Edinburgh Research Explorer

Review of Polybed pressure swing adsorption for hydrogen purification

Review of Polybed pressure swing adsorption for hydrogen purification

Mauro Luberti*, Hyungwoong Ahn

Institute for Materials and Processes, School of Engineering, The University of Edinburgh, Robert Stevenson Road, Edinburgh EH9 3FB, United Kingdom
*corresponding author: m.luberti@ed.ac.uk

Abstract

Hydrogen (H_2) will play a key role in the future low-carbon energy society. The industrial production of hydrogen involves chemical reactions and purification steps. Pressure Swing Adsorption (PSA) is a versatile process able to produce ultrapure hydrogen (99.99+%) from various gas mixtures, resulting in the most widespread purification technology worldwide. In particular, the Polybed PSA system, having more than six beds and a complex cycle configuration, has proven to maximize H_2 recovery and H_2 throughput, exceeding 90% and 240 MMSCFD (265,000 Nm^3 h^{-1}) per single train, respectively.

This paper systematically reviews the Polybed H_2 PSA process for the first time, highlighting the latest technical advances and discussing its optimal integration in industrial clusters. A bespoke Polybed PSA process designed for simultaneous production of high-purity hydrogen and carbon dioxide (CO_2) is also reviewed in light of the recent international directives aimed to reduce CO_2 emissions and produce blue hydrogen.

Keywords: *Hydrogen purification, Polybed pressure swing adsorption, Cycle scheduling, Layered bed, Carbon dioxide capture, Blue hydrogen*

1. Background

In recent years, climate change has become the most pressing issue that the world is facing. Since the early 19th century, the demand for fossil fuels, namely coal, oil and natural gas, has continued to grow rapidly, prompting a major increase in greenhouse gas (GHG) emissions. These atmospheric gaseous constituents of both natural and anthropogenic origins absorb outgoing infrared radiation from the Earth's surface, thus triggering the greenhouse gas effect (IPCC, 2020). In particular, the exponential increase in energy demand from 1780 to 2019 has contributed to a 48% growth in the atmospheric CO_2 concentration from 280 to 415 ppm in the northern hemisphere (NASA, 2019). Global carbon emissions as CO_2 are now expected to exceed 50 Gt by 2050 (Pacala and Socolow, 2004), provoking potentially detrimental effects on the planet's ecosystems and biodiversity, as well as the livelihoods of its nearly eight billion human inhabitants (Mora et al., 2013). As the largest source of GHG global emissions is the energy sector along with industry, transport and buildings, the International Energy Agency (IEA) identified advanced batteries, hydrogen electrolysers, and direct air capture and storage as the biggest innovation opportunities towards the net zero pathway by 2050 (IEA, 2021).

In particularly, hydrogen has been considered as a potential alternative to fossil fuels since the late 1980s with it being predicted to become commercially mature in the energy sector by 2030 (Bockris, 2013). However, it was not until recently that the potential of hydrogen as a fuel to replace fossil fuels and as a versatile energy carrier to store surplus renewable electricity was recognised internationally (Blanco et al., 2018; Acar and Dincer, 2020; Maestre et al., 2021). A future sustainable energy system built on hydrogen and renewable electricity has been identified as a viable long-term solution known as the *hydrogen economy* (Ball and Weeda, 2015; Dou et al., 2017; Abe et al., 2019). Its implementation will need a well-planned strategy, encompassing hydrogen production, distribution, utilization as well as increasing competitiveness with other energy carriers (Moliner et al., 2016; Dou et al., 2017; Oliveira et al., 2021). Particularly, the high cost of producing hydrogen from low-carbon energy and the slow development of hydrogen infrastructures are the major challenges that need to be solved urgently (IEA, 2019).

Despite being the most abundant element in the universe, hydrogen gas must be manufactured from feedstock containing hydrogen atoms, such as hydrocarbons, biomass and water. In the *Future of Hydrogen* report, the IEA identified around 72 million tonnes (Mt) of annual demand for ultrapure H_2 worldwide (IEA, 2019). The vast majority of hydrogen is produced from fossil fuels, and around 60% of it is produced in *dedicated* hydrogen production facilities, while one-third of global supply is *by-product* hydrogen, meaning that it comes from facilities and processes designed primarily to produce something else. In particular, most hydrogen is produced from natural gas (76%) via steam methane reforming, partial oxidation and autothermal reforming with the rest originating mainly from coal via gasification (22%). Electrolysis currently accounts for about 2% of the global hydrogen production, but its share is expected to grow significantly to respond to the demand for low-carbon emission hydrogen (IEA, 2019; Grimm et al., 2020; Anwar et al., 2021). Overall, less than 0.7% of the current hydrogen production is from renewable energy or from fossil fuel plants equipped with carbon capture and storage (CCS) technologies. In total, hydrogen production currently involves the emission of 830 Mt_{CO2} y^{-1} (IEA, 2019). Figure 1 shows the current worldwide hydrogen value chains in terms of supplies and demands.

From Figure 1 it is clear that the hydrogen use is dominated by industrial applications, including oil refining (33%), ammonia production (27%), methanol production (11%) and steel production via the direct reduction of iron ore (3%) (IEA, 2019). In refining complexes hydrogen is needed for operating their hydrotreating units that remove mainly sulphur and other impurities from raw petroleum products and hydrocracking units for upgrading low-grade heavy residues to more valuable diesel and lube base oils. There has been a continuous increase in the refining hydrogen demand over the last several decades due to more stringent environmental regulations on oil products' sulphur contents and the rapid change of crude oil properties from *light and sweet* to *heavy and sour* (Meyers, 2004; Umana et al., 2016). Due to the requirements of very high operational severity in both hydrotreating and hydrocracking units, ultrapure hydrogen should be utilised for the hydroprocessing. Accordingly, most refineries are forced to rapidly increase their hydrogen production capacities and are also considering to retrofit CCS technologies into their H_2 plants to reduce CO_2 emissions. The demands for ammonia and methanol are also expected to increase over the short to medium term, which will in turn require the hydrogen production capacity

to be augmented (IEA, 2019). Although less than 0.01 Mt y^{-1} of ultrapure hydrogen is currently used in fuel cell vehicles (FCEVs) (Figure 1), the transport sector is one of the areas where hydrogen will prove itself essential to reduce carbon emissions, especially for large commercial vehicles such as buses, trains, ships and planes (Gurz et al., 2017; Wilberforce et al., 2017; Hardman and Tal, 2018). Another sector where hydrogen is predicted to play an important role in the future low-carbon society is heating and power generation (Cappelletti and Martelli, 2017; Koç et al., 2020). The combustion of hydrogen is, in fact, very favourable compared to the combustion of fossil fuels, as it produces nearly three times as much energy in terms of lower heating value (LHV) with no CO_2 emissions. As hydrogen can be stored relatively easily as a compressed gas, a refrigerated liquefied gas, a cryo-compressed gas or in metal hydrides, it also offers a benefit over intermittent electricity produced by renewable energy (Gonzales et al., 2015; Barthelemy et al., 2017; Dawood et al., 2020).
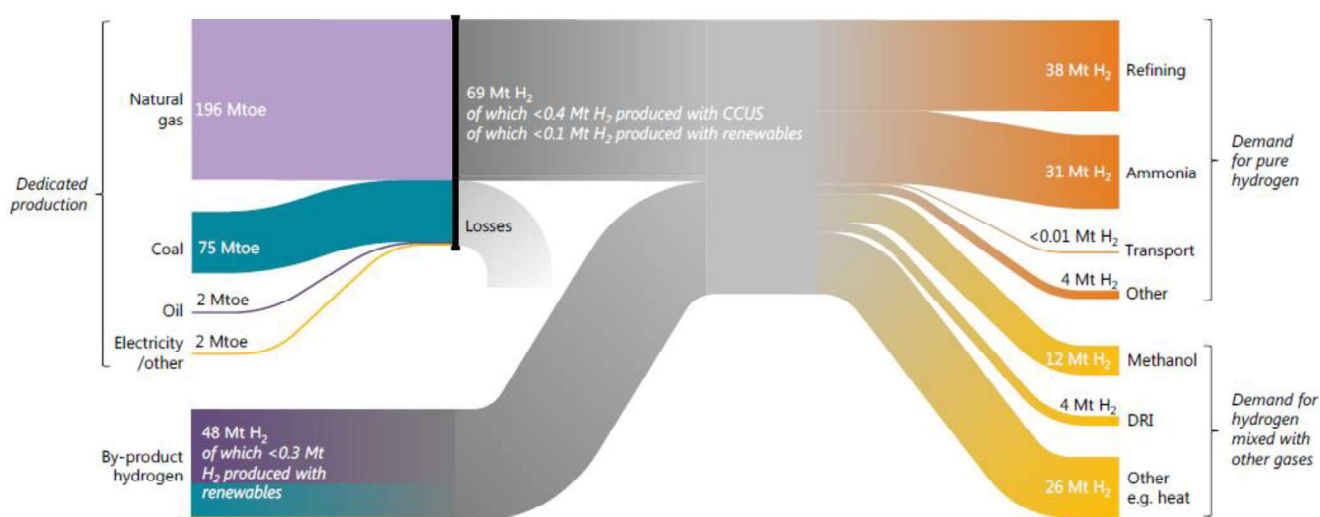
Figure 1: Sankey diagrams showing the worldwide hydrogen value chains (IEA, 2019)

Apart from the demands for hydrogen that does not have to be pure, such as methanol synthesis and other applications (heating, power generation, etc.), around 72 Mt y^{-1} of hydrogen need to be ultra-purified for its use in refineries, ammonia synthesis and fuel cells. Regardless of the fossil fuel feedstock and the technology employed to produce hydrogen, pressure swing adsorption imposed itself as the most techno-economically feasible technology for producing ultrapure hydrogen (99.99+%) due to the high adsorbent selectivity towards common impurities (Yang, 1987; Ruthven et al., 1994; Meyers, 2004; Voss, 2005). As a result, PSA units are most commonly designed in large-scale H_2 plants for hydrogen purification, as evidenced by their dominant share in the market with respect to cumulative capacity and number of units installed worldwide (Yang, 1987; UOP, 2015; Air Products, 2018a). Chemical absorption-based processes are also suitable for hydrogen purification at large-scale H_2 plants but they suffer from low H_2 purities ranging 95–97% and high steam consumption for solvent regeneration (UOP, 2016; Aasadnia et al., 2021). Likewise, cryogenic distillation is a highly energy intensive technology since it

requires extremely low operating temperatures, thus incurring significant OPEX for gas compression. Furthermore, the H_2 product is extracted with purity levels between 90 and 99%, which do not satisfy the application requirements (Air Products, 2018a; Aasadnia et al., 2021; Du et al., 2021). For medium-scale H_2 plants, polymeric membranes are a profitable technology for hydrogen upgrading since they are normally designed to produce hydrogen with 90–98% purity and 85–95% recovery (UOP, 2011; Air Products, 2018a; Air Liquide, 2021). In addition, the integration of polymeric membranes with PSA units is currently an option offered by some industrial H_2 plants licensors in order to increase the stand-alone PSA performance (Air Products, 2015; Linde, 2021). In fact, it has been reported that such hybrid systems could increase the overall H_2 recovery by 2–6% compared to the stand-alone PSA process (Sircar et al., 1999; Nikolic and Kikkinides, 2015; Li et al., 2016). At the same time, the hybrid systems likely exhibit higher CAPEX for installing membrane modules and higher OPEX for operating extra gas compressors. More recently, palladium alloy membranes have been proposed to obtain hydrogen with purities in excess of 99.9999%, which are particularly suitable for fuel cell applications (Al-Mufachi et al., 2015; Li et al., 2015; Du et al., 2021). However, their commercial spreading is highly limited by the high cost of the precious metal and, therefore, suitable only for small-scale and compact H_2 plants. Comprehensive techno-economic assessments of hydrogen purification technologies are available in the literature (Air Products, 2018a; Aasadnia et al., 2021; Du et al., 2021).

In designing a H_2 PSA unit it is essential to maximize H_2 recovery and H_2 throughput in order to improve the overall process economics and to avoid multiple trains operating in parallel. The Polybed PSA process was developed for this purpose, having seven to sixteen beds and a cycle configuration incorporating at least three pressure equalisation steps and at least two adsorbing beds at the same time. This paper aims to systematically review the Polybed H_2 PSA process for the first time, highlighting the latest technical advances that contribute to the continuous improvement of PSA performance and discussing its optimal integration in the refining, chemical and petrochemical industries. This technology will continue to play a key role in the future hydrogen economy. As well as the articles and textbooks, the relevant patents are reviewed in depth, given their significant share of information and innovations on this subject. For completeness, 6-bed H_2 PSA systems having at least three pressure equalisation steps and one adsorbing bed or at least two pressure equalisation steps and two adsorbing beds are also investigated. Furthermore, a bespoke Polybed PSA process that is capable of producing high purity CO_2 and ultrapure H_2 from synthesis gas (syngas) at the same time is reviewed in light of the recent international directives aimed to reduce CO_2 emissions and to produce blue hydrogen. This study also represents the first comprehensive assessment for this kind of technology.

2. PSA for hydrogen purification

Since the invention of the Skarstrom cycle in 1960, PSA has rapidly evolved into one of the most efficient gas separation processes. PSA is applied actively to various industrial separations, such as air drying, hydrogen purification, separation of branched and linear paraffins, landfill gas separation, small-to medium-scale air fractionation and, more recently, carbon capture and biogas upgrade (Ruthven et al.,

1994; Luberti et al., 2015; Luberti et al., 2017; Oreggioni et al., 2017). The first commercial H_2 PSA unit was installed in 1966 in conjunction with a steam reformer plant in Toronto and was composed of four adsorbers and a tail gas drum (Yang, 1987; UOP, 2015). Large-scale multi-bed processes (Polybed) were developed in the late 1970s, the first being a 10-bed, 42 MMSCFD (47,000 $Nm^3 h^{-1}$) unit at the Wintershall Lingen refinery in Germany in 1977 (Ruthven et al., 1994; UOP, 2015). Nowadays there are over 1,000 Polybed H_2 PSA systems in operation worldwide with up to 16 beds. Currently, a Polybed H_2 PSA system is capable of processing over 40 different types of feedstock and producing up to 240 MMSCFD (265,000 $Nm^3 h^{-1}$) of ultrapure hydrogen per single train (UOP, 2016).

The development of PSA technology for hydrogen purification in the 1980s coincided with the quest for more environmentally friendly transportation fuels. As an increasing number of hydrotreating and hydrocracking units went on stream, more steam reforming plants were installed to produce *on-purpose* hydrogen. The major steam reforming licensors quickly realised that the standard H_2 plant flowsheet equipped with two stages of water gas shift reactors, a carbon dioxide wet scrubbing system and a methanator to convert the remaining traces of carbon oxides to methane could be outperformed by a single stage of shift reactor and a PSA unit. PSA systems produce a very high purity hydrogen at 99–99.999+% whilst saving significantly the operating costs compared to the scrubbing system (UOP, 2016). Moreover, PSA units are easier to operate since they have neither rotating equipment nor circulating solutions (Yang, 1987; Meyers, 2004). The PSA also improves the plant energy efficiency by utilizing the low-pressure PSA tail gas to fuel the burners of the steam reformer, thus providing 60 to 90% of the total heat input. Depending on the feed gas composition, the PSA tail gas has, in fact, a LHV in the range of 4,000–8,000 kJ Nm^{-3} (UOP, 2016). The operating costs of a H_2 PSA unit are almost negligible, as the feed is already pressurized and the maintenance cost is very low (Yang, 1987; Ruthven et al., 1994). Common adsorbents used in industrial H_2 PSA units do not suffer from deactivation phenomena that are typical of their counterparts used as catalysts in refining processes such as isomerization, cracking and hydrotreating since PSA cycles are operated mostly at ambient temperature. Coking and sintering phenomena, in fact, occur at temperatures above 400–500°C or above 100°C in presence of olefins (Guisnet et al., 1997; Forzatti and Lietti, 1999; Boucheffa et al., 2001). Adsorbent poisoning is also very rare since syngas streams do not contain volatile organic compounds (VOCs) or high molecular weight hydrocarbons while hydrogen sulphide (H_2S) concentration is in the range of 5–10 and 40–60 ppmv for natural gas- and coal-based feedstock, respectively (DOE, 2002; IEA, 2017). As a result, the adsorbents of industrial PSA units can last more than 10 years without replacement (Wiessner, 1988; Dobladez et al., 2021; Xebec, 2021) and up to 30 years for hydrogen purification applications (Grande, 2016; UOP, 2016; Air Products, 2018b).

The interest and innovations in PSA technology for hydrogen purification have been very extensive in the last 50 years. Figure 2 shows the number of patents on H_2 PSA filed in the world between 1966 and 2020. The figures were obtained using the keywords *hydrogen* and *pressure swing adsorption* in the Global Patent Index database (Global Patent Index, 2021). A total of 7,488 patents were granted to more than 2,000 corporations, with a major surge in the five-year period 2011–2016 (Figure 2). The key claims of the

patents concern the development of new multi-bed configurations and advanced cycle scheduling or the application of novel adsorbents capable to maximize H_2 recovery, H_2 throughput and unit productivity whilst maintaining the high H_2 purity. A considerable effort was also made to improve the unit equipment, operation, maintenance and control (UOP, 2015).
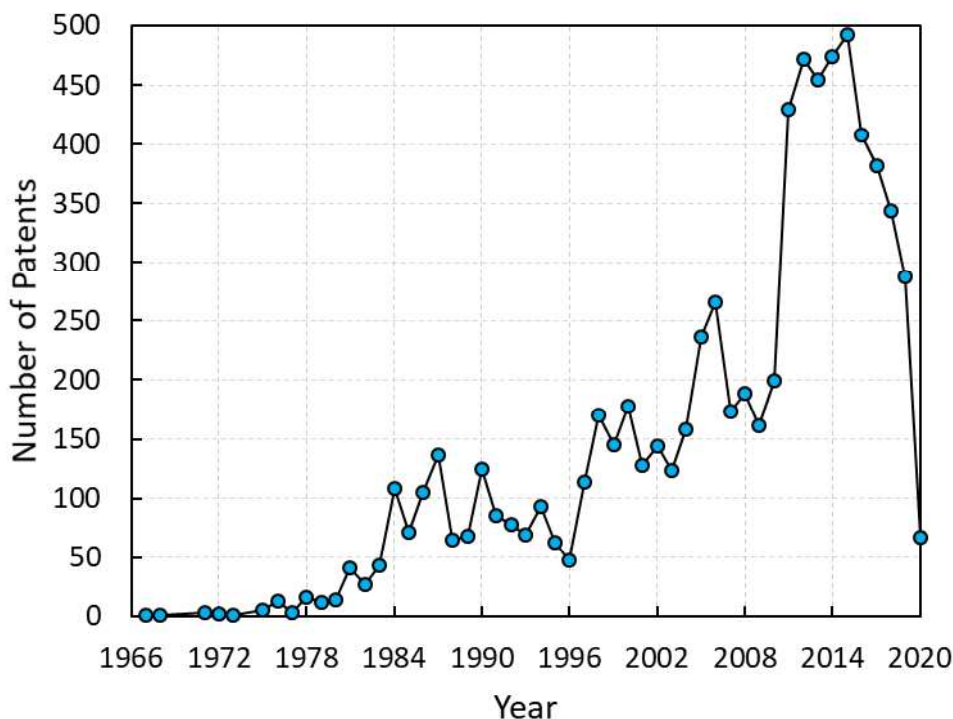
Figure 2: Survey of patents on H_2 PSA filed in the world between 1966 and 2020 (Global Patent Index, 2021)

2.1 Feed sources

Historically, steam reforming of light hydrocarbons, such as natural gas, LPG and light naphtha, has been the dominant technology for the production of syngas, and, hence, of hydrogen. Although the syngas has hydrogen as its major component, it also contains CO, CO_2, some unreacted CH_4, and other minor impurities such as N_2, O_2, Ar, H_2S, NH_3, etc., the presence of which depends on the feedstock and operating conditions (Grande, 2016). Since the 1980s Polybed PSA systems have been applied to the H_2-rich streams to purify hydrogen in order to meet the stringent purity requirements of the processes where hydrogen is used as feedstock. However, refiners soon realised that some refinery off-gases could also be fed to a H_2 PSA to produce a high purity hydrogen cost-effectively as long as they contained more than 50 mol% hydrogen. In this way, the route of producing hydrogen from the refinery off-gases became the second largest H_2 PSA usage (UOP, 2015). Globally, the purification of hydrogen from syngas and refinery off-gas account for about 65% of the installed H_2 PSA units. Next to these applications, the H_2 PSA is also actively used to purify a number of industrial H_2-rich effluents, such as ethylene off-gas, methanol off-gas, coke oven gas, ammonia off-gas, styrene off-gas, chlorine off-gas, steel industry gas and coal gasifier syngas

(UOP, 2015). Table 1 lists the major feed sources of a H_2 PSA along with their pressure, H_2 content, main and secondary impurities.

Table 1: Pressure and gas composition of various H_2 PSA feed sources (UOP, 2015; Grande, 2016; Sircar and Golden, 2000; Yang, 1987; Ruthven et al., 1994; Agahzamin et al., 2016; Ahn et al., 2001; DOE, 2010)

Feed source	Pressure (bar)	H_2 content (mol%)	Main impurity	Other impurities
Steam reformer syngas	20–30	70–80	CO_2	CH_4, CO, N_2
Refinery off-gas	8–22	65–85	CH_4	C_2H_6, C_3H_8, C_4H_{10}
Ethylene off-gas	25–35	70–90	CH_4	CO, C_2H_4, C_2H_6
Methanol off-gas	50–65	60–70	CO_2	CH_4, CO, N_2
Coke oven gas	5–15	55–60	CH_4	N_2, CO, CO_2
Coal gasifier syngas[a]	30–50	85–95	CO_2	CO, N_2, Ar

[a] Equipped with pre-combustion CO_2 capture

From Table 1 it is evident that the PSA process is extremely versatile and able to handle a wide variety of impurities including, but not limited to, light paraffins, light olefins, carbon oxides and atmospheric gases. The feed stream may also contain water vapour up to saturation. While for some applications it would be of interest to operate a PSA at higher temperatures, the feed temperature is in most cases close to ambient temperature, around 290–310 K (Grande, 2016). The adsorption pressure is fixed at either the available feed pressure or the required product pressure. Most of the feed streams are at 10–40 bar, but some outliers may have a pressure as low as 5 bar or as high as 65 bar (Table 1). The desorption pressure is usually fixed slightly above atmospheric pressure, in the range of 1–3 bar. The pressure drops along a H_2 PSA bed packed with adsorbent particles of 1–4 mm diameter can be up to 1 bar (Ruthven et al., 1994).

2.2 Adsorbents

The selection of the adsorbents is critical for achieving an excellent separation performance in the PSA process. A variety of commercial adsorbents for gas separation can be used for hydrogen purification due to their high selectivity for the gas impurities over hydrogen. Among them, silica gel, activated carbons and zeolites are often chosen in the common practice (Yang, 1987; Ruthven et al., 1994). The selective removal of these impurities is driven by the adsorbents having strong adsorption affinity for the impurities over the desired hydrogen, which makes H_2 PSA an equilibrium-driven process. Table 2 summarises the level of difficulty of impurity removal in H_2 PSA systems for silica gel, activated carbons and zeolites. Given the wide variety of feed compositions (Table 1) and the different level of difficulty of impurity removal per adsorbent (Table 2), the adsorption beds of H_2 PSA units are usually designed to have multiple adsorbent layers (Ruthven, 1984; Yang, 1987; Ruthven et al., 1994; Sircar and Golden, 2000). Multi-layered bed configurations exhibit better performances than single-layered bed configurations because it is unlikely to find an adsorbent that exhibits good working capacities and selectivities for all impurities in the raw H_2 feed. Multi-layered beds are also essential to remove the impurities to any desired low level, such as ppm or ppb (Meyers, 2004).

Table 2: Difficulty of impurity removal per adsorbent in H_2 PSA systems (Sircar and Golden, 2000; Meyers, 2004; Lopes et al., 2009; Liu et al., 2020)

	Silica gel	Activated carbons	Zeolites
H_2O	Very easy	Very difficult	Very easy
C_2H_4	Easy	Very easy	Very easy
C_4H_{10}	Easy	Very easy	Very easy
C_3H_8	Easy	Easy	Very easy
C_2H_6	Moderate	Easy	Very easy
CO_2	Moderate	Easy	Very easy
CH_4	Moderate	Easy	Moderate
CO	Moderate	Moderate	Easy
N_2	Difficult	Difficult	Moderate
Ar	Difficult	Difficult	Difficult
H_2	Very difficult	Very difficult	Very difficult

In case of H_2 PSA units designed to treat steam reformer syngases, each adsorption bed is usually configured as a layered bed with the bottom layer near the feed end packed with activated carbon and the top layer near the product end packed with 5A zeolite. The activated carbon layer acts as a guard bed, mainly adsorbing and desorbing CO_2 and CH_4, while the 5A zeolite layer removes mostly CO and N_2. Figures 3a and 3b show the adsorption isotherms of the main components of a steam reformer effluent at 303 K on activated carbon and 5A zeolite, respectively (Lopes et al., 2009). The zeolite layer is responsible for reducing the CO concentration to less than 10 ppm so that the purified hydrogen can be used in some types of fuel cells (IEA, 2019). The length ratio of the two layers in the bed is adjusted so as to ensure that CO_2 does not break through the activated carbon layer during the adsorption step. This is because CO_2 is adsorbed so strongly on zeolites that it cannot be desorbed easily by depressurisation, thus reducing the available adsorption capacity for the other gas impurities (Yang and Lee, 1998; Grande, 2016). The length ratio of the carbon to zeolite layers is therefore regarded as one of the key parameters that needs to be optimised for excellent performance (Park et al., 1998; Ahn et al., 2001; Ahn et al., 2012; Ribeiro, 2008).

Figures 4a and 4b show the adsorption isotherms of the main components of a refinery off-gas at 299 K on silica gel and activated carbon, respectively (Malek and Farooq, 1997; 1998; Lopes et al., 2009; Liu et al., 2020). Since activated carbon adsorbs C_3H_8 and C_4H_{10} very strongly, silica gel is used for the removal of these higher hydrocarbons, as they are relatively easy to desorb by depressurisation. On the other hand, activated carbon is preferred for the removal of CH_4 and C_2H_6 because it exhibits relatively large working capacities and high selectivities over H_2. Therefore, in case of H_2 PSA units designed to treat refinery off-gases, each adsorption bed is usually packed with silica gel near the feed end for removing C3+ hydrocarbons and activated carbon near the product end for capturing C1–C2 hydrocarbons. The effectiveness of this multi-layered PSA configuration has been addressed in the literature (Malek and Farooq, 1997; 1998). Since the raw H_2 feed streams are often saturated with water vapour, the use of a first bottom layer of alumina or silica gel in the PSA beds to retain the water has also been reported (Baksh

and Simo, 2013a; Baksh and Simo, 2013b; Grande, 2016). The initial steepness of the water isotherm is not excessive so that the adsorbed water vapour can be easily desorbed by depressurisation.
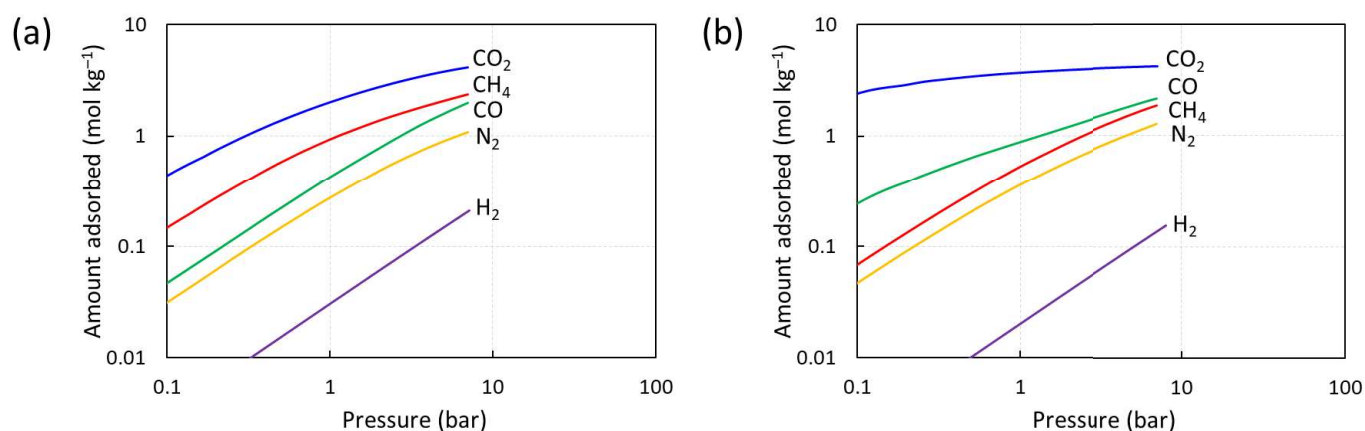

Figure 3: Adsorption isotherms of CO_2, CO, CH_4, N_2 and H_2 at 303 K on log-log scale on (a) activated carbon and (b) 5A zeolite (Lopes et al., 2009)
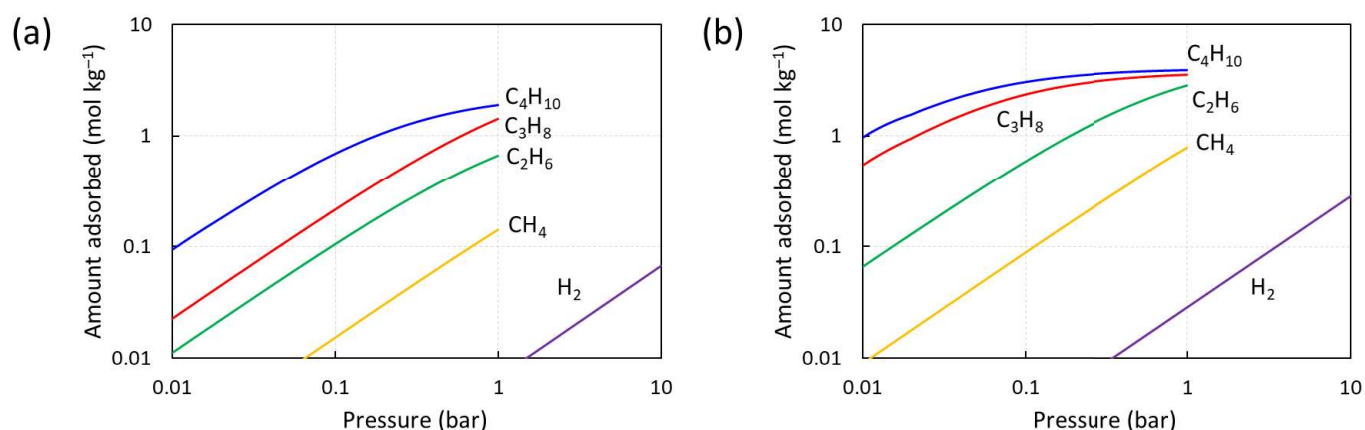
Figure 4: Adsorption isotherms of C_4H_{10}, C_3H_8, C_2H_6, CH_4 and H_2 at 299 K on log-log scale on (a) silica gel and (b) activated carbon. The H_2 isotherms on silica gel and on activated carbon are from (Liu et al., 2020) and (Lopes et al., 2009), respectively. All hydrocarbon isotherms are from (Malek and Farooq, 1997; 1998)

A lot of on-going research is endeavouring to develop advanced adsorbents that have good potential to improve the H_2 PSA performance further. Promising candidates, in fact, have shown enhanced adsorption capacities for some impurities and higher selectivities of those impurities over hydrogen, compared to the conventional activated carbon and 5A zeolite. A first class of novel adsorbents is represented by modified activated carbons, either activated in a different way (Lopes et al., 2011; Hong et al., 2021) or impregnated with a saline solution (Iyuke et al., 2000; Relvas et al., 2018; He et al., 2020). The modification of 5A and 13X zeolites by ion exchange of Na^+ with different cations has been suggested as an economic method to improve the H_2 PSA performance (Liu et al., 2009; Lopes et al., 2010; Brea et al., 2019a). Several types of metal organic frameworks (MOFs) have also been assessed for the purification of hydrogen, including MgMOF-74, UiO-66(Zr), IRMOF-11, Cu-BTC and UTSA-16 (Krishna and Long, 2011; Banu et al., 2013; Meng et al., 2013; Jamali et al., 2018; Brea et al., 2019b). Eventually, it was reported

that composite adsorbents of activated carbons and zeolites or zeolites and MOFs showed encouraging results (Ducrot-Boisgontier et al., 2010; Al-Naddaf et al., 2018). Table 3 lists the advanced adsorbents tested for hydrogen purification in terms of adsorbent class and improvements in the H_2 PSA process compared to the benchmark adsorbents.

Table 3: Advanced adsorbents for hydrogen purification (*AC* activated carbon, *ZE* zeolite, *MOF* metal organic framework)

Adsorbent name	Adsorbent class	Improvements in H_2 PSA	Reference
AC5-KS	Modified AC physically activated with CO_2	Enhanced CO_2 adsorption capacity, higher CO_2/H_2 selectivity	Lopes et al., 2011
Sn-AC	Modified AC impregnated with $SnCl_2 \cdot 2H_2O$	Enhanced CO adsorption capacity, higher CO/H_2 selectivity	Iyuke et al., 2000
Cu-AC	Modified AC impregnated with $CuCl_2 \cdot 2H_2O$		Relvas et al., 2018
Structured Ni-AC	Structured AC dip-coated with Ni foam	Enhanced CO_2 effective diffusivity, higher CO_2/H_2 selectivity, lower pressure drops	He et al., 2020
KOH-treated AC	Modified AC activated or impregnated with KOH	Enhanced adsorption capacity for CO_2, CO, CH_4, higher selectivity for CO_2, CO, CH_4 over H_2	Hong et al., 2021
5A-Sr ZE	Modified 5A ZE by ion exchange of Na^+ with Sr^{2+}	Enhanced CH_4 adsorption capacity, higher CH_4/H_2 selectivity	Liu et al., 2009
13X-Ba/Ca ZE	Modified 13X ZE by ion exchange of Na^+ with Ba^{2+}, Ca^{2+}	Enhanced N_2 adsorption capacity, higher N_2/H_2 selectivity	Lopes et al., 2010
13X-Ca/Mg ZE	Modified 13X ZE by ion exchange of Na^+ with Ca^{2+}, Mg^{2+}	Enhanced adsorption capacity for CO, CH_4, higher H_2 recovery in PSA cycle compared to 13X-Na	Brea et al., 2019a
MgMOF-74	Also denoted as MOF CPO-27-Mg or MOF Mg_2(dobdc)	Enhanced adsorption capacity for CO_2, CH_4, higher selectivity for CO_2, CH_4 over H_2	Krishna and Long, 2011
UiO-66(Zr)/-Br	Also denoted as MOF UiO-66(Zr) and UiO-66(Zr)-Br	Enhanced working capacity for CO, N_2, higher selectivity for CO, N_2 over H_2	Banu et al., 2013
IRMOF-11	Also denoted as isoreticular catenated MOF 11	Enhanced adsorption capacity for CO_2, CO, CH_4, higher selectivity for CO_2, CO, CH_4 over H_2	Meng et al., 2013
Cu-BTC	Also denoted as MOF Cu_3(BTC)$_2$	Higher H_2 purity in PSA cycle compared to AC, 5A ZE and AC / 5A ZE, improved layered bed	Jamali et al., 2018
UTSA-16	Also denoted as MOF UTSA-16	Similar performance in PSA cycle compared to AC (with 5A ZE as an extra common layer)	Brea et al., 2019b
FAU ZE / AC	Composite FAU-type ZE nanocasted carbon replica	Enhanced working capacity for CO_2, CH_4, N_2	Ducrot-Boisgontier et al., 2010
5A ZE / MgMOF-74	Composite 5A ZE and MgMOF-74 with core-shell structure	Enhanced adsorption capacity for CO_2, CO, CH_4, N_2, higher selectivity for CO_2, CO, CH_4, N_2 over H_2	Al-Naddaf et al., 2018

2.3 H$_2$ PSA cycle steps

Unlike distillation, absorption and liquid-liquid extraction that operate under steady state condition, cyclic adsorption processes using fixed-beds like PSA, are intrinsically dynamic, with the composition, pressure and temperature inside the bed varying with respect to time as well as position. PSA processes differ from one another with respect to the sequence of the elementary steps that constitute the PSA cycle and the way of operating each step. As the hydrogen product that a PSA unit produces is generally used as feedstock for other processes in refining, chemical and petrochemical industries, the PSA must be designed to operate continuously with an array of beds undergoing different steps simultaneously. Moreover, a *cyclic steady state* can be achieved in a PSA after repeating several cycles until the component concentrations oscillate around mean values in both *raffinate* and *extract* streams (Ruthven et al., 1994). In a H$_2$ PSA unit the effluent of the adsorption step is the purified hydrogen product, as the impurities are removed preferentially by adsorption. During the desorption steps a tail gas is extracted containing most of the impurities along with a portion of hydrogen that is retained in the bed at the start of the first desorption step. For the H$_2$ PSA cycle, the following elementary steps have been proposed (Yang, 1987; Ruthven et al., 1994; Wagner, 1969; Batta, 1971; Fuderer and Rudelstorfer, 1976; Weist Jr. et al., 2016):

a) *Adsorption*: The adsorption bed receives the raw H$_2$ feed stream at high pressure where the gas impurities are preferentially adsorbed in the different layers of the bed while a pure H$_2$ product is withdrawn from the product end. This step operates at the highest pressure of the PSA cycle.

b) *Co-current depressurising pressure equalisation*: The adsorption bed is co-currently depressurised to an intermediate pressure level between the high and the low pressure. A H$_2$-rich stream is withdrawn from the product end and is passed to another adsorption bed undergoing a complementary pressurising pressure equalisation step.

c) *Co-current providing purge*: The adsorption bed is co-currently depressurised to an intermediate pressure level between the high and the low pressure. A H$_2$-rich stream is withdrawn from the product end and is passed to at least another adsorption bed undergoing a complementary purge step.

d) *Counter-current blowdown*: The adsorption bed is counter-currently depressurised to the lowest pressure of the PSA cycle. An outgoing stream is extracted at the feed end containing a portion of the desorbed impurities.

e) *Counter-current purge*: The adsorption bed is counter-currently purged at low pressure by a H$_2$-rich stream withdrawn from at least another adsorption bed undergoing a complementary providing purge step. An outgoing stream is extracted at the feed end containing the remaining portion of the desorbed impurities. This step operates at the lowest pressure of the PSA cycle.

f) *Counter-current pressurising pressure equalisation*: The adsorption bed is counter-currently pressurised to an intermediate pressure level between the high and the low pressure. A H$_2$-rich

stream withdrawn from another adsorption bed undergoing a complementary depressurising pressure equalisation step is introduced at the product end.

g) *Counter-current product pressurisation*: The adsorption bed is counter-currently pressurised to the adsorption pressure by introducing at the product end a portion of H_2 product withdrawn during the adsorption step.

h) *Idle*: The adsorption bed is disconnected from the surroundings with no gas streams flowing into or out of the bed. This step may be required for bed synchronization purposes.

2.4 Methods to improve H_2 PSA performance

The performance of a PSA unit can be enhanced by process design and optimisation as well as using novel high-performance adsorbents. For instance, optimal ways of operating a PSA can be found by trialling various step sequences of a cycle and adjusting the step times (Voss, 2005; Grande, 2016). Determining a suitable step sequence of a cycle is a challenging task, especially for H_2 PSA systems having a large number of beds. However, several rules based on both heuristics and experience are available in the literature to assist in constructing an efficient cycle step sequence. Furthermore, many suitable PSA cycles have been studied, and modification of those cycles with other well-known steps is straightforward (Weist Jr. et al., 2016).

Ebner et al. (2009) and Mehrotra et al. (2010) derived graphical and arithmetic approaches, respectively, to obtain suitable PSA cycle scheduling. The approaches require *a priori* information about the step sequence, the constraints to meet and the number of beds. While the graphical methodology provides a systematic procedure to fill a 2-D grid representing the possible cycle schedules (Ebner et al., 2009), the arithmetic methodology requires solving a set of algebraic equations to get the same results. The scheduling methods can also be used to find the minimum number of beds required to operate the specified step sequence, the minimum number and location of idle steps to ensure alignment of coupled cycle steps and a simple screening technique to identify the best performing cycles that deserve further examination (Mehrotra et al., 2010).

For H_2 PSA systems the following methods to improve the unit performance have been proposed (Yang, 1987; Ruthven et al., 1994; Batta, 1971; Fuderer and Rudelstorfer, 1976; Weist Jr. et al., 2016):

a) *Multiple bed systems*: H_2 PSA cycles are generally carried out using more than one adsorption bed so that some beds produce the H_2 product while other beds are regenerated. In this way, hydrogen can be produced continuously with high throughputs. The larger number of adsorption beds a PSA has, the more complex step sequence it can operate with, which will result in improved performance. For instance, increasing the number of beds allows a PSA unit to incorporate in the cycle more pressure equalisation steps and/or a providing purge step, and to have multiple beds undergoing the adsorption step simultaneously, all of which will increase the H_2 recovery. However, for a required H_2 purity, e.g. 99.99+%, there exists a trade-off between the number of beds, hence the unit CAPEX, and the H_2 recovery (Yang, 1987).

b) *Multiple pressure equalisation steps*: Pressure equalisation steps can be regarded as hydrogen saving steps because they reduce the initial pressure of the blowdown step, thus minimising the hydrogen losses (Ruthven et al., 1994). Pressure equalisation steps also reduce the amount of H_2 product consumed in the final product pressurisation, as the adsorption bed would be already partially pressurised at the start of the pressurisation step (Yang, 1987). In particular, the performance of a H_2 PSA could be greatly enhanced by increasing the number of pressure equalisation steps, if the adsorption pressure was relatively high and the feed contained low impurity content. In case of a H_2 PSA unit designed to produce ultrapure hydrogen (99.99+%) from a steam reformer syngas, the H_2 recovery could be improved from 60–65% with one pressure equalisation step (Wagner, 1969) to 70–75% with two pressure equalisation steps (Batta, 1971), and up to 80–90% with three pressure equalisation steps (Fuderer and Rudelstorfer, 1976). Yavary et al. (2015) investigated three PSA cycles with one, two and three pressure equalisation steps, respectively, in a 6-bed PSA process for purifying hydrogen from a refinery off-gas. They concluded that, with the same operating conditions, increasing the number of pressure equalisation steps led to a significant gain in H_2 recovery with a little loss in H_2 purity. However, it has also been reported that increasing the number of pressure equalisation steps to more than four would have only a marginal benefit in H_2 recovery (Luberti et al., 2014a; Grande, 2016).

c) *Use of providing purge step*: Providing purge steps increase the H_2 recovery by avoiding the consumption of H_2 product in the purge step. Since the purge step is carried out at the lowest pressure of the cycle, the source of hydrogen can be taken from any other step in the cycle that are at a higher pressure, e.g. during a co-current depressurisation step at intermediate pressure (Yang, 1987). Often, the providing purge step is carried out in the cycle sequence after the final depressurising pressure equalisation step, that is to say, prior to the blowdown step. This is in line with the general principle proposed by Fuderer and Rudelstorfer (1976) for which, when more than one gas stream is discharged from a bed by depressurisation, the most impure discharged gas should be used to purge another bed at the lowest intermediate pressure while the purest discharged gas should be used to pressurise another bed to the highest intermediate pressure.

d) *Multiple beds on adsorption step*: This configuration splits the raw H_2 feed flowrate equally into more than one bed during the adsorption step, thus reducing the gas velocity along each bed. This would improve the H_2 recovery because lower gas velocities make the concentration fronts travel more sharply along the beds so that the length of unused bed (LUB) gets shorter (Weist Jr. et al., 2016). As a result, H_2 PSA units could benefit from this strategy by having a longer adsorption time or requiring smaller adsorption beds, leading to greater bed productivities and lower unit CAPEX (Luberti et al., 2014a; Grande, 2016).

The Polybed H_2 PSA system introduced by Fuderer and Rudelstorfer (1976) is the perfect embodiment of the PSA strategies mentioned above and designed to maximise the unit performance. Figure 5 shows, for instance, the flowsheet of the UOP Polybed H_2 PSA process having 10 beds and a cycle schedule

incorporating multiple pressure equalisation steps, a providing purge step and multiple beds on adsorption step at the same time.
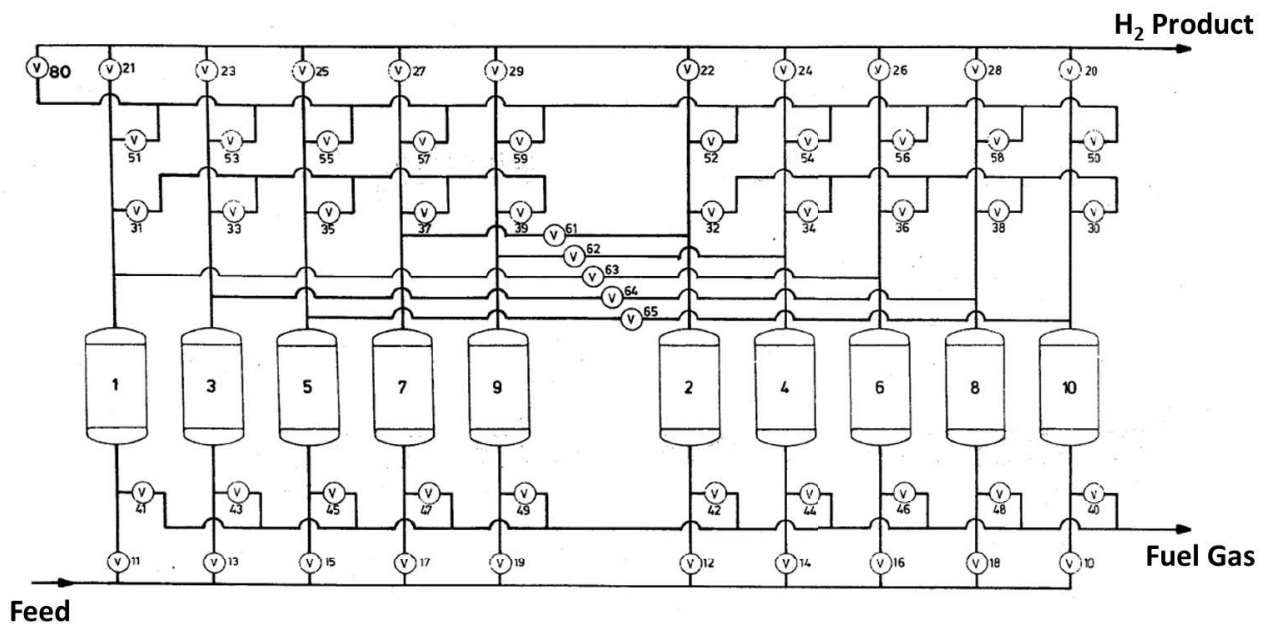

Figure 5: Flowsheet of the UOP Polybed H_2 PSA process (Fuderer and Rudelstorfer, 1976)

3. Polybed H_2 PSA

The Polybed process for hydrogen purification is an improvement of the 2-bed system developed by Wagner (1969) and the 4-bed system developed by Batta (1971). It features seven to sixteen beds and a cycle configuration incorporating at least three pressure equalisation steps and at least two beds receiving the feed gas at the same time (Fuderer and Rudelstofer, 1976). In order to deploy three-stage pressure equalisation, the absolute pressure ratio of the adsorption pressure to the purge pressure should be at least 7. Compared to the previous patents (Wagner, 1969; Batta, 1971), the Polybed system exhibits higher H_2 recoveries, higher H_2 throughputs, a smaller total volume of adsorption beds and a lower total inventory of adsorbent material.

A 6-bed H_2 PSA system can be designed to have either three pressure equalisation steps and only one bed undergoing the adsorption step or two pressure equalisation steps and two beds undergoing the adsorption step at the same time, as shown in Figures 6 and 7, respectively. Such systems represent two limiting configurations of the original Polybed system and were reported in the literature by Xu and Weist Jr. (2002) and Malek and Farooq (1997). It should be noted that, in order to accommodate the third pressure equalisation step, the cycle scheduling of the three pressure equalisation case (Figure 6) has the adsorption step time half as long as that of the two pressure equalisation case (Figure 7). One or two idle steps are also needed for bed synchronisation purposes. It is expected that the Polybed H_2 PSA system would benefit from both intensified pressure equalisation and reduced feed flowrate in one bed that each of the two 6-bed H_2 PSA system embeds. Figure 8 shows the step configuration of a 9-bed H_2 PSA cycle

with three pressure equalisations and three adsorbing beds at the same time, as disclosed by Fuderer and Rudelstorfer (1976).
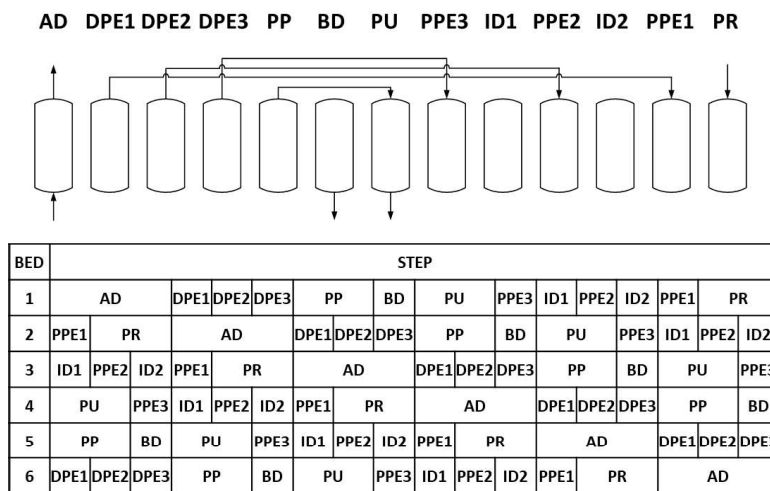
AD   DPE1 DPE2 DPE3   PP   BD   PU   PPE3   ID1   PPE2   ID2   PPE1   PR

BED	STEP												
1	AD	DPE1	DPE2	DPE3	PP	BD	PU	PPE3	ID1	PPE2	ID2	PPE1	PR
2	PPE1	PR	AD	DPE1	DPE2	DPE3	PP	BD	PU	PPE3	ID1	PPE2	ID2
3	ID1	PPE2	ID2	PPE1	PR	AD	DPE1	DPE2	DPE3	PP	BD	PU	PPE3
4	PU	PPE3	ID1	PPE2	ID2	PPE1	PR	AD	DPE1	DPE2	DPE3	PP	BD
5	PP	BD	PU	PPE3	ID1	PPE2	ID2	PPE1	PR	AD	DPE1	DPE2	DPE3
6	DPE1	DPE2	DPE3	PP	BD	PU	PPE3	ID1	PPE2	ID2	PPE1	PR	AD

Figure 6: Step configuration of a 6-bed H_2 PSA cycle with 3 pressure equalisations and 1 adsorbing bed (*AD* adsorption, *DPE* depressurising pressure equalisation, *ID* idle, *PP* providing purge, *BD* blowdown, *PU* purge, *PPE* pressurising pressure equalisation, *PR* pressurisation; $t_{AD} = t_{cycle}/6$; $t_{PP} = t_{PU} = t_{PR} = t_{cycle}/9$; $t_{BD} = t_{DPE} = t_{PPE} = t_{ID} = t_{cycle}/18$) (Xu and Weist Jr., 2002)

AD   DPE1   ID   DPE2   PP   BD   PU   PPE2   PPE1   PR

BED	STEP									
1	AD	DPE1	ID	DPE2	PP	BD	PU	PPE2	PPE1	PR
2	PPE1	PR	AD	DPE1	ID	DPE2	PP	BD	PU	PPE2
3	PU	PPE2	PPE1	PR	AD	DPE1	ID	DPE2	PP	BD
4	PP	BD	PU	PPE2	PPE1	PR	AD	DPE1	ID	DPE2
5	DPE1	ID	DPE2	PP	BD	PU	PPE2	PPE1	PR	AD
6	AD	DPE1	ID	DPE2	PP	BD	PU	PPE2	PPE1	PR	AD

Figure 7: Step configuration of a 6-bed H_2 PSA cycle with 2 pressure equalisations and 2 adsorbing beds (*AD* adsorption, *DPE* depressurising pressure equalisation, *ID* idle, *PP* providing purge, *BD* blowdown, *PU* purge, *PPE* pressurising pressure equalisation, *PR* pressurisation; $t_{AD} = t_{cycle}/3$; $t_{PP} = t_{PU} = t_{PR} = t_{cycle}/9$; $t_{BD} = t_{DPE} = t_{PPE} = t_{cycle}/18$) (Malek and Farooq, 1997)

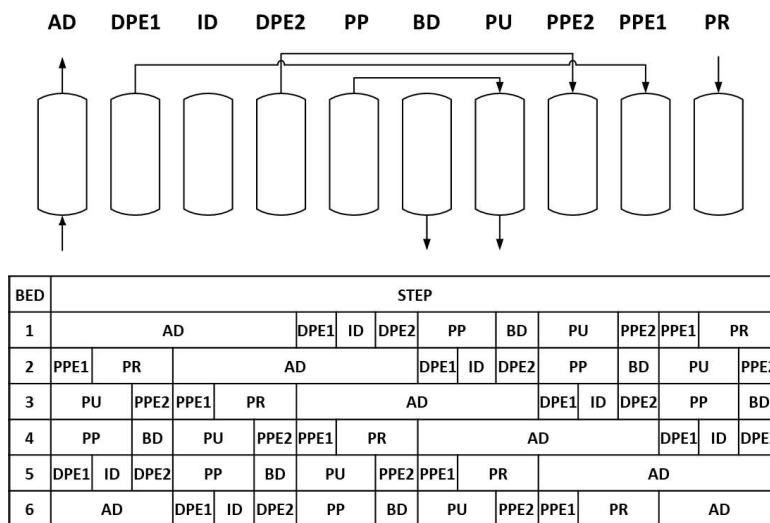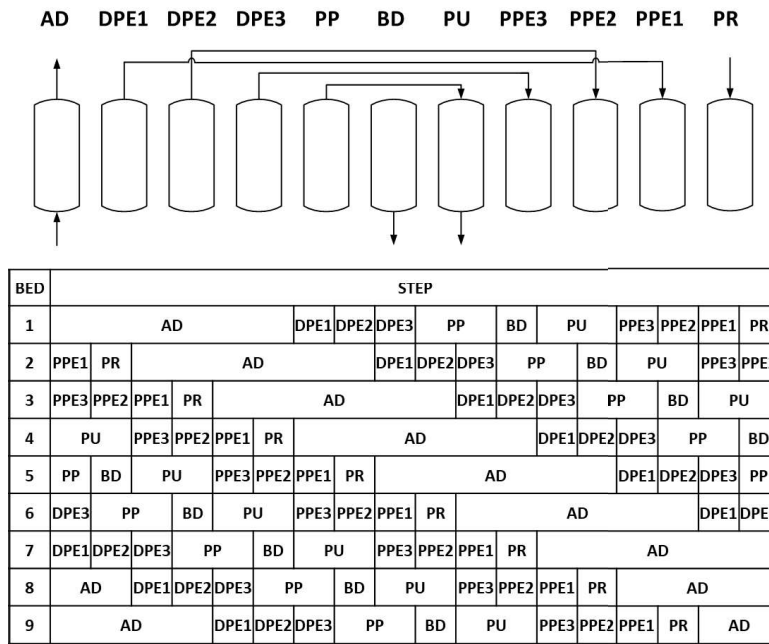| BED	STEP											
1	AD				DPE1	DPE2	DPE3	PP	BD	PU	PPE3	PPE2	PPE1	PR
2	PPE1	PR	AD			DPE1	DPE2	DPE3	PP	BD	PU	PPE3	PPE2
3	PPE3	PPE2	PPE1	PR	AD		DPE1	DPE2	DPE3	PP	BD	PU
4	PU	PPE3	PPE2	PPE1	PR	AD		DPE1	DPE2	DPE3	PP	BD
5	PP	BD	PU	PPE3	PPE2	PPE1	PR	AD		DPE1	DPE2	DPE3	PP
6	DPE3	PP	BD	PU	PPE3	PPE2	PPE1	PR	AD		DPE1	DPE2
7	DPE1	DPE2	DPE3	PP	BD	PU	PPE3	PPE2	PPE1	PR	AD	
8	AD	DPE1	DPE2	DPE3	PP	BD	PU	PPE3	PPE2	PPE1	PR	AD
9	AD		DPE1	DPE2	DPE3	PP	BD	PU	PPE3	PPE2	PPE1	PR	AD

Figure 8: Step configuration of a 9-bed H_2 PSA cycle with 3 pressure equalisations and 3 adsorbing beds (*AD* adsorption, *DPE* depressurising pressure equalisation, *ID* idle, *PP* providing purge, *BD* blowdown, *PU* purge, *PPE* pressurising pressure equalisation, *PR* pressurisation; $t_{AD} = t_{cycle}/3$; $t_{PP} = t_{PU} = t_{cycle}/9$; $t_{BD} = t_{DPE} = t_{PPE} = t_{PR} = t_{cycle}/18$) (Fuderer and Rudelstorfer, 1976)

In the next subsections industrial applications and technical advances of the Polybed H_2 PSA will be discussed in reference to both articles and patents. Various Polybed H_2 PSA systems that have been developed so far are classified by the PSA feed source, namely syngas from steam reforming, refinery off-gas and CO_2-depleted syngas from H_2 plants equipped with pre-combustion CO_2 capture. The last subsections will introduce several engineering solutions to enhance the performance of the Polybed systems as well as advanced mathematical modelling and optimization methods.

3.1 Syngas from steam reforming

The major application of the Polybed H_2 PSA is to purify hydrogen from steam reformer effluents, with a share accounting for more than 40% of the overall units installed worldwide (UOP, 2015). Among the academic articles, Nikolic et al. (2009) presented an optimization framework for designing complex PSA processes including an 8-bed, 10-step Polybed H_2 PSA system having three pressure equalisation steps. They compared two cases with respect to the adsorption bed configuration: one was single layered beds packed with activated carbon only and the other was dual layered beds packed with activated carbon and 5A zeolite. Given a feed gas containing 75.5% of H_2 balanced with CO_2, CO and CH_4 impurities, it was aimed to maximise the H_2 recovery with the H_2 purity maintained at 99.99%. The optimal operating conditions were searched for by varying the following operating variables: purge-to-feed ratio (0.5–2.5%), feed pressure (5–30 bar), bed length-to-diameter ratio (5–15) and carbon-to-zeolite ratio (0–1). It was found that the maximum achieved H_2 recovery was around 80.0% using the single layered beds and around 85.0% using the dual layered beds. Lopes et al. (2011) developed an adsorption uni-bed model

and simulated a Polybed H_2 PSA with a 10-step cycle including three pressure equalisation steps designed for purifying hydrogen from a gas mixture containing 79% of H_2 balanced with CO_2, CO, CH_4 and N_2 impurities. After a comprehensive simulation campaign they verified that ultrapure hydrogen (99.99+%) could be obtained using activated carbon AC5-KS adsorbent with a H_2 recovery of around 76% and a bed productivity of 160 mol_{H2} kg_{ads}^{-1} d^{-1}. Aside from the single layered beds, H_2 recoveries were low because the adsorption pressure was set to only 10 bar. Shi et al. (2018) carried out numerical simulations of a 10-bed, 13-step Polybed system having four pressure equalisation steps and a providing purge step as well as dual layered beds packed with activated carbon and 5A zeolite. The feed gas was at 22 bar and had a composition of 76% H_2, 20% CO_2, 3.5% CH_4, and 0.5% CO. By varying and assessing several operating variables, such as the feed flowrate, the carbon-to-zeolite ratio and the purge-to-feed ratio, they were able to achieve 99.99+% H_2 purity and 87.4% H_2 recovery, in line with the results reported by Nikolic et al. (2009). Two-train elevated temperature PSA processes to purify hydrogen using K-MG30 adsorbent were investigated by Zhu et al. (2018). By processing a typical coal-gasification shifted gas feed (29% CO_2, 40% H_2, 1% CO, and 30% H_2O) at 30 bar, the first train was an 8-bed, 13-step Polybed PSA system designed to produce a H_2-rich stream (> 95% purity), while the second train was a 2-bed, 7-step PSA system designed to further purify H_2 up to 99.99+%. The Polybed PSA cycle featured four pressure equalisation steps and a rinse step in which high-pressure steam at 673.15 K flowed through the bed for regeneration. By optimising the rinse-to-feed ratio and the purge-to-feed ratio the integrated two-train PSA unit was able to achieve an exceptionally high H_2 recovery of 97.5%.

Among the patents, Fuderer and Rudelstorfer (1976) developed various Polybed systems in the form of 7-, 8-, 9- and 10-bed configurations with the cycle schedules having 3–4 pressure equalisation steps, 2–3 beds on adsorption step, 1–2 beds on purge step and optional providing purge step. They claimed that 40 MMSCFD of ultrapure hydrogen could be produced in a dual layered 10-bed configuration processing a typical steam methane reformer syngas and obtaining a H_2 recovery of 86.0%. This H_2 recovery was 6% higher compared with that of the 4-bed PSA system developed by Batta (1971). In the effort of increasing the H_2 recovery, Fuderer (1982) also proposed to pre-treat 60% of the feed gas in a liquid absorber for CO_2 removal so that the CO_2 content was reduced from 22.9 to 3.0%, with the remaining 40% fed directly to an 8-bed, 11-step Polybed H_2 PSA. As a result, the H_2 recovery was increased from 86.0% to 89.8% because the greater H_2 mole fraction in the feed makes the co-current depressurisation steps more efficient, thus reducing the loss of hydrogen during the counter-current blowdown step. Another idea formulated to enhance the H_2 recovery in a Polybed PSA system was to carry out the bed regeneration with a purge step using a foreign gas followed by a displacement step. The adsorbed impurities could be purged by a weakly adsorbing foreign gas, e.g. N_2 or Ar, and then the adsorbed foreign gas could be displaced by a gas discharged during a co-current depressurisation step (Benkmann, 1983). The use of these measures ensured that no H_2 product was lost during the purge step, however the H_2 purity resulted highly sensitive to the introduction of a weakly adsorbing foreign specie. The performance of a Polybed H_2 PSA could also be improved by splitting the providing purge gas discharged from a bed and using some of it as a purge gas with the rest stored in an external vessel. The gas in this vessel could then be used to

partially repressurise the other bed. Using this approach, Whysall (1984) claimed that a 6-bed configuration with two pressure equalisation steps could achieve the same H_2 recovery as that of an 8-bed configuration with three pressure equalisation steps. The benefit for the unit CAPEX would be obvious due to the reduction of number of beds in the system. The further invention disclosed by Whysall and Wagemans (2001) greatly enhanced the Polybed PSA capacity up to 100 MMSCFD of ultrapure H_2 produced in a single train involving up to 16 beds. In general, PSA systems have limited scalability so that multiple PSA trains have to be configured in parallel for their very large-scale application, which results in high overall CAPEX. This is because PSA adsorption beds are limited to a diameter which can be transported to a construction site (maximum 4 meters) and to a height which should not overcome the crush strength of the adsorbent particles (Ruthven et al., 1994; Whysall and Wagemans, 2001). In the same patent (Whysall and Wagemans, 2001), the inventors also claimed that the unit productivity could be improved without deteriorating the H_2 recovery (87.2%) by increasing the purge step time relative to the adsorption step time and using a providing purge step. Xu and Weist Jr. (2002) and Xu et al. (2002) proposed novel cycle schedules in which a 6-bed system and a 10-bed system were configured with four pressure equalisation steps and at least one or two beds providing purge, respectively. It was claimed that ultrapure hydrogen could be produced with capacities ranging 80–84 MMSCFD and recoveries ranging 87.7–89.2%. Another good strategy to maximise the Polybed H_2 PSA productivity was to reduce the pressure equalisation time in a cycle to about 25 seconds, thereby reducing the overall cycle time, as disclosed by Xu et al. (2003). The invention showed multiple embodiments which can utilize combinations of 12, 14, or 16 beds, three or four beds on adsorption step, two or three beds on purge step, and four or five pressure equalisation steps. Partial pressure equalisations where the step ends before the equilibration of the two beds' pressures could also be embedded into the step sequence. Figures 9 and 10 show the step configurations of a 12-bed H_2 PSA cycle and a 16-bed H_2 PSA cycle, respectively, as reported by Xu et al. (2003). Advanced PSA cycles featuring turndown operation modes, continuous PSA tail gas flow, no need for purging storage tank and no idle steps were also proposed. In turndown mode the process is still able to operate efficiently in case of one or more beds are taken offline for operational reasons such as valve failure (Baksh and Simo, 2013a). The patent (Baksh and Simo, 2013a) also discussed the benefits of having an advanced bed layering with at least three layers of adsorbents (alumina, activated carbon and zeolite), where the activated carbon and zeolite adsorbents are layered based on particle size, thus reducing the pressure drops and enabling additional improvement in H_2 recovery. The inventors systematically investigated the previous enhancements in a 6-bed configuration having cycles with 2–4 pressure equalisation steps and 1–2 adsorbing beds. It was claimed that ultrapure hydrogen could be produced with capacities ranging 40–50 MMSCFD and H_2 recoveries ranging 85.0–88.0% (Baksh and Simo, 2013a). The same advanced PSA cycles, namely efficient operation in turndown mode and improved layered beds, were also applied to large scale Polybed PSA units ranging from 12 to 16 beds and producing 100–190 MMSCFD of ultrapure hydrogen (Baksh and Simo, 2013b). In particular, the patent disclosed 12-, 14- and 16-bed configurations where the number of pressure equalisation steps and the number of beds on adsorption step were 4-4, 5-5 and 6-6, respectively. It was reported that the 16-bed

configuration would be able to produce ultrapure H_2 with a capacity of 190 MMSCFD and an exceptional H_2 recovery of 92.0%.

Table 4 summarises the configuration and performance of the Polybed H_2 PSA systems designed for the syngas from steam reforming from patents in the literature.
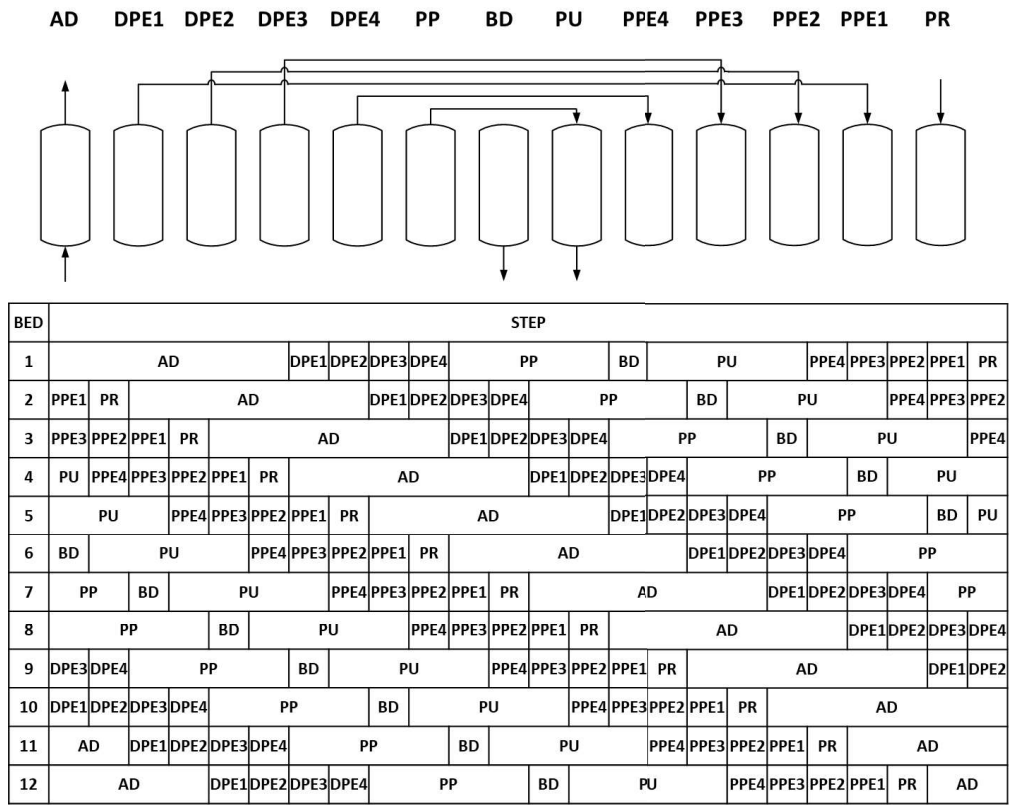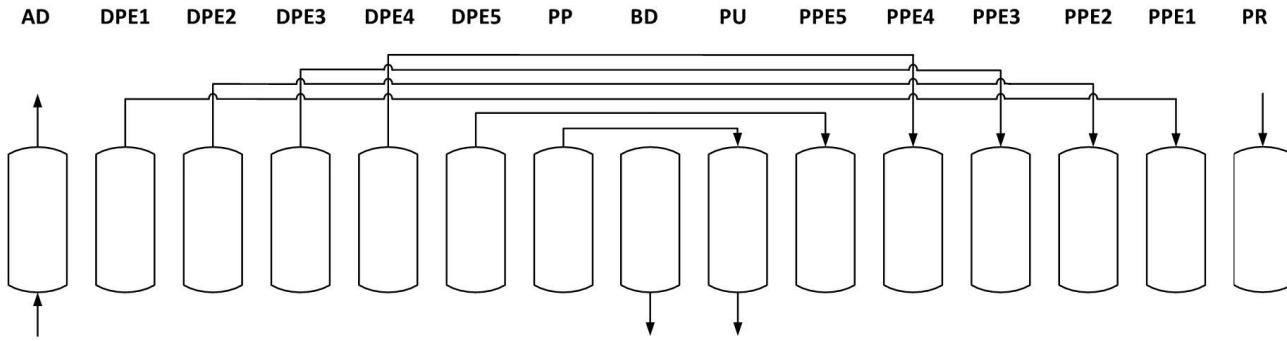

Column order (top of figure): AD DPE1 DPE2 DPE3 DPE4 PP BD PU PPE4 PPE3 PPE2 PPE1 PR

BED	STEP
1	AD | DPE1 | DPE2 | DPE3 | DPE4 | PP | BD | PU | PPE4 | PPE3 | PPE2 | PPE1 | PR
2	PPE1 | PR | AD | DPE1 | DPE2 | DPE3 | DPE4 | PP | BD | PU | PPE4 | PPE3 | PPE2
3	PPE3 | PPE2 | PPE1 | PR | AD | DPE1 | DPE2 | DPE3 | DPE4 | PP | BD | PU | PPE4
4	PU | PPE4 | PPE3 | PPE2 | PPE1 | PR | AD | DPE1 | DPE2 | DPE3 | DPE4 | PP | BD | PU
5	PU | PPE4 | PPE3 | PPE2 | PPE1 | PR | AD | DPE1 | DPE2 | DPE3 | DPE4 | PP | BD | PU
6	BD | PU | PPE4 | PPE3 | PPE2 | PPE1 | PR | AD | DPE1 | DPE2 | DPE3 | DPE4 | PP
7	PP | BD | PU | PPE4 | PPE3 | PPE2 | PPE1 | PR | AD | DPE1 | DPE2 | DPE3 | DPE4 | PP
8	PP | BD | PU | PPE4 | PPE3 | PPE2 | PPE1 | PR | AD | DPE1 | DPE2 | DPE3 | DPE4
9	DPE3 | DPE4 | PP | BD | PU | PPE4 | PPE3 | PPE2 | PPE1 | PR | AD | DPE1 | DPE2
10	DPE1 | DPE2 | DPE3 | DPE4 | PP | BD | PU | PPE4 | PPE3 | PPE2 | PPE1 | PR | AD
11	AD | DPE1 | DPE2 | DPE3 | DPE4 | PP | BD | PU | PPE4 | PPE3 | PPE2 | PPE1 | PR | AD
12	AD | DPE1 | DPE2 | DPE3 | DPE4 | PP | BD | PU | PPE4 | PPE3 | PPE2 | PPE1 | PR | AD

Figure 9: Step configuration of a 12-bed H_2 PSA cycle with 4 pressure equalisations, 3 adsorbing beds and 2 purging beds (*AD* adsorption, *DPE* depressurising pressure equalisation, *ID* idle, *PP* providing purge, *BD* blowdown, *PU* purge, *PPE* pressurising pressure equalisation, *PR* pressurisation; $t_{AD} = t_{cycle}/4$; $t_{PP} = t_{PU} = t_{cycle}/6$; $t_{BD} = t_{DPE} = t_{PPE} = t_{PR} = t_{cycle}/24$) (Xu et al., 2003)

Top diagram column labels: AD DPE1 DPE2 DPE3 DPE4 DPE5 PP BD PU PPE5 PPE4 PPE3 PPE2 PPE1 PR

BED	STEP															
1	AD	DPE1	DPE2	DPE3	DPE4	DPE5	PP	BD	PU	PPE5	PPE4	PPE3	PPE2	PPE1	PR	
2	PPE1	PR	AD	DPE1	DPE2	DPE3	DPE4	DPE5	PP	BD	PU	PPE5	PPE4	PPE3	PPE2	
3	PPE3	PPE2	PPE1	PR	AD	DPE1	DPE2	DPE3	DPE4	DPE5	PP	BD	PU	PPE5	PPE4	
4	PPE5	PPE4	PPE3	PPE2	PPE1	PR	AD	DPE1	DPE2	DPE3	DPE4	DPE5	PP	BD	PU	
5	PU	PPE5	PPE4	PPE3	PPE2	PPE1	PR	AD	DPE1	DPE2	DPE3	DPE4	DPE5	PP	BD	PU
6	PU	PPE5	PPE4	PPE3	PPE2	PPE1	PR	AD	DPE1	DPE2	DPE3	DPE4	DPE5	PP	BD	PU
7	PU	PPE5	PPE4	PPE3	PPE2	PPE1	PR	AD	DPE1	DPE2	DPE3	DPE4	DPE5	PP	BD	
8	PP	BD	PU	PPE5	PPE4	PPE3	PPE2	PPE1	PR	AD	DPE1	DPE2	DPE3	DPE4	DPE5	PP
9	PP	BD	PU	PPE5	PPE4	PPE3	PPE2	PPE1	PR	AD	DPE1	DPE2	DPE3	DPE4	DPE5	PP
10	PP	BD	PU	PPE5	PPE4	PPE3	PPE2	PPE1	PR	AD	DPE1	DPE2	DPE3	DPE4	DPE5	PP
11	DPE5	PP	BD	PU	PPE5	PPE4	PPE3	PPE2	PPE1	PR	AD	DPE1	DPE2	DPE3	DPE4	
12	DPE3	DPE4	DPE5	PP	BD	PU	PPE5	PPE4	PPE3	PPE2	PPE1	PR	AD	DPE1	DPE2	
13	DPE1	DPE2	DPE3	DPE4	DPE5	PP	BD	PU	PPE5	PPE4	PPE3	PPE2	PPE1	PR	AD	
14	AD	DPE1	DPE2	DPE3	DPE4	DPE5	PP	BD	PU	PPE5	PPE4	PPE3	PPE2	PPE1	PR	AD
15	AD	DPE1	DPE2	DPE3	DPE4	DPE5	PP	BD	PU	PPE5	PPE4	PPE3	PPE2	PPE1	PR	AD
16	AD	DPE1	DPE2	DPE3	DPE4	DPE5	PP	BD	PU	PPE5	PPE4	PPE3	PPE2	PPE1	PR	AD

Figure 10: Step configuration of a 16-bed H_2 PSA cycle with 5 pressure equalisations, 4 adsorbing beds and 3 purging beds (*AD* adsorption, *DPE* depressurising pressure equalisation, *ID* idle, *PP* providing purge, *BD* blowdown, *PU* purge, *PPE* pressurising pressure equalisation, *PR* pressurisation; $t_{AD} = t_{cycle}/4$; $t_{PP} = t_{PU} = 3t_{cycle}/16$; $t_{BD} = t_{DPE} = t_{PPE} = t_{PR} = t_{cycle}/32$) (Xu et al., 2003)

Table 4: Performance of Polybed H_2 PSA applied to steam reformer syngas from patents in the literature. H_2 purity is 99.99+% in all studies (*AD* adsorption, *PE* pressure equalisation)

Configuration	No. beds on AD step	No. PE steps	Adsorbent	H_2 Recovery (%)	H_2 Product Rate (MMSCFD*)	Reference
10-bed, 11-step[a]	3	3	AC / 5A	86.0	40.0	Fuderer and Rudelstorfer, 1976
8-bed, 11-step[b]	2	3	AC / 5A	89.8	11.3	Fuderer, 1982
16-bed, 13-step[c]	4	4	AC / 5A	87.2	100.0	Whysall and Wagemans, 2001
6-bed, 13-step[d]	1	4	AC / 5A	87.7	N/A	Xu and Weist Jr., 2002
10-bed, 14-step[d]	2	4	AC / 5A	88.0	83.5	Xu et al., 2002
10-bed, 13-step[d]	2	4		89.2	79.9	
6-bed, 13-step[e]	1	4	Alumina / AC / 5A	88.0	40.3	Baksh and Simo, 2013a
6-bed, 9-step[e]	2	2		85.0	48.8	
6-bed, 11-step[e]	2	3		86.0	49.4	
12-bed, 13-step[e]	4	4	Alumina / AC / 5A	90.3	130.0	Baksh and Simo, 2013b
14-bed, 15-step[e]	5	5		92.0	163.0	
16-bed, 17-step[e]	6	6		92.0	190.0	

[*] 1 MMSCFD = 1,116 Nm^3 h^{-1}

[a] P_{ads} = 21 bar, P_{des} = 1 bar, Feed composition (mol%) $H_2/CO_2/CO/CH_4$ = 77.1/22.5/0.35/0.01

[b] P_{ads} = N/A, P_{des} = N/A, Feed composition (mol%) $H_2/CO_2/others$ = 79.8/12.1/8.1

[c] P_{ads} = 22 bar, P_{des} = 1.6 bar, Feed composition (mol%) $H_2/CO_2/CO/CH_4/N_2$ = 72.5/19.2/2.04/5.57/0.67

[d] P_{ads} = 30 bar, P_{des} = 1 bar, Feed composition (mol%) $H_2/CO_2/CO/CH_4/N_2$ = 74.0/16.0/3.5/6.0/0.5

[e] P_{ads} = 25.8 bar, P_{des} = 1.3 bar, Feed composition (mol%) $H_2/CO_2/CO/CH_4/N_2/H_2O$ = 73.87/16.37/3.31/5.94/0.23/0.3

3.2 Refinery off-gas

Refinery off-gases are produced in various refining processes, such as catalytic cracking and reforming, and account for more than 25% of the overall H_2 PSA units installed worldwide, resulting in the second largest feed source of the Polybed process (UOP, 2015). In case of refinery off-gases, the main impurity of the raw H_2 feed is often methane, with the more strongly adsorbed higher hydrocarbons constituting the other impurities. Maurer (1993) disclosed a strategy to attain enhanced H_2 recovery and working capacity for adsorbate hydrocarbons. In the invention, it was proposed that PSA cycles should be designed with two counter-current depressurisation steps and a counter-current purge step in-between the two depressurisation steps. In addition, the second counter-current depressurisation step should be carried out at a pressure slightly lower than the atmospheric pressure. An ejector would be needed for

the sub-atmospheric pressure and the effluent gas of the first depressurisation step would be taken as a motive gas. As an example, a Polybed H_2 PSA system was designed to process a binary gas mixture of 80 mol% H_2 balanced with CH_4 with a flowrate of 60 MMSCFD and a pressure of 41.3 bar. The Polybed was a 10-bed, 15-step system comprising three pressure equalisation steps and a providing purge step. The inventor compared two different step sequences: one had a conventional single stage depressurisation and the other had the novel dual stage depressurisation with the purge step in-between. It was claimed that the novel PSA cycle scheduling could boost H_2 recovery from 84.4% to 87.0%. Malek and Farooq (1997) developed a mathematical model of a 6-bed, 10-step PSA process to purify hydrogen from a feed with 72% H_2 and three hydrocarbon impurities (methane, ethane and propane) using activated carbon as an adsorbent. The cycle step configuration is reported in Figure 7. After carrying out a sensitivity analysis on the total cycle time and adsorption pressure, it was found that ultrapure hydrogen could be produced with a H_2 recovery of around 70% by swinging the bed pressure between 22.0 and 2.8 bar and fixing the cycle time to 720 seconds. In a follow up paper the same authors extended the numerical simulations by considering butane as an extra impurity in the feed and dual layered beds packed with silica gel and activated carbon adsorbents (Malek and Farooq, 1998). As a result of the new simulation campaign, the H_2 recovery was improved up to around 72% with the same PSA operating conditions as those in the previous study. Furthermore, the mathematical model was fully validated through the performance of an industrial 6-bed H_2 PSA unit in operation at a refinery.

3.3 Syngas from H_2 plants equipped with pre-combustion CO_2 capture

Carbon capture, storage and utilisation (CCSU) technologies have been actively developed in the last decade to decarbonise the power and industrial plants and tackle the exacerbating climate change. In particular, a lot of research has been recently carried out to capture CO_2 from the CO_2-rich streams of H_2 plants, such as steam reformer syngas and coal gasifier syngas (Table 1). A carbon capture unit is designed to primarily remove CO_2 from a gas mixture and produce a high purity CO_2 (95+%) stream, while the other impurities as well as the remaining CO_2 are retained in the H_2-rich stream. This resulting H_2-rich stream will have a H_2 purity of 85–95% at most, thus requiring additional purification to reach 99.99+%. In this regard, Liu et al. (2020) designed and simulated a 6-bed, 15-step PSA system to produce ultrapure hydrogen from the H_2-rich stream leaving a VSA unit that captures CO_2 selectively from a SMR effluent stream. The new PSA feed comprised 94.36% H_2 balanced with CO_2, CO and CH_4 at 22 bar. Using dual layered beds packed with activated carbon and 5A zeolite and a cycle configuration having four pressure equalisation steps and a providing purge step, ultrapure hydrogen could be produced with a recovery of 74.1%. The H_2 recovery would drop to 71.2% considering the hydrogen loss in the first VSA process. The low H_2 recovery could be explained by the loss of hydrogen during the blowdown step due to the higher affinity of H_2 for activated carbon (near the feed end) compared to 5A zeolite (near the product end).

IGCC power plants are one of the emerging clean coal technologies, which paves the way for producing power from coal with a higher net plant efficiency than conventional coal-fired power plants since a carbon capture unit can be applied to a gas stream having a higher CO_2 partial pressure. Luberti et

al. (2014a) were the first to design and numerically investigate a novel H_2 PSA unit to produce ultrapure hydrogen from the syngas that is generated by coal gasification and treated by a dual-stage Selexol process for CO_2 pre-combustion capture. The effluent stream from the CO_2 capture unit had a composition of 88.75% H_2 balanced with CO_2, CO, N_2 and Ar at 34 bar. In the simulation study, it was sought to maximise the H_2 recovery by increasing the complexity of the PSA cycle configuration based on 6, 9 and 12 beds packed with 5A zeolite adsorbent. As a result, the H_2 recovery was enhanced by increasing the number of beds and reached 92.7% in a Polybed system having 12 beds and a cycle configuration with three beds on adsorption step simultaneously and four pressure equalisation steps. The same authors also improved the overall H_2 plant performance by implementing the H_2 PSA tail gas recycle to the shift reactor since it could improve the H_2 product yield and help to alleviate the power consumption at the pre-combustion capture unit (Luberti et al., 2014b). Therefore, it was demonstrated that even in this scenario the Polybed H_2 PSA unit could be designed to achieve 90% of H_2 recovery, with an expected drop in performance due to the larger beds needed to accommodate the higher feed flowrate and to remove more impurities. Moon et al. (2018) analysed the performance of an 8-bed H_2 PSA system using dual layered beds packed with activated carbon and zeolite LiX adsorbents and processing the same H_2-rich feed from an IGCC plant equipped with pre-combustion carbon capture. Three cycle configurations were assessed in detail, namely: a 17-step cycle with four pressure equalisation steps and a product purge step, a 15-step cycle with three pressure equalisation steps and a providing purge step at high intermediate pressure, and a 15-step cycle with three pressure equalisation steps and a providing purge step at low intermediate pressure. As expected, the latter configuration achieved the highest H_2 recovery of 89.7% because, even if the number of pressure equalisation steps was one less, it could reduce the hydrogen loss the most as the providing purge was taken instead of the product purge and the step was carried out at the lowest intermediate pressure. Riboldi and Bolland (2016) applied a two-stage PSA configuration to an IGCC-derived syngas stream in which the first PSA train extracted high purity CO_2 and the second PSA train produced ultrapure H_2. They designed and simulated a first 7-bed, 12-step PSA cycle for capturing CO_2 and a second 6-bed, 13-step PSA cycle comprising three pressure equalisation steps and a providing purge step for purifying H_2. The simulated H_2 PSA cycle operated between 38.8 and 1.8 bar but unfortunately the authors did not provide information on the feed composition nor the achieved H_2 recovery.

Table 5 lists the performance of the Polybed H_2 PSA systems applied to syngas from H_2 plants, including both steam reforming and coal gasification, equipped with pre-combustion CO_2 capture from articles in the literature.

Configuration	No. beds on AD step	No. PE steps	Adsorbent	H_2 Recovery (%)	H_2 plant	Reference
6-bed, 15-step[a]	1	4	AC / 5A	74.1	SMR	Liu et al., 2020
6-bed, 10-step[b]	2	2		84.4		
6-bed, 13-step[b]	1	3	5A	86.3	IGCC	Luberti et al., 2014a
9-bed, 11-step[b]	3	3		91.9		
12-bed, 13-step[b]	3	4		92.7		
8-bed, 17-step[c]	2	4		86.6		
8-bed, 15-step[c]	2 / 3	3	AC / LiX	85.0	IGCC	Moon et al., 2018
8-bed, 15-step[c]	2 / 3	3		89.7		

[a] P_{ads} = 22 bar, P_{des} = 1 bar, Feed composition (mol%) $H_2/CO_2/CO/CH_4$ = 94.36/1.85/0.53/3.26
[b] P_{ads} = 34 bar, P_{des} = 1 bar, Feed composition (mol%) $H_2/CO_2/CO/N_2/Ar$ = 88.75/2.12/2.66/5.44/1.03
[c] P_{ads} = 35 bar, P_{des} = 1.1 bar, Feed composition (mol%) $H_2/CO_2/CO/N_2/Ar$ = 88.75/2.12/2.66/5.44/1.03

3.4 Engineering enhancements

As Polybed H_2 PSA systems increased in size and complexity over time, developments in control system, equipment, operation and maintenance have been instrumental to enable the improvements in the PSA technology. In particular, most of the engineering enhancements concerned the *stacked skid* that houses all automatic process switching valves, manual isolation valves, feed, product and tail gas piping as well as internal connection headers and local instrumentation, all of which are connected to the adsorbers (UOP, 2015). Since H_2 PSA units are integrated in refineries, chemical and petrochemical plants, they could be limited by their large product gas flow fluctuations. These fluctuations require sizeable storage or surge tanks to allow proper function of downstream process equipment connected to the PSA systems. Due to the multiple pressure equalisation steps embedded in the cycle, Polybed H_2 PSA systems are also subject to limitations in terms of high parts count. Not only this complexity significantly increases the probability of a component failure but it also significantly increases the system size, assembly time and material cost. To mitigate these issues, Lomax Jr. et al. (2005) developed a modular Polybed H_2 PSA system that facilitates the unit to be repaired while operating and reduces the flow pulsations through a system of feed and product manifolds (Figure 11a). The same invention also provided an apparatus to eliminate the bending moments at the adsorption bed end connections through an integral structural cover, including lateral panels and valve covers (Figure 11b). To improve the Polybed H_2 PSA operability and drastically reduce the valve inventory, Gittleman et al. (2005) proposed a system where the adsorbers are connected to a feed manifold, a product manifold and an exhaust manifold through suitable conduits, where the gas flows are controlled by a feed rotating valve and a product rotating valve. These rotary valve PSA systems have the advantage of being more simple, compact and quiet than conventional PSA systems equipped with a large number of pneumatically or electrically controlled valves. Rotary valve PSA systems also have the advantage of being able to operate with faster cycles, therefore enhancing the bed productivity. Specifically, the inventors presented in the patent a rotary feed valve with two feed gas ports

and two exhaust gas ports appropriately spaced (Figure 12a) and a rotary product valve with two product gas ports, eight equalisation ports and two purge gas ports appropriately spaced (Figure 12b), thus allowing the Polybed H_2 PSA to operate with all the conventional cycle step configurations (Gittleman et al., 2005). A further innovation in the Polybed H_2 PSA control system has been recently disclosed in relation to the remote monitoring of PSA processes, providing advanced alarm and asset management, and adjusting operating conditions to optimise in real time the PSA unit performance (Bjorklund et al., 2019). There are many process performance indicators that may be monitored, including flowrates, gas compositions, temperatures and pressures. In addition, valve operation may be monitored, including opening speed, closing speed and performance. In the patent it was claimed that the system may adjust one or multiple operating variables in real time to offset the difference between the actual operating performance and the optimal operating performance (Bjorklund et al., 2019).
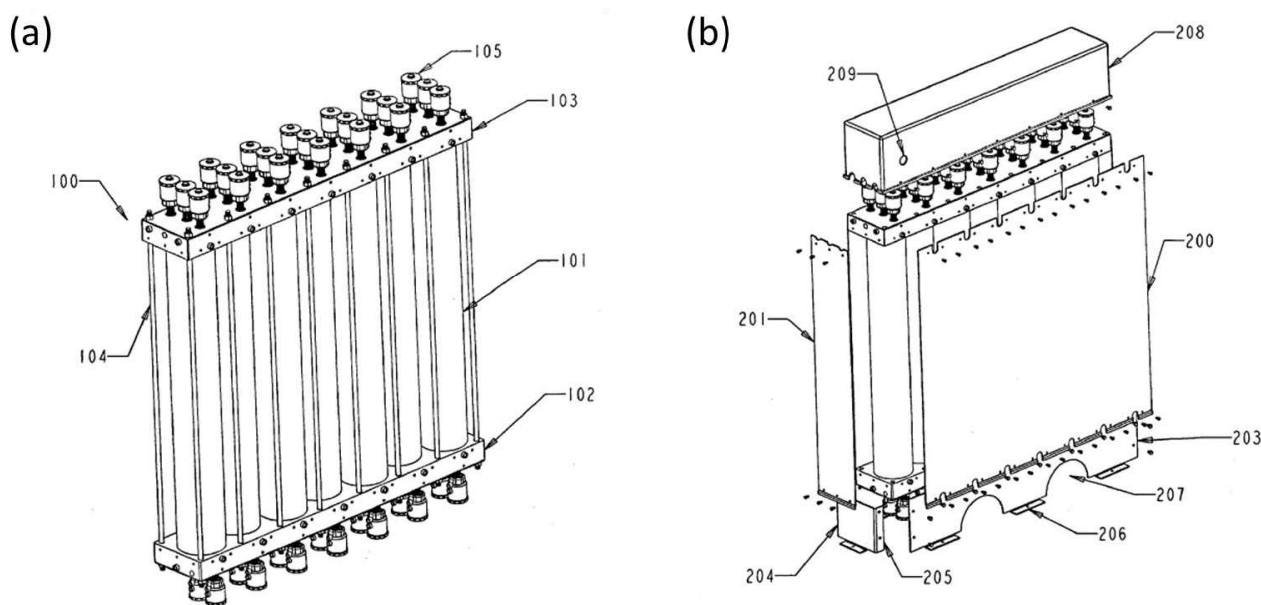
Figure 11: Modular Polybed H_2 PSA system with reduced flow pulsations showing: (a) adsorbers, valves, feed and product manifolds; (b) structural panels and valve covers (Lomax JR. et al., 2005)
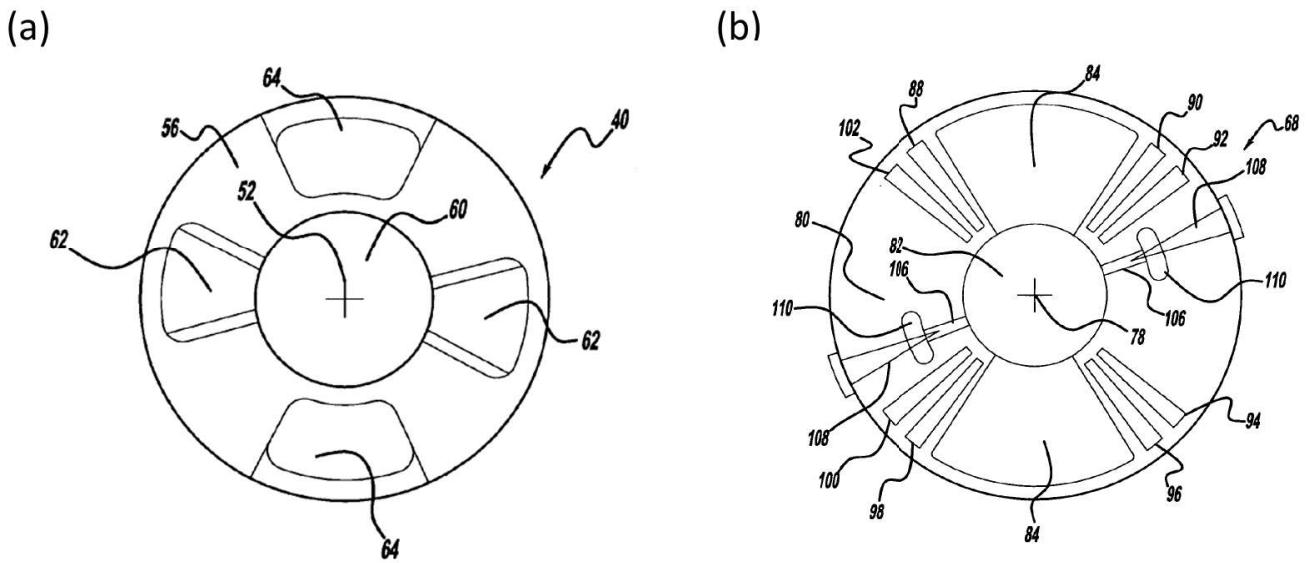
Figure 12: Plan view of (a) rotary feed valve and (b) rotary product valve in a Polybed H_2 PSA system (Gittleman et al., 2005)

3.5 Advanced mathematical modelling and optimization methods

Mathematical modelling is a powerful tool for understanding, designing and predicting process performance in the chemical industry, relying on the conservation of mass, momentum and energy. The simulation and optimization of adsorption processes are challenging, as they are intrinsically dynamic and subject to reverse flows during the cycle. To rigorously model such systems a set of stiff nonlinear partial differential equations (PDEs) and nonlinear algebraic equations (AEs) needs to be solved (Yang et al., 1987; Ruthven et al., 1994; Luberti and Ahn, 2021). In addition, adsorption cycles have to be simulated repetitively until the *cyclic steady state* (CSS) is achieved (Yang et al., 1987; Ruthven et al., 1994; Nilchan and Pantelides, 1998). Given this cyclic behaviour, the optimization of PSA processes requires a significant computational effort since a large variety of cycle steps and step times can be evaluated as decision variables as well as operating conditions and bed dimensions.

Among the formal optimization works focussing on H_2 PSA systems, Jiang et al. (2004) used a black box optimization approach to maximize the H_2 recovery of a 5-bed, 11 step PSA process designed to purify hydrogen from a conventional SMR effluent. Valve constants, step times, flowrates and bed geometry were selected as decision variables while H_2 purity and pressure specifications were set as constraints. The authors also implemented advanced mathematical tools to reduce the computational time, including a *unibed* approach equipped with storage buffers to mimic bed interactions and a Newton-based approach able to accelerate CSS convergence. Knaebel et al. (2005) and Huang et al. (2008) carried out optimization routines to purify hydrogen from a H_2/CH_4 mixture using a 1-bed, 4-step PSA cycle and activated carbon as an adsorbent. By varying adsorption pressure, purge time, feed and purge velocities, the system power requirement was minimized and the H_2 recovery was maximized at the same time, whilst keeping H_2 purity at 99.9+%.

To reduce the computational load of PSA optimization processes reduced-order or surrogate models have been proposed. These models can speed up the optimizations without compromising the accuracy since they are constructed using statistical techniques such as decision trees, Gaussian process regressions, artificial neural networks, response surface methodologies, etc. (Subraveti et al., 2019; Pai et al., 2020). In addition, surrogate modelling is data-driven as the statistical algorithms can be trained using data obtained from rigorous mathematical models or experiments. The selected machine-learning algorithms will also exhibit different training efforts, depending on the application (Subraveti et al., 2019; Pai et al., 2020).

In the context of H_2 PSA systems, Agarwal et al. (2009) developed a reduced-order model based on proper orthogonal decomposition and applied it to the optimization of a 2-bed, 4-step PSA process for the separation of hydrogen from methane. The reduced-order model successfully decreased the computational time while maximizing the H_2 recovery by manipulating operating pressures, step times, feed and purge velocities, and yet meeting the required H_2 purity. Zhang et al. (2021) used the Box–Behnken design, one of the popular response surface approaches, to optimize an activated carbon/5A zeolite layered 2-bed, 6-step PSA process for the purification of hydrogen from coke oven gas. Following the algorithm training, quadratic regressions were obtained for H_2 purity, H_2 recovery and bed productivity as a function of adsorption time, pressure equalization time and purge-to-feed ratio. The first attempt to apply a neural network to a H_2 PSA system designed to produce hydrogen from a natural gas cracked stream was reported by Sundaram (1999). The author discussed different machine-learning training sets and used the trained neural network to obtain the H_2 recovery of a 2-bed, 6-step PSA process as a regressed polynomial function of adsorption time, adsorption pressure, feed velocity and CO_2 feed composition. More recently, a few works successfully trained an artificial neural network algorithm through a detailed parametric study and used it to optimize various H_2 PSA units. Among them, Ye et al. (2019) studied a 2-bed, 4-step PSA to purify a SMR-based $H_2/CO_2/CO$ ternary mixture on a Cu-BTC adsorbent bed; Xiao et al. (2020) studied a 2-bed, 6-step PSA to purify a coke oven gas on an activated carbon/5A zeolite layered bed; and Yu et al. (2021) studied a 4-bed, 8-step PSA to purify a SMR effluent on an activated carbon/5A zeolite layered bed. All studies performed a tri-objective optimization to maximize H_2 purity, H_2 recovery and bed productivity simultaneously. Various decision variables were evaluated, including adsorption pressure, adsorption time, flowrates, carbon-to-zeolite ratio and purge-to-feed ratio. The conclusions demonstrated that it was feasible and cost-effective to find optimal operation parameters of the H_2 PSA process by machine-learning algorithms based on the artificial neural network (Ye et al., 2019; Xiao et al., 2020; Yu et al., 2021).

4. Co-production of H_2 and CO_2

The shifted syngas from steam reformers and coal gasifiers contains significant quantities of carbon dioxide, which, by appropriate design of the separation process, could be recovered as a by-product. Furthermore, concentrating a high purity CO_2 stream suitable for geological sequestration would allow to effectively decarbonise the H_2 plants, thus producing blue hydrogen. A specially designed Polybed PSA for

simultaneous production of ultrapure H_2 and high purity CO_2 from such a shifted syngas was developed by Air Products and Chemicals in 1979 (Sircar, 1979). The original configuration (Gemini-9) used 9 adsorption beds in a series-parallel arrangement (Figure 13), where 6 parallel beds contained NaX zeolite adsorbent for selective removal of H_2O and CO_2 from the feed gas (the *A beds*) while 3 parallel beds contained a mixture of NaX and 5A zeolite adsorbents for selective removal of CO, CH_4 and N_2 impurities from the hydrogen product (the *B beds*). Overall, the B beds went through two complete cycles while the A beds went through only one cycle so that each B bed handled the gas flow from two A beds during the complete cycle. A key feature is that the A and B beds were connected in series during the adsorption step but they were regenerated by two different sequences, including a high-pressure CO_2 rinse step for the A beds and a shared pressure equalisation step (Sircar and Kratz, 1988). According to experiments carried out in a pilot unit, the Gemini-9 process was able to produce ultrapure hydrogen (99.99+%) with a recovery of 87.1% when the adsorption pressure was set to 18 bar. The purity of the secondary CO_2 product was 99.4% with a recovery of 94.0% (Sircar and Kratz, 1988). Another advantage of the Gemini-9 process was that the CO_2 concentration in the off-gas was low (< 10%) so that this stream could be recycled as a more valuable fuel gas due to its higher lower heating value. The drawback of the process was also obvious, since CO_2 was produced during the evacuation step at sub-atmospheric pressure (0.13– 0.2 bar). In addition, the CO_2 stream needed to be recompressed to the adsorption pressure during the high-pressure rinse step, thus incurring in a considerable OPEX.
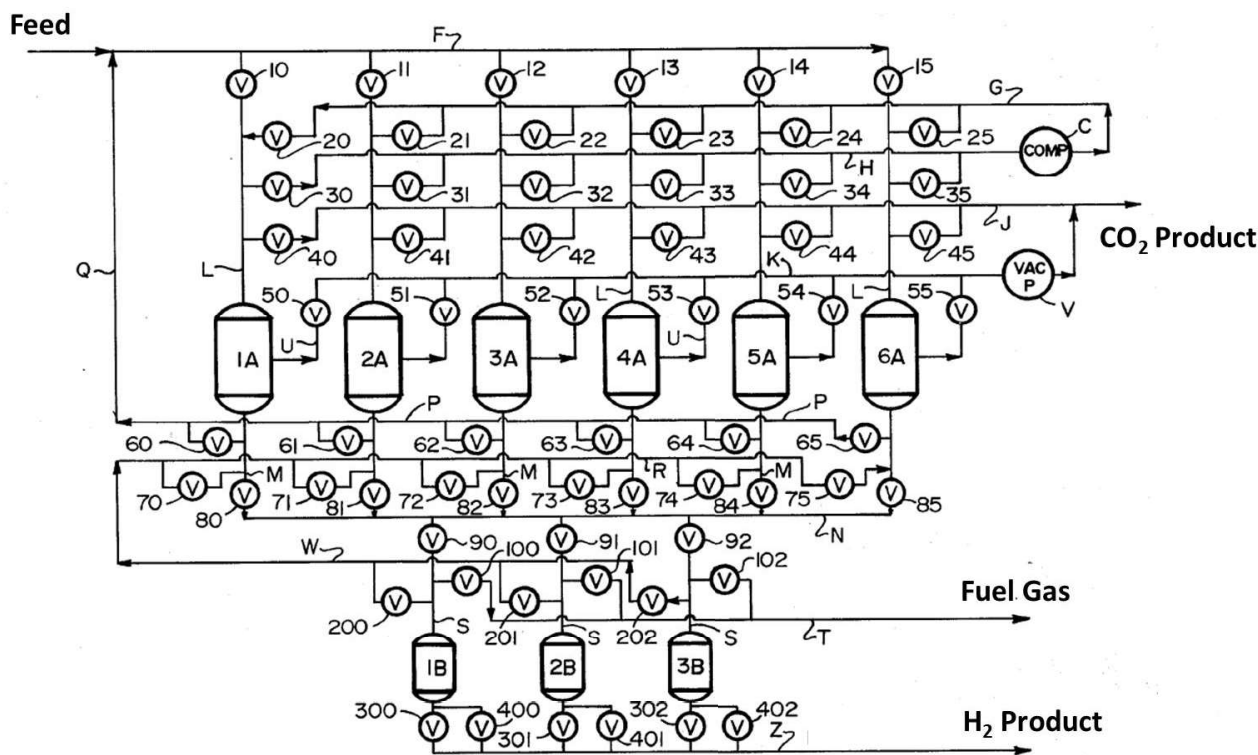

Figure 13: Flowsheet of the Gemini PSA process for simultaneous production of H_2 and CO_2 (Sircar, 1979)

Since the introduction of the original Gemini-9 process several improvements have been proposed to enhance the Polybed PSA performance and the overall unit economics. Among them, the Gemini-8 process featured 4 A beds and 4 B beds packed with the same adsorbents as in the Gemini-9 process. The main difference lied in the cycle configuration which lacked the high-pressure CO_2 rinse step in the A beds, thus reducing significantly the quantity of recycle gas that needed to be recompressed (Kumar, 1990). The elimination of one net bed along with 18 switch valves resulted in CAPEX savings as compared to the Gemini-9 process. An additional benefit was the elimination of a product surge tank required in the original configuration to balance the hydrogen product flowrate over the cycle. However, the savings in OPEX and CAPEX came with the sacrifice of H_2 recovery that was reduced from 87.1% to 86.0% as well as with poorer performance in relation to CO_2 purity (97.0+%) and CO_2 recovery (86.0%) (Kumar et al., 1992). About 10 years after developing the Gemini-9 process, Sircar (1988) disclosed a novel Polybed PSA configuration (Gemini-11) having 6 A beds, 3 B beds and additional 2 C beds for further recovery of hydrogen product from a tertiary fuel gas product stream. This stream, in fact, contained over 60% of hydrogen that could be purified by selective adsorption of impurities. By employing a Skarstrom cycle over the C beds and packing them with a mixture of NaX and 5A zeolite adsorbents, it was claimed that that overall H_2 recovery of the unit could be increased from 87.1% to 95.2%. The performance of CO_2 purity and CO_2 recovery remained unchanged compared to the Gemini-9 process (Sircar, 1988). Another idea to improve the Gemini-9 process was proposed by Kumar and Kratz (1992) by incorporating in both A and B bed cycle configurations a new pressure equalisation step where an A bed was partially repressurised after undergoing the evacuation step by a gas discharged by a B bed before undergoing the blowdown step. Although the feed composition was different than that used in the original process, it was claimed that the H_2 recovery could be improved by two percentage points over the original process (Kumar and Kratz, 1992).

More recently, the co-production of high purity H_2 and CO_2 has been assessed through a single Polybed VPSA process rather than the two trains of the Gemini process by Streb et al. (2019). The basic configuration of the Polybed VPSA system involved 7–10 adsorption beds having a cycle with 3–4 pressure equalisation steps and a high-pressure rinse step. In a follow up paper the same research group applied this novel VPSA process to different syngas feeds at 25 bar from typical steam reforming and autothermal reforming plants (Streb and Mazzotti, 2020). Through process modelling and optimisation, it was reported that three cycle configurations could achieve H_2 purity levels of 99.90% and 99.97% with H_2 recovery above 90%, whilst recovering more than 90% of CO_2 with a purity greater than 96%. Furthermore, as the minimum energy consumption required for the separation was in the range of 300–500 kJ kg_{CO2}^{-1}, the Polybed VPSA process compared well to the state of the art of carbon capture technologies, exhibiting similar energy requirements as the liquid absorption process using a piperazine (PZ)/methyldiethanolamine (MDEA) solution and up to twice higher unit productivity.

A comparison of Polybed PSA system performance applied to H_2 plants for co-production of H_2 and CO_2 is summarised in Table 6.

Table 6: Performance of Polybed PSA applied to H$_2$ plants for co-production of H$_2$ and CO$_2$ from articles and patents in the literature (*AD* adsorption, *PE* pressure equalisation)

Configuration	No. beds on AD step	No. PE steps	Adsorbent	H$_2$ Purity (%)	H$_2$ Recovery (%)	CO$_2$ Purity (%)	CO$_2$ Recovery (%)	Reference
A: 6-bed, 6-step[a] B: 3-bed, 7-step[a]	A: 1 B: 1	A: 1 B: 1+1	A: NaX B: NaX / 5A	99.99+	87.1	99.4	94.0	Sircar and Kratz, 1988
A: 4-bed, 5-step[b] B: 4-bed, 7-step[b]	A: 1 B: 1	A: 1 B: 1+1	A: NaX B: NaX / 5A	99.99+	86.0	97.0+	86.0	Kumar et al., 1992
A: 6-bed, 6-step[c] B: 3-bed, 7-step[c] C: 2-bed, 4-step[c]	A: 1 B: 1 C: 1	A: 1 B: 1+1 C: 0	A: NaX B: NaX / 5A C: NaX / 5A	99.99+	95.2	99.4	94.0	Sircar, 1988
9-bed, 12-step[d]	1	3	13X	99.90	90.0+	96.0+	90.0+	Streb and Mazzotti, 2020
10-bed, 12-step[d]	1	3		99.97	90.0+	96.0+	90.0+	

[a] Gemini-9, P$_{ads}$ = 18 bar, P$_{des}$ = 0.13–0.20 bar, Feed composition (mol%) H$_2$/CO$_2$/CH$_4$/CO = 75.4/19.9/3.73/0.96
[b] Gemini-8, P$_{ads}$ = 18 bar, P$_{des}$ = 0.13–0.20 bar, Feed composition (mol%) H$_2$/CO$_2$/CH$_4$/CO = 75.4/19.9/3.73/0.96
[c] Gemini-11, P$_{ads}$ = 18 bar, P$_{des}$ = 0.13–0.20 bar, Feed composition (mol%) H$_2$/CO$_2$/CH$_4$/CO = 75.4/19.9/3.73/0.96
[d] VPSA, P$_{ads}$ = 25 bar, P$_{des}$ = 0.1 bar, Feed composition (mol%) H$_2$/CO$_2$/CH$_4$/CO/N$_2$ = 75.81/16.31/3.03/4.65/0.2

5. Integration with industrial clusters

As already mentioned, environmental restrictions, new transportation fuel specifications and increased processing of heavier and sourer crude oils are leading to a substantial increase of hydrogen consumption in the refining, chemical and petrochemical industries. In addition, the development of a hydrogen economy is prompting the use of hydrogen in novel and hard-to-abate emission sectors, including transport, heating and power generation. Therefore, in the last two decades the management of hydrogen networks across the industrial clusters has become a critical issue. The optimization of hydrogen distribution networks is intrinsically related to the recovery of hydrogen from refinery off-gases and waste streams, which is mainly carried out by Polybed H$_2$ PSA units (Liao et al., 2016; Li et al., 2020).

Typical design process methods to optimize hydrogen networks involve pinch analysis techniques and superstructure-based mathematical programming approaches. Alves and Towler (2002) proposed for the first time the concept of hydrogen pinch to analyse hydrogen distribution systems by setting targets for the minimum purity and flowrate of fresh hydrogen required. This method allowed to find the optimal placement of H$_2$ PSA units and provided valuable theoretical insights into the impact of hydrogen purification on the performance of hydrogen networks. The hydrogen pinch technique was further refined by Ding et al. (2011) who optimized a refinery hydrogen network taking also into account pressure constraints and finding the optimal placement of compression equipment. Foo and Manan (2006) systematically assessed multiple-pinch problems and the appropriate selection of hydrogen purification techniques using a novel cascade analysis for a utility hydrogen network.

Superstructure- based mathematical methods have also been employed to optimally integrate H$_2$ PSA units into hydrogen networks. Hallale and Liu (2001) first used this method to maximize the H$_2$ recovery

across an industrial site. They also discussed in detail the optimal placement of H_2 PSA units and compressors to provide significant economic and environmental benefits. Among the studies focussing on the retrofit of refinery hydrogen networks, Liao et al. (2010) used a systematic approach to develop multiple hydrogen structure possibilities for the optimal placement of H_2 PSA units by means of short-cut models. A case study demonstrated that the proposed methodology could achieve a reduction of 22.8% in the total annual cost of the refinery hydrogen network. Deng et al. (2020) developed a combined hydrogen pinch analysis and super-structure modelling approach to optimize a hydrogen network integrated with a light hydrocarbon recovery process. H_2 PSA was found to be the key unit to upgrade the refinery off-gases. For new refinery hydrogen networks, Liao et al. (2016) rigorously assessed the influence of the design parameters of H_2 PSA units such as adsorbent selectivity and pressure ratio. It was found that they had a much stronger influence on the performance of the hydrogen network compared to other network parameters. Li et al. (2020) used a surrogate-modelling technique to design simultaneously hydrogen distribution networks and H_2 PSA units and found optimal design parameters for both structures. The overall total annual cost of the refinery hydrogen network decreased by 19% compared to the base case. As regards hydrogen networks in petrochemical complexes, Jeong and Han (2011) presented a hydrogen recycling network to optimize the use of by-product hydrogen, which otherwise would be used as a fuel. By appropriate design of six H_2 PSA units it was confirmed that the economic profits could increase by 7.4%.

The above studies all focussed on the intra-plant hydrogen network level but, more recently, integration of inter-plant hydrogen networks has also drawn attention. Deng et al. (2017) proposed a novel super-structure for the optimal design of inter-plant hydrogen networks in a petrochemical complex, including a fertilizer plant and an ethylene plant. By incorporating a short-cut model for the H_2 PSA unit in the optimization framework, the H_2 recovery could be related to pressure ratio, adsorbent selectivity and feed composition. Following an assessment of the impacts of design conditions of the PSA process on the network performance, the total annual cost was reduced by 18.1% compared to the base case. Lou et al. (2019) developed a novel two-step method that combined hydrogen pinch analysis and mathematical programming to optimize an inter-plant network with a shared H_2 PSA unit. Both flowrate of hydrogen utilities and total annualized cost were minimized along with the number of inter-plant connections. Eventually, Deng et al. (2019) designed and assessed a refinery hydrogen network integrated with a shared H_2 PSA unit in a hydrogen production plant. After the optimization of the network, results showed that the integrated configuration could successfully reduce both flowrate of hydrogen utilities and raw material consumption for the H_2 plant.

6. Conclusions

This paper systematically reviewed for the first time the Polybed H_2 PSA process, regarded as the most techno-economically feasible technology for producing ultrapure hydrogen (99.99+%) with high throughputs (> 240 MMSCFD) and high recoveries (> 90%). Hydrogen is a key feedstock for conventional

refining, chemical and petrochemical processes and a versatile energy carrier, making it an efficient fuel source for the future low-carbon transport, heating and power generation sectors.

H_2 PSA units have been designed to purify different types of H_2-rich feedstock through the selection of adsorbents, often packed in layered beds, which optimize the working capacity and selectivity of hydrogen over the impurities. However, besides the adsorbents, it was shown that PSA processes could be enhanced by appropriately designing the type and the sequence of steps in the cycle scheduling. To increase H_2 throughput and H_2 recovery several methods were proposed including the use of multiple bed systems, multiple pressure equalisation steps, a providing purge step and multiple beds on adsorption step simultaneously. As a result, the Polybed H_2 PSA system was the perfect embodiment of all these strategies, having seven to sixteen beds and a cycle configuration incorporating at least three pressure equalisation steps and two adsorbing beds at the same time. Over the decades, Polybed H_2 PSA systems have been improved in terms of process economics through more advanced configurations and cycle schedules as well as enhanced unit equipment, operation, maintenance and control.

Although Polybed H_2 PSA units have been traditionally applied to steam reformer effluents and refinery off-gases, there have been recent studies on their application to H_2 plants equipped with pre-combustion carbon capture technologies such as SMR and IGCC plants. Furthermore, in the effort to combat climate change, a specially designed Polybed PSA process could also be deployed to treat shifted syngas streams in order to produce blue H_2 with CO_2 capture. Once the major barriers hindering the hydrogen economy will be solved, i.e., the high costs of producing low-carbon hydrogen and the development of hydrogen infrastructures, the Polybed H_2 PSA systems of the future will feature even higher performances and will be better integrated in the industrial clusters.

References

Aasadnia, M., Mehrpooya, M., Ghorbani, B.: A novel integrated structure for hydrogen purification using the cryogenic method. Journal of Cleaner Production 278, 123872 (2021)

Abe, J.O., Popoola A.P.I., Ajenifuja, E., Popoola, O.M.: Hydrogen energy, economy and storage: Review and recommendation. International Journal of Hydrogen Energy 44, 15072–15086 (2019)

Acar, C., Dincer, I.: The potential role of hydrogen as a sustainable transportation fuel to combat global warming. International Journal of Hydrogen Energy 45, 3396–3406 (2020)

Agahzamin, S., Mirvakili, A., Rahimpour, M.R.: Investigation and recovery of purge gas streams to enhance synthesis gas production in a mega methanol complex. Journal of CO_2 Utilization 16, 157–168 (2016)

Agarwal, A., Biegler, L.T., Zitney, S.E.: Simulation and optimization of pressure swing adsorption systems using reduced-order modelling. Ind. Eng. Chem. Res. 48, 2327–2343 (2009)

Ahn, H., Yang, J., Lee, C.-H.: Effects of feed composition of coke oven gas on a layered bed H_2 PSA process. Adsorption 7, 339–356 (2001)

Ahn, S., You, Y.-W., Lee, D.-G., Kim, K.-H., Oh, M., Lee, C.-H.: Layered two- and four-bed PSA processes for H_2 recovery from coal gas. Chemical Engineering Science 68, 413–423 (2012)

Air Liquide: Hydrogen membrane overview (2021). Available at https://www.airliquideadvancedseparations.com/our-membranes/hydrogen

Air Products: PRISM® membrane systems for petrochemical applications (2015). Available at https://www.airproducts.com/-/media/airproducts/files/en/523/523-15-015-glb-prism-membrane-systems-for-petrochemical-applications.pdf?la=en&hash=06C6AF0D51299DFE61161F009C06E026#:~:text=PRISM%20Membrane%20Systems%20recover%20hydrogen,from%20high%2Dpressure%20petrochemical%20streams.

Air Products: Recovering hydrogen − and profits − from hydrogen-rich offgas (2018a). Available at https://www.airproducts.com/-/media/airproducts/files/en/312/312-18-002-us-recovering-hydrogen-and-profits-from-hydrogen-rich-offgas.pdf

Air Products: Hydrogen PSA Technology (2018b). Available at: https://www.airproducts.co.uk/equipment/psa-hydrogen-purification

Al-Mufachi, N.A., Rees, N.V., Steinberger-Wilkens, R.: Hydrogen selective membranes: A review of palladium-based dense metal membranes. Renewable and Sustainable Energy Reviews 47, 540–551 (2015)

Al-Naddaf, Q., Thakkar, H., Rezaei, F.: Novel zeolite-5A@MOF-74 composite adsorbents with core−shell structure for H_2 purification. ACS Appl. Mater. Interfaces 10, 29656–29666 (2018)

Alves, J.J., Towler, G.P.: Analysis of refinery hydrogen distribution systems. Ind. Eng. Chem. Res. 41, 5759–5769 (2002)

Anwar, S., Khan, F., Zhang, Y., Djire, A.: Recent development in electrocatalysts for hydrogen production through water electrolysis. International Journal of Hydrogen Energy 46, 32284–32317 (2021)

Baksh, M.S.A., Simo, M.: Six bed pressure swing adsorption process operating in normal and turndown modes. US Patent 8491704 B2 to Praxair Technology, Inc. (2013a)

Baksh, M.S.A., Simo, M.: Large scale pressure swing adsorption systems having process cycles operating in normal and turndown modes. US Patent 8496733 B2 to Praxair Technology, Inc. (2013b)

Ball, M., Weeda, M.: The hydrogen economy e Vision or reality? International Journal of Hydrogen Energy 40, 7903–7919 (2015)

Banu, A.-M., Friedrich, D., Brandani, S., Duren, T.: A multiscale study of MOFs as adsorbents in H_2 PSA purification. Industrial and Engineering Chemistry Research 52, 9946–9957 (2013)

Barthelemy, H., Weber, M., Barbier, F.: Hydrogen storage: Recent improvements and industrial perspectives. International Journal of Hydrogen Energy 42, 7254–7262 (2017)

Batta, L.B.: Selective adsorption process. US Patent 3564816 to Union Carbide Corporation (1971)

Benkmann, C.: Pressure swing adsorption process. US Patent 4371380 to Linde Aktiengesellschaft (1983)

Bjorklund, C.E., Kelley, S., Guenther, J., McCool, R.: Remote monitoring of pressure swing adsorption units. WO 2019/055993 A1 to UOP LLC (2019)

Blanco, H., Nijs, W., Ruf, J., Faaij, A. : Potential for hydrogen and Power-to-Liquid in a low-carbon EU energy system using cost optimization. Applied Energy 232, 617–639 (2018)

Bockris, J.O.M.: The hydrogen economy: Its history. International Journal of Hydrogen Energy 38, 2579–2588 (2013)

Boucheffa, Y., Joly, G., Magnoux, P., Guisnet, M., Jullian, S.: Origin of deactivation of 5A adsorbents during the separation of n and isoalkanes. Studies in Surface Science and Catalysis 139, 367–374 (2001)

Brea, P., Delgado, J.A., Agueda, V.I., Gutierrez, P., Uguina, M.A.: Multicomponent adsorption of H_2, CH_4, CO and CO_2 in zeolites NaX, CaX and MgX. Evaluation of performance in PSA cycles for hydrogen purification. Microporous and Mesoporous Materials 286, 187–198 (2019a)

Brea, P., Delgado, J.A., Agueda, V.I., Uguina, M.A.: Comparison between MOF UTSA-16 and BPL activated carbon in hydrogen purification by PSA. Chemical Engineering Journal 355, 279–289 (2019b)

Cappelletti, A., Martelli, F.: Investigation of a pure hydrogen fueled gas turbine burner. International Journal of Hydrogen Energy 42, 10513–10523 (2017)

Dawood, F., Anda, M., Shafiullah, G.M.: Hydrogen production for energy: An overview. International Journal of Hydrogen Energy 45, 3847–3869 (2020)

Deng, C., Zhou, Y., Jiang, W., Feng, X.: Optimal design of inter-plant hydrogen network with purification reuse/recycle. International Journal of Hydrogen Energy 42, 19984–20002 (2017)

Deng, C., Liu, J., Zhou, Y., Feng, X.: Design of hydrogen network integrated with the shared purifier in hydrogen production plant. Ind. Eng. Chem. Res. 58, 10466–10481 (2019)

Deng, C., Zhu, M., Liu, J., Feng, X.: Systematic retrofit method for refinery hydrogen network with light hydrocarbons recovery. International Journal of Hydrogen Energy 45, 19391–19404 (2020)

Ding, Y., Feng, X., Chu, K.H.: Optimization of hydrogen distribution systems with pressure constraints. Journal of Cleaner Production 19, 204–211 (2011)

Dobladez, J.A.D., Mate', V.I.A., Torrellas, S.A., Larriba, M., Brea, P. Efficient recovery of syngas from dry methane reforming product by a dual pressure swing adsorption process. International Journal of Hydrogen Energy 46, 17522–17533 (2021)

DOE NETL: Wabash River coal gasification repowering project: A DOE assessment (2002). Available at https://www.osti.gov/biblio/790376-wabash-river-coal-gasification-repowering-project-doe-assessment

DOE NETL: Cost and performance baseline for fossil energy plants (2010). Available at https://www.nrc.gov/docs/ML1327/ML13274A052.pdf

Dou, Y., Sun, L., Ren, J., Dong, L.: Opportunities and future challenges in hydrogen economy for sustainable development. Hydrogen Economy, Chapter 10, 277–305 (2017)

Ducrot-Boisgontier, C., Parmentier, J., Faour, A., Patarin, J., Pirngruber, G.D.: FAU-type zeolite nanocasted carbon replicas for CO_2 adsorption and hydrogen purification. Energy Fuels 24, 3595–3602 (2010)

Du, Z., Liu, C., Zhai, J., Guo, X., Xiong, Y., Su, W., He, G.: A review of hydrogen purification technologies for fuel cell vehicles. Catalysts 11, 393 (2021)

Ebner, A.D., Mehrotra, A., Ritter, J.A.: Graphical approach for complex PSA cycle scheduling. Adsorption 15, 406–421 (2009)

Foo, D.C.Y., Manan, Z.A.: Setting the minimum utility gas flowrate targets using cascade analysis technique. Ind. Eng. Chem. Res. 45, 5986–5995 (2006)

Forzatti, P., Lietti, L.: Catalyst deactivation. Catalysis Today 52, 165–181 (1999)

Fuderer, A., Rudelstorfer, E.: Selective adsorption process. US Patent 3986849 to Union Carbide Corporation (1982)

Fuderer, A.: Two-feed pressure swing adsorption process. US Patent 4333744 to Union Carbide Corporation (1976)

Gittleman, C.S., Appel, W.S., Winter, D.P., Sward, B.K.: Hydrogen purification process using pressure swing adsorption for fuel cell applications. US Patent 2005/0098034 A1 to General Motors Corporation (2005)

Global Patent Index (2021). Available at https://www.epo.org/searching-for-patents/technical/espacenet/gpi.html

Gonzales, E.L., Llerena, F.I., Perez, M.S., Iglesias, F.R., Macho, J.G.: Energy evaluation of a solar hydrogen storage facility: Comparison with other electrical energy storage technologies. International Journal of Hydrogen Energy 40, 5518–5525 (2015)

Grande, C.A.: PSA technology for H_2 separation. Hydrogen Science and Engineering: Materials, Processes, Systems and Technology, First Edition. Wiley-VCH, Weinheim (2016)

Grimm, A., de Jong, W.A., Jan Kramer, G.: Renewable hydrogen production: A technoeconomic comparison of photoelectrochemical cells and photovoltaic-electrolysis. International Journal of Hydrogen Energy 45, 22545–22555 (2020)

Guisnet, M., Magnoux, P., Martin, D.: Roles of acidity and pore structure in the deactivation of zeolites by carbonaceous deposits. Studies in Surface Science and Catalysis 111, 1–19 (1997)

Gurz, M., Baltacioglu, E., Hames, Y., Kaya, K.: The meeting of hydrogen and automotive: A review. International Journal of Hydrogen Energy 42, 23334–23346 (2017)

Hallale, N., Liu, F.: Refinery hydrogen management for clean fuels production. Advances in Environmental Research 6, 81–98 (2001)

Hardman, S., Tal, G.: Who are the early adopters of fuel cell vehicles? International Journal of Hydrogen Energy 43, 17857–17866 (2018)

He, B., Liu, J., Zhang, Y., Zhang, S., Wang, P., Xu, H.: Comparison of structured activated carbon and traditional adsorbents for purification of H_2. Separation and Purification Technology 239, 116529 (2020)

Hong, S.-H., Chung, K., Bang, G., Kim, K.-M., Lee, C.-H.: Adsorption equilibria and kinetics of CO_2, CH_4, CO, N_2, and H_2 on KOH-treated activated carbon pellets up to 1000 kPa. Chemical Engineering Journal, https://doi.org/10.1016/j.cej.2021.133396 (2021)

Huang, Q., Malekian, A., Eic, M.: Optimization of PSA process for producing enriched hydrogen from plasma reactor gas. Separation and Purification Technology 62, 22–31 (2008)

IEA: Techno-Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CSS (2017). Available at https://ieaghg.org/component/content/article/49-publications/technical-reports/784-2017-02-smr-based-h2-plant-with-ccs

IEA: The Future of Hydrogen (2019). Available at https://www.iea.org/reports/the-future-of-hydrogen

IEA: Net Zero by 2050 (2021). Available at https://www.iea.org/reports/net-zero-by-2050

IPCC: Climate Change and Land (Special Report) (2020). Available at https://www.ipcc.ch/srccl/

Iyuke, S.E., Daud, W.R.W., Mohamed, A.B., Kadhum, A.A.H., Fisal, Z., Shariff, A.M.: Application of Sn-activated carbon in pressure swing adsorption for purification of H_2. Chemical Engineering Science 55, 4745–4755 (2000)

Jamali, S., Mofarahi, M., Rodrigues, A.E.: Investigation of a novel combination of adsorbents for hydrogen purification using Cu-BTC and conventional adsorbents in pressure swing adsorption. Adsorption 24, 481–498 (2018)

Jeong, C., Han, C.: Byproduct hydrogen network design using pressure swing adsorption and recycling unit for the petrochemical complex. Ind. Eng. Chem. Res. 50, 3304–3311 (2011)

Jiang, L., Fox, V.G., Biegler, L.T.: Simulation and optimal design of multiple-bed pressure swing adsorption systems. AIChE Journal 50, 2904–2917 (2004)

Knaebel, S., Ko, D., Biegler, L.T.: Simulation and optimization of a pressure swing adsorption system: recovering hydrogen from methane. Adsorption 11, 615–620 (2005)

Koç, Y., Yagli, H., Gorgulu, A., Koç, A.: Analysing the performance, fuel cost and emission parameters of the 50 MW simple and recuperative gas turbine cycles using natural gas and hydrogen as fuel. International Journal of Hydrogen Energy 45, 22138–22147 (2020)

Krishna, R., Long, J.R.: Screening metal organic frameworks by analysis of transient breakthrough of gas mixtures in a fixed bed adsorber. Journal of Physical Chemistry C 115, 12941–12950 (2011)

Kumar, R.: Adsorption process for recovering two high purity gas products from multicomponent gas mixture. US Patent 4913709 to Air Products and Chemicals, Inc. (1990)

Kumar, R., Kratz, W.C.: Separation of multicomponent gas mixtures by selective adsorption. US Patent 5133785 to Air Products and Chemicals, Inc. (1992)

Kumar, R., Kratz, W.C., Guro, D.E., Rarig, D.L., Schmidt, W.P.: Gas mixture fractionation to produce two high purity products by pressure swing adsorption. Separation Science and Technology, 27, 509–522 (1992)

Li, P., Wang, Z., Qiao, Z., Liu, Y., Cao, X., Li, W., Wang, J., Wang, S.: Recent developments in membranes for efficient hydrogen purification. Journal of Membrane Science 495, 130–168 (2015)

Li, B., He, G., Jiang, X., Dai, Y., Ruan, X.: Pressure swing adsorption/membrane hybrid processes for hydrogen purification with a high recovery. Front. Chem. Sci. Eng. 10, 255–264 (2016)

Li, H., Liao, Z., Sun, J., Jiang, B., Wang, J., Yang, Y.: Simultaneous design of hydrogen allocation networks and PSA inside refineries. Ind. Eng. Chem. Res. 59, 4712–4720 (2020)

Liao, Z., Wang, J., Yang, Y., Rong, G.: Integrating purifiers in refinery hydrogen networks: a retrofit case study. Journal of Cleaner Production 18, 233–241 (2010)

Liao, Z., Tu, G., Lou, J., Jiang, B., Wang, J., Yang, Y.: The influence of purifier models on hydrogen network optimization: Insights from a case study. International Journal of Hydrogen Energy 41, 5243–5249 (2016)

Linde: Hydrogen extraction from hydrogen blended natural gas (2021). Available at https://www.technologieland-hessen.de/mm///mm001/02_Purrucker_Linde.pdf

Liu, Y., Xu, J., Jin, L., Fang, Y., Hu, H.: Synthesis and modification of zeolite NaA adsorbents for separation of hydrogen and methane. Asia-Pac. J. Chem. Eng. 4: 666–671 (2009)

Liu, B., Yu, X., Shi, W., Shen, Y., Zhang, D., Tang, Z.: Two-stage VSA/PSA for capturing carbon dioxide (CO_2) and producing hydrogen (H_2) from steam methane reforming gas. International Journal of Hydrogen Energy 45, 24870–24882 (2020)

Lomax Jr., F.D., Hickman, T., Lettow, J.S., Streeks, M., Prasad, V.: Modular pressure swing adsorption process and apparatus. US Patent 2005/0005771 A1 to H2Gen Innovations, Inc. (2005)

Lopes, F.V.S., Grande, C.A., Ribeiro, A.M., Loureiro, J.M., Evaggelos, O., Nikolakis, V., Rodrigues, A.E.: Adsorption of H_2, CO_2, CH_4, CO, N_2 and H_2O in activated carbon and zeolite for hydrogen production. Separation Science and Technology 44, 1045–1073 (2009)

Lopes, F.V.S., Grande, C.A., Ribeiro, A.M., Vilar, V.J.P., Loureiro, J.M., Rodrigues, A.E.: Effect of ion exchange on the adsorption of steam methane reforming off-gases on zeolite 13X. Journal of Chemical Engineering Data 55, 184–195 (2010)

Lopes, F.V.S., Grande, C.A., Rodrigues, A.E.: Activated carbon for hydrogen purification by pressure swing adsorption: multicomponent breakthrough curves and PSA performance. Chemical Engineering Science 66, 303–317 (2011)

Lou, Y., Liao, Z., Sun, J., Jiang, B., Wang, J., Yang, Y.: A novel two-step method to design inter-plant hydrogen network. International Journal of Hydrogen Energy 44, 5686–5695 (2019)

Luberti, M., Friedrich, D., Brandani, S., Ahn, H.: Design of a H_2 PSA for cogeneration of ultrapure hydrogen and power at an advanced integrated gasification combined cycle with pre-combustion capture. Adsorption 20, 511–524 (2014a)

Luberti, M., Friedrich, D., Ozcan, D.C., Brandani, S., Ahn, H.: A novel strategy to produce ultrapure hydrogen from coal with pre-combustion carbon capture. Energy Procedia 63, 2023–2030 (2014b)

Luberti, M., Kim, Y.H., Lee, C.H., Ferrari, M.C., Ahn, H.: New momentum and energy balance equations considering kinetic energy effect for mathematical modelling of a fixed bed adsorption column. Adsorption 21, 353–363 (2015)

Luberti, M., Oreggioni, G.D., Ahn, H.: Design of a rapid vacuum pressure swing adsorption process for post-combustion CO_2 capture from a biomass-fuelled CHP plant. Journal of Environmental Chemical Engineering 5, 3973–3982 (2017)

Luberti, M., Ahn, H.: Design of an industrial multi-bed (V)PSA unit for argon concentration. Separation and Purification Technology 261, 118254 (2021)

Maestre, V.M., Ortiz, A., Ortiz, I.: Challenges and prospects of renewable hydrogen-based strategies for full decarbonization of stationary power applications. Renewable and Sustainable Energy Reviews 152, 111628 (2021)

Malek, A., Farooq, S.: Study of a six-bed pressure swing adsorption process. AIChE Journal 43, 2509–2523 (1997)

Malek, A., Farooq, S.: Hydrogen purification from refinery fuel gas by pressure swing adsorption. AIChE Journal 44, 1985–1992 (1998)

Maurer, R.T.: Pressure swing adsorption process with multiple desorption steps. US Patent 5203888 to UOP (1993)

Mehrotra, A., Ebner, A.D., Ritter, J.A.: Arithmetic approach for complex PSA cycle scheduling. Adsorption 16, 113–126 (2010)

Meng, Z., Lu, R., Rao, D., Kan, E., Xiao, C., Deng, K.: Catenated metal-organic frameworks: Promising hydrogen purification materials and high hydrogen storage medium with further lithium doping. International Journal of Hydrogen Energy 38, 9811–9818 (2013)

Moliner, R., Lazaro, M.J., Suelves, I.: Analysis of the strategies for bridging the gap towards the Hydrogen Economy. International Journal of Hydrogen Energy 41, 19500–19508 (2016)

Moon, D.-K., Park, Y., Oh, H.-T., Kim, S.-H., Oh, M., Lee, C.-H.: Performance analysis of an eight-layered bed PSA process for H_2 recovery from IGCC with pre-combustion carbon capture. Energy Conversion and Management 156, 202–214 (2018)

Mora, C., Frazier, A., Longman, R. et al.: The projected timing of climate departure from recent variability. Nature 502, 183–187 (2013)

Meyers, R.A.: Handbook of petroleum refining processes 3rd Edition. McGraw-Hill, New York (2004)

NASA (2019). Available at https://climate.nasa.gov/news/2915/the-atmosphere-getting-a-handle-on-carbon-dioxide/

Nikolic, D., Kikkinides, E.S., Georgiadis, M.C.: Optimization of multibed pressure swing adsorption processes. Industrial and Engineering Chemistry Research 48, 5388–5398 (2009)

Nikolic, D.D., Kikkinides, E.S.: Modelling and optimization of hybrid PSA/membrane separation processes. Adsorption 21, 283–305 (2015)

Nilchan, S., Pantelides, C.C.: On the optimisation of periodic adsorption processes. Adsorption 4, 113–147 (1998)

Oliveira, A.M., Beswick, R.R., Yan, Y.: A green hydrogen economy for a renewable energy society. Current Opinion in Chemical Engineering 33, 100701 (2021)

Oreggioni, G.D., Luberti, M., Reilly, M., Kirby, M.E., Toop, T., Theodorou, M., Tassou, S.A.: Techno-economic analysis of bio-methane production from agriculture and food industry waste. Energy Procedia 123, 81–88 (2017)

Pacala, S., Socolow, R.: Stabilization wedges: Solving the climate problem for the next 50 years with current technologies. Science 305, 968–972 (2004)

Pai, K.N., Prasad, V., Rajendran, A.: Experimentally validated machine learning frameworks for accelerated prediction of cyclic steady state and optimization of pressure swing adsorption processes. Separation and Purification Technology 241, 116651 (2020)

Park, J.-H., Kim, J.-D., Yang, R.T.: Adsorber dynamics and optimal design of layered beds for multicomponent gas adsorption. Chemical Engineering Science 53, 3951–3963 (1998)

Relvas, F., Whitley, R.D., Silva, C., Mendes, A.: Single-stage pressure swing adsorption for producing fuel cell grade hydrogen. Industrial and Engineering Chemistry Research 57, 5106–5118 (2018)

Ribeiro, A.M., Grande, C.A., Lopes, F.V.S., Loureiro, J.M., Rodrigues, A.E.: A parametric study of layered bed PSA for hydrogen purification. Chemical Engineering Science 63, 5258–5273 (2008)

Riboldi, L., Bolland, O.: Pressure swing adsorption for coproduction of power and ultrapure H_2 in an IGCC plant with CO_2 capture. International Journal of Hydrogen Energy 41, 10646–10660 (2016)

Ruthven, D.M.: Principles of adsorption and adsorption processes. Wiley, New York (1984)

Ruthven, D.M., Farooq, S., Knaebel, K.S.: Pressure swing adsorption. VCH Publishers, New York (1994)

Shi, W., Yang, H., Shen, Y., Fu, Q., Zhang, D., Fu, B.: Two-stage PSA/VSA to produce H_2 with CO_2 capture via steam methane reforming (SMR). International Journal of Hydrogen Energy 43, 19057–19074 (2018)

Sircar, S.: Separation of multicomponent gas mixtures. US Patent 4171206 to Air Products and Chemicals, Inc. (1979)

Sircar, S.: Fractionation of multicomponent gas mixtures by pressure swing adsorption. US Patent 4790858 to Air Products and Chemicals, Inc. (1988)

Sircar, S., Kratz, W.C.: Simultaneous production of hydrogen and carbon dioxide from steam reformer off-gas by pressure swing adsorption. Separation Science and Technology, 23, 2397–2415 (1988)

Sircar, S., Waldron, W.E., Rao, M.B., Anand, M.: Hydrogen production by hybrid SMR–PSA–SSF membrane system. Separation and Purification Technology 17, 11–20 (1999)

Sircar, S., Golden, T.C.: Purification of hydrogen by pressure swing adsorption. Separation Science and Technology 35, 667–687 (2000)

Streb, A., Hefti, M., Gazzani, M., Mazzotti, M.: Novel adsorption process for co-production of hydrogen and CO_2 from a multicomponent stream. Industrial and Engineering Chemistry Research 58, 17489–17506 (2019)

Streb, A., Mazzotti, M.: Novel adsorption process for co-production of hydrogen and CO_2 from a multicomponent stream–Part 2: Application to steam methane reforming and autothermal reforming gases. Industrial and Engineering Chemistry Research 59, 10093–10109 (2020)

Subraveti, S.G., Li, Z., Prasad, V., Rajendran, A.: Machine learning-based multiobjective optimization of pressure swing adsorption. Ind. Eng. Chem. Res. 58, 20412–20422 (2019)

Sundaram, N.: Training neural networks for pressure swing adsorption processes. Ind. Eng. Chem. Res. 38, 4449-4457 (1999)

Umana, B., Zhang, N., Smith, R.: Development of vacuum residue hydrodesulphurization– hydrocracking models and their Integration with refinery hydrogen networks. Industrial and Engineering Chemistry Research 55, 2391–2406 (2016)

UOP: Optimising hydrogen production and use (2011). Available at https://www.honeywell-uop.cn/wp-content/uploads/2011/08/PTQ_Q311_Hydrogen_Optimization_Paper.pdf

UOP: 50 years of PSA technology for H_2 purification (2015). Available at https://honeywell-uop.azurewebsites.net/processing-solutions/gas-processing/50-years-of-hydrogen-purification-innovation/

UOP: UOP Polybed™ pressure swing adsorption (PSA) systems (2016). Available at https://honeywell-uop.azurewebsites.net/?document=psa-systems-for-hydrogen-production-by-steam-reforming&download=1

Voss, C.: Applications of pressure swing adsorption technology. Adsorption 11, 527–529 (2005)

Wagner, J.L.: Selective adsorption process. US Patent 3430418 to Union Carbide Corporation (1969)

Weist Jr., E.L., Wu, D., Xu, J., Herb, B.E., Hoke Jr., B.C.: Pressure swing adsorption process. US Patent 9381460 B2 to Air Products and Chemicals, Inc. (2016)

Whysall, M.: Pressure swing adsorption process. US Patent 4482361 to Union Carbide Corporation (1984)

Whysall, M., Wagemans, L.J.M.: Very large-scale pressure swing adsorption processes. US Patent 6210466 B1 to UOP LLC (2001)

Wiessner, F.G.: Basics and industrial applications of pressure swing adsorption (PSA), the modern way to separate gas. Gas Separation & Purification 2, 115–119 (1988)

Wilberforce, T., El-Hassan, Z., Khatib, F.N., Al Makky, A., Baroutaji, A., Carton, J.G., Olabi, A.G.: Developments of electric cars and fuel cell hydrogen electric cars. International Journal of Hydrogen Energy 42, 25695–25734 (2017)

Xebec: Pressure Swing Adsorption (PSA) Systems for Ultra-Pure Hydrogen & Other Industry Gas Purification (2021). Available at: https://xebecinc.com/hydrogen-purification/

Xiao, J., Li, C., Fang, L., Bower, P., Wark, M., Benard, P., Chahine, R.: Machine learning–based optimization for hydrogen purification performance of layered bed pressure swing adsorption. Int. J. Energy Res. 44, 4475–4492 (2020)

Xu, J., Weist Jr., E.L.: Six bed pressure swing adsorption process with four steps of pressure equalization. US Patent 6454838 B1 to Air Products and Chemicals, Inc. (2002)

Xu, J., Weist Jr., E.L., Rarig, D.L., Occhialini, J.M., Pillarella, M.L.: Pressure swing adsorption process with multiple beds on purge and/or with ten beds and four pressure equalization steps. US Patent 6379431 B1 to Air Products and Chemicals, Inc. (2002)

Xu, J., Rarig, D.L., Cook, T.A., Hsu, K.-K., Shoonover, M., Agrawal, R.: Pressure swing adsorption process with reduced pressure equalization time. US Patent 2003/001509 A1 to Air Products and Chemicals, Inc. (2003)

Yang, R.T.: Gas separation by adsorption processes. Butterworths, Boston (1987)

Yang, J., Lee, C.-H.: Adsorption dynamics of a layered bed PSA for H_2 recovery from coke oven gas. AIChE Journal 44, 1325–1334 (1998)

Yavary, M., Ebrahim, H.A., Falamaki, C.: The effect of number of pressure equalization steps on the performance of pressure swing adsorption process. Chemical Engineering and Processing 87, 35–44 (2015)

Ye, F., Ma, S., Tong, L., Xiao, J., Benard, P., Chahine, R.: Artificial neural network based optimization for hydrogen purification performance of pressure swing adsorption. International Journal of Hydrogen Energy 44, 5334–5344 (2019)

Yu, X., Shen, Y., Guan, Z., Zhang, D., Tang, Z., Li, W.: Multi-objective optimization of ANN-based PSA model for hydrogen purification from steam methane reforming gas. International Journal of Hydrogen Energy 46, 11740–11755 (2021)

Zhang, N., Benard, P., Chahine, R., Yang, T., Xiao, J.: Optimization of pressure swing adsorption for hydrogen purification based on Box-Behnken design method. International Journal of Hydrogen Energy 46, 5403–5417 (2021)

Zhu, X., Shi, Y., Li, S., Cai, N.: Two-train elevated-temperature pressure swing adsorption for high-purity hydrogen production. Applied Energy 229, 1061–1071 (2018)