CHAPTER I

INTRODUCTION

1.1 Introduction

Hydrogen has great potential as an energy carrier. The data from multimedia research group indicates that the overall US hydrogen market is estimated at $798.1 million in 2005 and is expected to rise to $1,605.3 million in 2010.

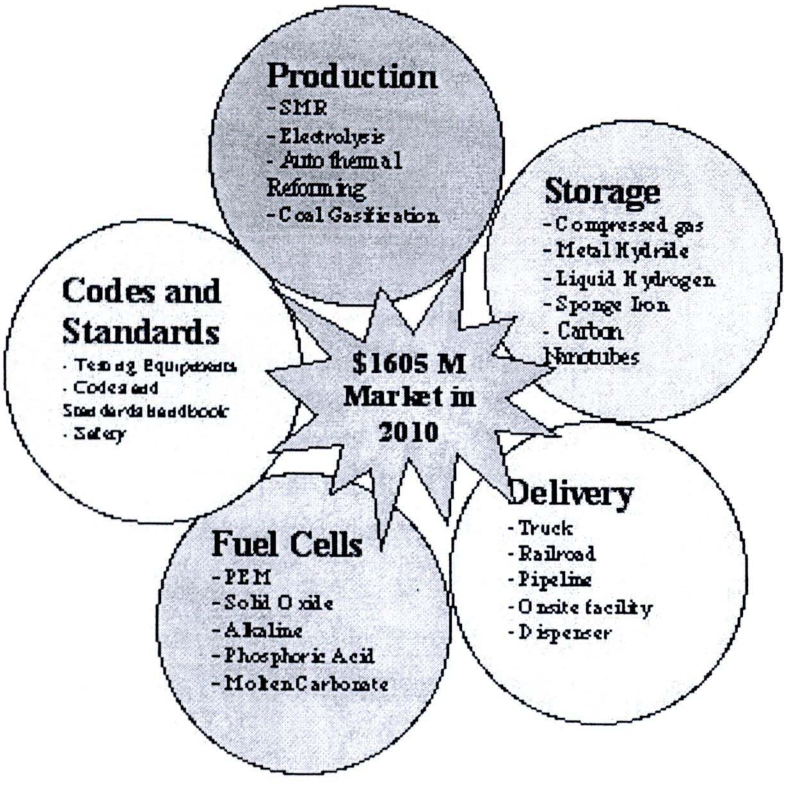

Figure 1.1 U.S. Hydrogen market.

Source: FKU (Fuji-Keizai USA)

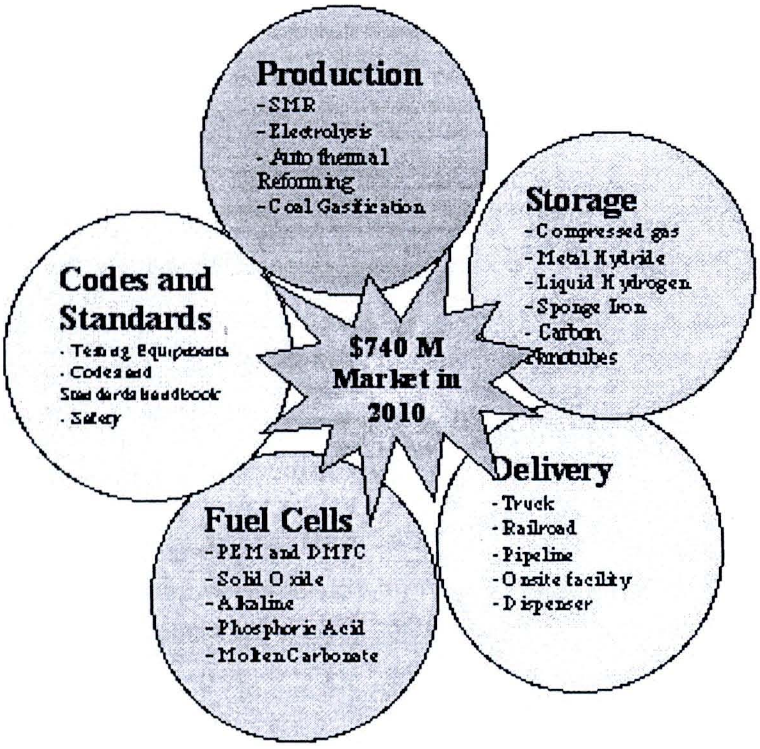

Figure 1.2 European Hydrogen Market.
Source: FKU (Fuji-Keizai USA)

The overall European hydrogen market is estimated to be about $368 million in 2005 and is expected to grow at an average annual growth rate of 15 percent to $740 million in 2010. European community is funding various projects on hydrogen production, storage and hydrogen refueling stations.

Increased demand for lighter fuels and products, a desire for higher-performance products, and an insistence on more environmentally acceptable products require refiners to alter processing conditions and technologies so that they can successfully meet the demands of today's society. These demands relate to product slate or quality, they also have a significant impact on a valuable but often overlooked refinery by-product: hydrogen, which is important as both a commodity and a reactant in the total refinery. The hydrogen balance in a typical refinery is straightforward: hydrogen supplied by the feedstock leaves in the products, by-products, and wastes. In the 1950s, catalytic reforming provided refiners with a relatively pure hydrogen stream as a by-product of normal refining practice. Refiners had a ready-made source of hydrogen, which could be used as a reagent in the chemistry of their refining schemes. In the 1990s, increasingly demanding product specifications require more hydrogen content in the products as well as removal of contaminants [1].

To avoid investing in a new hydrogen-producing plant, a refiner with a light hydrogen balance needs to consider three main issues:

- Maximizing the hydrogen yield from the refinery with particular attention to the primary source: the catalytic reformer.
- Determining the hydrogen required to produce increasing amounts of high-performance products.
- Considering the hydrogen management technologies required to convey hydrogen from the source to the user under the most-appropriate conditions [2].

Because of large market value and application of hydrogen make it is interesting to develop hydrogen technology to meet the today's demand and quality.

1.1.1 Technical data of hydrogen

Molecular weight	2.02 g./mol
Boiling point	-252.77°C at 101.3 KPa
Specific volume	11.967 m^3kg^{-1} at 20°C, 101.3 KPa
Critical temperature	-239.77°C
Critical pressure	1298 KPa
Heat capacity	1432 J $kg^{-1}K^{-1}$ at 25°C, 101.3 KPa
Flammable limits in air	4-74.5 percent
TLV (Threshold Limit Values)	not established (considered non toxic)

1.1.2 Sources of hydrogen

Gasesous hydrogen can be made using several commercially feasible processes. These include:

- Electrolysis of water
- Thermal-catalytic dissociation of ammonia
- Thermal-catalytic dissociation of methanol
- Steam-iron conversion of reducing gas
- Patial oxidation of hydrocarbon
- Catalytic steam-reforming of hydrocarbons
- Catalytic steam-reforming of hydrocarbons
- The water-gas process

Table 1.1 compare production costs for various methods for a typical capacity of 2,865 kg of hydrogen per day (basis = 2005)

Table 1.1 Cost comparison [3]

Process	**Hydrogen production cost (per kg)**
Gas Reformation	\$1.15
Wind Electrolysis	\$3.10
Nuclear Electrolysis	\$1.48
PV Plate Electrolysis	\$7.40
CPV Electrolysis	\$3.18

1.1.3 Uses of hydrogen

A significant amount of gaseous hydrogen is produced by steam reforming of natural gas or naphtha and consumed in a downstream process. One notable example is in the fertilizer industry, where NH_3 synthesis gas is produced by steam reforming of hydrocarbon followed by air addition and secondary reforming to produce a mixture which contains H_2 and N_2 in a ratio approximately 3:1. A second important area of the process industry which produces and uses hydrogen is oil refining. Many refineries have reformers which produce relatively pure hydrogen for use on site by hydrogen-consuming processes. These processes include hydrotreating, hydrodealkylation, hydrodesulphurization, hydrogenation, and hydrocracking of heavy residues.

These processes require hydrogen of 90-99 percent purity by volume and all take place at ambient and higher temperatures, and so do not often use cryogenic technology.

Typical operations involved may be reforming, CO_2 removal by absorption and final upgrading by methanation, and sometimes adsorption.

The bulk of the hydrogen is made at moderate purities but in vast quantities and is consumed in situ or in downstream processing units. The hydrogen balance is one of the fundamental parts of the make-up of a sophisticated refinery and many cryogenic processes have been effectively utilized to remove medium purity hydrogen to improve the hydrogen balance when refineries turn to more severe processing of their crudes.

The remaining users of hydrogen are highly varies, but have two things in common: first, they consume much smaller amounts of hydrogen; secondly they require much higher purities.

Also many of the small consumers require liquid hydrogen and hence require cryogenic technology for its production. These areas include:

- liquid hydrogen engines
- liquid hydrogen rockets
- metallurigical applications

Liquid hydrogen engines were researched extensively in the 1950s in the USA with encouraging results. The test program began with military intentions but the results were also applied by the NASA space program. The program began with conversions of aircraft jet engines to be fired on hydrogen and resulted in rocket engines of the 1970s and 1980s which ultimately carried the famous Shuttles into space. Hydrogen was advantageous as a fuel due to its high performance with minimum weight for fuel storage in the booster rockets. The use of hydrogen and oxygen propellants is not without its hazards, as highlighted in the ill-fated Challenger flight in January 1986 which resulted in the deaths of seven astronauts.

Although hydrogen/oxygen combustion is a common means of propulsion in rocketry, another more effective method has also been seriously investigated. Liquid hydrogen can also be used as a coolant and propellant in a nuclear reactor and this energy provides the thrust for a rocket. An extensive test programme to investigate this was undertaken in the USA in the late 1950s. Liquid hydrogen is also used in a variety of test programmes in atomic physics areas, but the quantities involved are much smaller than the military and space programmes, In all cases, liquid hydrogen is of a very high purity, as necessary in order to allow liquefaction without freezing problems.

High purity gaseous hydrogen is also use in some chemical and metal industries, e.g. hydrogenation of fats and edible oils and in nickel refining [4].

There are lots of applications for hydrogen as energy-source, if people really want to use it. The most important application for hydrogen as energy-source is the car. Cars are very important for this new technique, because a lot of the carbon dioxide (CO_2) pollution is coming from the emission of cars. If cars in the future are driving on hydrogen-gas instead of petrol, the emission will be vapor instead of pollution with CO_2.

The hydrogen Fuel initiative provides funding to accelerate R&D of hydrogen fuel and infrastructure technology. The goal is to enable industry to make commercialization decisions by 2015, so that hydrogen fuel cell vehicles can be available for purchase in showrooms by 2020. Success will require hydrogen production and distribution at a price that is competitive with gasoline, as well as hydrogen fuel cell vehicles that are competitive with gasoline and electric-hybrid vehicles.

The hydrogen-rich gas mixture produced via reforming or gasification contains 40-70% hydrogen and a variety of contaminants including carbon monoxide, carbon dioxide, nitrogen, methane, water, sulfur, and possibly tar and ash. The necessary purity of hydrogen in a polymer electrolyte membrane (PEM) fuel cell is not clearly elucidated by the percentage; while some chemicals do not affect membrane performance even in large amounts, others can cause detrimental effects in small quantities. Common safe chemicals (such as nitrogen) are considered diluting agents and must be removed simply to reduce compression and storage volumes. Dangerous agents (such as carbon monoxide, sulfur, and ammonia) are considered impurities and must be almost entirely removed. PEMs are poisoned by CO at more than 10 parts per million and by sulfur at the parts-per-billion level. Based on current available PEM fuel cell information, the tentative contaminant targets are; <10ppb sulfur, <1 ppm carbon monoxide, <100 ppm carbon dioxide, < 1 ppm ammonia, < 100 ppm non-methane hydrocarbon on a C-1 basis, oxygen, nitrogen and argon can not exceed 2% in total, particulate levels must meet ISO standard 14787. Future information on contaminant limits for on-board storage may add additional constraints. By contrast, solid-oxide fuel cells (SOFCs) for stationary applications can accept a less pure hydrogen feed, since they are not poisoned by carbon monoxide (CO) and can tolerate some sulfur [5].

1.1.4 Hydrogen purities and forms

Hydrogen is available in purities which broadly fall into two groups, the first having purities up to 99.9 percent and the second greater than 99.9 per cent by volume. The majority of hydrogen is produced at purities up to 99 percent and is usually consumed as soon as it is produced in a down stream process, e.g. ammonia synthesis. This hydrogen is invariably made only in gaseous form. Typical uses and purities are given in table 1.2.

The second category of hydrogen product is generally for special uses such as welding, hydrogenation of edible oils and fats, reduction of metal oxides, research, and as a rocket fuel. BOC limited produces four typical grades of high-purity gases and these are listed in Table 1.3. These grades are usually supplied in gas bottles, although research and space exploration establishments us liquid hydrogen. In order to liquefy this hydrogen, a comparable purity must be generated [4].

Table 1.2 Uses and purities of hydrogen.

Hydrogen user	Typical purity (%)	Typical impurities (%)
Ammonia synthesis	74-75*	24% nitrogen – used in ammonia synthesis Approx. 1-1.5% argon + methane
Hydrocracking	97-99	Methane
Hydrodealkylation	90-98	Methane Traces of ethane
Hydrotreating	90-98	Methane and other light hydrocarbons
Methanol synthesis	65-75	Carbon oxides used in reaction to form methanol

*85-90 percent for hydrogen recycled from ammonia purge gas recovery.

Table 1.3 Commercial grade hydrogen purities (maximum impurity level in v.p.m.).

Impurity	Grade			
	N4.0	N5.0	N5.5	N6.0
Oxygen	2	1	1	0.1
Nitrogen	30	5	1	0.4
Hydrocarbons	32	1	1	0.05
Carbon dioxide	3	0.05	0.05	0.05
Carbon monoxide	1	1	1	0.05
Water	2	2	1	0.5
Minimum hydrogen content (mol.%)	99.99	99.999	99.9995	99.9999

* v.p.m. = ppm by volume

1.1.5 Hydrogen purification technology

The purity of the hydrogen available to consumers can have a significant effect on the design and operation of the consuming units which is generally a hydro-processing unit. The three main hydrogen purification technologies used in refineries are 1. adsorption process, 2. selective permeation using polymer membranes, and 3. cryogenic separation. Each of these processes is based on a different separation principle, and consequently, the process characteristics differ significantly. Selecting the appropriate H_2 purification technology depends not only on the economics, but also on such project considerations as process flexibility, reliability, and ease of future expansion. This part reviews the purification process characteristics and equipment as well as other project considerations for these technologies. General selection guidelines are presented along with process integration that takes advantage of the complementary characteristics of the three processes.

- Adsorption Process

Adsorption, as applied to gas purification, is the selective concentration of one or more components of a gas at the surface of a microporous solid. The mixture of adsorbed components is called the adsorbate, and the microporous solid is the adsorbent. The attractive forces holding the adsorbate on the adsorbent are weaker than those of chemical bonds, and the adsorbate can generally be releases (desorbed) by raising the temperature or reducing the partial pressure of the component in the gas phase in a manner analogous to the stripping of an adsorbed component from solution. When an adsorbed component react chemically with the solid, the operation is called chemisorption and desorption is generally not possible [9].

- Membrane Process

POLYSEP^{TM} membrane systems are based on the difference in permeation rates between hydrogen and impurities across a gas-permeable polymer membrane. Permeation involves two sequential mechanisms: the gas-phase component must first dissolve into the membrane and then diffuse through it to the permeate side. Different components have different solubility and permeation rates. Solubility depends primarily on the chemical composition of the membrane and diffusion on the structure of the membrane. Gases can have high permeation rates as a result of high solubility, high diffusivity, or both. The driving force for both solution and diffusion is the partial pressure difference across the membrane between the feed and permeate sides. Gases with higher permeability, such as H_2, enrich on the permeate side of the membrane, and gases with lower permeability enrich on the non-permeate side of the membrane because of the depletion of components with high permeability. The first fraction of the gas to permeate through the membrane consists primarily of the components with the highest permeability. As a larger fraction of the feed gas is allowed to permeate, the relative amount of the components with lower permeability increases in the permeate stream. In hydrogen separations, higher purity hydrogen is associated with lower recovery, and lower purity hydrogen is associated with higher recovery. The effect of hydrogen purity on recovery is much more dramatic with membrane systems than with PSA or cryogenics units. A fairly small change in hydrogen purity can change the recovery significantly as show in Figure 1.3.

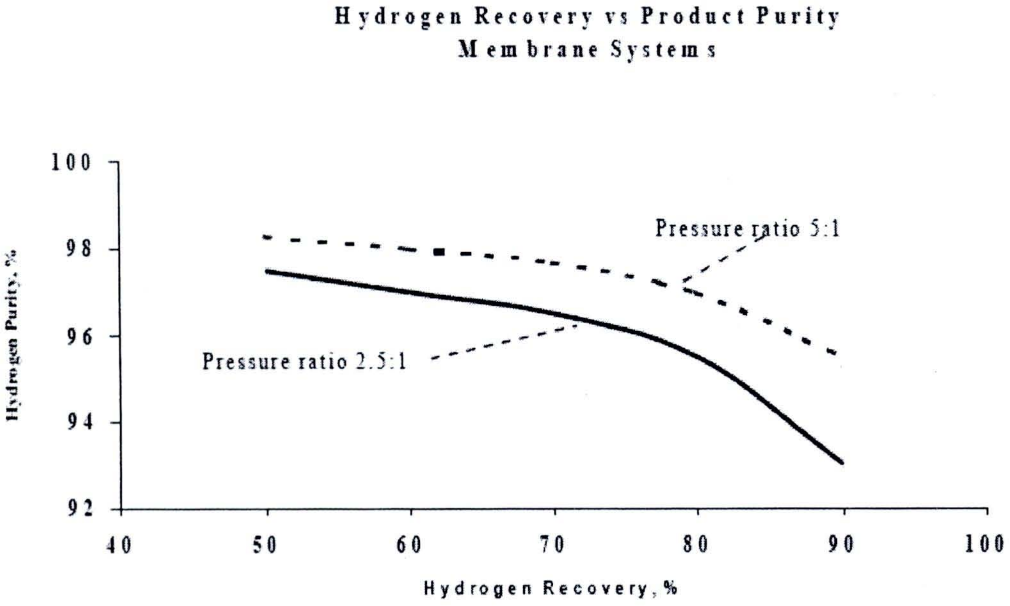

Figure 1.3 Hydrogen recovery vs product purity membrane systems.

Higher hydrogen recovery also requires that more membrane area be provided. The membrane area required when feed composition and system pressure levels are fixed increases exponentially at high hydrogen recovery. The performance of a specific membrane system, that is, the recovery versus the product purity for a given feedstock, is primarily dependent on the ratio of feed to permeate pressure and is largely independent of the absolute pressure level. However, the area requirement is inversely proportional to the feed pressure. Hence, compressing the feed gas rather than the permeate, even though the permeate flow is smaller, is often preferable when the objective is to achieve the required pressure ratio.

- Cryogenic Process

Cryogenic units are based on the difference in boiling temperatures (relative volatility) of the feed components. Hydrogen has a high relative volatility compared with hydrocarbons. The process condenses the required amount of feed impurities by cooling the feed stream against the warming product and tail-gas streams in brazed aluminum multi-pass heat exchangers. The refrigeration required for the process is obtained by Joule-Thomson refrigeration, which is derived from throttling the condensed liquid hydrocarbons. Additional refrigeration, if required, can be obtained by external refrigeration packages or by turbo expansion of the hydrogen product. The partial condensation process is normally applied to hydrogen-hydrocarbon separations. The feed needs to be pretreated to remove water and other components that could freeze in the system. The pretreated feed at high pressure, 300 to 1,200 psig, is cooled against a stream leaving the cryogenic unit to a temperature at which the majority of the C2+ hydrocarbons condense. The two-phase stream is sent to a separator where the H_2-CH_4 vapor stream is taken overhead and further cooled to a temperature low enough to give the desired hydrogen purity. The cooled stream is fed to another separator, and the hydrogen product is taken overhead. Before leaving the cryogenic unit, the hydrogen is heated by heat exchange against the hydrogen methane from the first separator and the feed. The liquid CH_4 from the second separator is expanded to a suitable pressure so that it will vaporize against the hydrogen-methane stream from the first separator. Additional cooling is provided by expanding part of the C2+ hydrocarbons product, if necessary. Thus, the cryogenic unit typically splits the feed into three products: a high purity hydrogen stream, a methane rich stream at fuel gas pressure, and C2+ hydrocarbons product, which may be two phase. By using additional separators, additional products, such as ethane-propane and LPG streams, can also be produced. If the feed stream does not contain sufficient hydrocarbons to achieve the necessary cooling by the Joule-Thomson effect alone, then additional refrigeration can be provided by expansion of the hydrogen product or a package refrigeration system, normally at 5 to -40°F [2].

This research studies the suitable condition for hydrogen purification by adsorption process which is economic when impurities are present in quantities significantly greater than a few v.p.m. (ppm by volume) to obtain the higher purity of hydrogen. The gas adsorption properties of alumina, zeolite 3A, 4A, 5A, 13X and beta are also studied.

1.2 Objective and scope of the research

1.2.1 Objective

a) To find out the best condition and suitable adsorbent for hydrogen purification by adsorption process.

b) To study gas adsorption properties of zeolite 3A, 4A, 5A, 13X and beta.

1.2.2 Scope of the research

This research studies the suitable condition for hydrogen purification by adsorption system. The various parameters such as type of adsorbents, temperature, size of adsorbents, an inlet pressure, ratio between alumina and zeolite and the life time of adsorbents were studied.