HYDROGEN SEPARATION AND HANDLING

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Summary

Various processes based on phase change, absorption, adsorption, permeation through membranes, and chemical reactions are available for separation, recovery and purification of hydrogen. Some of these processes are employed in practical operations according to operating conditions, specifications, and end uses for removed and recovered components. The prime technology is the pressure swing adsorption processes, which have several advantages over the other methods. Technical progress for improvement of hydrogen recovery and energy consumption can be made mainly by

research and development of separation media such as absorbents, adsorbents, polymer membranes and hydrogen storage alloys to achieve superior performances in selectivity, rate-capability, capacity, and durability.

Addition of hydrogen to natural gas is a possible way to enlarge the use of hydrogen into energy fields. For this purpose, a beneficial effect in terms of improving combustion properties and reducing polluting emissions can be obtained for burner combustion of town gas and lean-burn operation of internal combustion engines.

Safe handling of hydrogen and its mixtures, and the hazards and damage resulting from its physical and chemical properties and combustion characteristics are outlined with respect to its three forms of gas, liquid, and metal hydride. As hydrogen is colorless and odorless, burns with a nearly invisible flame, and can embrittle some metals, detectors of gaseous hydrogen and its flame and materials suitable for equipment are also described. Hydrogen can be handled as safely as other fuels. However, gaseous hydrogen is a highly flammable and explosive gas with wide flammability limits, a low minimum ignition energy, and a fast burning velocity. Liquid hydrogen is an extremely low-temperature liquid with a normal boiling point of 20 K. Adequate handling and safety measures of hydrogen are obviously important for both current and emerging uses of hydrogen as a feedstock and a fuel.

1. Introduction

Hydrogen is an important commodity in various industrial fields such as ammonium production, petroleum processing, chemical and petrochemical industries, metallurgical processing, the electronics industry, town gas, and the aerospace industry. It is normally manufactured by removing other components or recovering it from gaseous mixtures generated in various chemical processes. The crude hydrogen-based gases produced from hydrocarbons by steam reforming or partial oxidation contain various co-products, by-products, and residual reactants such as carbon dioxide, water vapor, carbon monoxide, and methane. Moisture and traces of oxygen exist in hydrogen generated by water electrolysis. Unreacted or by-product hydrogen is obtained in its mixed or fairly pure state in hydrocracking, hydrotreating, and brine electrolysis processes. Product hydrogen with a specified purity is prepared from these hydrogen-rich gases through separation and purification operations.

The term “separation” is generally used for all first-stage operations to increase hydrogen concentration, whereas the term “purification” is used for secondary operations to upgrade product hydrogen. Various processes to separate and purify hydrogen are available. They are based on physical or chemical principles, and are classified into, for example, phase change, absorption, adsorption, permeation through membranes, and chemical reaction. Some of these processes are employed in practical operations according to operating conditions, specifications, and end uses for removed and recovered components. Among them, the prime separation technology is the pressure swing adsorption (PSA) process, which has several advantages over the other methods and is widely used in various fields of hydrogen separation. The other methods are also available for pretreatment of the crude hydrogen or final purification to a highly purified level. In addition to performance improvement of conventional separation processes based on phase change, absorption and adsorption, technical progress is being made on new ones using palladium membranes, polymer membranes, or metal hydrides.

Hydrogen is also expected to be more diversely and widely utilized as an energy carrier for the purpose of reducing the large dependence on fissile fuels and mitigating local and global environmental problems. Town gases which are manufactured from hydrocarbons and coals and contain a considerable amount of hydrogen, have been safely handled in commercial and residential areas for many years, although they are mostly being replaced by natural gas which mainly consists of methane. Addition of hydrogen produced from water and renewable energy sources to town gas derived from natural gas is considered to be an approach for the gradual transfer to the age of hydrogen energy systems. A trade-off between the reduction of NOx emission and increase of backfiring, which is inevitable for burner combustion of pure hydrogen, can be significantly avoided by burning hydrogen together with methane. Another possible use of hydrogen as an additive is in fuels for internal combustion engines of both spark and compression types. For these engines, methane mixed with hydrogen has been shown to have beneficial effects in terms of improving combustion properties and reducing polluting emissions, especially in lean-burn operation. A significant reduction in emission of nitrogen oxides, carbon monoxide, and hydrocarbons from automobiles is expected when fueled with this mixture. A transportation system using natural gas containing hydrogen would be an effective way of mitigating environmental concerns in urban areas, as well as introducing hydrogen into the energy supply infrastructure.

Hydrogen and its mixtures are routinely handled and used on a large or small scale. However, handling of hydrogen in the three forms of compressed gas, cryogenic liquid, or metal hydride involves hazards resulting from its physical and chemical properties and combustion characteristics. Gaseous hydrogen, with its wide flammability limits, wide detonability limits, low minimum ignition energy and fast burning velocity, is highly flammable and explosive. Although its flammable mixture with air rapidly disperses into the atmosphere or deflagrates with a relatively weak impulse in an open space, its deflagration in a totally or partially confined space is accompanied by a severe pressure impulse and a potential transition to detonation. It is colorless and odorless, and can embrittle some metals. Therefore, for safe handling of gaseous hydrogen, attention must be paid to its possible leakage, likely formation of a flammable mixture, avoidance of ignition sources, and selection of appropriate container materials, especially in a confined space. The same considerations apply to liquid hydrogen and metal hydrides, since these yield gaseous hydrogen either spontaneously or during process operation. Liquid hydrogen is accompanied by hazards related to its low temperature; viz., fast evaporation, line-blocking due to solidification of moisture and air, thermal stress and cold embrittlement of construction materials, and handlers' frostbite. Metal hydrides allow hydrogen to be stored at moderate pressure and ambient temperature. However, the fine particles produced during repetitive cycles of hydrogen absorption and desorption are often pyrophoric, and may induce an internal stress that causes rupture of the container. Adequate handling and safety measures of hydrogen in each form are obviously important for both current and emerging uses of hydrogen as a feedstock and a fuel.

2. Separation and Purification of Hydrogen

2.1 Partial Condensation

Partial condensation processes involve a gas-liquid separation method that makes use of relatively large differences in volatility among feed components. This method is suited for removal of easily condensable components like water vapor from hydrogen-rich gases, recovery of moderately high purity hydrogen from crude gases of relatively small hydrogen content or low hydrogen partial pressure, and simultaneous separation of hydrogen and valuable components from their rich gases in continuous and large-scale operation, because gaseous impurities such as hydrocarbons, water vapor, carbon dioxide, carbon monoxide, and nitrogen condense at much higher temperatures than hydrogen. Partial condensation at a cryogenic temperature was the representative method of hydrogen separation, mainly for recovery of hydrogen from petrochemical off-gases. However, the cryogenic separation processes are not so popular these days.

2.2 Absorption Methods

Absorption methods are also gas–liquid separation ones, which use absorbents to remove soluble components from crude hydrogen gases. The equipment consists of an absorption column in which soluble components are trapped in an absorbent at a higher pressure or a lower temperature, followed by a regeneration column in which the absorbed components are released at a lower pressure or a higher temperature. The absorbent is circulated between the two columns. Such operations as washing out of soluble impurities into a liquid absorbent are often called “washing.” Water washing is the oldest absorption process and was used mainly to remove carbon dioxide contained in crude hydrogen gases. The absorption processes are roughly classified into *physical* ones that utilize the differences in solubility between hydrogen and other components, and *chemical* ones based on chemical reactions between impurity components and the absorbent.

Physical absorption processes, in which solubility of gaseous components generally obeys Henry’s law, are mostly applied to separation of hydrogen from feed gases at considerably high pressures and high impurity concentrations for removal of residual impurities, and have the advantages that the product hydrogen leaving the absorption column is near the feed pressure and the regeneration of absorbents is relatively easy. The representative applications are removal of carbon dioxide by the use of organic solvents or solutions, removal of methane, nitrogen and argon by scrubbing pre-purified hydrogen gas at a cryogenic temperature, and removal of heavy hydrocarbons and separation of light hydrocarbons from gases rich in hydrogen by the use of heavy hydrocarbons such as gasoline, oil, toluene, or methyl cyclohexane as solvent.

Chemical absorption is suitable for complete removal of specific impurities from crude hydrogen and recovery of hydrogen from that at its relatively low pressure or low concentration in comparison with physical absorption. This chemical absorption method is used mainly for separation of acidic substances such as carbon dioxide, hydrogen sulfide, carbonyl sulfides, and hydrogen cyanide from raw hydrogen gases produced from hydrocarbons and coals. Hot alkaline or amine solutions are used as the absorbing agents to remove the acidic impurities.

2.3 Adsorption Methods

Adsorption separation methods utilize the preferential adsorption of some constituent species other than hydrogen mainly due to the difference in adsorption equilibrium. Representative adsorbents are silica gel, activated carbon, activated aluminum and molecular sieves. Most of the conventional separation units are operated in a dual mode of adsorption by passing the feed hydrogen gas and regeneration by means of heating, pressure reduction, gas purge, or a combination of these methods. They are widely applied to removal of impurities such as water vapor, dusts, tars, heavy hydrocarbons, mists and acidic components, and upgrading of moderately high purity hydrogen. The adsorption processes at cryogenic temperatures are indispensable for the final removal of residual impurities in the production of the ultra-high-purity hydrogen with an overall impurity level of less than 0.1 parts per million (ppm), which is required in hydrogen liquefaction and semiconductor industries.

In the 1960s, a new separation technology, the so-called “pressure swing adsorption (PSA) process”, was developed. A PAS unit consists of four to twelve vertical columns containing specific adsorbents. The columns are connected through valves in order to perform pressurization and depressurization (pressure swing) by sophisticated charge and discharge of hydrogen gases. Each column is operated in a sequential cycle, which consists of adsorption of impurities, equilibration of pressures, desorption of impurities, purge of impurities and pressurization. PSA processes in hydrogen separation offer several features, such as simultaneous recovery of hydrogen in a product gas and other constituents in a purge gas, separation to highly pure hydrogen at a moderate hydrogen recovery, product hydrogen pressure near the feed pressure, minor influence on the design of the separation unit and the purity and recovery of product hydrogen by variations in composition in feed hydrogen, amenability to automatic operation with little consumption of utilities, and low operating cost. Owing to these advantages, PSA processes of various types are under widespread development and in commercial use in both small and large systems for production and recovery of hydrogen.

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Biographical Sketch

Itsuki Uehara, born April 4, 1950, in Kyoto Prefecture, Japan, graduated from Nagoya Institute of Technology in 1973. He received his ME degree in chemical engineering from Nagoya University in 1975 and Doctor of Engineering degree in electrochemistry from Kyoto University; has worked for Osaka National Research Institute on hydrogen energy systems and applications of hydrogen storage alloys (1975–1999); has worked as the Chief of the Central Research Institute, Toyama Industrial Technology Center (1999-2001); is presently the Human Resource Coodinator, National Institute of Advanced Industrial Science and Technoloy;and has published some 100 papers and 5 books.