

Comparative Analysis of Pressure Swing Adsorption and Supersonic Separators for High-Purity Hydrogen Applications

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In a hydrogen-based economy, many high-purity applications are required, so innovative and ultra-efficient purification processes are crucial. There are a variety of methods to separate and purify hydrogen and they can be classified mainly as physical and chemical methods, among the physical processes, PSA technology has been around for some time and is characterized by low operating costs and long service life. On the other hand, PSA has some disadvantages like the need for process optimization to reach high levels of hydrogen purity. An unusual separation technology that can be used to purify H₂ is supersonic separators (SS) a new approach to condensing and separating water and heavy hydrocarbons from natural gas already in use in the natural gas industry, and which can also be applied in the sector of hydrogen. Compared with traditional processing, the main advantage of supersonic separation technology is its small size and flexible structure. This work aims to analyse both technology's advantages and disadvantages, evaluating the SS's technical viability for hydrogen purification through numerical modelling.

1. Introduction

Hydrogen is used daily as a gas and liquid by many industries, including the petroleum industry, and in manufacturing processes to produce chemicals, food, and electronics. Unlike carbon-based fuels, hydrogen does not produce harmful by-products during combustion. which makes it the perfect fuel as it only generates energy, heat, and clean water when used in reactions.

In the face of all these advantages, a significant effort is being made to transform our economy into a hydrogen-based economy. For this, processes currently based on fossil fuels, which emit large amounts of carbon, are being rethought to use hydrogen as the main raw material. In a hydrogen-based economy, many high-purity applications are required, this includes mobility applications such as fuel cell vehicles, stationary electricity production using fuel cells, and laboratory applications for analysis using advanced equipment such as mass spectrometers, spectrophotometers, chromatographs, among others. (Ligen et al. 2020)

Nowadays the main way to produce hydrogen is a process called steam reforming of methane where natural gas or methane reacts with steam to produce hydrogen. But this process comes from fossil fuel and produces hydrogen with large amounts of carbon monoxide and dioxide, in addition to other contaminants. Thus, water electrolysis becomes an amazing way to produce hydrogen, carbon-free and with low amounts of contaminants. The main water electrolysis technologies are:

- Alkaline electrolyzers operate via the transport of hydroxide ions (OH⁻) through the electrolyte from the cathode to the anode with hydrogen being generated on the cathode side. This technology with a 100-year history is the most mature, durable, and cheapest. The integration with renewable energy is expected to improve the dynamic of operations.
- SOE electrolysis, which uses a solid ceramic material as the electrolyte that selectively conducts negatively charged oxygen ions (O²⁻) at elevated temperatures, generates hydrogen in a slightly different way and the technology experiences are being demonstrated, still with relatively high costs.

- In a PEM electrolyser, the electrolyte is a solid special polymeric material. Introduced in the 1960s and commercialized in the last decade, these systems have a wider dynamic range (0–200%), more suitable for intermittent power supply. However, capital costs are currently approximately twice those of alkaline electrolysers, and cell lifetimes need to be improved. (Simões, et al. 2021)

The most probable hydrogen contaminants in the electrolysis are a) Nitrogen, from Purge and inerting phases and fed-in water; b) oxygen from Gas solubility, Cross over; and c) water, from the process. H₂ purification technology is a crucial link from H₂ production to H₂ utilization. Stable, reliable, and low-cost H₂ sources represent a base for large-scale applications of fuel cell vehicles. Thus, high-efficient and low-power H₂ purification technologies for fuel cell vehicles play an underlying role in the development of the H₂ energy industry. To attend the ISO 14687:2019 for ultra-purity hydrogen applications, removal techniques are used to purify the hydrogen. The hydrogen purification technologies can be classified into two main categories: 1) Physical and 2) chemical methods, as described on figure 1. (Du, et al. 2021)

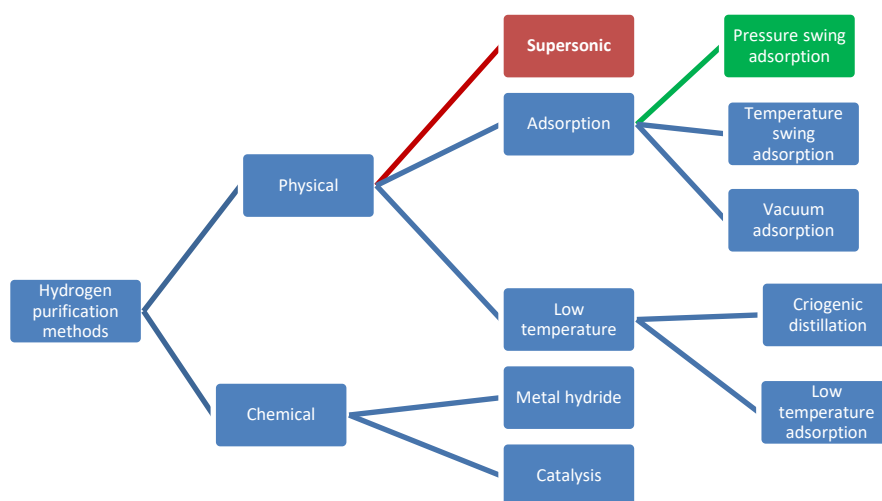


Figure 1: Classification of hydrogen purification technologies.

Catalytic recombination (Deoxo) and Pressure Swing Adsorption (PSA) are the most common separation processes. PSA technology relies on differences in the adsorption properties of gases to separate them under pressure. It uses a solid reagent to remove water from the gas, implemented by periodical pressure changing based on the difference in the adsorbent (desiccants) capacity for different gases. The PSA separation effect primarily depends on the type of adsorbent and the technical process used. (Du, et al. 2021).

In this context, an unusual separation technology that can be used to purify H₂ is supersonic separators (SS), a new approach to condensing and separating water and heavy hydrocarbons from natural gas already in use in the natural gas industry, which can also be applied in the sector of hydrogen. The purification technologies shown in Figure 1 are the same as those for natural gas conditioning, and SS was introduced to overcome some of the shortcomings of those purification techniques, and it is still not widely used for NG conditioning, but the technology has good application potential and has been studied worldwide (Karimi, 2006). Supersonic separators (SS) are compact devices that separate gases and liquids near their bubble point or dew point, gas-liquid mixtures, and other compressible fluids. SS consists of Laval (converging-diverging) nozzles in which the high-pressure fluid swirls, generating a supersonic fluid expansion; during expansion, an extreme drop in temperature occurs in the fluids, which results in the condensation of certain components. The structure of the equipment promotes the formation of a strong high-velocity vortex, causing the condensate particles to tend to the walls of the pipe, forming a film of liquid at the ends, favouring phase segregation. This mechanism is facilitated by an application at high speeds, in this way, SS adiabatic flow transformations are determined by the Mach number. Besides, SS is a technology already successfully used to separate natural gas liquids in large units, with many applications, as in air separations, gas conditioning, and natural gas separations.

This work aims to analyze the technologies for removing hydrogen contaminants to meet the quality requirements of ultrapure hydrogen according to ISO 14687-2019, comparing the technical and economic feasibility of PSA and SS technologies in the purification of green hydrogen from water electrolysis. Evaluating the technical viability of SS for hydrogen purification through numerical modeling. And analyzing the advantages and disadvantages of both technologies.

2. Study design/ methods

This work was developed in a two steps methodology, firstly, numerical modelling to evaluate the SS's technical viability for hydrogen purification was run out with Aspen HYSYS support. With that, the proposal could be validated in terms of viability and efficiency to find out whether the supersonic technology was able to dehydrate the hydrogen, and furthermore, whether the removal efficiency was high enough to meet the requirements of high-pure hydrogen, according to ISO 14687:2019.

Starting from the first step, it is achievable or not to compare the PSA technology, which is already used for the purposes of the ISO standard for hydrogen purification in electrolysis plants, with the supersonic separation technology. Thus, once technically validated, the second methodological step was a literature review to find the potential characteristics, advantages, and drawbacks of each technology, and place them side by side.

3. Technologies discussion and highlights

The following sections discuss the technical specifications of each technology. In addition, a brief overview of the operation and phenomena involved are presented in each section for the pressure swing adsorption technology and the supersonic separation.

3.1 Pressure swing adsorption technology

As previously mentioned in the introduction section, PSA is considered suitable for hydrogen purification. Due to the small size of hydrogen molecule, it significantly differs from most other gas molecules present in a process stream. The scheme of a conventional PSA technology can be described as the flow of a gas mixture under pressure through a bed, with a high selectivity adsorbent to a determined stream component. After the depressurization of the system, the component adsorbed is removed and the adsorbent is regenerated. This scheme allows an efficient H_2 separation with low costs and without the use of solvent. Normally, the traditional adsorbents used are zeolite molecular sieves, activated carbon, activated alumina, and silica gel, moreover, novel adsorbents and modifications are being studied to improve performance and efficiency. Dry bed dehydration is a semi-continuous process. A conventional system of PSA is operated in cycles with two parallel beds (one vessel adsorbing while the other is regenerating) so that the process could be operated continuously, however, literature has reported many studies that optimize this scheme of operation with the use of four or more beds and different configurations, in these cases, purity levels required and the composition of the inlet stream are the most dependent variables to achieve better results. The major disadvantage of this technology is the requirement of components that are not strongly adsorbed in the adsorbent, thus, as water and oxygen are the contaminants in a hydrogen product gas within the electrolysis process, PSA shows as a good option to purify hydrogen (Du, et al. 2021) (Neves & Schwartzman, 2005).

Even the elementary steps varying depending on each case, the three mains are pressurization, adsorption, and depressurization. The pressurization step pressurizes the feed gas till the operating condition, creating a rich product gas at the end of bed and a stationary phase with the adsorbent and the components absorbed. The adsorption step occurs when part of the product gas is withdrawn, the stream is composed by the components less absorbed. Lastly, during the depressurization step, the bed is fed in counter-current and a rich gas with the components most absorbed is create, this process partially regenerates the bed. Although, these three steps are not enough in terms of reaching high purity, thus, to improve efficiency and performance new steps can be added to the cycle. The time of each cycle, adsorption pressure, and other operational variables can be optimized. Most of the processes that use PSA purification applies multiple beds and cycles Neves & Schwartzman (2005).

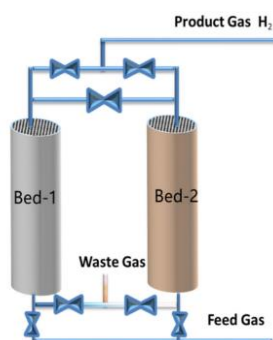


Figure 2: Pressure Swing Adsorption basic structure, Du et al. (2021).

3.2 Supersonic separation technology

Supersonic separators are a recent technology with the most practical applications in natural gas (NG) industry. Currently, the process has shown good performance in CO₂ removal from NG gas processing. The equipment has the advantages like simple structure, process intensification elements, energy integration with the process involved, and environmentally friendly use since there is no need of a regeneration system due to the short residence time of the stream, consequently, reducing dirt and fouling inside the equipment. The basic structure is composed of a Laval Nozzle (LN), a Cyclone, and a Diffuser. According to the US Patent no. 6,524,368 B2, Supersonic Separator Apparatus and Method are focused on removing a selected component from a stream with a plurality of other components. The phenomenon of separation is reached when the flow at supersonic velocity passes through a conduit, then, with the decreasing temperature of the fluid (project temperature) the selected component is condensed and removed sideways in a collecting zone. The product stream flows through a shock wave decreasing the axial velocity to subsonic and being collected downstream.

The device components are detailed as the LN, which promotes the contraction of the fluids (subsonic speed), then, at the throat of the LN the flow reaches sonic speeds and lastly, at the expansion section the fluid expands at supersonic speeds resulting in pressure and temperature of separation. The Cyclone structure is located at the end of the device and collects the droplets in the mixture of gas in a centrifugal system. The dry gas, thereby, flows through the Diffuser and recovers a maximum of 80% of the initial pressure (Magalhães, 2019).

Concerning the vantages and disadvantages of each technology described, this work aims to evaluate the possibility of using supersonic separators instead of PSA technology in hydrogen purification within an electrolysis system. Efficient separation of gases, dry gas as a product, low cost of operation, area and equipment size required are the main reasons to test supersonic separation in the process. The mixture of gas analyzed is composed of water, oxygen, and hydrogen. The dew point difference between each component can benefit the supersonic operation and depend on the purification result, the deoxidizer within the electrolysis system can be removed.

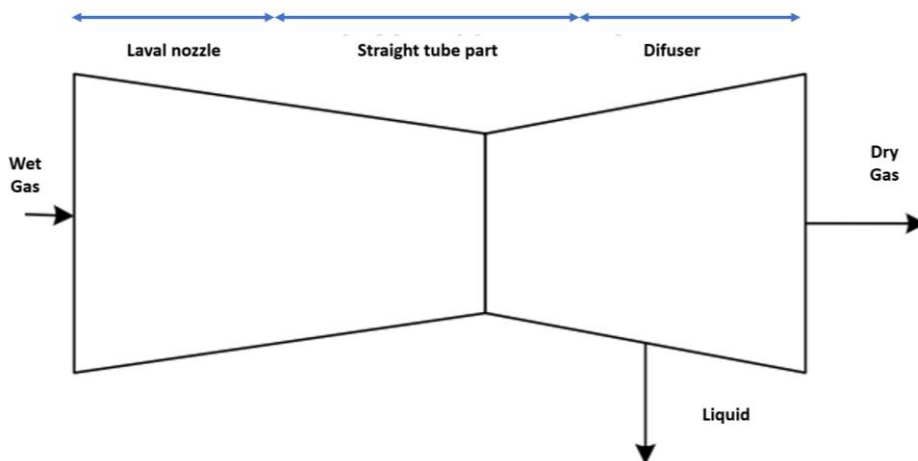


Figure 3: Supersonic Separator basic structure.

4. Main Results

The modelling and efficiency of separation for the supersonic separation was evaluated according to Ávila (2022), and an inlet stream specification before the purification process of an electrolysis plant was considered (Ligen, 2020), moreover, a 1 MW system was adopted as a base case for the mass flow of product. Thereby, the supersonic separator was located after the electrolyser and deoxidizer steps for hydrogen purification. According to the methodology of Ávila (2022), the modelling process of supersonic is based on several studies that use supersonic separators in the natural gas industry, the model was improved with sound speed calculation methodology and optimizations by the SENAI CIMATEC in partnership with Petrobras and the results can be seeing on table 1.

Table 1: Results of SS simulation

Component	Inlet SS	Outlet SS
H ₂	99,9	99,999
H ₂ O	0,1	0,001

Numerical modelling of the nozzle shows that its technology is suitable for hydrogen dehydration, and due to its high efficiency of removal, could be easily used to purify hydrogen into ISO 14687/2019 requirements, with an outlet stream of hydrogen with less than 5 ppm of water, thus, being able to substitute PSA technically. Still, in addition to the technical evaluation to know if the purpose of the technology can achieve the proposed objective, it is necessary a detailed study of both vantages and disadvantages of the technologies. Therefore, the comparison between PSA and SS technologies depends on attributes, discussed in Table 2. These attributes were taken from the literature on both technologies.

Table 2: Comparative Analysis of PSA and Supersonic Separators

Attributes	Pressure Swing Adsorption	Supersonic Separator	Reference
Cost	Low	High	Kim, et al. (2015); Magalhães (2019)
Efficiency	High	High	Cao, et al. (2019); Du, et al. (2019)
Solvent Requirement	N/A	N/A	–
Complexity	Medium	Low	Ligen (2020); Bian, et al. (2016)
Power Consumption	Medium	High	Kim, et al. (2015); Machado, et al. (2012)
Maintenance	Low	Low	Cao, et al. (2019); Du, et al. (2019)
Equipments necessary	4	3	–
Residence Time	High	Low	Neves & Schwartzman (2005); Ávila, et al. (2022)
Continuous Process	No	Yes	–
Regeneration System	Yes	N/A	Zeng, et al. (2022); Ávila, et al. (2022)
Literature Assessment for H ₂ Purification	High	Low	–
TRL	9	9	–

Main advantages and considerations of SS are, as Table 1 illustrates: The low complexity, due to its basic structure and less space required and absence of moving parts with contributes for the modularity of the equipment; Efficiency, in terms of separation and system operability, promoting a high pure product stream of hydrogen; Power consumption, since electrical energy is provided to the cyclone part of equipment and compressors associated, it has an advantage when compared to other thermal separation processes. Although compared to the PSA it has a higher consumption, mainly due to its continuous process while the PSA operates in a semi-continuous process; It is not necessary solvent in SS system since the phenomena of separation occur by physical properties, this also contributes to sustainable processes; Maintenance, that is less required than PSA once the adsorbents have a lifetime shorter than the SS system; Number of equipment, there are low compared to other conventional systems of separation like DEA and MDEA. Are considered essential equipment for the SS: a compressor, the SS equipment, and a product tank. PSA was considered essential the two beds, one compressor, and a product tank; Residence time, once the fluid reaches supersonic speeds through the equipment the fouling process is considerably reduced; Continuous process, different from PSA that needs two beds for better operation and in order to operate semi-continuously, SS equipment promotes fluids separation with the diffuser continuously in normal operation; Literature assessment of SS for hydrogen purification and

TRL: the use of SS especially in natural gas industry, even being a recent technology, it has numerous industrial cases, promoting the technique to TRL of 9, however, there is very limited literature for the application in hydrogen purification; Cost: since the SS equipment is constructed depending on each process it increases the project cost, the PSA, in contrast, has a higher availability since it is used largely for separation in processes.

5. Conclusions

For years, H₂ has been used for various purposes, either as a reagent or as an energy source. However, it is necessary to carry out the purification of green hydrogen from PEM electrolysis process, in which oxygen and water, in ppm amounts, are the main impurities, where Catalytic recombination (Deoxo) and Pressure Swing Adsorption (PSA) are the most common separation processes. Likewise, supersonic separators (SS) are compact devices that separate gases and liquids, The numerical modelling shows SS as a good possibility to promote the separation between H₂ and water, substituting the traditional PSA processes.

SS is shown to be less expensive in terms of OPEX, once there is no need for changes and regenerations of the adsorber. Moreover, the CAPEX of SS is a bottleneck, making research and development studies necessary to reduce it and make it competitive, turning the process less expensive than when utilizing the PSA separator.

Acknowledgments

A special thanks to the SENAI-CIMATEC's university centre for the financial support, and to Competence Centre for Green Hydrogen (CCH2V) for the technical assessment.

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