SAE J2719 Quality Hydrogen: Guidelines to Select the Most Suitable Purification Technology

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ABSTRACT

Hydrogen (H_2) is a gas widely used in several industrial applications. Hydrogen usage will be expanding as it is the main fuel for fuel cell technology and is used to store the excess energy generated by renewable sources such as solar and wind. In these applications the degree of H_2 purity is crucial and advanced purification systems are typically used to guarantee the purity. This article will review the types of purification technologies that are currently available to generate high-purity H_2, starting from an already clean source that is at least 99.9% pure. Other technologies also widely used in gas purification, like pressure swing adsorption (PSA) and polymeric membrane separation, that are more suitable to handle a lower degree of H_2 purity will not be discussed. This article will review the advantages and disadvantages of adsorbers, getters, cryogenic, and palladium (Pd) purification technologies with guidelines on how to select the most appropriate technology depending on the application and the experimental conditions.

INTRODUCTION

Hydrogen has the potential to become a significant source of clean energy.[1] All the major car manufacturers have developed cars powered by proton exchange membrane (PEM) fuel cells, with thousands of cars being introduced to the market starting in 2015. This technology is a great step ahead in the introduction of clean cars because the exhaust consists of only water vapor. A necessary requirement for the mass adoption of this new vehicle technology is the development of a suitable infrastructure capable of filling car tanks at high pressure, 700 bars, with high-purity H_2. Per the hydrogen fuel quality specifications for polymer electrolyte fuel cells in road vehicles, published by the U.S. Department of Energy, impurities such as carbon monoxide (CO) and sulphur compounds, are very tight, down to 200 ppb or even less. This is because of their ability to deplete the lifetime of the fuel cells.[2–4]

This article will review the most common technologies used to improve H_2 quality down to at least 8 nines (8N) quality, explaining where each technology has advantages.

PURIFICATION TECHNOLOGIES

The technologies widely used for H_2 purification discussed in this paper are:

- Adsorber
- Getter
- Cryogenic
- Palladium

Adsorber Purifiers

Adsorber purifiers consist of a cylindrical column filled with high surface area materials that are suitable for the chemisorption and physisorption of impurities, Figure 1.

Figure 1. Adsorber purifiers.

An adsorber purifier is operated at room temperature and removes reactive impurities such as oxygen (O_2), water (H_2O), CO, carbon dioxide (CO_2), non-methane hydrocarbons (NMHC), ammonia (NH_3), nitrogen oxides (NO_x), and sulphur (S) compounds to ppb_v or sub-ppb_v levels. It is completely transparent to, and thus not suitable for removing nitrogen (N_2), methane (CH_4), and rare gases. If these gases are considered to be critical impurities in H_2 other purification technologies should be considered.

Figure 2 demonstrates a typical application to maintain a low and constant concentration of H_2O and O_2 in H_2 from a high-pressure cylinder. When H_2 is progressively used from a gas cylinder, there is a continual decrease of the pressure, which affects the moisture content in the delivered gas. Figure 2 shows the water vapor and oxygen content in H_2 vs. cylinder pressure when a constant flow of 4.6 L/min from a 4.5N cylinder is delivered.

H_2O and O_2 Trend versus Cylinder Pressure

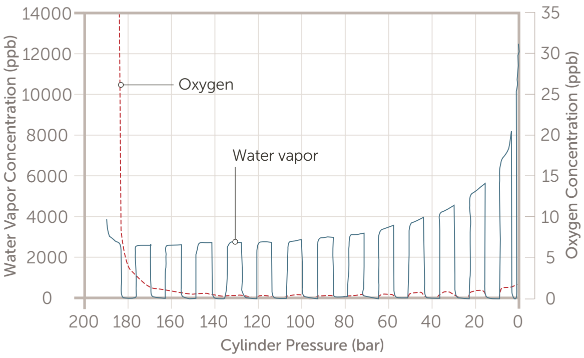

Figure 2. Water vapor and oxygen trend vs. cylinder pressure.

The H_2O and O_2 content in H_2 was analyzed by means of a Delta F DF-760E; every 30 minutes an adsorber MicroTorr® H_2 purifier was switched between bypass and on-line to continuously monitor the delivered gas and the purified gas. It is clear that when the cylinder is approaching 80 bar (5.5 psig), the water vapor concentration in H_2 starts significantly increasing. Simultaneously the H_2 from the purifier remains below 1 ppb independent of the inlet concentration guaranteeing not only a high degree of purity but also consistency.

Once saturated with impurities, the purifier can be regenerated to fully recover the initial capacity and efficiently to sorb impurities. If this technology is used with relatively clean inlet gas, e.g., 5N or preferably 6N, the purifier is normally regenerated off-line at the factory. Since the quality of the inlet gas is already fairly good, the lifetime of an adsorber purifier could be several years. An accurate estimation of the lifetime is possible if the average impurity level, the average flow rate, and the duty cycle are known.

The cost of ownership of these purifiers is low: in fact, they do not require any power to operate or any loss of H_2 due to venting. However, if the loading of impurities is high, the purifier could be saturated in a very short time. Mishandling, such as lack of purging the gas lines during installation, could easily contaminate the purifier due to residual air saturating the purifier active sites, drastically reducing the estimated lifetime.

The flow rate managed by these purifiers typically ranges from a few sccm up to thousands of slpm.

If the H_2 purity is not as high, such as 4.5N or 5N, and/or the flow rate is higher than 50 – 100 standard m^3/h, it could be more convenient to use the same purification technology with two columns mounted in parallel in a so-called automatically regenerable purifier. Such a purifier assembly includes valves, heaters, and a microprocessor to continuously cycle between the two columns, Figure 3. The purification logic is very simple and effective: while one column purifies the gas, the other is either undergoing regeneration or is in standby mode. This type of purifier is used when the H_2 flow rates are relatively high ranging from 10 m^3/h to many hundreds of m^3/h. The higher the flow rate handled by the purifier is, use of a more complex unit is further justified.

Figure 3. A two-column purifier assembly.

The cost of ownership of this purifier is also low: it requires energy to heat up the vessel under regeneration for a period of about 8 – 12 hours every week or whenever it is necessary to regenerate the purifier. During this process about 5% of the purified H_2 is used to purge the column under regeneration to remove previously sorbed impurities.

In high flow rate purifiers it is also convenient to use N_2 for the regeneration gas in order to minimize the amount of H_2 consumed in every regeneration cycle.

The final achievable purity and the impurities removed are the same for the single column and the dual column regenerable purifiers, down to less than 1 ppb, Table 1.

Getter Purifiers

Getter purifiers are another widely used technology for the purification of H_2 based on zirconium alloys. They must be run at high temperature and can remove O_2, H_2O, CO, CO_2, NH_3, NO, NO_2, N_2, CH_4, and other hydrocarbons while they are transparent to rare gases. The zirconium alloy forms stable compounds like oxides, carbides, and nitrides, and differently from the adsorber technology, cannot be regenerated. Once the getter column has been saturated with impurities it has to be replaced.

Capacity of a getter column is much higher than an adsorber column of the same volume; as a reference, in the case of O_2 and H_2O impurities, the getter column has 10 to 50 times higher capacity.

While the use of heat exchangers helps to save energy, since the gas must be heated 100% of the time, the cost of ownership of a getter purifier is higher compared to the adsorber technology.

Depending on the impurity concentration in H_2, the lifetime of a typical getter-based column is in the range of three to five years. However, it is not uncommon for a getter-based cartridge to last more than eight years.

To minimize the consumption of the getter-based cartridge, an adsorber column could be installed upstream of the getter column. In this way all of the getter capacity will be used to trap N_2 and CH_4 impurities.

The flow rates for a getter-based purifier, Figure 4 range from a few L/min up to hundreds of m³/h.

Figure 5 shows the typical very low concentration of impurities at the outlet of a getter purifier measured by a Thermo Scientific (APIMS) atmospheric pressure ionization mass spectrometry.[5]

Figure 4. Example of getter purifier up to 10 m³/h and 100 m³/h.

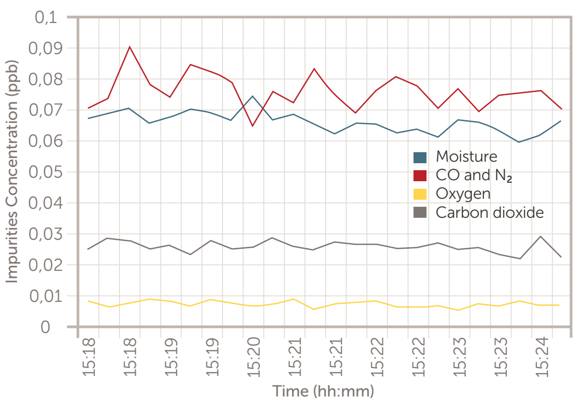

Figure 5. Typical impurities concentration at the outlet of a getter purifier.

Cryogenic Purifiers

In the cryogenic purification of H_2, the stream is cooled down to cryogenic temperatures through a column filled with a high-surface media. In this manner all impurities, including some inert impurities, with the exception of helium (He) are trapped onto the cryogenic column.

The cryogenic purifier works with two columns in parallel so that one is in operation while the other is under regeneration, similarly to the adsorber purifier but at different operating temperatures.

This technology is quite efficient but requires a high cost infrastructure because it is necessary to continuously supply liquid N_2 to maintain the columns' low operation temperature. If the vaporized N_2 is used in the plant for equipment purging, the running cost is reduced. It also requires power to warm up the column during regeneration and uses a small percentage of the purified H_2 during regeneration.

This technology can also reduce argon (Ar) in H_2 from ppbs down to ppts.

Potentially this technology can be used starting from medium flow rates, e.g., 10 m³/h, but the high cost of the infrastructure and the consumption of liquid N_2 make it practical only when the flow rates are at least 100 m³/h. The running cost of the purifier is strongly influenced by the location and the availability of liquid nitrogen.

Palladium Purifiers

This technology is specific for H_2 purification because H_2 is the only atom capable of diffusing across a hot Pd membrane, Figure 6. This technology allows the removal of all impurities from H_2 even the rare gases such as He and Ar. Hydrogen diffusion is driven by the inlet gas pressure and by the Pd membrane operating temperature, 350° – 400°C (662° – 752°F), with no need for cycling or switching valves during operation.[6]

H_2 Flow Rate: Inside/out

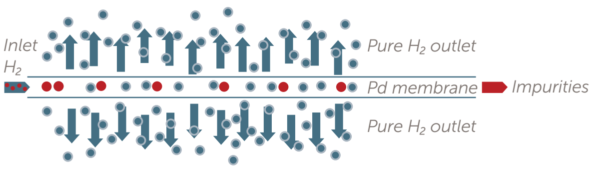

Figure 6. Palladium purifier principle of operation.

Figure 7. Example of a palladium purifier.

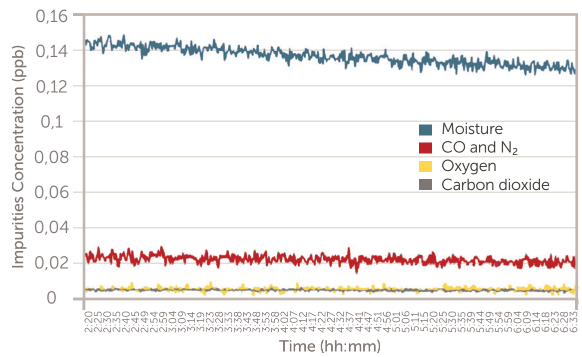

Figure 8. Impurities concentration at the outlet of a palladium purifier.

Palladium purifiers, Figure 7, have unlimited lifetime as long as the Pd membrane integrity is maintained and, in terms of footprint, these purifiers are also significantly more compact compared to the other purifier technologies.

To keep removing the impurities upstream of the Pd membrane and prevent their build-up, a few percent of the incoming H_2 flow, typically 2%, is vented along with the impurities.[7]

Figure 8 shows a realization of a Pd purifier using multiple Pd tubes mounted in parallel to achieve a high surface area in a small volume and the typical impurities concentration. The running cost of this purifier is determined by the power consumption and the loss of H_2 from the bleed flow. In general terms and compared to heated getter or cryogenic purifiers, the cost of ownership will be relatively low if the unit is well engineered with heat exchangers to recover a large part of the energy.

New generations of Pd purifiers based on supported membranes are currently under development.[8–10] They have characteristics similar to the self-standing Pd purifiers but use thinner Pd layers in the 2 – 10 micron range. The lower Pd thickness has two main advantages:

- The need for a small quantity of an expensive precious metal
- High H_2 permeance across the membrane

Table 1. Comparison of purifier technologies under general conditions

Because purifiers based on the same technology but made by different manufacturers could have different specifications, this table provides general purification conditions.

Technology	Inlet gas purity	Impurities removed	Impurities not removed	Flow range	Operating temperature	Pressure drop	Maintenance	Comment
Adsorber	5N	O_2, H_2O, CO, CO_2, HC>C_5, NO_X, S	N_2, CH_4, rare gases	0.1 – 120 m^3/h	Room temperature	Low	Regeneration every 1 – 3 years	The better the inlet gas purity, the longer the lifetime Less expensive technology with limited performance
Regenerable adsorber	4.5N	O_2, H_2O, CO, CO_2, HC>C_5, NO_X, S	N_2, CH_4, rare gases	10 – 1,000 m^3/h	Room temperature	Low	None	Suitable for very high flow rate Low running cost No N_2 removal
Getter	6N	O_2, H_2O, CO, CO_2, N_2, CH_4, NO_X, S	Rare gases	0.1 – 300 m^3/h	300° – 600°C (572° – 1112°F)	Low	Getter column replacement every 3 – 8 years	Good when the gas is relatively clean Removes all impurities, N_2 included
Cryogenic	4N	O_2, H_2O, CO, CO_2, N_2, CH_4, NO_X, S	He	20 – 1,000 m^3/h	-180°C (-292°F)	Low	None	Requires complex infrastructure to manage liquid N_2 High running cost Removes all impurities except He Competitive for high flow rates
Palladium membrane	3.5N	O_2, H_2O, CO, CO_2, N_2, CH_4, rare gases, NO_X, S	None	0.1 – 100 m^3/h	400°C (752°F)	High	None	Removes all impurities, rare gases included Very compact Compatible with high inlet gas purity Sensitive to S contamination
Supported palladium membrane	3.5N	O_2, H_2O, CO, CO_2, N_2, CH_4, rare gases, NO_X, S	None	0.1 – 500 m^3/h	400°C (752°F)	Medium-low	None	Removes all impurities, rare gases included Very compact Compatible with high inlet gas purity Sensitive to S contamination

CONCLUSION

Purification technologies suitable to purify H_2 and reduce the impurities concentration down to the ppb and ppt range have been briefly discussed and compared. Each one has its own peculiarities and it is up to the customer to decide on the most appropriate purifier technology for the application based on the inlet H_2 purity, the desired specifications, and the target purity levels.

Installing a gas purifier will achieve a very low concentration of the impurities of concern and maintain it over time, even when the incoming H_2 purity is not consistent.

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