	Energy balance dimensionless parameter	
R_g^h	Energy balance dimensionless parameter	
R_g^s	Energy balance dimensionless parameter	
T	Temperature	K
t	Time	s
u	Interstitial velocity	m s ⁻¹
V	Volume	m ³
x	Dimensionless spatial coordinate	
y	Gas phase molar fraction	
z	Spatial coordinate	m

Greek Symbol	Description	Units
α	Dimensionless d'Arcy parameter	
ΔH	Heat of adsorption	J mol ⁻¹
μ	Viscosity	kg m ⁻¹ s ⁻¹
ρ	Density	kg m ⁻³
t_b	Time bed constant	s
θ	Dimensionless time variable	
ζ_a	Adsorbed phase capacity factor	
ζ_g	Gas phase capacity factor	

Acronym	Description
AD	Adsorption step
BD	Blowdown step
BF	Backfill step
CSS	Cyclic steady state
DPE	Depressurization pressure equalization step

LDF	Linear driving force
PDE	Partial differential equation
PG	Purge step
PPE	Pressurization pressure equalization step
Subscripts	Description
ads	Adsorbent
ad	Adsorption
b	Bed
EQ	Equalization
H	High
i	Component I / interstitial velocity
in	Inside / initial
j	Component j
<i>L</i>	Length
max	Maximum
mix	Mixture
nc	Number of components / Not calculated
p	Particle
ref	Reference
T	Thermal
w	Wall

5.7. References

1. Kumar, R., et al., *A versatile process simulator for adsorptive separations*. Chemical Engineering Science, 1994. **49**(18): p. 3115-3125.

2. Biegler, L.T., L. Jiang, and V.G. Fox, *Recent advances in simulation and optimal design of pressure swing adsorption systems*. Separation & Purification Reviews, 2005. **33**(1): p. 1-39.
3. Agarwal, A., L.T. Biegler, and S.E. Zitney, *Simulation and optimization of pressure swing adsorption systems using reduced-order modeling*. Industrial & Engineering Chemistry Research, 2009. **48**(5): p. 2327-2343.
4. Todd, R.S., et al., *Fast finite-volume method for PSA/VSA cycle simulation experimental validation*. Industrial & Engineering Chemistry Research, 2001. **40**(14): p. 3217-3224.
5. Kvamsdal, H. and T. Hertzberg, *Optimization of PSA systems—studies on cyclic steady state convergence*. Computers & chemical engineering, 1997. **21**(8): p. 819-832.
6. Ding, Y. and M.D. LeVan, *Periodic states of adsorption cycles III. Convergence acceleration for direct determination*. Chemical Engineering Science, 2001. **56**(17): p. 5217-5230.
7. Todd, R.S., et al., *Improved ODE integrator and mass transfer approach for simulating a cyclic adsorption process*. Computers & chemical engineering, 2003. **27**(6): p. 883-899.
8. Capra, F., et al., *MO-MCS, a derivative-free algorithm for the multiobjective optimization of adsorption processes*. Industrial & Engineering Chemistry Research, 2018. **57**(30): p. 9977-9993.
9. Webley, P.A., et al. *Optimization of PSA systems for Air Separation*. in *The Sixth Conference on Fundamentals of Adsorption (FOA6)*. 1998. Elsevier.
10. Jiang, L., L.T. Biegler, and V.G. Fox, *Simulation and optimization of pressure-swing adsorption systems for air separation*. AIChE Journal, 2003. **49**(5): p. 1140-1157.
11. Khajuria, H. and E.N. Pistikopoulos, *Optimization and control of pressure swing adsorption processes under uncertainty*. AIChE Journal, 2013. **59**(1): p. 120-131.
12. Sankararao, B. and S.K. Gupta, *Multi-objective optimization of pressure swing adsorbers for air separation*. Industrial & engineering chemistry research, 2007. **46**(11): p. 3751-3765.

13. Boukouvala, F., M.F. Hasan, and C.A. Floudas, *Global optimization of general constrained grey-box models: new method and its application to constrained PDEs for pressure swing adsorption*. Journal of Global Optimization, 2017. **67**(1-2): p. 3-42.
14. Pai, K.N., V. Prasad, and A. Rajendran, *Experimentally validated machine learning frameworks for accelerated prediction of cyclic steady state and optimization of pressure swing adsorption processes*. Separation and Purification Technology, 2020. **241**: p. 116651.
15. Pai, K.N., V. Prasad, and A. Rajendran, *A generalized, adsorbent-agnostic, artificial neural network framework for rapid simulation, optimization and adsorbent-screening of adsorption processes*. Industrial & Engineering Chemistry Research, 2020.
16. Grande, C.A., *Advances in pressure swing adsorption for gas separation*. ISRN Chemical Engineering, 2012. **2012**.
17. Sun, W., et al., *A systematic simulation and proposed optimization of the pressure swing adsorption process for N₂/CH₄ separation under external disturbances*. Industrial & Engineering Chemistry Research, 2015. **54**(30): p. 7489-7501.
18. Cruz, P.J.R.d., *Simulação e otimização de processos cíclicos de adsorção: Aplicação à produção de oxigénio a partir do ar e separação/purificação do hélio*. 2003.
19. Hindmarsh, A.C., *ODEPACK, a systematized collection of ODE solvers*. Scientific computing, 1983: p. 55-64.
20. Cruz, P., et al., *Cyclic adsorption separation processes: analysis strategy and optimization procedure*. Chemical Engineering Science, 2003. **58**(14): p. 3143-3158.
21. Chou, C.-t. and W.-C. Huang, *Simulation of a four-bed pressure swing adsorption process for oxygen enrichment*. Industrial & engineering chemistry research, 1994. **33**(5): p. 1250-1258.
22. Yáñez, M., et al., *PSA purification of waste hydrogen from ammonia plants to fuel cell grade*. Separation and Purification Technology, 2020. **240**: p. 116334.
23. Relvas, F., et al., *Single-stage pressure swing adsorption for producing fuel cell grade hydrogen*. Industrial & Engineering Chemistry Research, 2018. **57**(14): p. 5106-5118.

24. Santos, J., F. Magalhaes, and A. Mendes, *Contamination of zeolites used in oxygen production by PSA: effects of water and carbon dioxide*. Industrial & engineering chemistry research, 2008. **47**(16): p. 6197-6203.
25. Sircar, S. and T.C. Golden, *Pressure swing adsorption technology for hydrogen production*. Hydrogen and syngas production and purification technologies, 2009. **10**: p. 414-450.

Chapter 6. General conclusions and future work

High purity hydrogen is needed for the PEMFC market. Pressure swing adsorption is the preferred technology to obtain the desired purity degree. While large-scale units with up to 16-beds can produce +99.999 % H₂ at a high recovery rate (ca. 90 %), in small-scale applications PSA scale-down leads to lower recoveries of ca. 70 %, owing to lower operating pressure and reduced number of columns, typically four. In addition, commercially available adsorbents present low adsorption capacity for CO, which needs to be removed down to sub-ppm levels, thus limiting the efficiency of the separation.

A commercial hydrogen PSA prototype was optimized and adapted to operate in VPSA mode. The objective was to produce stationary PEMFC grade hydrogen, according to ISO 14687-3, from a mixture of 70 % H₂, 25 % CO₂, 4 % CH₄, and 1 % CO. After optimization through a design of experiments, the VPSA operating mode allowed improving the hydrogen recovery from 69.8 % (PSA mode) to 73.2 % (VPSA mode), for a targeted CO concentration of 10.0 ppm, meeting the required hydrogen purity.

To improve the CO adsorption capacity, CO-selective adsorbents were investigated, namely preparing π -complexation adsorbents from a commercial activated carbon by wetness impregnation of copper chloride. The copper loading led to enhanced CO adsorption capacity which was assigned to the formation of π -complexation bonds between the CO and Cu⁺. On the other hand, a decrease in the surface area in the Cu-AC led to a decrease in adsorption capacity towards CO₂, CH₄, N₂, and H₂, whose adsorption is only assigned to van der Waals interactions with the activated carbon surface. At 1 bar and 30 °C, the CO adsorption capacity in the Cu-AC-5 sample was 5-fold higher than the pristine AC, 2.48 mol·kg⁻¹ vs. 0.466 mol·kg⁻¹.

The performance of the modified Cu-AC in hydrogen purification was assessed using a 4-bed lab-scale unit, targeting automotive PEMFC grade hydrogen, according to ISO 14687-2 (CO below 0.2 ppm). The feed mixture was based on the same 70 % H₂, 25 % CO₂, 4 % CH₄, and 1 % CO used in the commercial prototype. Cu-AC-2 sample (2 mol_{Cu}/kg_{AC}) was chosen due to its high enough CO selectivity for an effective CO removal and because CO₂ still has adequate adsorption capacity. After optimization using a design of experiments approach, hydrogen with a purity >99.97 % was obtained, with 76.19 % recovery and a carbon monoxide concentration of 0.17 ppm. This result presents an important outcome in PSA technology for hydrogen purification, particularly for small-scale applications.

Finally, a PSA simulator was developed in a Fortran routine and an efficient optimization procedure was proposed. The optimization was based on a self-adaptive cycle time strategy and involved heuristic rules to determine the optimum systematically. The strategy allowed optimizing the adsorption time and the purge-to-feed ratio simultaneously and proved to accelerate the CSS convergence. Comparing to fixed-time simulations, the self-adaptive cycle time can be more than 3 times faster, with the additional advantage of finding the optimum cycle time for the given conditions. The PSA simulator was experimentally validated using the 4-bed lab-scale PSA.

The work here developed led to the creation of the spin-off company *Amnis Pura, Lda*, dedicated to gas separation by Pressure Swing Adsorption. The company received the *FEUP Prime* seal in 2019 and is one of the 15 startups selected amongst +100 to participate in the CleanTech Camp – 2021 edition, promoted by EIT InnoEnergy, Naturgy, Enagás Empreende, CRH, and PRIO.

6.1. Future work

In this work, important steps were taken towards efficient hydrogen purification using pressure swing adsorption technology.

The development of the CO-selective Cu-AC adsorbent allowed producing hydrogen with CO concentration at a sub-ppm level. Further research using this adsorbent may therefore be useful namely:

- Combining the Cu-AC with other adsorbents in layered-bed PSA;
- Using Cu-AC for CO purification;
- Using Cu-AC for co-production of H₂ and CO in mixtures rich in both H₂ and CO (e.g. syngas);
- Evaluate the potential of Cu-AC in other separations, namely olefin/paraffin, desulphurization, etc.;
- Preparing π -complexation adsorbent using other substrates, including activated alumina, zeolites, etc.

In addition, further developments in the simulator should also be considered, namely implementing parallelization in the coding to speed up the computation time; introducing other optimization methodologies; and testing new numerical methods. Moreover, other PSA operating variables should be added to the optimization strategy. A very interesting approach would be implementing the self-adaptive cycle time strategy in a real context, where the PSA cycle time could be adjusted according to the concentration of contaminants measured in the produced stream. To do this, care should be taken to avoid oscillations in the process response. In addition, the response time delay of the gas analyzers should be taken into account.

Finally, other cycles configuration and unit designs should be considered, namely based on rapid cycle PSAs.

A. Appendix – Experimental adsorption equilibrium data

A.1. Experimental data

A.1.1. 2GA-H2

Table A.1 – Experimental adsorption equilibrium data of CO on AC at 30 °C, 40 °C, and 50 °C.

CO (Kuraray 2GA-H2)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.115	0.062	0.090	0.039	0.119	0.041
0.260	0.138	0.179	0.076	0.217	0.075
0.438	0.224	0.395	0.160	0.464	0.145
0.741	0.361	0.678	0.263	0.672	0.213
1.038	0.485	0.930	0.348	0.994	0.305
1.513	0.663	1.374	0.488	1.601	0.464
2.214	0.895	2.223	0.721	2.495	0.672
3.137	1.161	3.371	0.994	3.638	0.903
4.309	1.450	4.338	1.189	4.619	1.077
5.456	1.697	5.032	1.316	5.563	1.230
-	-	5.685	1.428	-	-

Table A.2 – Experimental adsorption equilibrium data of CO₂ on AC at 30 °C, 40 °C, and 50 °C.

CO ₂ (Kuraray 2GA-H2)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.032	0.187	0.026	0.114	0.033	0.101
0.102	0.489	0.090	0.332	0.139	0.366
0.224	0.880	0.254	0.751	0.328	0.727
0.381	1.277	0.408	1.064	0.619	1.164
0.647	1.811	0.619	1.429	0.907	1.520
0.955	2.313	0.858	1.774	1.309	1.941
1.364	2.869	1.270	2.278	1.872	2.433
1.934	3.487	1.871	2.876	2.624	2.972
2.765	4.192	2.579	3.447	3.534	3.506
3.569	4.734	3.510	4.058	4.440	3.948
4.546	5.268	4.596	4.611	5.271	4.295
5.320	5.614	5.305	4.916	-	-

Table A.3 – Experimental adsorption equilibrium data of CH₄ on AC at 30 °C, 40 °C, and 50 °C.

CH ₄ (Kuraray 2GA-H2)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.064	0.104	0.079	0.097	0.096	0.093
0.225	0.323	0.222	0.251	0.255	0.233
0.442	0.563	0.372	0.393	0.418	0.358
0.622	0.734	0.558	0.549	0.678	0.631
0.877	0.947	0.836	0.754	0.928	0.785
1.220	1.194	1.314	1.055	1.344	1.010
1.799	1.545	2.073	1.442	1.902	1.270
2.530	1.905	3.168	1.883	2.739	1.597
3.533	2.306	4.355	2.265	3.636	1.890
4.892	2.739	5.375	2.543	4.670	2.179
5.591	2.937	-	-	5.517	2.390

Table A.4 – Experimental adsorption equilibrium data of N₂ on AC at 30 °C, 40 °C, and 50 °C.

N ₂ (Kuraray 2GA-H2)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.044	0.015	0.041	0.013	0.109	0.026
0.087	0.032	0.044	0.012	0.250	0.059
0.217	0.081	0.087	0.025	0.337	0.080
0.468	0.170	0.217	0.063	0.479	0.109
0.823	0.286	0.468	0.134	0.712	0.159
1.251	0.415	0.823	0.227	1.019	0.225
1.848	0.578	1.251	0.333	1.407	0.299
2.573	0.756	1.848	0.468	1.992	0.416
3.648	0.985	2.573	0.618	2.927	0.574
4.316	1.112	3.648	0.816	3.955	0.740
5.371	1.295	4.316	0.929	4.905	0.868
-	-	5.371	1.093	5.784	0.982
-	-	5.696	1.149	-	-

Table A.5 – Experimental adsorption equilibrium data of H₂ on AC at 30 °C, 40 °C, and 50 °C.

H ₂ (Kuraray 2GA-H2)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.284	0.010	0.417	0.013	0.426	0.010
1.011	0.036	1.078	0.033	1.043	0.025
2.976	0.103	3.126	0.095	2.108	0.050
4.415	0.152	4.390	0.133	3.114	0.074
5.503	0.188	5.533	0.167	5.017	0.118

A.1.2. Cu-AC-0.5

Table A.6 – Experimental adsorption equilibrium data of CO on Cu-AC-0.5 at 30 °C, 40 °C, and 50 °C.

CO (Cu-AC-0.5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g^{-1}	Pressure bar	q_{CO} mmol g^{-1}	Pressure bar	q_{CO} mmol g^{-1}
0.000	0.000	0.000	0.000	0.000	0.000
0.052	0.152	0.017	0.069	0.056	0.089
0.164	0.270	0.057	0.137	0.333	0.264
0.283	0.353	0.173	0.250	0.513	0.339
0.499	0.469	0.389	0.379	0.688	0.403
0.819	0.609	0.650	0.492	0.910	0.475
1.216	0.758	0.902	0.582	1.237	0.571
1.729	0.927	1.523	0.769	1.584	0.667
2.436	1.131	2.069	0.908	2.169	0.814
3.432	1.378	3.168	1.147	2.705	0.931
4.611	1.630	4.241	1.346	3.412	1.072
5.586	1.813	5.380	1.530	4.191	1.214
-	-	-	-	5.419	1.415

Table A.7 – Experimental adsorption equilibrium data of CO₂ on Cu-AC-0.5 at 30 °C, 40 °C, and 50 °C.

CO ₂ (Cu-AC-0.5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g^{-1}	Pressure bar	q_{CO} mmol g^{-1}	Pressure bar	q_{CO} mmol g^{-1}
0.000	0.000	0.000	0.000	0.000	0.000
0.048	0.207	0.014	0.060	0.077	0.171
0.132	0.481	0.045	0.152	0.173	0.352
0.227	0.737	0.127	0.363	0.293	0.549
0.395	1.116	0.292	0.711	0.506	0.851
0.593	1.488	0.502	1.070	0.808	1.209
0.901	1.968	0.884	1.595	1.334	1.724
1.376	2.566	1.363	2.120	1.868	2.155
1.958	3.161	2.014	2.694	2.677	2.693
2.793	3.825	3.039	3.389	3.701	3.246
3.971	4.542	4.066	3.928	4.836	3.743
5.061	5.051	5.173	4.411	5.573	4.105

Table A.8 – Experimental adsorption equilibrium data of CH₄ on Cu-AC-0.5 at 30 °C, 40 °C, and 50 °C.

CH ₄ (Cu-AC-0.5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.048	0.056	0.032	0.034	0.094	0.067
0.180	0.194	0.070	0.070	0.274	0.190
0.330	0.333	0.180	0.168	0.466	0.305
0.508	0.484	0.406	0.348	0.715	0.443
0.719	0.645	0.630	0.503	0.969	0.570
1.008	0.840	0.891	0.666	1.398	0.762
1.494	1.122	1.388	0.933	1.734	0.899
2.056	1.399	2.177	1.282	2.258	1.094
2.848	1.726	3.186	1.639	3.428	1.459
3.851	2.090	4.264	1.953	4.391	1.712
4.934	2.404	5.275	2.201	5.432	1.950
5.552	2.561	-	-	-	-

Table A.9 – Experimental adsorption equilibrium data of N₂ on Cu-AC-0.5 at 30 °C, 40 °C, and 50 °C.

N ₂ (Cu-AC-0.5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.039	0.012	0.021	0.005	0.023	0.004
0.086	0.026	0.048	0.011	0.056	0.011
0.229	0.068	0.069	0.016	0.074	0.014
0.441	0.129	0.135	0.032	0.148	0.028
0.673	0.193	0.240	0.055	0.249	0.047
0.842	0.238	0.460	0.105	0.503	0.092
0.970	0.271	0.696	0.156	0.760	0.137
1.559	0.413	0.974	0.213	1.012	0.179
2.390	0.593	1.856	0.383	2.015	0.338
3.273	0.760	2.787	0.543	3.009	0.478
4.225	0.917	4.186	0.750	4.495	0.664
5.322	1.076	5.676	0.938	5.932	0.822

Table A.10 – Experimental adsorption equilibrium data of H₂ on Cu-AC-0.5 at 30 °C, 40 °C, and 50 °C.

H ₂ (Cu-AC-0.5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.200	0.006	0.268	0.007	0.426	0.010
1.044	0.032	1.108	0.029	1.043	0.025
2.543	0.079	2.159	0.057	2.191	0.051
4.357	0.132	3.492	0.092	3.120	0.077
5.485	0.165	4.495	0.119	5.017	0.121
-	-	5.502	0.145	-	-

A.1.3. Cu-AC-2

Table A.11 – Experimental adsorption equilibrium data of CO on Cu-AC-2 at 30 °C, 40 °C, and 50 °C.

CO (Cu-AC-2)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.016	0.237	0.009	0.136	0.026	0.163
0.062	0.485	0.049	0.337	0.087	0.338
0.143	0.715	0.113	0.518	0.234	0.581
0.310	0.955	0.289	0.812	0.441	0.792
0.647	1.192	0.559	1.033	0.846	1.041
0.957	1.330	0.924	1.215	1.115	1.153
1.367	1.451	1.466	1.390	1.716	1.323
1.923	1.577	2.119	1.538	2.412	1.476
2.933	1.756	3.114	1.706	2.826	1.547
3.992	1.903	4.148	1.844	3.515	1.652
4.952	2.019	5.208	1.963	4.495	1.774
5.719	2.101	-	-	5.448	1.877

Table A.12 – Experimental adsorption equilibrium data of CO₂ on Cu-AC-2 at 30 °C, 40 °C, and 50 °C.

CO ₂ (Cu-AC-2)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.041	0.100	0.062	0.111	0.081	0.104
0.105	0.230	0.142	0.233	0.164	0.194
0.180	0.364	0.322	0.463	0.256	0.287
0.323	0.586	0.485	0.643	0.515	0.519
0.545	0.871	0.679	0.831	0.806	0.742
0.767	1.118	1.002	1.104	1.103	0.943
1.170	1.499	1.475	1.439	1.551	1.208
1.269	1.579	2.041	1.775	2.340	1.598
2.162	2.191	3.103	2.280	3.458	2.044
3.135	2.693	3.985	2.613	4.434	2.359
3.989	3.044	5.202	2.987	5.419	2.631
4.808	3.319	-	-	-	-
5.540	3.551	-	-	-	-

Table A.13 – Experimental adsorption equilibrium data of CH₄ on Cu-AC-2 at 30 °C, 40 °C, and 50 °C.

CH ₄ (Cu-AC-2)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.077	0.051	0.084	0.045	0.102	0.042
0.165	0.105	0.181	0.091	0.216	0.085
0.311	0.187	0.274	0.133	0.379	0.144
0.453	0.260	0.458	0.212	0.670	0.242
0.699	0.376	0.753	0.328	0.939	0.313
0.911	0.469	1.061	0.436	1.399	0.443
1.387	0.670	1.642	0.613	2.091	0.595
1.533	0.710	2.146	0.750	3.012	0.792
2.541	1.006	3.144	0.983	4.123	0.993
3.380	1.213	4.085	1.171	5.305	1.176
4.889	1.512	5.445	1.399	-	-
-	-	-	-	-	-

Table A.14 – Experimental adsorption equilibrium data of N₂ on Cu-AC-2 at 30 °C, 40 °C, and 50 °C.

N ₂ (Cu-AC-2)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.042	0.010	0.088	0.014	0.094	0.012
0.126	0.028	0.265	0.041	0.224	0.028
0.275	0.059	0.549	0.083	0.541	0.066
0.535	0.107	0.875	0.129	0.834	0.100
0.750	0.145	1.334	0.191	1.136	0.134
1.029	0.195	1.826	0.252	1.663	0.192
1.495	0.265	2.340	0.312	2.208	0.248
2.353	0.383	3.194	0.406	2.743	0.300
3.394	0.507	4.399	0.525	3.268	0.350
4.898	0.663	5.152	0.593	3.834	0.402
-	-	5.863	0.656	4.597	0.469
-	-	-	-	5.501	0.544

Table A.15 – Experimental adsorption equilibrium data of H₂ on Cu-AC-2 at 30 °C, 40 °C, and 50 °C.

H ₂ (Cu-AC-2)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.206	0.004	0.303	0.004	0.230	0.004
0.522	0.011	1.179	0.019	1.061	0.016
1.646	0.033	2.411	0.039	2.138	0.036
3.040	0.057	4.400	0.070	3.265	0.054
5.041	0.093	5.522	0.089	4.450	0.078
-	-	-	-	-	-

A.1.4. Cu-AC-3.5

Table A.16 – Experimental adsorption equilibrium data of CO on Cu-AC-3.5 at 30 °C, 40 °C, and 50 °C.

CO (Cu-AC-3.5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g^{-1}	Pressure bar	q_{CO} mmol g^{-1}	Pressure bar	q_{CO} mmol g^{-1}
0.000	0.000	0.000	0.000	0.000	0.000
0.008	0.108	0.011	0.100	0.066	0.347
0.021	0.297	0.033	0.265	0.102	0.461
0.068	0.650	0.103	0.615	0.243	0.792
0.135	0.935	0.306	1.111	0.542	1.168
0.386	1.459	0.692	1.500	0.713	1.284
0.622	1.699	0.934	1.638	1.012	1.440
0.865	1.856	1.342	1.818	1.760	1.711
1.317	2.039	2.506	2.106	2.612	1.901
2.190	2.299	3.698	2.260	3.944	2.086
3.234	2.440	4.243	2.308	4.452	2.137
4.294	2.543	5.433	2.421	5.680	2.261
5.469	2.651	-	-	-	-

Table A.17 – Experimental adsorption equilibrium data of CO₂ on Cu-AC-3.5 at 30 °C, 40 °C, and 50 °C.

CO ₂ (Cu-AC-3.5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g^{-1}	Pressure bar	q_{CO} mmol g^{-1}	Pressure bar	q_{CO} mmol g^{-1}
0.000	0.000	0.000	0.000	0.000	0.000
0.030	0.046	0.113	0.144	0.148	0.120
0.070	0.113	0.216	0.248	0.373	0.316
0.203	0.301	0.363	0.390	0.533	0.433
0.375	0.505	0.528	0.537	0.827	0.607
0.598	0.729	0.865	0.777	0.984	0.689
1.010	1.070	1.233	0.997	1.405	0.897
1.480	1.389	2.027	1.399	2.343	1.281
2.153	1.757	3.014	1.795	2.993	1.504
3.127	2.171	4.026	2.122	3.849	1.739
4.137	2.504	5.281	2.424	4.643	1.938
5.297	2.829	-	-	5.743	2.212

Table A.18 – Experimental adsorption equilibrium data of CH₄ on Cu-AC-3.5 at 30 °C, 40 °C, and 50 °C.

CH ₄ (Cu-AC-3.5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.037	0.018	0.023	0.010	0.100	0.036
0.088	0.044	0.056	0.023	0.194	0.066
0.211	0.103	0.074	0.031	0.400	0.129
0.445	0.205	0.148	0.061	0.568	0.181
0.670	0.293	0.249	0.100	0.658	0.203
0.924	0.384	0.503	0.189	0.867	0.256
1.410	0.538	0.760	0.272	1.016	0.293
2.244	0.759	1.012	0.346	1.491	0.402
3.275	0.985	2.015	0.596	1.989	0.504
4.370	1.182	3.009	0.786	3.019	0.677
5.189	1.310	4.495	1.023	4.049	0.828
-	-	5.632	1.200	5.243	0.993

Table A.19 – Experimental adsorption equilibrium data of N₂ on Cu-AC-3.5 at 30 °C, 40 °C, and 50 °C.

N ₂ (Cu-AC-3.5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.044	0.005	0.094	0.011	0.020	0.002
0.092	0.012	0.179	0.019	0.044	0.004
0.219	0.030	0.605	0.065	0.068	0.006
0.448	0.060	1.057	0.111	0.130	0.012
0.710	0.093	1.772	0.177	0.225	0.020
0.923	0.118	2.478	0.237	0.458	0.040
1.412	0.174	2.875	0.272	0.678	0.060
2.310	0.268	3.460	0.319	0.934	0.081
3.301	0.362	4.127	0.366	1.775	0.146
4.313	0.447	4.701	0.404	2.799	0.221
5.371	0.527	5.693	0.471	4.160	0.312
-	-	-	-	5.660	0.402

Table A.20 – Experimental adsorption equilibrium data of H₂ on Cu-AC-3.5 at 30 °C, 40 °C, and 50 °C.

H ₂ (Cu-AC-3.5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.134	0.004	0.088	0.001	0.097	0.002
0.485	0.010	0.641	0.011	0.317	0.005
1.017	0.019	1.358	0.022	0.697	0.011
2.156	0.038	2.317	0.038	1.400	0.021
3.177	0.054	4.552	0.071	2.365	0.035
4.071	0.067	5.802	0.086	3.317	0.048
5.293	0.087	-	-	4.737	0.068
-	-	-	-	5.796	0.081

A.1.5. Cu-AC-5

Table A.21 – Experimental adsorption equilibrium data of CO on Cu-AC-5 at 30 °C, 40 °C, and 50 °C.

CO (Cu-AC-5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.008	0.217	0.048	0.466	0.011	0.096
0.037	0.542	0.116	0.793	0.069	0.421
0.118	1.008	0.196	1.048	0.220	0.868
0.235	1.401	0.386	1.446	0.372	1.137
0.479	1.858	0.530	1.623	0.645	1.424
0.901	2.281	0.714	1.795	0.792	1.532
1.434	2.516	1.028	2.025	1.175	1.771
1.984	2.657	1.760	2.342	1.920	2.074
2.774	2.780	2.918	2.594	3.054	2.342
3.806	2.885	4.042	2.746	3.907	2.447
5.175	2.975	5.231	2.852	4.991	2.587
-	-	-	-	5.518	2.630

Table A.22 – Experimental adsorption equilibrium data of CO₂ on Cu-AC-5 at 30 °C, 40 °C, and 50 °C.

CO ₂ (Cu-AC-5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.056	0.072	0.048	0.047	0.111	0.080
0.112	0.133	0.176	0.154	0.309	0.194
0.196	0.215	0.386	0.300	0.506	0.296
0.391	0.379	0.714	0.496	0.802	0.435
0.580	0.518	1.123	0.689	1.253	0.606
0.799	0.660	1.783	0.948	2.009	0.848
1.075	0.819	2.160	1.078	3.033	1.121
1.432	0.999	3.177	1.375	4.002	1.336
1.967	1.227	4.422	1.664	5.188	1.558
2.750	1.500	5.231	1.817	5.671	1.637
3.766	1.782	-	-	-	-
4.923	2.032	-	-	-	-
5.567	2.151	-	-	-	-

Table A.23 – Experimental adsorption equilibrium data of CH₄ on Cu-AC-5 at 30 °C, 40 °C, and 50 °C.

CH ₄ (Cu-AC-5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.042	0.013	0.054	0.018	0.113	0.029
0.096	0.035	0.136	0.041	0.216	0.054
0.219	0.077	0.250	0.074	0.363	0.086
0.343	0.120	0.390	0.112	0.528	0.123
0.560	0.181	0.635	0.169	0.865	0.184
0.917	0.272	0.950	0.233	1.233	0.243
1.483	0.391	1.536	0.338	2.027	0.354
1.904	0.469	2.375	0.463	3.014	0.468
2.807	0.610	3.338	0.583	4.026	0.568
4.827	0.852	4.535	0.709	5.281	0.675
5.388	0.915	5.674	0.813	-	-

Table A.24 – Experimental adsorption equilibrium data of N₂ on Cu-AC-5 at 30 °C, 40 °C, and 50 °C.

N ₂ (Cu-AC-5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.048	0.005	0.113	0.008	0.054	0.003
0.105	0.010	0.216	0.016	0.136	0.008
0.194	0.018	0.363	0.026	0.250	0.015
0.403	0.035	0.528	0.039	0.390	0.025
0.658	0.057	0.865	0.062	0.635	0.038
0.845	0.073	1.233	0.086	0.950	0.056
1.339	0.109	2.027	0.137	1.536	0.089
1.949	0.156	3.014	0.196	2.375	0.135
2.941	0.227	4.026	0.252	3.338	0.183
3.957	0.291	4.981	0.303	4.535	0.240
4.965	0.349	5.691	0.339	5.325	0.275
5.568	0.380	-	-	-	-

Table A.25 – Experimental adsorption equilibrium data of H₂ on Cu-AC-5 at 30 °C, 40 °C, and 50 °C.

H ₂ (Cu-AC-5)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.113	0.002	0.504	0.007	0.319	0.004
0.481	0.007	1.012	0.014	1.043	0.013
1.053	0.015	2.275	0.031	2.044	0.026
2.313	0.034	3.002	0.042	3.158	0.041
3.496	0.055	4.125	0.057	4.310	0.055
5.089	0.076	5.491	0.075	5.437	0.069

A.1.6. Cu-AC-6

Table A.26 – Experimental adsorption equilibrium data of CO on Cu-AC-6 at 30 °C, 40 °C, and 50 °C.

CO (Cu-AC-6)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.008	0.190	0.071	0.642	0.045	0.344
0.016	0.352	0.120	0.844	0.070	0.457
0.041	0.611	0.149	0.951	0.127	0.676
0.090	0.930	0.277	1.291	0.223	0.930
0.196	1.359	0.491	1.610	0.617	1.439
0.403	1.847	0.803	1.905	1.058	1.743
0.811	2.285	1.100	2.105	1.706	2.040
1.590	2.612	2.060	2.481	2.474	2.269
2.679	2.857	3.279	2.717	3.373	2.449
3.741	2.960	4.477	2.847	4.371	2.589
5.131	3.049	5.809	2.938	5.525	2.723

Table A.27 – Experimental adsorption equilibrium data of CO₂ on Cu-AC-6 at 30 °C, 40 °C, and 50 °C.

CO ₂ (Cu-AC-6)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.057	0.060	0.011	0.009	0.051	0.031
0.092	0.093	0.048	0.037	0.139	0.079
0.162	0.154	0.092	0.071	0.234	0.127
0.247	0.222	0.176	0.129	0.396	0.204
0.413	0.336	0.325	0.218	0.632	0.298
0.638	0.472	0.577	0.345	0.979	0.418
0.910	0.613	1.054	0.549	1.641	0.618
1.332	0.801	1.823	0.811	2.535	0.839
1.803	0.980	2.823	1.079	3.536	1.043
2.490	1.195	4.055	1.336	4.683	1.238
3.249	1.392	5.455	1.565	5.653	1.377
4.784	1.693	-	-	-	-
5.500	1.810	-	-	-	-

Table A.28 – Experimental adsorption equilibrium data of CH₄ on Cu-AC-6 at 30 °C, 40 °C, and 50 °C.

CH ₄ (Cu-AC-6)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.038	0.012	0.075	0.019	0.090	0.019
0.086	0.026	0.183	0.042	0.204	0.039
0.176	0.051	0.287	0.066	0.309	0.060
0.491	0.130	0.488	0.109	0.512	0.096
0.720	0.182	0.796	0.167	0.804	0.142
0.935	0.227	1.190	0.232	1.207	0.200
1.379	0.311	1.100	0.218	2.031	0.304
1.870	0.394	2.060	0.360	3.007	0.409
2.526	0.492	3.281	0.508	4.016	0.503
3.312	0.595	4.817	0.657	5.177	0.597
4.251	0.701	5.866	0.743	-	-
5.215	0.798	-	-	-	-

Table A.29 – Experimental adsorption equilibrium data of N₂ on Cu-AC-6 at 30 °C, 40 °C, and 50 °C.

N ₂ (Cu-AC-6)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.042	0.003	0.032	0.002	0.049	0.003
0.113	0.009	0.134	0.008	0.181	0.009
0.269	0.020	0.254	0.016	0.319	0.017
0.540	0.040	0.472	0.030	0.545	0.029
0.759	0.055	0.829	0.051	0.878	0.044
1.040	0.074	1.360	0.080	1.331	0.066
1.505	0.105	2.173	0.122	1.985	0.095
2.319	0.155	3.124	0.168	2.755	0.128
3.442	0.216	3.970	0.205	3.491	0.157
4.769	0.274	4.668	0.233	4.172	0.183
5.245	0.289	5.401	0.261	4.772	0.204
-	-	-	-	5.589	0.232

Table A.30 – Experimental adsorption equilibrium data of H₂ on Cu-AC-6 at 30 °C, 40 °C, and 50 °C.

H ₂ (Cu-AC-6)					
30 °C		40 °C		50 °C	
Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹	Pressure bar	q_{CO} mmol g ⁻¹
0.000	0.000	0.000	0.000	0.000	0.000
0.040	0.001	0.356	0.005	0.556	0.007
0.444	0.004	0.942	0.013	1.130	0.014
0.915	0.012	2.275	0.031	2.544	0.031
1.916	0.029	3.748	0.052	4.043	0.051
3.434	0.050	5.218	0.071	5.513	0.069
5.005	0.075	-	-	-	-
5.535	0.081	-	-	-	-

A.2. Dual-site Langmuir isotherm parameters

Table A.31 - Dual-site Langmuir equation parameters of CO, CO₂, CH₄, N₂ and H₂ adsorption isotherms on AC Kuraray 2GA-H2.

Parameter	Pristine AC (Kuraray 2GA-H2)				
	CO	CO ₂	CH ₄	N ₂	H ₂
$q_{\text{max},1} / \text{mol kg}^{-1}$	3.91	8.42	1.33	0.976	7.48×10^{-3}
$b_{\infty,1} / \text{bar}^{-1}$	3.61×10^{-5}	1.68×10^{-5}	9.84×10^{-4}	6.28×10^{-5}	1.18×10^{-4}
$\Delta H_1 / \text{kJ mol}^{-1}$	20.7	23.9	17.1	20.5	10.3
$q_{\text{max},2} / \text{mol kg}^{-1}$	0.249	1.04	6.36	4.67	2.95
$b_{\infty,2} / \text{bar}^{-1}$	2.63×10^{-5}	5.21×10^{-5}	2.35×10^{-4}	2.96×10^{-5}	5.71×10^{-5}
$\Delta H_2 / \text{kJ mol}^{-1}$	19.6	28.2	14.4	17.9	13.5

Table A.32 - Dual-site Langmuir equation parameters of CO, CO₂, CH₄ N₂ and H₂ adsorption isotherms on Cu-AC-0.5.

Cu-AC-0.5					
Parameter	CO	CO ₂	CH ₄	N ₂	H ₂
$q_{\max,1} / \text{mol kg}^{-1}$	0.288	7.95	5.44	0.414	0.0164
$b_{\infty,1} / \text{bar}^{-1}$	5.78×10^{-8}	1.74×10^{-5}	7.07×10^{-5}	9.22×10^{-5}	2.64×10^{-4}
$\Delta H_1 / \text{kJ mol}^{-1}$	49.2	23.8	18.2	18.3	11.0
$q_{\max,2} / \text{mol kg}^{-1}$	3.70	0.870	0.794	2.82	3.47
$b_{\infty,2} / \text{bar}^{-1}$	1.24×10^{-4}	5.21×10^{-5}	4.66×10^{-4}	3.68×10^{-5}	1.12×10^{-4}
$\Delta H_2 / \text{kJ mol}^{-1}$	17.4	27.8	18.9	19.6	11.1

Table A.33 - Dual-site Langmuir equation parameters of CO, CO₂, CH₄ N₂ and H₂ adsorption isotherms on Cu-AC-2.

Cu-AC-2					
Parameter	CO	CO ₂	CH ₄	N ₂	H ₂
$q_{\max,1} / \text{mol kg}^{-1}$	1.25	5.79	3.47	2.14	0.029
$b_{\infty,1} / \text{bar}^{-1}$	9.29×10^{-8}	1.44×10^{-5}	3.79×10^{-5}	2.19×10^{-4}	4.85×10^{-4}
$\Delta H_1 / \text{kJ mol}^{-1}$	43.0	23.9	20.4	15.1	7.76
$q_{\max,2} / \text{mol kg}^{-1}$	0.977	0.705	0.259	0.833	5.53
$b_{\infty,2} / \text{bar}^{-1}$	5.06×10^{-5}	5.06×10^{-5}	7.34×10^{-5}	1.39×10^{-6}	2.28×10^{-4}
$\Delta H_2 / \text{kJ mol}^{-1}$	26.6	26.6	24.0	17.9	6.77

Table A.34 - Dual-site Langmuir equation parameters of CO, CO₂, CH₄ N₂ and H₂ adsorption isotherms on Cu-AC-3.5.

Cu-AC-3.5					
Parameter	CO	CO ₂	CH ₄	N ₂	H ₂
$q_{\max,1} / \text{mol kg}^{-1}$	1.55	4.89	3.20	2.98	0.0610
$b_{\infty,1} / \text{bar}^{-1}$	3.72×10^{-8}	1.51×10^{-5}	2.60×10^{-5}	3.55×10^{-5}	4.59×10^{-4}
$\Delta H_1 / \text{kJ mol}^{-1}$	43.4	23.6	20.1	4.86	8.36
$q_{\max,2} / \text{mol kg}^{-1}$	1.21	0.523	0.547	1.95	0.681
$b_{\infty,2} / \text{bar}^{-1}$	1.92×10^{-5}	2.50×10^{-4}	3.24×10^{-3}	8.89×10^{-5}	1.66×10^{-3}
$\Delta H_2 / \text{kJ mol}^{-1}$	33.4	22.2	12.7	16.8	7.05

Table A.35 - Dual-site Langmuir equation parameters of CO, CO₂, CH₄ N₂ and H₂ adsorption isotherms on Cu-AC-5.

Cu-AC-5					
Parameter	CO	CO ₂	CH ₄	N ₂	H ₂
$q_{\max,1} / \text{mol kg}^{-1}$	2.19	3.70	2.41	3.02	5.87
$b_{\infty,1} / \text{bar}^{-1}$	1.26×10^{-8}	1.87×10^{-5}	1.79×10^{-5}	3.60×10^{-5}	7.23×10^{-5}
$\Delta H_1 / \text{kJ mol}^{-1}$	47.4	23.3	20.6	4.95	7.57
$q_{\max,2} / \text{mol kg}^{-1}$	0.981	0.249	0.374	1.67	3.78
$b_{\infty,2} / \text{bar}^{-1}$	3.78×10^{-5}	5.32×10^{-5}	2.62×10^{-3}	1.40×10^{-4}	3.63×10^{-4}
$\Delta H_2 / \text{kJ mol}^{-1}$	32.8	27.1	13.8	14.9	3.86

Table A.36 - Dual-site Langmuir equation parameters of CO, CO₂, CH₄ N₂ and H₂ adsorption isotherms on Cu-AC-6.

Cu-AC-6					
Parameter	CO	CO ₂	CH ₄	N ₂	H ₂
$q_{\max,1} / \text{mol kg}^{-1}$	2.22	3.11	2.26	2.97	4.29
$b_{\infty,1} / \text{bar}^{-1}$	1.08×10^{-8}	1.91×10^{-5}	2.20×10^{-5}	3.53×10^{-5}	5.11×10^{-5}
$\Delta H_1 / \text{kJ mol}^{-1}$	47.4	23.2	19.8	4.80	7.90
$q_{\max,2} / \text{mol kg}^{-1}$	1.10	0.218	0.401	1.06	2.46
$b_{\infty,2} / \text{bar}^{-1}$	3.78×10^{-5}	5.32×10^{-5}	2.90×10^{-3}	1.36×10^{-4}	3.57×10^{-4}
$\Delta H_2 / \text{kJ mol}^{-1}$	32.8	27.0	12.4	15.8	6.12

B. Experimental setups

B.1.1. Adsorption measuring setup – Volumetric method

The setup used to determine the experimental adsorption equilibrium isotherms is shown in Figure B.4. The setup comprises two tanks (A and B) with accurately known volumes connected through a manual on-off valve. The sample is placed in Tank B, while tank A is fed with the measuring gas. A pressure sensor is placed in tank A for pressure monitoring, and a thermocouple is placed in tank B, for temperature monitoring. The tanks are placed in a thermostatic bath to ensure isothermal operation. The vacuum pump is used to evacuate the samples.

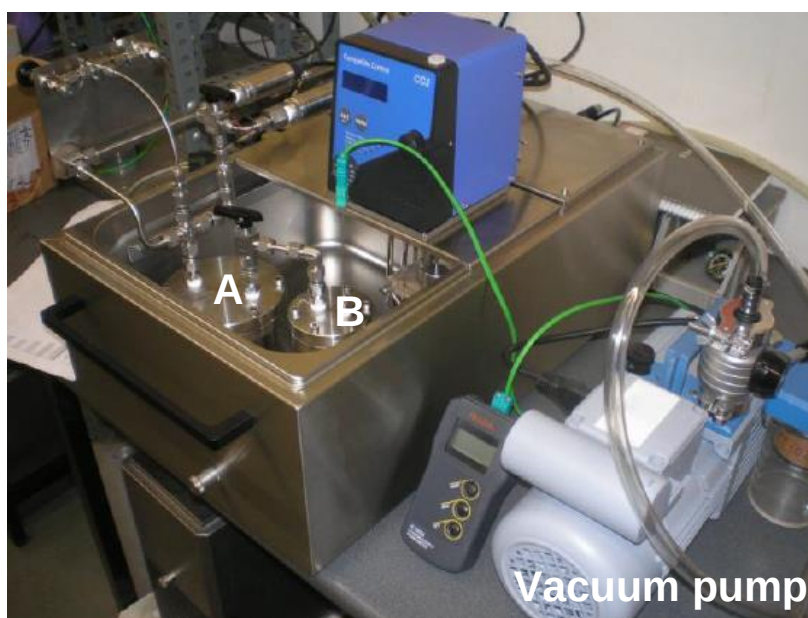


Figure B.1 – Picture of the volumetric method setup.

B.1.2. Breakthrough setup

The breakthrough experiments presented in Chapter 4 were carried out in the setup shown in Figure B.2.

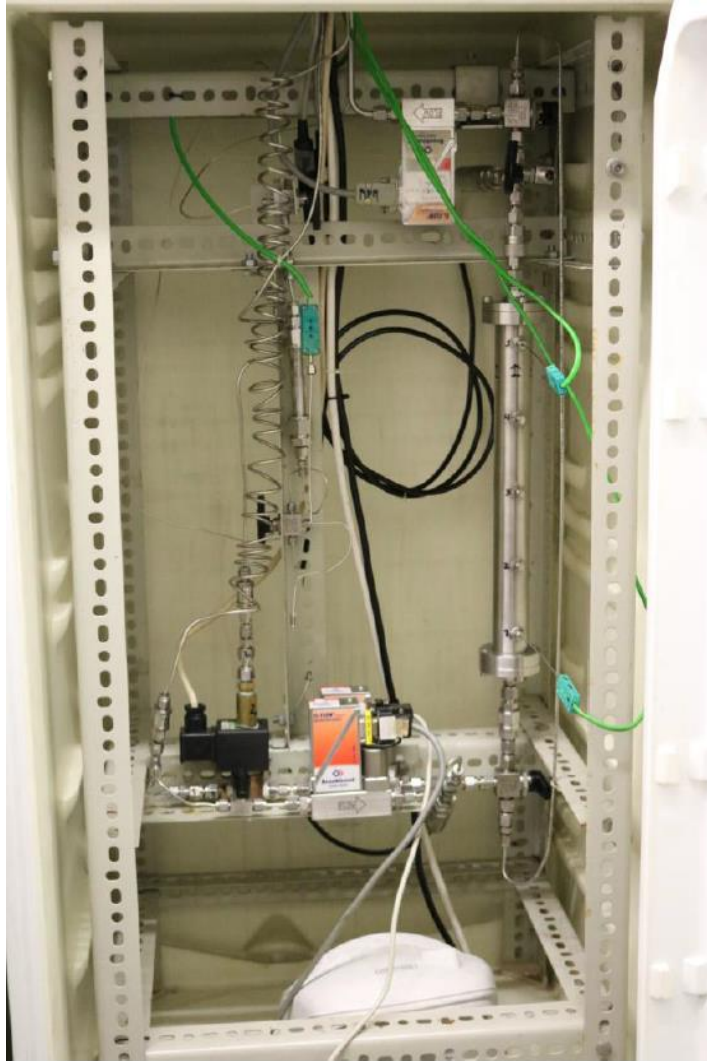


Figure B.2 – Picture of the breakthrough experimental setup.

B.1.3. Lab-scale PSA

The in-house built lab-scale PSA unit used in the hydrogen purification experiments is shown in Figure B.3.



Figure B.3 – Picture of the 4-column lab PSA.

The unit comprises four columns loaded with an adsorbent and a fifth column used to store part of the product. The feed flow rate is controlled using a series of mass flow controllers, while the purge and backfill flow rates are regulated using a needle valve. The purge and product flow rates are measured using inline mass flowmeters. The product can be either controlled using a pressure controller or a mass flow controller. Four pressure

transducers, placed at the bottom of each column, are used to obtain the pressure history inside adsorption beds during operation. A set of solenoid and check valves are used to direct the flow according to the adsorption cycle.

B.1.4. PSA prototype

The PSA prototype comprises 4-columns packed with a commercial activated carbon from UOP. The unit is designed as a “plug & play” device for producing fuel cell quality hydrogen out of syngas, with a capacity of $3 \text{ m}^3 \cdot \text{h}^{-1}$. The PSA prototype is part of a reformed ethanol fuel cell system, where syngas is produced from ethanol reforming, followed by water gas shift. The PSA is used afterward to obtain fuel cell quality hydrogen.

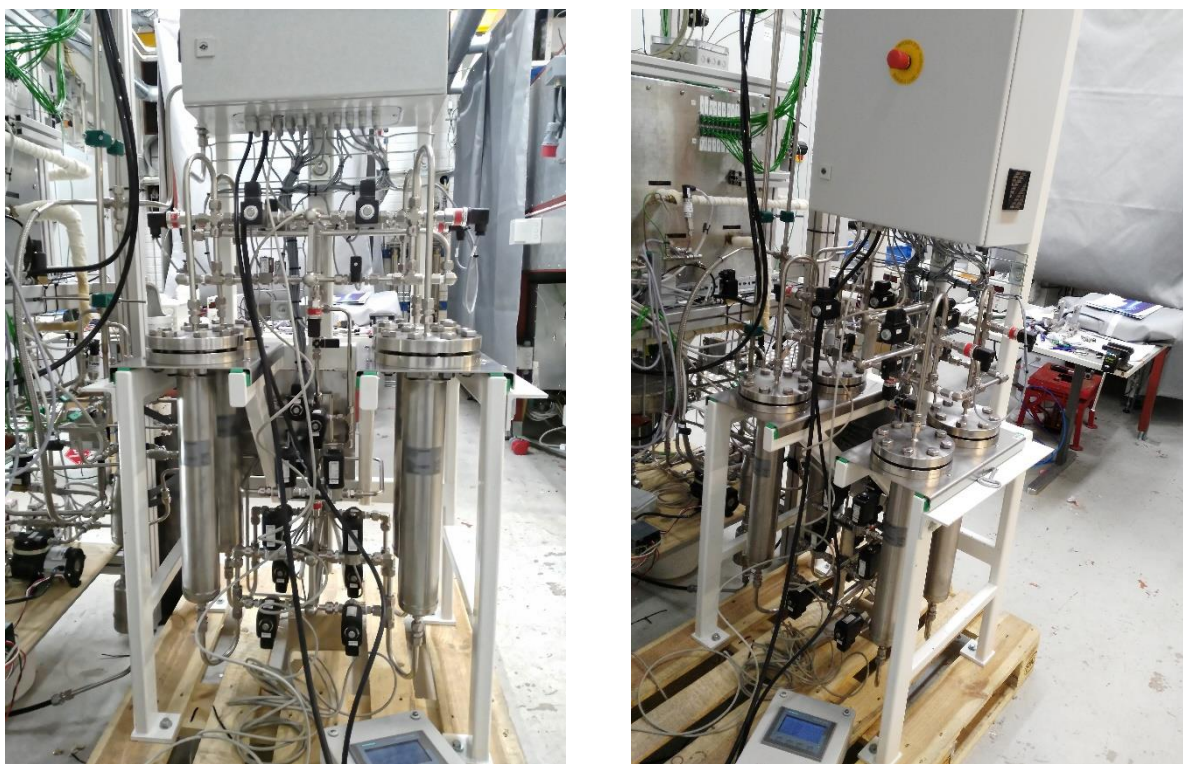


Figure B.4 – Pictures of the PSA prototype.



Figure B.5 – Picture of the reformed ethanol system container - outside

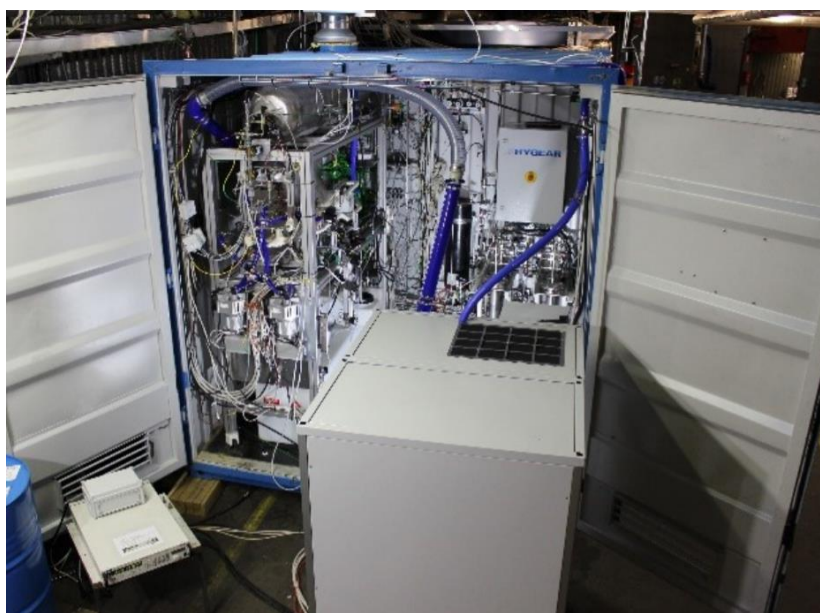


Figure B.6 – Picture of the reformed ethanol system container - inside.