Off-Gases Optimization in a Hydrogen Network Refinery

For optimization of a hydrogen network, a steam reformer is associated to the feedstock and linear programming (LP) is applied. The investigated network consists of one steam reformer and two feedstocks. By exerting LP and the mentioned association, total annual cost decreasing is achieved in a case study in which natural gas and off-gas were considered as feedstocks. The optimization problems of the hydrogen network comprise the hydrogen network retrofit design and the feedstock selection with respect to their cost. Nonlinear programming (NLP) and mixed-integer nonlinear programming (MINLP) models are developed for optimization based on a two-case study: for the first one, an existent optimization method on hydrogen networks is investigated and for the second one, revision of a recent optimization method on hydrogen networks associated by an LP model in the steam reformer unit is applied. These two cases resulted in total annual cost reductions of 34 % and 45.9 %, respectively.

Keywords: Hydrogen management, Hydrogen network, Refinery, Steam reformer

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1 Introduction

Environmental legislation and market forces increase the demand for hydrogen in oil refineries. Hydrocarbon steam reforming is an important process for hydrogen production. Generally, hydrogen networks are involved in steam reforming processes. The refineries are being forced to increase consumption of hydrogen that results from the market for heavy crude oils (hydrocracking and hydrotreating) and stringent air emission regulations [1]. Hydrogen as a clean energy has the potential to compensate the global warming problem. It is also one of the alternatives to replace the current fossil fuels energy system [2]. The processes for generating hydrogen in refineries comprise steam reforming of methane and other hydrocarbons, partial oxidation of heavier hydrocarbons, and hydrogen recovery from off-gases or fuel gases from refineries [3]. Generally, the effective cost is the initial option for using of source species [4].

A steam reformer plant is studied as one of the producers of hydrogen in the hydrogen network. More specifically, the steam reformer that uses hydrocarbon feedstocks such as natural gas, naphtha, or the existing off-gases can be improved for application in the hydrogen network. The main objective is to apply a systematic optimizing approach considering the multiple feeds in a steam reformer unit that provides optimum use of off-gases in the hydrogen network.

2 Background and Previous Works on Hydrogen Management

Hydrogen management leads to reduce consumption of hydrogen utilities, optimize hydrogen networks, and eliminate additional costs in a refinery. It has been performed in graphical and mathematical models. The first systematic approach for the assessment of hydrogen resources of a hydrogen network was proposed by Towler et al. [5] based on cost and value composite curves. Alves and Towler [6] developed a framework of sinks and sources for the hydrogen network similar to pinch analysis for a heat exchanger network. El-Halwagi et al. used graphical methods and mass exchanger networks (MENs) to minimize fresh sources [7].

Unlike the graphical models, pressure constraints, adding new equipments, and the optimal equipment emplacements are considered in mathematical models. Hallale and Liu [8] proposed a mathematical approach for determining the minimum utility consumption and the maximum recovery of the hydrogen network. Fonseca et al. [9] employed the linear programming model to optimize a hydrogen network refinery,
leading to a 30% reduction in hydrogen utility usage. Khajehpour et al. [2] proposed objective functions that minimize waste flows containing hydrogen and reduce hydrogen production. Liao et al. [10] used relations for compressors and purifiers to solve the mixed-integer nonlinear programming (MINLP) model obtained from the network structure to minimize the total annual cost.

Kumar et al. [4] noted that the effect of the cost parameter on optimum distribution of hydrogen is the most important study parameter. They considered the ability of the MINLP model to evaluate many complexities of a real refinery system in two case studies. The results indicated an average 26.6% reduction in hydrogen consumption. Recently, Liao et al. [11, 12] proposed a method combining the pinch insight with a rigorous mathematical optimization technique. The method addresses both threshold and pinch problems. Initially the analysis is restricted to systems with no purification and one hydrogen purification unit.

One of the hydrogen production methods is recovery of hydrogen from refinery off-gases by purifiers. The cost of this process can be significantly lower than for buying or producing hydrogen [3]. Various studies have been performed on the management of hydrogen networks with purifiers and hydrogen recovery from off-gases [3, 8, 10, 13, 14]. These studies normally emphasize the purifiers’ design and/or provide mathematical models of purifiers in hydrogen networks. Peramanu et al. [15] evaluated the economic performance of different purification processes for off-gases. Liao et al. developed a systematic approach that provides more network structure possibilities for the placement of compressors and purifiers [10]. Zhang et al. [16] developed an ensuing graphical method for targeting the pinch point and minimum utility consumption of the hydrogen system with purification reuse. In most cases, the purity of hydrogen in off-gas streams is not adequately high to be recycled. Therefore, it decreases the efficiency of the purifiers. Off-gases can be used for feedstocks of a steam reformer in addition to the fuel system.

3 General Linear Model of the Steam Reformer

One of the most important industrial processes for production of hydrogen is steam reforming of natural gas [2]. The steam reforming processes convert natural gas, refinery off-gases, LPG (liquefied petroleum gas), naphtha, and methanol as the feedstock with steam in the presence of a catalyst into a hydrogen-rich synthesis gas [1, 17]. Generally, the use of feedstocks on a steam reformer is dependent on two parameters: their availability and economic problems [17]. Various feedstock representations were proposed by Tehrani Nejad [18] who applied a simplex linear programming (LP) model to connect oil products and to allocate CO2 for different crude oil feeds.

The developed mathematical models were based on the following assumptions: (i) The feedstock of the steam reformer unit consists of natural gas and one of the off-gases streams (ii) the LP model mentioned above [18] was extended merely for hydrogen optimization; (iii) the purity of the produced hydrogen from various feedstocks in the steam reformer unit is considered different and is assumed constant in optimization; (iv) costs of feed, fuel, boiler feed water, power, and cooling water, and generation of export steam as utility usage are the major operating cost in hydrogen production. In this study, it is assumed that the cost of feed obtains the overall production cost of hydrogen.

The steam reformer process with its input and output in this work is presented as a plant including two feedstocks (Fig. 1). The overall process reaction expressed for the steam reformer process is as follows:

\[ C_nH_m + H_2O \rightarrow H_2 + CO_2 + CO + CH_4 + H_2O \]  

where \( F_{in,steam-reformer} \) and \( F_{out,steam-reformer} \) are the feed and reformer gas product of the steam reformer plant, respectively. Here, \( F_{in} \) contains natural gas and off-gas from other units. In fact, there is a trade-off between the amounts of natural gas and off-gas.

\[ F_{in,steam-reformer} \rightarrow \text{Steam Reformer Plant} \rightarrow F_{out,steam-reformer} \]

The components’ purity is given by:

\[ F_{i,product} = F_{i,product}F_{out,steam-reformer} \]  

Based on Eqs. (1)–(4), the products from the steam reformer can be formulated as:

\[ a_1F_{i,product} = \beta_1 F_{NG} + \beta_2 F_{off-gas} \]  

where \( a_1 \) and \( a_2 \) are the quantities of production of each component in various feeds of the steam reformer process. The following equation represents the amount of the reformer gas product:

\[ \beta_1 F_{NG} + \beta_2 F_{off-gas} \geq \text{demand for Hydrogen} \]  

\[ \beta_1 F_{NG} + \beta_2 F_{off-gas} \geq \text{demand for reformer gas-product} \]
4 Hydrogen Network System

4.1 Overview

A hydrogen network system comprises three major components [10]: (i) hydrogen distribution network, (ii) purifiers, and (iii) compressors. The hydrogen distribution network includes the whole source, sinks, and connections between them. Fig. 2 depicts the hydrogen network for this case study in a typical Iranian refinery.

4.1.1 Hydrogen Sources

The sources of hydrogen are the streams containing hydrogen, which can be sent to the consumers [8]. The total amount of gas sent to the hydrogen network must equal the amount available from the source:

\[ \sum_j F_{i,j} = F_{\text{source},i} \]  

(9)

4.1.2 Hydrogen Sinks

Hydrotreaters and hydrocrackers are the major consumers of hydrogen in a refinery plant. The amount of gas entering the sink and the hydrogen purity must be kept constant and are calculated by:

\[ F_{\text{sink},i} \leq \sum_j F_{i,j} \]  

(10)

\[ F_{\text{sink},i} y_{\text{sink},i} \leq \sum_j F_{i,j} y_j \]  

(11)
4.1.3 Purifiers

Purifiers are interception units that upgrade the hydrogen purity of sources. Hydrogen purifiers may receive gas from several sources and produce a product stream and a residue stream which can be sent to other sinks [8]. The schematic diagram of a purifier is illustrated in Fig. 3.

The feed stream flow rate and the feed purity are defined as:

\[
F_{\text{in.pur}} = \sum_i F_{i,\text{pur}}
\]  
(12)

\[
y_{\text{in.pur}} = \sum_i F_{i,\text{pur}} y_{i,\text{pur}}
\]  
(13)

Product flow rate:

\[
F_{\text{prod.pur}} = R F_{\text{in.pur}} y_{\text{in.pur}}
\]  
(14)

Residue flow rate and purity:

\[
F_{\text{resid.pur}} = F_{\text{in.pur}} - F_{\text{prod.pur}}
\]  
(15)

\[
F_{\text{resid.pur}} y_{\text{resid.pur}} = (R - 1) F_{\text{in.pur}} y_{\text{in.pur}}
\]  
(16)

where \( R \) is the hydrogen recovery which depends on the purifier variables. Its relationship is expressed as follows [3, 10]:

\[
R = f(F_{\text{in.pur}}, y_{\text{in.pur}}, y_{\text{prod.pur}})
\]  
(17)

4.1.4 Compressors

Compressors are used to provide the hydrogen source pressure to send the stream to hydrogen sinks. The amount of gas fed to the compressor must be equal to the amount that leaves it as well as its gas purity.

Mass balance:

\[
\sum_i F_{\text{comp},i} = \sum_i F_{i,\text{comp}}
\]  
(18)

\[
\sum_i F_{\text{comp},i} y_{\text{comp}} = \sum_i F_{i,\text{comp}} y_{i}
\]  
(19)

Capacity limit:

\[
\sum_i F_{i,\text{comp}} \leq F_{\text{max.comp}}
\]  
(20)

4.1.5 Adding New Equipment

According to the objective function for using hydrogen-rich off-gases streams, two logical constraints for each binary variable (existence or non-existence of equipment) of new equipment like compressors must be added [2].

\[
\sum_i F_{i,\text{new equipment}} - Y_n U_P \leq 0
\]  
(21)

\[
\sum_i F_{i,\text{new equipment}} - Y_n U_P \geq 0
\]  
(22)

\[Y_n (\text{new equipment}) = \{0, 1\}\]

4.2 Economic Considerations

In order to evaluate the economics of any hydrogen utility steam reformer, an economic model can calculate the capital cost and associate with the production flow rate [10]:

\[
C_{H_2} = \left[ (c_{\text{hydrogen}}) F_{\text{reformer gas product}} \right]
\]  
(23)

Considering the relation between flow rate and different feedstocks of the steam reformer, the capital cost is evaluated with the feedstock:

\[
C_{H_2} = (\delta_1 \beta_1 F_{\text{NG}} + \delta_2 \beta_2 F_{\text{off-gas}})
\]  
(24)

where \( \delta_1 \) and \( \delta_2 \) are the cost of hydrogen obtained by natural gas and off-gas feedstocks, respectively. Accordingly, feedstock prices are assumed where \( \delta_1 \) is more than \( \delta_2 \).
Also further costs can be calculated via the following formulations. The fuel value is obtained by heat value calculation [2, 8, 10]:

\[ C_{\text{fuel}} = F_{\text{fuel}} e_{\text{fuel}} (\gamma - 1) \left( \frac{P_{\text{out}}}{P_{\text{in}}} \right)^{\gamma - 1} \]

where \( \Delta H_L \) is the standard heat of combustion and \( e_{\text{fuel}} \) is the price of the fuel system.

The pipe installation cost only refers to new pipelines [8]:

\[ C_{\text{pipe}} = \left( a_{\text{pipe}} + b_{\text{pipe}} \right) A_f L \]

where \( u \) is the superficial gas velocity, \( L \) is the length of piping, and \( a_{\text{pipe}} \) and \( b_{\text{pipe}} \) are constants.

Sources can only feed sinks with higher pressures through compressors, hence, the compressors for raising the pressure need power [2, 8]:

\[ \text{Power} = \frac{C_{\text{power}}}{\eta} \left( \frac{P_{\text{out}}}{P_{\text{in}}} \right)^{\gamma - 1} \]

where \( \text{power} \) represents the power consumption of a compressor, \( F \) is the flow rate of hydrogen, and the compressor power cost is defined as follows:

\[ C_{\text{power}} = \sum_{i \in \text{comp}} \text{power}_i \]

The cost of a new compressor is calculated by:

\[ C_{\text{comp}} = a_{\text{comp}} b_{\text{comp}} \times \text{power} \]

where \( a_{\text{comp}} \) and \( b_{\text{comp}} \) are constants.

5 Objective Function

The objective is minimization of the total annual cost (TAC) for the hydrogen network: objective function = min TAC [8, 10].

\[ \text{TAC} = (C_{\text{H}_2} + C_{\text{power}} - C_{\text{fuel}}) t + A_f \left( \sum_{i \in \text{comp}} C_{\text{new equipment}} \right) \]

where \( t \) represents the annual operating hours, \( A_f \) is the annual interest percentage, \( (C_{\text{H}_2} + C_{\text{power}} - C_{\text{fuel}}) \) is the operating cost, and \( A_f \left( \sum_{i \in \text{comp}} C_{\text{new equipment}} \right) \) is the investment cost, including new equipment investment costs (piping, compressor, purifier).

6 Case Study

The current hydrogen distribution network is presented in Fig. 2. There are three consumers and hydrogen is supplied from a catalytic reformer (CCR) as well as a hydrogen plant. The purities and capacity of the hydrogen produced by the hydrogen plant and catalytic reformer are summarized in Tab. 1.

<table>
<thead>
<tr>
<th>Source</th>
<th>Flow rate [Nm³/h]</th>
<th>Purity [%]</th>
<th>Pressure [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP off-gas</td>
<td>8600</td>
<td>81.4</td>
<td>24.5</td>
</tr>
<tr>
<td>LP off-gas</td>
<td>7600</td>
<td>51</td>
<td>5.2</td>
</tr>
</tbody>
</table>

There are four compressors to increase pressure and send the hydrogen to the consumer processes, but one of the compressors is shut down. The compressors data are given in Tab. 2.

<table>
<thead>
<tr>
<th>Compressor</th>
<th>Operation flow [Nm³/h]</th>
<th>Maximum flow [Nm³/h]</th>
<th>Inlet pressure [bar]</th>
<th>Outlet pressure [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>54 300</td>
<td>76 000</td>
<td>21.3</td>
<td>198</td>
</tr>
<tr>
<td>C2</td>
<td>59 000</td>
<td>65 000</td>
<td>4.5</td>
<td>24.5</td>
</tr>
<tr>
<td>C3</td>
<td>90 000</td>
<td>10 000</td>
<td>24.5</td>
<td>55</td>
</tr>
<tr>
<td>C4 (shutdown)</td>
<td>–</td>
<td>16 400</td>
<td>4.8</td>
<td>30</td>
</tr>
</tbody>
</table>

It is assumed that the compressors could be described as having a maximum capacity and that the inlet and outlet pressures are fixed regardless of the flow rate through the compressor. The dotted line streams are presented in Fig. 2. There are the existing pipe streams in the network but these have been shut down. The process data of all hydrogen sources and sinks are given in Tabs. 3 and 4.

<table>
<thead>
<tr>
<th>Sources</th>
<th>Flow rate [Nm³/h]</th>
<th>Purity [%]</th>
<th>Pressure [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocracker</td>
<td>Min 35 000</td>
<td>92–99.9</td>
<td>198</td>
</tr>
<tr>
<td></td>
<td>Normal 57 000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Max 63 000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heavy naphtha</td>
<td>Min 1500</td>
<td>80–92</td>
<td>55</td>
</tr>
<tr>
<td>Heavy diesel</td>
<td>Min 7500</td>
<td>80–92</td>
<td>55</td>
</tr>
<tr>
<td>Hydrogen plant</td>
<td>Min 8600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feedstock</td>
<td>Max 7600</td>
<td>51</td>
<td>30</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sink</th>
<th>Flow rate [Nm³/h]</th>
<th>Purity [%]</th>
<th>Pressure [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
<td>–</td>
<td>–</td>
<td>4.5</td>
</tr>
</tbody>
</table>
As indicated in Fig. 2, the plants PSAI and PSAII are the purification systems (PSA: pressure swing adsorption). The operating parameters of purifiers are listed in Tab. 5. Several operating constraints apply for purifiers: (i) The feed PSAI only is from the hydrogen plant; (ii) the pressure variation between feed and product is 0.5 bar; (iii) the feed purities for PSAI and PSAII must be more than 73 % and 80 %, respectively.

<table>
<thead>
<tr>
<th>Table 5. Data for purifiers.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed (max) [Nm(^3)h(^{-1})]</td>
</tr>
<tr>
<td>-------------------------------</td>
</tr>
<tr>
<td>PSAI 80 000</td>
</tr>
<tr>
<td>PSAII 50 000</td>
</tr>
</tbody>
</table>

In this work, natural gas and low-pressure (LP) off-gas (amine gas) are considered as two feeds to the hydrogen plant (steam reformer) feedstocks. The existing amount of natural gas consumed by the hydrogen plant is 8900 Nm\(^3\)h\(^{-1}\), also only quantities of hydrogen (\(a_1 - a_2\)) are surveyed. The operating data are listed in Tab. 6.

### 7 Optimization Case Study

The case study is optimized to solve two model options of the hydrogen network. Nonlinear programming (NLP) and MINLP models are applied to minimize the total annual cost. The costs of electricity, fuel, \(\delta_1\), and \(\delta_2\) are assumed as 0.08 $ kWh\(^{-1}\), 0.004 $/MJ, 0.08 $ Nm\(^{-3}\), and 0.06 $ Nm\(^{-3}\), respectively. Annual operating hours are 8200 h and the annual interest percentage is 0.5.

The optimal hydrogen network for the NLP model is indicated in Fig. 4. By solving the model, the optimal network and the costs are determined. The optimal stream hydrogen plant and CCR plant are 28 750 Nm\(^3\)h\(^{-1}\) and 43 800 Nm\(^3\), respectively. The amount used by the hydrogen plant in this model for natural gas is about 600 Nm\(^3\)h\(^{-1}\). The total annual cost for the NLP model of the case study decreased the total annual cost by 34 %.

The MINLP model applied to network optimization involves one binary variable. A new compressor (C4) is applied for sending the LP off-gas by the hydrogen plant and only the cost power of this compressor is evaluated. As optimal amounts of the CCR plant and hydrogen plant 48 900 Nm\(^3\)h\(^{-1}\) and 27 900 Nm\(^3\)h\(^{-1}\) are obtained, respectively. The optimal feedstocks of the hydrogen plant are 5100 Nm\(^3\)h\(^{-1}\) for LP off-gas and 0 for natural gas. The total annual cost is 27.277 million $ per year, which comprises the operating cost with 27.266 million $ per year and the annual capital cost with 0.011 million $ per year. The results are illustrated in Fig. 5 and Tabs. 7–9. The PSA efficiency depends on the feed purity. According to the restriction of the PSAII purity, all of the LP off-gas cannot be sent to the PSAI. Therefore, the amount of 5100 Nm\(^3\)h\(^{-1}\) of LP off-gas is fed to the steam reformer.

### Table 6. Operating data for hydrogen plant feedstocks.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Hydrogen purity [%]</th>
<th>(a_1)</th>
<th>(a_2)</th>
<th>(\beta_1)</th>
<th>(\beta_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>0</td>
<td>0.76</td>
<td>4.5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>LP off-gas</td>
<td>51</td>
<td>0.73</td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 7. Summarized results.

<table>
<thead>
<tr>
<th></th>
<th>Existing hydrogen network</th>
<th>Optimum hydrogen network 1</th>
<th>Optimum hydrogen network 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAC (total annual cost) [million $]</td>
<td>50.418</td>
<td>33.071</td>
<td>27.277</td>
</tr>
<tr>
<td>Operating cost</td>
<td>50.418</td>
<td>32.992</td>
<td>27.266</td>
</tr>
<tr>
<td>Electricity [million $/year]</td>
<td>7.519</td>
<td>7.666</td>
<td>7.901</td>
</tr>
<tr>
<td>Fuel [million $/year]</td>
<td>$15,999</td>
<td>$6,23</td>
<td>$5,41</td>
</tr>
<tr>
<td>Annual capital cost</td>
<td>0.0</td>
<td>0.079</td>
<td>0.011</td>
</tr>
<tr>
<td>Piping [million $]</td>
<td>–</td>
<td>0.158</td>
<td>0.022</td>
</tr>
</tbody>
</table>

### Table 8. Results optimized for purifiers.

<table>
<thead>
<tr>
<th></th>
<th>Existing operating conditions</th>
<th>Optimized operating conditions for state 1</th>
<th>Optimized operating conditions for state 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSAI R1 [%]</td>
<td>45.3</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>yPI [%]</td>
<td>99.9</td>
<td>99.9</td>
<td>99.9</td>
</tr>
<tr>
<td>yRI [%]</td>
<td>38</td>
<td>24.1</td>
<td>21.3</td>
</tr>
<tr>
<td>yfI [%]</td>
<td>76</td>
<td>76</td>
<td>73</td>
</tr>
<tr>
<td>PSAII RII [%]</td>
<td>69.1</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>yPII [%]</td>
<td>99.9</td>
<td>99.9</td>
<td>99.9</td>
</tr>
<tr>
<td>yRII [%]</td>
<td>69</td>
<td>30.4</td>
<td>34.2</td>
</tr>
<tr>
<td>yfII [%]</td>
<td>92</td>
<td>81.3</td>
<td>83.8</td>
</tr>
</tbody>
</table>

RI, hydrogen recovery ratio to PSAI; RII, hydrogen recovery ratio to PSAII; yPI, product purity to PSAI; yPII, product purity to PSAII; yRI, residual purity to PSAI; yRII, residual purity to PSAII; yfI, feed purity to PSAI; yfII, feed purity to PSAII.
8 Conclusions

Some factors such as market demand, environmental regulation, clean fuel (low-sulfur fuel), and converting of heavy oils to light products increase the hydrogen requirement in refineries. Formerly, in hydrogen network, off-gases were injected to the fuel system and purifier unit due to increasing hydrogen purity. The problem of this approach is the decrease of the unit performance by injection of low-purity off-gases to PSA. Steam reforming of hydrocarbons is considered as a large hydrogen economic generation in refineries. The described approach for a steam reformer is useful for modeling of the total process. By applying and understanding the quantities of production ($a_i$), the component production in a steam reformer can be calculated. CO$_2$ is the other generated steam in reforming processes which is mentioned as a green-house gas. By using this methodology, CO$_2$ emission in hydrogen networks can be constrained. Retrofit results obtained for the optimum network

![Optimal Structure for the NLP Model of the Case Study](image_url)

Table 9. Case study optimization results.

<table>
<thead>
<tr>
<th></th>
<th>Existing hydrogen network</th>
<th>Optimum hydrogen network 1</th>
<th>Optimum hydrogen network 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCR plant</td>
<td>59,000</td>
<td>43,800</td>
<td>48,900</td>
</tr>
<tr>
<td>Compressor C1</td>
<td>54,300</td>
<td>61,600</td>
<td>60,200</td>
</tr>
<tr>
<td>Compressor C2</td>
<td>59,000</td>
<td>43,800</td>
<td>48,900</td>
</tr>
<tr>
<td>Compressor C3</td>
<td>9,000</td>
<td>10,000</td>
<td>10,000</td>
</tr>
<tr>
<td>Compressor C4</td>
<td>0</td>
<td>0</td>
<td>7,600</td>
</tr>
<tr>
<td>H$_2$ plant</td>
<td>40,500</td>
<td>28,750</td>
<td>27,900</td>
</tr>
<tr>
<td>PSAI product</td>
<td>24,200</td>
<td>19,700</td>
<td>18,300</td>
</tr>
<tr>
<td>PSAII product</td>
<td>30,100</td>
<td>37,000</td>
<td>37,800</td>
</tr>
<tr>
<td>Hydrocracker</td>
<td>54,300</td>
<td>57,000</td>
<td>57,000</td>
</tr>
<tr>
<td>Heavy diesel</td>
<td>7,500</td>
<td>8,050</td>
<td>7,500</td>
</tr>
<tr>
<td>Hydrotreating</td>
<td>1,500</td>
<td>1,650</td>
<td>1,600</td>
</tr>
</tbody>
</table>

Figure 4. Optimal structure for the NLP model of the case study.
indicate the change of natural gas feedstocks to LP off-gas and a decrease of the total annual cost by 45.9%. It is concluded that LP off-gases should be sent to the steam reformer for the following reasons: (i) low cost of LP off-gases (\(d_1\) and \(d_2\)) compared to natural gas; (ii) feedstock amount and purity of PSA II limitations (see Tab. 5); (iii) low purity content of hydrogen in LP off-gases compared to high-pressure (HP) off-gases.

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**Symbols used**

- \(C\) [\$] cost
- \(C_p\) [\(1 \text{ kg}^{-1} \text{K}^{-1}\)] heat capacity at constant pressure
- \(D\) [m] pipe diameter
- \(F\) [\(\text{Nm}^3\text{h}^{-1}\)] flow rate
- \(P\) [bar] pressure
- \(R\) [–] hydrogen recovery ratio
- \(T\) [K] temperature
- \(\text{UP, LO}\) [\(\text{Nm}^3\text{h}^{-1}\)] upper and lower bounds of flow rate that can be sent to new equipments
- \(\gamma\) [%] hydrogen purity

**Greek letters**

- \(\Delta H_c\) [\(\text{J Nm}^{-3}\)] heat of combustion
- \(\delta\) [\(\text{S Nm}^{-3}\)] cost of hydrogen
- \(a\) [–] quantities of production for steam reformer

*Figure 5. Optimal structure for the MINLP model of the case study.*
$\beta$ [-] product deficiency of feedstocks
$\gamma$ [-] ratio of heat capacity at constant pressure to that at constant volume
$\rho$ [kg m$^{-3}$] density
$\eta$ [-] compressor efficiency

Indices

i sources
j sinks

References