

## HYDROGEN MANAGEMENT IN REFINERIES

Zahra Rabiei

*Oil & Chemical Engineering Development, Sharif University of Technology, Tehran, Iran,*  
[rabeiez@ripi.ir](mailto:rabeiez@ripi.ir).

Received August 6, 2012, Accepted November 30, 2012

---

### Abstract

Environmental restrictions, new transportation fuel specifications, and increased processing of heavier more-sour curds are leading substantial increases in refinery hydrogen consumption for hydro-desulfurisation, aromatic and olefin saturation and improvement of product quality and reduces in refinery hydrogen production from catalytic reformers as a by-product. Therefore above factors make hydrogen management, a critical issue. Generating, recovering and purchasing of hydrogen have significant impact on refinery operating costs. More importantly, overall refinery operations, may be constrained by the availability of hydrogen. Primary consideration, however, should be given to the recovery of hydrogen contained in various purge gasses, since this is a very attractive way from the viewpoint of economy. This paper discusses three process for recovery and purification of hydrogen : adsorption by using of pressure swing adsorption, permeation using membranes, cryogenic and then compares these options from the viewpoint of economy. Then, revamping of hydrogen distribution network will be studied using actual data of an refinery in four alternatives from viewpoint of economy.

**Keywords:** hydrogen recovery; hydrogen purification; Hydrogen Management; PSA; membrane; cryogenic; economy; refinery.

---

### 1. Introduction

A refinery consist of many processes that convert crude oils into valuable products such as gasoline, jet fuel and diesel by consuming of hydrogen, etc. The required hydrogen in some processes can be supplied from other processes which are producers of hydrogen.

In the past, production capacity or product slate of refineries have rarely been limited by hydrogen availability. However, in recent years, the oil refining industry uses, increasingly, large quantities of hydrogen. Current trends in refining industries, are reducing the availability of hydrogen to the point where most refineries are concerned about their future hydrogen balance. The new specification for low-sulfur fuels, require increase hydrogen consumption in hydrotreaters. At the same time, limits on the aromatics content of gasoline and requirements for oxygenates have led to lower severity in the catalytic reformer and so less hydrogen is produced in this unit. The use of heavier crude oils and more bottom-of-the-barrel processing increase the hydrogen demand in hydrocracking and heavy oil hydrotreating units.

The refinery produces a wide range of products and intermediates from a variety of crude oil and feed stocks. Change in crude or product slates from the design basis can make it for even a new refinery to operate efficiently. The demand for gasoline and middle distillate means crude oil will require greater processing and thus more hydrogen. In future, practically all fractions of sour crude will subjected to catalytic processes that involve hydrogen. The total quantity of fractions directed to hydrotreating, hydrocracking and hydrodesulfurization will amount to 90% of the total crude run. Correspondingly, the demand for hydrogen will increase to the extent where it must be recovered from refinery gas.

Hydrogen is usually regarded as a utility in oil refining. The supply of hydrogen, which represents a cost to the refinery, must be maintained to avoid constraints on the refinery operations. If the demand for hydrogen exceeds the availability supply, then the incremental demand must be met by increasing hydrogen plant production (turning up productions or revamping existing equipment), building a new hydrogen plant, purchasing hydrogen from outside suppliers , or recovery of hydrogen that was going to fuel by installing a hydrogen purification unit or lower-cost alternative of optimizing and revamping the

hydrogen distribution network. In any case, it is very important to know the minimum hydrogen required by the system.

## 2. Hydrogen Sources within the Refinery

The primary source of hydrogen within the refinery has been the catalytic naphtha reforming unit which supplies the needs of hydrocracking and hydrotreating processes. If the hydrogen from catalytic reforming is insufficient, additional hydrogen requirements may be supplied by building a hydrogen plant that produces the gas by steam reforming of natural gas, LPG or naphtha and partial oxidation. Alternatively, hydrogen may be imported via a pipeline. Hydrogen that is obtained from a hydrogen plant or import is termed as a utility. A survey of hydrogen sources in refineries is presented in Table 1, with some typical hydrogen yields.

## 3. Hydrogen consumers within the refinery

Figure 1 shows a flow diagram of a high-conversion refinery, highlighting the hydrogen consuming processes. Hydrotreating and hydrocracking processes are not the only consumers in refineries. Other hydrogen-consuming processes include lubricant plants, isomerization process, and petrochemical processes that can be integrated with the refinery hydrogen network. The refinery might also export hydrogen across the fence, which can be considered as an additional amount consumed.

Table 1. Typical hydrogen production data for different refinery processes [1]

Process	% wt on feed	% wt on crude
Catalytic reforming:		
• Semiregeneration	1,4-2,0	0,15-0,
• Continuous	3,5	0,35-0,6
Steam reforming of methane	30	-
Partial oxidation	20-25	1,0-5,0
Catalytic cracking	0,05-0,01	0,01-0,04

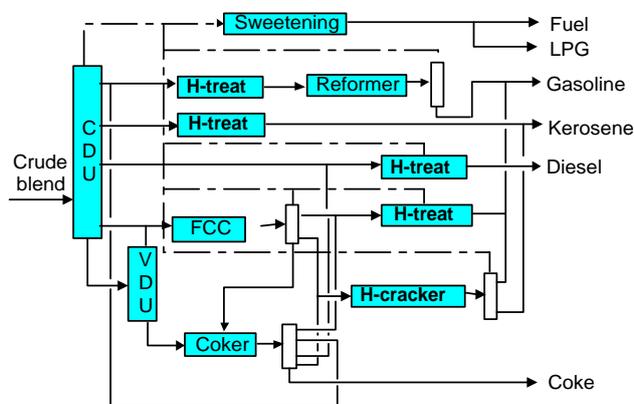


Figure 1. Simplified flow diagram of a high conversion refinery [2].

The amount of hydrogen required for a particular application depends on the hydrogen content of the feed and products, and the amount of heteroatoms (sulfur, nitrogen, etc.) to be removed. Typical hydrogen consumption data for various refinery processes are presented in table 2.

Figure 2 shows a schematic diagram of a typical hydrogen consumer (hydrotreater or hydrocracker). A liquid hydrocarbon feed is mixed with a hydrogen-rich gas stream, heated and fed to the hydrotreating or hydrocracking reactor. Some of the hydrogen is consumed in the reactor and light hydrocarbon compounds (methane, ethane, propane) and other gases ( $H_2S$ ,  $NH_3$ ) are formed. The stream from reactor is cooled and sent to a gas-liquid high pressure separator. The gas stream from separator, which is at pressure of 13.8-20.7 Mpa typically contains 70-85% hydrogen, with  $C_1-C_6$ ,  $H_2S$  and other impurities, is often treated in an amine unit to remove  $H_2S$  [4]. Then part of this gas stream is recompressed and recycled to the reactor inlet. The remaining hydrogen-rich gas stream is purged in order to prevent the build-up of contaminants in the recycle loop. This purge stream may be re-used else- here, but often is sent to the fuel system, where it is burned for its

heating value, or flared. This figure, shows the sink and source of hydrogen, clearly. Note that these are not the hydrogen make-up and purge streams, respectively. Instead, the sink is the gas stream entering the reactor and the source is the gas stream existing the separator. The sink and source data can be determined from the make-up, purge and recycle data.

Table 2. Typical hydrogen consumption data for various refinery processes <sup>[1]</sup>

Process	% wt on feed	% wt on crude
Hydrotreating		
• Straight run naphtha	0,05	0,01
• Cracked naphtha	0,7-1,0	0,05-0,1
Hydrodesulfurization		
• Low sulfur gas-oil to 0.05% S	0,15	0,04
• High sulfur gas-oil to 0.05% S	0,35	0,05
Cycle oils hydrogenation	3	0,3
Hydrocracking vacuum gas-oil	2-3	0,5-0,8

#### 4. Hydrogen recovery

Many refineries are inclined to avoid capital investment in hydrogen production facilities because the hydrogen plant is regarded as a utility and not a profit center. Over-the-fence supply may be cost-effective in some cases, but it inevitably makes the refinery critically dependent on an external supplier. Although installing hydrogen purification units is usually an attractive option, it involves complex decisions such as :

- Which stream or streams to recover?
- Which recovery technology to use?
- What inlet and outlet pressure to use?
- that trade-off to make between product purity, recovery, and capital cost?

As shown in figure 2 some of hydrogen consumer have a rich-hydrogen purge gas stream. If the pure gas stream is high enough purity and pressure, it can be cascaded to downstream hydrotreaters, and if it is low pressure or low purity it will likely be used as fuel gas. Neither of these practices is always the most economic and it may be economically advantageous to recover hydrogen from this purge gas in a hydrogen recovery unit (HRU) and use it as part of hydrogen make-up requirements.

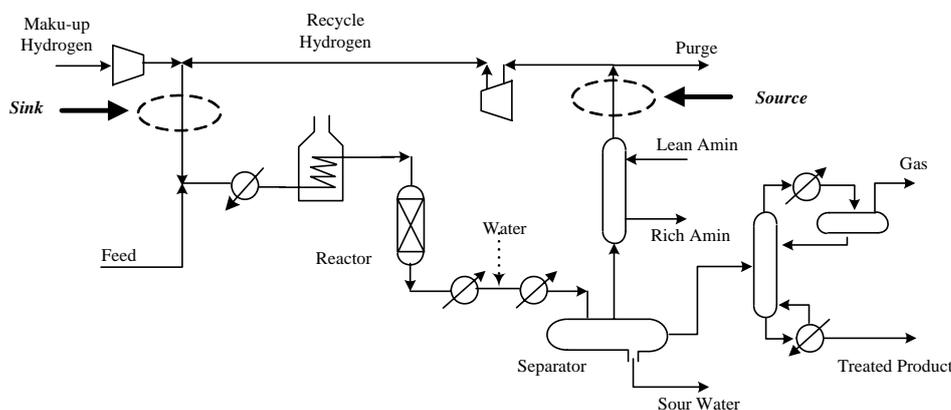


Figure 2. Schematic diagram of a typical hydrogen consumer showing the correct source and sink location <sup>[3]</sup>.

To justify hydrogen recovery from off gas or purge, it is important to clearly identify the cost and incentives on which the comparisons will be based. If the capacity of an existing hydrogen plant is limited, hydrogen recovery from off-gas or purge streams may postpone the need for incremental hydrogen production facilities or additional hydrogen plant. Any amount of hydrogen that can be recovered will reduce the size of a new hydrogen plant, which can reduce investment for this new plant or lower operating costs for natural gas feed and fuel to an existing plant. It will also be advantageous to recover the hydrogen at the highest possible pressure to reduce the compression costs. If recovered hydrogen is available as feed to it's second or third stage, depending on the pressure of the recovered hydrogen, the size and operating horsepower of the make-up compressor may be reduced. The tail gas from hydrogen recovery unit, depending on it's hydrogen content and pressure,

is used as fuel or as feed to hydrotreater. Its value as fuel gas will probably be less than hydrotreater feed gas. The value of fuel gas is its energy content as equivalent natural gas, and the value of hydrotreater feed gas is hydrogen content of it. The economic incentives for hydrogen recovery for a new plant may differ with an existing plant with existing equipment. In a new plant, the designer, depending on reliability and operating factors, may not want to downsize the hydrogen plant based on capability of hydrogen recovery unit (HRU). In this case, if hydrogen make-up capacity and compression is already installed, only operating cost savings are realized by the HRU.

## 5. Hydrogen purification technologies

The purity and pressure of the hydrogen stream available to consumers have significant effect on the design and operating of these units which is generally a hydro-processing unit. The three main hydrogen purification technologies used in refineries are pressure swing adsorption (PSA), selective permeation using membranes, and cryogenic separation. Each of these options based on a different separation principle, and consequently, the characteristics of these processes differ significantly. The appropriate hydrogen purification technology selection, depends not only on the economics, but also, on flexibility, reliability, and easy of future process expansion.

### 5.1. Pressure swing adsorption (PSA)

PSA is a hydrogen purification process in which the impurities consist of  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ , etc. in a gas stream are removed in adsorbent beds. PSA units are based on the ability of adsorbents to adsorb more impurities at high gas-phase partial pressure than at low partial pressure. The adsorbents, depending on specific application, are usually made of molecular sieve, activated carbon, activated alumina or silica gel. In this UOP process, impurities are adsorbed in an adsorber at higher partial pressure and then, desorbed at lower partial pressure. By using of this process, hydrogen is recovered at high pressure and impurities, because very little hydrogen is adsorbed relative to methane and other light hydrocarbons. The impurity partial pressure is reduced by swing the adsorber pressure from the feed pressure to the tail gas pressure and then purging with a portion of the product hydrogen. Commercial PSA units normally use between 4 and 12 adsorbers. More adsorbers are used for higher hydrogen recovery or increasing capacity.

The driving force for separation in this process is the difference in impurity partial pressure between the feed and tail gas. Minimum pressure ratio of approximately 4:1 between the pressure of feed and tail gas is usually required for hydrogen purification [5]. Since hydrogen is essentially not adsorbed in the PSA process and comes out from first stage of PSA cycle, it is available near feed pressure (typical pressure drop between the feed and hydrogen product is less than 10 psi [5]). Two advantages of this process are its ability to produce a high pressure and high purity (excess of 99 vol% and frequently 99.999 vol% [4]) hydrogen stream. Removal of  $\text{CO}$  and  $\text{CO}_2$  to a volume level of 0.1 to 10 ppm is commonly achieved. In this process the amount of hydrogen recovery is moderate (65-90% depending on the tail gas pressure) because a part of produced hydrogen is consumed for regeneration the beds. A correlation by UOP [6] indicated that recovery is fairly insensitive to feed and tail gas pressure. In refinery application the optimum pressure is in the range of 13.79-27.58 MPa. But, more important than the feed pressure is the tail gas pressure. The optimum tail gas pressure is as low as possible. It was found, with low pressure tail gas (0.034 MPa) having 15-20% better recovery than 0.41 MPa tail gas pressure. However the cost to compress low pressure tail gas to enter the 0.41 MPa fuel gas system can be significant and the operating pressure of a PSA unit should be optimized. PSA systems are insensitive to change in feed composition for constant hydrogen purity and recovery.

### 5.2. Membrane process

Membrane systems are based on the difference between in permeation rates between hydrogen and impurities across a gas-permeable polymer membrane. Permeation involves two sequential mechanisms: the component of gas phase 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 on the chemical composition of the membrane and diffusion on the structure of the membrane. Components with higher permeability, such as hydrogen, dissolve in to the polymer membrane on the high pressure side and diffuse to the low pressure side and components with lower permeability, are retained on the high pressure side because of the depletion of components with high permeability. High

permeation rates are due to high solubilities, high diffusivities, or both. The driving force is the difference in partial pressure, with the highest driving force giving the highest recovery. The polymeric membranes used for separation consist of cellulose acetate, polyacetate, polysulfonate, polyamide and polyimide. Membrane units can recover hydrogen at moderate purity (90-95%) and moderate recovery (85-90%) [4]. A correlation by UOP [6] indicates with a significant decrease in recovery the purity increase slightly. The effect of hydrogen purity on recovery with membrane systems is much more dramatic than with PSA or cryogenic units. The performance of a specific membrane system, that is, the recovery versus the product purity for a given feedstock, is dependent on the ration of feed to permeate pressure and is largely independent of the absolute pressure level. Hence, even when permeate flow is smaller, if the objective is achieving of the required pressure ratio, compressing the feed gas before permeate, is often preferable. The pressure of tail gas from membrane unit is near feed pressure and must be reduced for use as fuel gas. If the flow rate of tail gas is significant, the Energy from pressure reducing could drive a turbine.

When a membrane unit is installed, a preheater exchanger and separator is required to remove any heavy components that could be condense and damage the membrane. H<sub>2</sub>S can damage the membrane and must be removed from the feed gas, usually by amine treating.

Changes in feed composition will have a large effect on product purity. Membranes have no moving parts and are reliable.

### 5.3 Cryogenic process

The cryogenic process using partial oxidation removes the hydrocarbon impurities from the hydrogen stream. Cryogenic units are based on the difference in volatility (boiling temperature) of the feed components. Hydrogen has a high relative volatility compared with methane and other light hydrocarbons. In this process, the required amount of feed impurities is condensed by cooling the feed stream against warming the product and tail gas streams in multi-pass heat exchanger. The refrigeration required for the process is obtained by Joule-Thomson refrigeration derived from throttling the condensed liquid hydrocarbons. If additional refrigeration is required, it can be obtained by external refrigeration packages or turbo expansion of the hydrogen product.

This process is typically applied for separation of hydrogen-hydrocarbon. If the feed contains water and other components that could freeze in the system, rather than entering to cryogenic unit should be preheated. The preheated feed at high pressure, 700-1200 psig, is cooled against a stream from the cryogenic unit to a temperature at which the majority of C<sub>2</sub><sup>+</sup> hydrocarbons condense. The two-phase stream is sent to a separator and then the hydrogen-hydrocarbon vapor from overhead of it is cooled to a low temperature enough for obtaining the desired hydrogen purity. The cooled stream is sent to another separator and the hydrogen product from overhead of this separator, before leaving the unit, is heated against the hydrocarbon-methane from the first separator and the feed. The liquid methane stream 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, if required, can be obtained by expanding part of the C<sub>2</sub><sup>+</sup> hydrocarbons.

Thus the cryogenic unit, typically separate the feed into three product, a high purity hydrogen stream, a methane-rich stream at fuel gas pressure, and a C<sub>2</sub><sup>+</sup> hydrocarbons product, which may be two phase. Additional products, such as ethane-propane and LPG, can be produced using additional separators.

When the feed pressure is low, the feed hydrogen content is less than 40% and there are higher concentration of heavier hydrocarbons which can be easily condensed, cryogenic process can be the best process for hydrogen purification. There is a correlation between hydrogen purity, recovery, and tail gas pressure, moderate purity (90-95%) will achieve with high recovery (90-95%) when the tail gas pressure is kept low (0.07Mpa) [4].

Cryogenic process is cost intensive and in processing varying feed composition has less flexibility and sometimes requires supplemental refrigeration and is considered less reliable than PSA or a membrane and the feed needs pretreatment. Due to disadvantages of cryogenic process for hydrogen purification, typically not used in refineries and therefore it was not considered in this study.

## 6. Technology selection for hydrogen recovery from refinery off-gases

The hydrogen content and operating pressure of the refinery off-gasses have a large influence on both the process recovery selection and the capital investment for the recovery unit. Higher purity hydrogen is usually more valuable for hydrotreater feed or as make-

up hydrogen. Purified Hydrogen with higher pressure will be more valuable because of reducing the make-up compression cost. Table 3 presents hydrogen content (vol%) and pressure of various hydrogen-rich gases that are obtained in petroleum processing. Hydrogen recovery is appropriate for most of these processes except for catalytic cracker off gas.

Table 3. Hydrogen content and pressure in refinery off-gases [1]

Process	Hydrogen content, (% vol.)	Initial pressure (MPa)
Catalytic reforming	40-85	2,8
Catalytic cracking (off-gas)	10-30	5,5
Hydrocracking (off-gas)	40-60	1,7-2,86
Hydrotreating (purge)	25-35	4,5
Thermal hydrodealkylation	50-75	2,8-2,6
Hydrogenation (purge)	85	-

Both of performance criteria (hydrogen recovery and feed and product conditions) and operational requirements (flexibility, reliability, pretreatment of feed and by-product recovery) are influenced on selection of hydrogen purification technology. Table 4 has summarize these factors for each of the three technologies.

All of three hydrogen recovery technologies (PSA, membrane, cryogenic) can give product with more than 90 vol% hydrogen purity. Since, off gas from catalytic reformer unit in refineries dose not contain impurities that are available in other off gases, PSA is appropriate for hydrogen recovery from this off gas for use in hydro-processing units. For hydrogen recovery from catalytic cracker off gas, cryogenic is appropriate, but generally, for justifying a project, recovery of C<sub>2</sub> components and LPG, not hydrogen alone, is necessary. As shown in Table 4 the PSA process requires the feed with relatively high hydrogen purity (typically above 50 vol %) at moderate pressure, but produces a high purity product with little pressure drop and good hydrogen recovery from the feed. The high purity hydrogen from a PSA unit helps obtain a recycle gas with high purity in the hydro-processing unit and the small pressure drop across this unit avoids excessive recompression.

Membrane systems product hydrogen stream with moderate purity at low pressure but with high recovery. Therefore, such systems because of operation under sizeable pressure drop, are more appropriate to recovering hydrogen from high pressure purge gasses. catalytic reformer off gas, because of high hydrogen concentration, enhances membrane performance. However, membrane can produce hydrogen with purity less than PSA unit.

In cryogenic units, hydrogen pressure loss is much less than membrane systems and this process is most attractive if the hydrogen content of the feed is low (30-50 vol%). By using cryogenic units, recovering of by-products, such as ethane and methane is possible. The cryogenic process is thermodynamically the most efficient hydrogen purification technology, but PSA process, despite it's lower hydrogen recovery, is the most commonly hydrogen purification technology.

Sometimes, a combination of purification technologies is the most appropriate selection. For getting high recovery and high purity of hydrogen at high pressure with by-product recovery, cryogenic in integration with PSA is the best combination, can provide the required high purity hydrogen at high overall recovery, probably [5].

Table 4. Process and operational consideration for hydrogen purification technologies [5]

Cryogenic	Membrane	PSA	Factors
Minimum feed H <sub>2</sub> , %	15	15	50
Feed pressure, psig	200-1,200	200-2,000	150-1,000
H <sub>2</sub> purity, %	97 max.	98 max.	99.9 +
H <sub>2</sub> recovery, %	Up to 98	Up to 97	Up to 90
CO + CO <sub>2</sub> removal	No	No	Yes
H <sub>2</sub> product pressure	App. Feed	Much less than feed	App. feed
Feed pretreatment	Yes	Yes	No
Flexibility	Average	High	Very high
Reliability	Average	High	High
By-product recovery	Yes	Possible	No
Ease of expansion	Low	High	Average

## 7. Cost analysis of hydrogen recovery in refineries

A gas containing hydrogen can always be purified to deliver approximately pure hydrogen to any unit that consume hydrogen, except when the cost of purification is too expensive. Therefore, deriving force for recovery of hydrogen is set by economics. Hydrogen is consumed to add value to feedstock. Therefore, the difference between the recovery cost and the value added represents the deriving force for hydrogen transfer. In reality, we should only recover hydrogen when there is a financial incentive to do so: i.e., when the net value generated in the hydrogen consumer process is sufficient to cover all of the hydrogen recovery costs. For any process that is a source of hydrogen we can plot the marginal cost of recovering hydrogen against the amount recovered [7].

When the refinery has a hydrogen plant, it can be thought of as an external utility, which the size of it is fixed in the design stage. The cost of hydrogen from the hydrogen plant is mainly a function of feedstock price and dose not depend strongly on the hydrogen plant size. In some cases, hydrogen is even purchased "over the fence", in which case a fixed price applies regardless of the amount purchased. If the cost of recovered hydrogen is more expensive than that produced by hydrogen plane hydrogen recovery is not economical. Therefore, any portion of the source with a higher recovery cost than the hydrogen plant represents an amount of hydrogen that is not economically recoverable and should be sent to fuel system.

The value added per unit hydrogen consumed in each individual process minus the cost of the feed (not including hydrogen) and any capital charge and other operating costs, all divided the rate of hydrogen consumption [7].

$$VA_H Q' = \sum_i w_i p_i - \sum_j v_j f_j - \sum_k C_{o,k} - C_C \quad (1)$$

$$v_j = w_c + u_j \quad (2)$$

### 7.1. Operating Costs

Hydrogen is usually recovered from refinery off gases using either membrane diffusion or pressure swing adsorption (PSA). The cost of recovered hydrogen,  $C_H$ , is given by [7]:

$$C_H = C_F + C_W + C_R \quad (3)$$

#### 7.1.1. Fuel Cost

The fuel value of the hydrogen,  $C_F$ , is the cost of providing extra fuel to compensate for the calorific value of the hydrogen that is removed from the off gas. This value depends on the site fuel balance and varies from zero when the site has a net fuel surplus to the cost of an equivalent amount of natural gas when the site has a net fuel deficit. For the case study in this paper,  $C_F$  was taken as 0.431 \$/kmol (0.544 \$/Mscf).

#### 7.1.2. Compressor Power Cost

The compressor work,  $C_W$ , includes both feed and product compression and is given by [7]:

$$C_W = \frac{c_p T_1}{\eta} \left[ \left( \frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} - 1 \right] \quad (4)$$

#### 7.1.3. Hydrogen Recovery Process Cost

##### a. Pressure swing adsorption Process

For PSA process, the cost of the purification can be estimated from eq 5 [7].

$$C_R (\$/_{1994} / kmol) = \frac{18.04}{Q} + \frac{0.2364}{Y_z} \quad (5)$$

In typical refinery applications, the cost of process is almost independent of the purity of hydrogen produced.

##### b. Membrane Process

For the membrane process, the area required,  $A$ , is given by [7]:

$$A = \frac{YGz}{R_P P_L \left[ r \left( \frac{z - x_r}{\ln\left(\frac{z}{x_r}\right)} \right) - y \right]} \quad (6)$$

Concentration in the residual gas, given by :

$$x_r = \frac{y(1-Y)z}{(y-Yz)} \quad (7)$$

For membrane process, the cost of the recovery can be estimated from eq 8 [7].

$$C_R (\$/_{1994} / kmol) = 0.0391 + 0.0114 \frac{AR_P P_L}{Q} \quad (8)$$

The cost is not strongly dependent on purity, so for convenience the purity of recovered hydrogen is set at 99%. The above equations are used for finding the cost of hydrogen recovery from any off-gas at different values of recovery yield,  $Y$ . Since the recovered hydrogen is essentially pure, the amount of hydrogen recovered can be calculated as :

$$Q = GYz \quad (9)$$

The total cost,  $C_T$ , is :

$$C_T = QC_H \quad (10)$$

and the marginal cost  $C_M$  (\$/kmol or \$/Mscf) is:

$$C_M = \frac{\delta C_T}{\delta Q} \quad (11)$$

## 7.2. Investment Costs

The investment cost is consist of the costs of new compressors, new purifiers and piping.

### 7.2.1. Compressors

The capital cost of a compressor as given in Peter and Timmerhaus [8], is the linear function of power consumption, i.e.:

$$C_{comp.} (\$) = a_{comp.} + b_{comp.} \times Power(kw) \quad (12)$$

For case study  $a_{comp.} = 115000$  ,  $b_{comp.} = 1910$ .

### 7.2.2. Purifiers

The cost of a PSA unit is calculated as a linear function of the feed flow rate [7]:

$$C_{PSA} (\$) = a_{PSA} + b_{PSA} \times F_{in(PSA)} (MMscfd) \quad (13)$$

For case study  $a_{PSA} = 503800$  ,  $b_{PSA} = 347400$ .

### 7.2.3. Piping

The piping cost in case study is taken as 10% of total investment cost. Because the detail information about piping length between refinery process units was not available.

## 8. Case Study

A simplified hydrogen distribution system for a typical refinery is shown in figure 3 (the unit of flow rate is Kmol/hr) . This system consists of hydrogen producers [e.g., hydrogen generation unit (HGU), atalytic reformer (CCR)], consumers [e.g., hydrocacking unit (HCU), naphtha hydrotreater (NHT)]. One of the two hydrogen producers is the hydrogen generation unit (HGU), where high-purity hydrogen is produced. The other producers is the catalytic reformer (CCR), where hydrogen is generated as a byproduct. Hydrogen consumers require hydrogen at different purities and pressures.

As shown in this figure, 3 streams with relatively high-purity hydrogen is sent to fuel system of refinery. To use hydrogen efficiently, some these gases, can be purified in hydrogen

recovery process such as pressure swing adsorption (PSA). The purified hydrogen can then be sent to hydrocracker unit (HCU) as a hydrogen make-up. The rest of the purge gases with small amount of hydrogen that are not worth recovering are delivered to the refinery fuel plant.

The make-up gas rates of most hydrogen consumers (e.g. hydrotreaters and hydrocrackers) depend heavily on the hydrogen purity in the gas make-up. In other words, the make-up gas with purer hydrogen, the lower gas flow rate, and thus, the less compression work required for the same liquid throughput. However to increase the hydrogen purity, low purity hydrogen needs to be purified, which results in hydrogen loss and extra operating cost. Therefore there is tradeoff between the hydrogen purity, the gas flow rate and the cost penalties. In addition the feed conditions of the purification process are another important issue in hydrogen network optimization, as the processes at different purity and pressures as feed. Overall the objective of optimizing the hydrogen network is to minimize the hydrogen operating costs, including the feedstock cost for the hydrogen generation unit and the total compression cost.

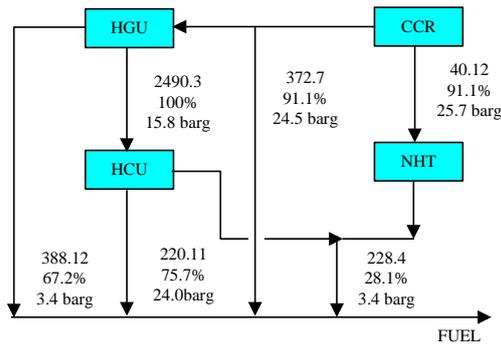


Figure 3. Hydrogen distribution system in a real typical refinery.

In this study, two alternative for hydrogen recovery from fuel streams contained of hydrogen are recommended and compared from the view point of investment and operating cost and profit and payback time.

At first alternative, two high pressure streams from hydrocracker unit (HCU) and catalytic reformer (CCR) are used for purification and delivering to hydrocracker unit as hydrogen make-up. The simplified hydrogen distribution diagram after modification is shown in fig. 4a.

At second alternative, it is assumed to use of fuel stream from hydrogen generation unit (HGU) for purification. For this purpose, at first, this stream after passing through a compressor, is pressurized to 24.5 barg. The simplified hydrogen distribution diagram after modification is shown in figure 4b.

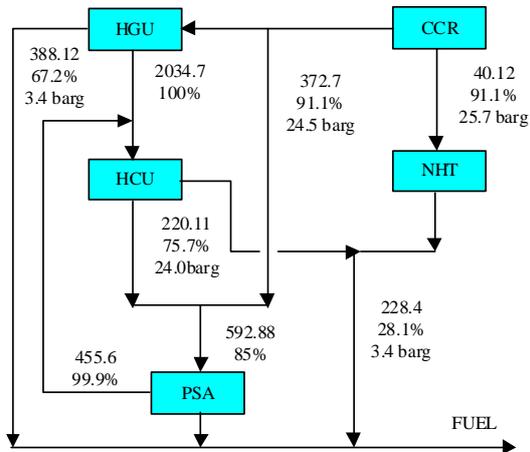


Figure 4a. Modified hydrogen distribution system (first alternative)

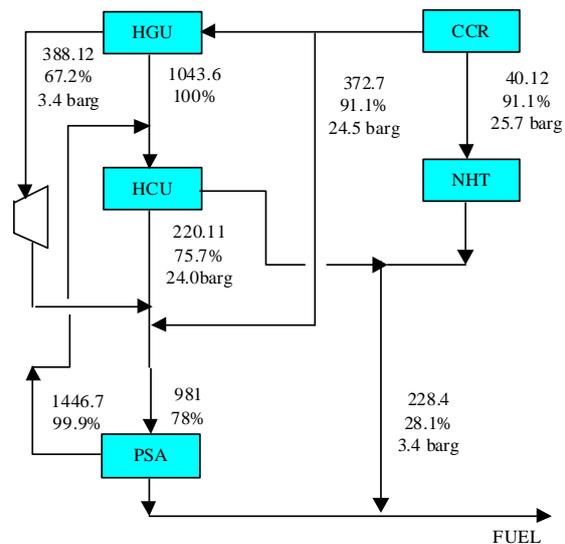


Figure 4b. Modified hydrogen distribution system (second alternative)

The calculation results related to operating and investment cost and profit and payback time are given meanwhile these results have been obtained using several practical constraints consist of :

1. The PSA production purity is given as 99% and the recovery is 90%.
2. Hydrogen production cost in hydrogen plant is at least 2\$/Kmol.
3. Pressure drop in PSA unit is between 7.5 to 10 psi.
4. Fuel value is  $C_F = 0.431\$/Kmol$ .

Table 5. Comparison of two alternatives for modification of hydrogen distribution system

Alternative	Operating Cost (million \$/year)	Investment Cost (million \$)	Profit (million \$/year)	Payback Time (month)
First alternative (Figure 4.a)	Fuel : 1.72 PSA : 1.53 Total : 3.25	PSA : 4.42 Piping : 0.49 Total : 4.91	4.73	18
Second alternative (Figure 4.b)	Fuel : 2.61 Compressor : 0.92 PSA : 1.69 Total : 5.22	Compressor : 2.68 Piping : 1.07 Total : 10.73	5.95	22

## 9. Conclusion

Now, by considering the summarized economic results in table 5 and refinery operating limitations and the main purpose of hydrogen network modification in this real refinery, one of these two alternatives may be recommended.

## Nomenclature

A	membrane area (m <sup>2</sup> or ft <sup>2</sup> )
$C_{Comp.}$	capital cost of compressor (\$)
$C_F$	fuel value of recovered hydrogen (\$/kmol or \$/Mscf)
$C_H$	cost of recovered hydrogen (\$/kmol or \$/Mscf)
$C_{O,K}$	operating cost of utility k consumed in a process unit (\$/day)
$C_{PSA}$	capital cost for PSA unit (\$)
$C_R$	cost of the recovery process (\$/kmol or \$/Mscf)
$C_T$	total cost of hydrogen production (&)
$C_W$	cost of compressor work per unit hydrogen recovered (\$/kmol or \$/Mscf)
$c_p$	gas average heat capacity (J mol <sup>-1</sup> K <sup>-1</sup> )
$f_j$	flow rate of feed j consumed in a process unit (m <sup>3</sup> /day or bbl/day)
G	gas feed rate (Kmol/hr or MMscf/day)
$P_1$	compressor inlet pressure
$P_2$	compressor outlet pressure
$P_L$	delivery pressure for gas produced in a membrane separator
$p_i$	flow rate of product i produced
Q	flow rate of hydrogen (kmol/hr or Mscf/day)
$R_p$	membrane permeability (kmol N <sup>-1</sup> h <sup>-1</sup> or MMscf/(ft <sup>2</sup> psi day)
r	pressure ratio in membrane process
$T_1$	compressor gas inlet pressure (K)
$U_j$	processing cost incurred in upstream units (\$/m <sup>3</sup> or \$/bbl)
$VA_H$	value added per unit hydrogen consumed (\$/kmol or \$/Mscf)
$v_j$	cost of feed j (\$/m <sup>3</sup> or \$/bbl)
$W_c$	compressor work (W)
$w_c$	price of crude oil (\$/m <sup>3</sup> or \$/bbl)
$w_i$	price of product i (\$/m <sup>3</sup> or \$/bbl)
$x_r$	hydrogen concentration in the residual gas from the membrane process
Y	recovery yield of hydrogen
y	hydrogen purity
z	feed mole fraction of hydrogen

- $\gamma$  ratio of gas specific heats  
 $\eta$  isentropic efficiency of compressor

### **Abbreviations**

- CCR catalytic reformer  
 CDU crude oil distillation unit  
 HCU Hydrocracker unit  
 HGU hydrogen generation unit  
 NHT Naphtha hydrotreater unit  
 PSA pressure swing adsorption  
 VDU vacuum distillation unit

### **References**

- [1] Aitani, A.M., "Process to Enhance Refinery- Hydrogen Production", Petroleum and Gas Technology Division, The Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia, 11 July 1995.
- [2] Alves, J.J., Towler, G.P., "Analysis of Refinery Hydrogen Distribution Systems", *Ind.Eng.Chem.Res.*, 2002, vol.41, 5759-5769.
- [3] Hallale, N., Liu, F., "Refinery Hydrogen Management for Clean Fuels Production", *Advances in Environmental Research*, 2001, vol. 6, 81-98.
- [4] Permanu, S., Cox, B.G., Pruden, B., "Economic of Hydrogen Recovery process for the purification of Hydroprocessor Purge and Off-gases", *International Journal of Hydrogen Energy*, 1999, vol.24, 405-425.
- [5] Whysall, M., Picioccio, K.W., "Selection and Revamp of Hydrogen Purification Processes", UOP LLC, Des Plaines, Illionios, Prepared for Presentation at the 1999 AIChE Spring Meeting, Houston, Texas, 13<sup>th</sup>-18<sup>th</sup> March, 1999.
- [6] Miller GQ, Stocker J., "Selection of a Hydrogen Separation Process", NPRA Annual Meeting, San Francisco, California, 19-21 March, 1989.
- [7] Towler, G.P., Mann, R., Serriere, A.j., Gabaude, C.M.D., "Refinery Hydrogen Management: Cost Analysis of Chemically-Integrated Facilities", *Ind. Eng. Chem. Res.*, 1996, vol.35, 2378-2388.
- [8] Peter, M. X., Timmerhause, K. D.: "Plant Design and Economics for Chemical Engineers", McGraw –Hill, New York 1990.