Hydrogen Recovery from Refinery Off-gases

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Abstract: Separation of hydrogen from an existing refinery off-gas stream represents an opportunity to achieve significant cost reductions in refineries in the coming years providing that the efficient and economical technologies are available for retrofit of the existing hydrogen plant or to build a new plant. Three different techniques have been evaluated from the literature for the hydrogen separation from off-gases i.e., pressure swing adsorption, cryogenic and membrane. All these processes are simulated using sequential modular and equation oriented processes. The first two processes can be retrofitted to existing units, they ensure significant amount of energy to recover hydrogen for subsequent sequestration. This study presents a techno-economic comparison of the performance of these techniques. The results show that all processes are expensive options to recover hydrogen from refinery off-gases. However, the membrane technology, based on the hydrogen permeation, appears to be more attractive and feasible. A perfect mixing model was adopted to describe the flow pattern in the membrane module.

Key words: Hydrogen recovery, off-gas, separation, PSA, cryogenic, membrane

INTRODUCTION

Hydrogen is one of the main intermediate products largely utilized in oil and petrochemical industries. Its usage has been constantly growing in modern refineries, chemical and petrochemical complexes in order to treat heavier oil feedstock. In some refining processes, hydrogen is both used as a raw material and obtained in some processes as a by-product. Generally, in refineries or petrochemical complexes, the off-gas streams contain considerable amount of hydrogen, which are mostly incinerated in refinery flares as a waste gas. At the same time valuable hydrocarbons are converted into hydrogen in reformers in order to produce the hydrogen needed for hydrogen consuming processes. The hydrogen demand in refineries is constantly growing due to more severe environmental regulations. This leads to higher capital cost needed to build new hydrogen plants or increase the capacity of the existing ones. Therefore, the hydrogen recovery from the off-gases could be considered as a promising approach to make effective use of the existing facilities. The novel approach may considerably decrease the hydrogen production cost in the refineries. The recovered hydrogen can either be used as a raw material in a refinery or can be sold as a new product to downstream industries.

Separation techniques and one retrofit/revamp: There are some techniques developed for the separation of hydrogen from off-gases. These techniques are:

- Cryogenic Technology (CT)
- Pressure Swing Adsorption technology (PSA)
- Membrane Technology (MT)

These techniques, their application to hydrogen separation technology and their advantages and limitations are described below.

Cryogenic technique: Cryogenic technology is based on the difference in the relative component volatility at low temperatures. Since hydrogen has a higher volatility than the other components presented in the off-gas stream, it remains as a gas, while the other components become condensed easily when the temperature is lowered extensively. This would result in condensating the impurities of the off-gas, which in turn, leads to separate the gaseous hydrogen from these impurities. The disadvantages of this method, which result in higher capital cost of such purification unit, are as followings:

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Off-gases are usually available at low pressure and have to be compressed up to at least 20 bars in order to be able to return to the hydrogen main header. Therefore, additional equipment, i.e., two centrifugal compressors and two after coolers have to be employed\(^6\).

Off-gases usually contain about 8% CO\(_2\) (mole) as an impurity that may be freeze out during low temperature process\(^5\). Consequently, a CO\(_2\) separation plant, as a pretreatment stage, has to be considered before passing the gas into the cryogenic process. Therefore, the auxiliary unit should be included using this technique for CO\(_2\) separation, however in this way, the compressed CO\(_2\)-free off-gas enters the cryogenic section.

There are three options to be considered in the cryogenic process\(^5\):

- Using a Joule-Thomson valve
- Using a turbo-expander
- Using plate-fin heat exchangers

In order to have a low pressure off- gas stream inherently, Using a Joule-Thomson valve or a turbo-expander process is not recommended\(^5\) because hydrogen content in the final product stream would be low (less than 90% mole). However, plate-fin heat exchangers would produce the desired hydrogen purity up to 97% (mole)\(^5\). Such high purity could be achieved using two plate-fin heat exchangers. In addition to the use of cold process streams, which are produced in the separators and then used as the refrigerant in the heat exchangers, employing an auxiliary refrigerant such as liquefied nitrogen is necessary to provide enough cooling. This process is simulated using the sequential modular approach.

PSA technique: The PSA is a cyclic process used for the separation of hydrogen from the off-gas stream\(^3\). This technique is based on the pressure changes effect on adsorption of hydrogen in a fixed bed. In this technique, an adsorbent (e.g., Zeolit-5A)\(^3\) is used to separate hydrogen from the pressurized off-gases. This separation process consists of four steps, i.e., re-compression, adsorption, desorption and blow-down\(^3\). This process is rather complex in nature and could not be easily simulated using the sequential modular approach. Thus, an equation oriented approach is needed to simulate this process. The details are given below.

Assumptions and constrains made for developing the model, are listed below:

- The off-gas is a binary mixture of hydrogen and methane. This assumption is justified by low concentration of other components in the industrial off-gas stream.
- The mixture is ideal.
- Axial pressure gradients are neglected.
- Axial dispersion is negligible.
- A Linear Driving Force (LDF) model is assumed.
- Equilibrium isotherm is linear.
- The process is isothermal. This is justified due to low adsorption heat.

Material balance for the separation of hydrogen in fixed beds is\(^3\):

\[
\frac{\partial y_i}{\partial \tau} = \left( \frac{-u_t}{L} \right) \frac{\partial y_i}{\partial Z} + \frac{1-e}{\epsilon} \left( \frac{RT q_{\text{scale}}}{p_{t_{\text{end}}}} \right) \frac{\partial q_i}{\partial \tau}
\]  
(1)

And according to LDF model:

\[
\frac{\partial q_i}{\partial \tau} = k_{\text{op}} t_{\text{end}} \left( q_i^* - q_{\text{scale}} q_i^- \right)
\]  
(2)

Assumption of the linear equilibrium isotherm results in:

\[
q_i^* = \frac{k_e y_i}{R.T}
\]  
(3)

Combining Eqs. 1-3, leads to the following expression:

\[
\frac{\partial q_i}{\partial \tau} = A \frac{\partial y_i}{\partial Z} - B y_i + C
\]  
(4)

Where:

\[
A = \frac{-u_t}{L}
\]  
(5)

\[
B = \frac{1-e}{\epsilon} \frac{p_{t_{\text{end}}}}{\rho_b} k_{\text{op}} \left( k_e + \frac{1}{\rho_b} \right)
\]  
(6)

\[
C = \frac{1-e}{\epsilon} k_{\text{op}} y_0 t_{\text{end}}
\]  
(7)

Eq. 4 could be solved by the Laplace transform method in each step of PSA, individually.

Membrane technology: Hydrogen enrichment using membrane technology is one of the economical methods to recover hydrogen from off-gases due to low costs (i.e., operating and capital) and ease of operation\(^6\). The Membrane technology is based on the selective separation properties of a polymeric membrane. The small molecules are separated from larger molecules in the membrane systems due to their higher permeation capability. Hydrogen is one of the high permeability
gases, which can be separated from the other components of the off-gas through the polymeric membrane. The driving force needed for the separation in this technique is partial differential pressure across the membrane module\(^{10}\). This process also has to be simulated using the equation oriented approach. The details are given below.

Assumptions made for developing the model are listed below:

- A glassy polymer (polyvinyltrimethylsilane) is used.
- perfect mixing model (Fig. 8) is used.
- A multicomponent mixture is assumed.

Considering the above-mentioned assumptions, the process could be simulated using the following equation:

\[
Z_i = \frac{P_{RX_i}}{Q_iA_i} = \frac{\Phi L_i I_i + P_F + P_P}{1 - \Phi} (1 - \Phi)
\]  

Usage of off-gases in hydrogen production plant: Steam reforming is the most ordinary process to produce hydrogen from natural gas. This process is based on the reforming of natural gas in a catalytic reformer at high temperature and pressure. The off-gas streams could be consumed inside the hydrogen production plant as a raw material and two options may be taken into account accordingly:

- Hydrogen production plant’s retrofit, in this case off-gas stream is used as a raw material inside the hydrogen production plant with considering constant plant capacity.
- Hydrogen production plant’s revamp.

In order to have an off-gas stream with a high flow rate, revamping of hydrogen production plant is not recommended because, the simulation results show that heat exchangers are not adequate. Also, when the capacity is increased, the reformer duty and the consumption rate will be accordingly increased leading to an enlargement in reformer size. However, usage of off-gas stream with considering constant plant capacity could be considered. Due to check usage of the off-gas in existing hydrogen production plant, existing plant could be simulated using the sequential modular approach.

RESULTS AND DISCUSSION

In order to choose the feasible technique among the separation techniques for the hydrogen recovery from the off-gas stream, several factors have to be considered\(^{11}\):

- off-gas stream properties (composition, pressure, flow rate)
- recovering gas properties (purity, pressure)

Sample industrial data of an off-gas stream are shown in Table 1 and were used as the base case in this work.

Cryogenic: The information about the cryogenic operation such as hydrogen concentration at the end of operation and the choice of operating conditions are presented as followings:

CO\(_2\) separation unit is simulated by a sequential modular approach with Di-ethanol Amin (DEA) in an amine contactor. Figure 1 shows number of trays versus CO\(_2\) concentration in the product gas. As expected, CO\(_2\) concentration decreases as the number of trays go up in the amine contactor because of more surface area. In this figure, minimum CO\(_2\) concentration 100 ppm can be reached with 30 trays.

![Figure 1: Effect of no. of trays on CO\(_2\) mole fraction in a DEA amine contactor](image)

![Figure 2: Variation of enthalpy vs. pressure curve for off-gas stream (cryogenic technique)](image)
Figure 2 shows the variation of Enthalpy vs. pressure for CO₂-free off-gas stream. Outlet stream from CO₂ separation unit is located in point A. It could be seen in this figure that the enough cooling of gaseous compressed off-gas stream leads to a two-phase flow and then gaseous hydrogen could be separated from liquefied hydrocarbons. Expansion types i.e., Joule-Thomson or turbo-expander, could be compared in this figure easily because Joule-Thomson is an isenthalpic process but turbo-expander is an isentropic process.

Figure 3-5 show the flow diagram of the process using Joule-Thomson method, turbo-expander method and plate-fin heat exchangers method respectively. Joule-Thomson and turbo-expander methods could not be capable of separation of hydrogen from the typical off-gas stream due to low pressure in feed. But plate-fin heat exchanger method (Fig. 5), with using of 482 kg h⁻¹ liquefied nitrogen as a refrigerant (because process cold streams producing in separators have not enough potential to prepare enough cooling) leads to a 97% (molar) hydrogen stream.

**PSA:** In this section the PSA operation results were presented based on the mathematical model developed in the previous section. Solution of Eq. 4 with considering model parameters in Table 2 provides a stream with %65 (mole) hydrogen in purity.

Figure 6 shows H₂ purity changes in adsorption step versus bed length. This figure illustrates that the hydrogen concentration increases with increasing of the bed length for a constant bed diameter. Simulation results show that obtaining a highly-pured H₂ with a short bed is impossible due to low content of H₂ in feed stream[2].

Figure 7 shows H₂ purity changes in adsorption step versus the bed diameter. This figure illustrates that the hydrogen concentration increases with increasing of the bed diameter for a constant bed length. Simulation results show that obtaining a highly-pured H₂ with shallow beds is impossible due to low content of H₂ in feed stream[2].

**Membrane:** Figure 8 shows the schematic of the membrane used in this study. Simulation results showed with 10⁻9 m² polymer surface area, the product stream may reach to 99% (mole) hydrogen while it depends on the that dimensions of membrane vessel and pressure of feed.

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**Table 1: Industrial off-gas stream specification**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass flow rate (Kg h⁻¹)</td>
<td>5800.00</td>
</tr>
<tr>
<td>Pressure (bara)</td>
<td>1.20</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition (% mol)</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>i-C₄</th>
<th>n-C₄</th>
<th>i-C₅</th>
<th>n-C₅</th>
<th>C₆</th>
<th>CO</th>
<th>CO₂</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>45.74</td>
<td>5.46</td>
<td>3.84</td>
<td>0.98</td>
<td>0.59</td>
<td>0.18</td>
<td>0.07</td>
<td>0.04</td>
<td>0.64</td>
<td>8.84</td>
<td>33.62</td>
</tr>
</tbody>
</table>

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**Table 2: Typical simulation parameters for PSA system**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε</td>
<td>0.3</td>
</tr>
<tr>
<td>Pₛ</td>
<td>750</td>
</tr>
<tr>
<td>D</td>
<td>4.5</td>
</tr>
<tr>
<td>L</td>
<td>9</td>
</tr>
<tr>
<td>kₑ</td>
<td>0.007</td>
</tr>
<tr>
<td>kₑ₀</td>
<td>0.021*10⁻³</td>
</tr>
<tr>
<td>tₑ₀</td>
<td>600</td>
</tr>
</tbody>
</table>
stream. This part of results provides the membrane operation results based on the hydrogen permeation through a glassy polymer.

Figure 9 shows area needed versus feed pressure. This figure illustrates that the needed area decrease with increasing feed pressure because of an increase in differential pressure as a driving force. Therefore, initial costs could be minimized if high feed pressure is provided.

Existing hydrogen production plant: Figure 10 shows the variation of natural gas flow rate versus hydrogen mole fraction at the outlet of the reformer. The production rate is decreased, if the off-gas stream were used as a raw material. It can be concluded that the off-gas stream can not be considered as a raw material (Fig. 10).

Economical aspects: The performance of the H₂ separation techniques were evaluated by a techno-economic analysis. Cost estimation results have been reported in Table 3 for these separation technologies. As expected, membrane technique has a low capital and operating costs. Cash position diagram has been shown in Fig. 11 to calculate payback period. It can be concluded from this figure that membrane technology has the lowest payback period among the separation techniques and its usage is recommended as an

<table>
<thead>
<tr>
<th>Table 3: Comparison of H₂ capture cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
</tr>
<tr>
<td>compression</td>
</tr>
<tr>
<td>PSA</td>
</tr>
<tr>
<td>Cryogenic</td>
</tr>
<tr>
<td>Joule-Thomson</td>
</tr>
<tr>
<td>Turboexpander</td>
</tr>
<tr>
<td>Plate fin heat exchangers</td>
</tr>
<tr>
<td>Membrane</td>
</tr>
</tbody>
</table>

Fig. 9: Effect of feed pressure on polymeric membrane area

Fig. 10: Effect of adding off-gas as feed into the existing hydrogen production plant
CONCLUSION

A number of important conclusions can be drawn with respect to the validity and performance of these techniques and revamp/retrofit option:

- All processes, (CT, PSA, MT, retrofit/revamp) are closely simulated using the modular and equation oriented approaches and the proper models were presented in each case.
- The simulation results show that the retrofit option could not be considered as an economical way of using off-gas stream, since it lowers the hydrogen production rate at the reformer outlet.
- The simulation results and experimental data reported in the literature show that the revamping of hydrogen plant in order to add off-gas to feed stream leads to reformer enlargement for high hydrogen mole fraction in the reformer outlet.
- The models developed in this study can be considered as a prediction tool to simulate the performance of the existing technology.
- Due to the low capital and operating costs and ease of operation, high quality $H_2$ can be obtained by membrane technology to recover the hydrogen from the refinery off-gases with the typical throughput.

NOMENCLATURE

$y_i$ mole fraction of $i$th component in adsorption bed
$y_{i0}$ inlet mole fraction of $i$th component
$Z_i$ mole fraction of $i$th component in permeate side
$P$, pressure, (Pa)
$P_f$, feed pressure, (Pa)
$P_r$, permeate pressure, (Pa)
$l$, membrane thickness (m)
$A$, membrane surface area (m$^2$)
$L_f$, feed flow rate (kmole/h)
$Q_i$, permeability coefficient of $i$th component (kmole. m/hr. m$^2$.pa)
$t$, time, (sec)
$t_{end}$, cycle time, (sec)
$T$, temperature, (K)
$u$, superficial gas velocity, (m/sec)
$k_w$, linear driving force coefficient, (sec$^{-1}$)
$k_{eq}$, adsorption equilibrium constant, (m$^3$/kg of adsorbent)
$k_{eq}$, equilibrium amount adsorbed solid phase, (kg/kg of adsorbent)
$q_i$, amount adsorbed on solid phase, (kg/kg of adsorbent)
$q_i$, dimensionless amount adsorbed on solid phase
$L$, adsorption bed length, (m)
$Z$, Dimensionless axial distance
$R$, gas constant, (m$^3$.pa/ kgmole.°K)
$D$, adsorption bed diameter, (m)

GREEK LETTERS

$\varepsilon$, Porosity of adsorption bed
$\rho_b$, bed density, (kg/m$^3$)
$\tau$, Dimensionless time, $t/t_{end}$
$\Phi$, stage cut, dimensionless

REFERENCES