Relative Concentration based Mathematical Optimization for Improving Fresh Hydrogen Utilization Efficiency of Multi-Impurity Hydrogen Networks

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The traditional methods of hydrogen network integration generally minimize hydrogen consumption and rarely discuss the characterization of hydrogen utilization efficiency (HUE). And some definition of HUE are also not accurate enough. Based on relative concentration property, this paper constructs a nonlinear mathematical model encompassing all necessary constraints to synthesize the multi-impurity hydrogen networks. Result shows that this model is superior to all ones with absolute concentration basis. Through observation and analysis of hydrogen to oil ratio (HTO), a practical and important operation parameter of refinery, we can know the actual hydrogen demand of one hydrogen network. So, in this paper we compare two different kinds of HUE. Conclusion is: Efficiency₂, calculated by actual hydrogen demand, is more reasonable than Efficiency₁, calculated by hydrogen discharge.

1. Introduction

Nowadays refinery hydrogen consumption increases by about 8% a year. Therefore, hydrogen resources saving are of great significance. Alves and Towler (2002) used the diagram of surplus hydrogen to target minimum fresh hydrogen consumption. But this method computation efficiency is very low. El-Halwagi et al. (2003) put forward a graphical method with contaminant versus flow rate diagram. Then, Foo et al. (2006) put forward algebraic calculation instead of visual solution and ultimately achieved the purpose of maximum resource recovery. Zhang et al. (2011) put forward an improved graphical method for the hydrogen networks with purification. Liu et al. (2013) further performed the research on the relationship between the Pinch Point location and the inlet, outlet concentration of purification equipment. As for mathematical programming methods, they usually build superstructure and a corresponding mathematical model. Hallale and Liu (2001) first established a superstructure model to optimize the hydrogen network. Zhou et al. (2012) added a desulfurization device. Gradually, other factors such as uncertainty (Zuwei et al. 2010), multi-objective (Jiao et al. 2013), multi-period (Liang et al. 2016), etc. were considered. With reference to water networks, Zhang et al. (2016) established relative concentration constraints and further reduced hydrogen consumption. In this paper, a multi-impurity, relative concentration basis, nonlinear programming mathematical model is established to analysis two different characterizations of HUE. According to the actual operation parameter, HTO, the best one is selected to explain and analyze the ability and potential of hydrogen resources saving.

2. Theory

2.1 Superstructure

Superstructure showed in Figure 1 includes hydrogen sources (sr), sinks (sk), and purifier psa (Pressure Swing Adsorption). \(\{1,2,\ldots,a\}\) is the number of sources and \(\{1,2,\ldots,b\}\) is the number of sinks. Each source can supply hydrogen to any sink and each sink can also receive hydrogen from any source. Besides, \(sr\) could part or all be sent to one or more \(sk\), or similarly to \(psa\) or fuel gas.
The hydrogen demand of sk can be satisfied by one or more sources and/or psa. This paper builds mathematical model with this superstructure, and the target is to minimize fresh hydrogen consumption and maximize HUE.

2.2 Mathematical model

2.2.1. Calculation of relative concentration

The main reference of relative concentration (RC) in this paper is research of Zhang et al. (2016).

$$RC_{sr, i, k} = \frac{m_{i, k}}{ysr_i}$$ (1)

$$RC_{sk, j, k} = \frac{n_{j, k}}{ysk_j}$$ (2)

$m_{i, k}$ and $n_{j, k}$ are absolute concentration (AC) of contaminant $k$ in $sr_i$ and the ceiling AC of $k$ in $sk_j$. $RC_{sr, i, k}$ and $RC_{sk, j, k}$ are corresponding RC. Compared with AC, RC is used to quantify the impurity concentration and the hydrogen flow rate is employed to quantify flow rate. It releases the total flow rate and concentration normalization constraints. In other words, it is relaxation, so it is superior to absolute basis.

2.2.2. Constraint equations of $sr$

The main constraint for every source is availability of hydrogen resource.

$$Hsr_i = Fsr_i \cdot ysr_i$$ (3)

$$Z_i \cdot s_i + \sum_{j=1}^{b} Hy_{j, i} \cdot d_{i, j} \leq Hsr_i$$ (4)

The sum of hydrogen flow rate $Z_i$ (from $sr_i$ to $psa$), $Hy_{j, i}$ (from $sr_i$ to $sk_j$) should be less than total hydrogen flow rate of $sr_i$ ($Hsr_i$). In Eq(4), $s_i$ is the connection relationship between $sr_i$ and $psa$; $d_{i, j}$ is matrix of network structure.

2.2.3. Constraint equations of $sk$

For every sink, there are two constraints: first is amount of hydrogen provided by $sr$ and $psa$ must meet the demand of $sk_j$. Second is the impurity concentration should be less than the upper limit of $sk_j$.

$$X_j = Xsk_j \cdot (1 + e_j)$$ (5)

$Xsk_j$ is the current oil processing capacity, when there is a fluctuation $e_j$ in $sk_j$, it turns to $X_j$.

$$Hsk_j = l_j \cdot X_j \cdot c_j$$ (6)

$Hsk_j$ is the actual hydrogen demand of $sk_j$, and $l_j$, $c_j$ are known correction coefficients.
\[
O_j \cdot ss_j \cdot RCpsa_k + \sum_{i=1}^{a} Hy_{j,i} \cdot d_{i,j} \cdot RCsr_{i,k} = RCsk_{j,k} \cdot (O_j \cdot ss_j + \sum_{i=1}^{a} Hy_{j,i} \cdot d_{i,j})
\]

(7)

\[
O_j \cdot ss_j + \sum_{i=1}^{a} Hy_{j,i} \cdot d_{i,j} = Hsk_j
\]

(8)

\(O_j\) is hydrogen flow rate from psa to sk\(j\), ss\(j\) is the connection relationship. RCpsa\(k\) is RC of contaminant k in psa outlet. Eq(7) is impurity constraint of sk\(j\). Eq(8) means the constraint of hydrogen demand of sk\(j\).

2.2.4. Constraint equations of psa

Constraint for psa is about mathematical relationship with its inlet and outlet.

\[
\sum_{i=2}^{a} Z_i \cdot s_i \cdot psa_M = \sum_{j=1}^{b} O_j \cdot ss_j
\]

(9)

\[
\sum_{i=2}^{a} Z_i \cdot s_i \cdot RCsr_{i,k} \cdot psa_{k2} = (b \sum_{j=1}^{a} O_j \cdot ss_j) \cdot RCpsa_k
\]

(10)

Eq(9) is psa hydrogen flow rate relationship and Eq(10) is impurity relationship between psa inlet and outlet, where psa\(_{11}\), psa\(_{12}\) are constants of psa hydrogen recovery rate, impurities removal rate.

2.2.5. Objective function

In this paper, objective function is minimum hydrogen consumption: FSRH.

\[
FSRH = \frac{b \sum_{j=1}^{H} {Hy_{j,i} \cdot d_{i,j}}}{ysr_{1}}
\]

(11)

And at the same time, we use following variables to do some useful analysis:

\[
HTO_j = \frac{O_j \cdot ss_j + \sum_{i=1}^{a} Hy_{j,i} \cdot d_{i,j}}{X_j}
\]

(12)

\[
e_{fuel} = \frac{1}{\text{FSRH} \cdot ysr_{1}}
\]

(13)

\[
\text{Efficiency}_1 = \frac{1}{\text{efuel}}
\]

(14)

\(\text{efuel}\) is fuel gas to fresh hydrogen consumption ratio. \(\text{Efficiency}_1\) is one HUE.

\[
\text{Efficiency}_2 = \frac{b \sum_{j=1}^{H} Hsk_j \cdot Hy_{j,i} \cdot d_{i,j}}{\text{FSRH} \cdot ysr_{1}}
\]

(15)

\(\text{Efficiency}_2\) is HUE calculated by the actual hydrogen demand.

The relative concentration model consists of Eq(1) ~ Eq(15), which is a nonlinear programming (NLP) model.

3. Case studies

Case in this paper is based on actual data of a refinery. Table 1 shows the detail data of sources and sinks.

<table>
<thead>
<tr>
<th>F (Nm(^3)/h)</th>
<th>(y_x) (mol%)</th>
<th>(m_{ij}) (mol%)</th>
<th>Xsk(j) (t/h)</th>
<th>(y_{sk}) (mol%)</th>
<th>(n_{ij}) (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sources</td>
<td>H(_2)S</td>
<td>N</td>
<td>C</td>
<td>Hydrogen Sinks</td>
<td>H(_2)S</td>
</tr>
<tr>
<td>sr(_1)</td>
<td>0.995</td>
<td>0.0099</td>
<td>0.003</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>sr(_2)</td>
<td>16000</td>
<td>0.915</td>
<td>0.007</td>
<td>0.016</td>
<td>0.062</td>
</tr>
<tr>
<td>sr(_3)</td>
<td>90000</td>
<td>0.899</td>
<td>0.0216</td>
<td>0.063</td>
<td>0.016</td>
</tr>
<tr>
<td>sr(_4)</td>
<td>32000</td>
<td>0.88</td>
<td>0.037</td>
<td>0.041</td>
<td>0.042</td>
</tr>
<tr>
<td>sr(_5)</td>
<td>7500</td>
<td>0.9</td>
<td>0.056</td>
<td>0.022</td>
<td>0.022</td>
</tr>
<tr>
<td>sr(_6)</td>
<td>6500</td>
<td>0.87</td>
<td>0.026</td>
<td>0.083</td>
<td>0.021</td>
</tr>
<tr>
<td>sr(_7)</td>
<td>24600</td>
<td>0.88</td>
<td>0.037</td>
<td>0.041</td>
<td>0.042</td>
</tr>
<tr>
<td>sr(_8)</td>
<td>8864</td>
<td>0.87</td>
<td>0.026</td>
<td>0.083</td>
<td>0.021</td>
</tr>
<tr>
<td>sr(_9)</td>
<td>14000</td>
<td>0.44</td>
<td>0.123</td>
<td>0.166</td>
<td>0.271</td>
</tr>
</tbody>
</table>
When fluctuations in $s_{k_2}$, $s_{k_3}$, $s_{k_5}$, use 2.2 model we get Table 2. Results of AC is got by traditional methods. There are 9 sources and $s_{r_1}$ is fresh hydrogen, as well as 7 sinks. And it is a multi-impurity hydrogen network. Figure 2 (a), Figure 2 (b) and Figure 3 (a) are constructed by the results in Table 2, where the X axis is different $X_j$, Y axis is hydrogen utilization efficiency. In Figure 2, (a) is about Efficiency$_1$, while (b) is about Efficiency$_2$.

**Table 2: Results by relative concentration basis and absolute concentration basis**

<table>
<thead>
<tr>
<th>$\theta_{e_2}, \theta_{e_3}, \theta_{e_5}$</th>
<th>-0.2</th>
<th>-0.16</th>
<th>-0.12</th>
<th>-0.08</th>
<th>0</th>
<th>0.04</th>
<th>0.08</th>
<th>0.12</th>
<th>0.16</th>
<th>0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSRH (Nm$^3$/h)</td>
<td>52,993</td>
<td>55,253</td>
<td>57,513</td>
<td>59,773</td>
<td>62,033</td>
<td>64,293</td>
<td>66,553</td>
<td>68,813</td>
<td>71,285</td>
<td>73,364</td>
</tr>
<tr>
<td>Efficiency$_1$</td>
<td>0.326</td>
<td>0.407</td>
<td>0.481</td>
<td>0.551</td>
<td>0.616</td>
<td>0.676</td>
<td>0.733</td>
<td>0.786</td>
<td>0.833</td>
<td>0.882</td>
</tr>
<tr>
<td>Efficiency$_2$</td>
<td>0.326</td>
<td>0.407</td>
<td>0.481</td>
<td>0.551</td>
<td>0.616</td>
<td>0.676</td>
<td>0.733</td>
<td>0.786</td>
<td>0.833</td>
<td>0.882</td>
</tr>
<tr>
<td>FSRH (Nm$^3$/h)</td>
<td>55,650</td>
<td>58,044</td>
<td>60,437</td>
<td>62,830</td>
<td>65,425</td>
<td>68,631</td>
<td>71,831</td>
<td>76,471</td>
<td>80,359</td>
<td>82,359</td>
</tr>
<tr>
<td>Efficiency$_1$</td>
<td>0.396</td>
<td>0.471</td>
<td>0.541</td>
<td>0.606</td>
<td>0.664</td>
<td>0.714</td>
<td>0.759</td>
<td>0.786</td>
<td>0.818</td>
<td>0.865</td>
</tr>
<tr>
<td>Efficiency$_2$</td>
<td>0.311</td>
<td>0.388</td>
<td>0.459</td>
<td>0.526</td>
<td>0.585</td>
<td>0.636</td>
<td>0.681</td>
<td>0.710</td>
<td>0.743</td>
<td>0.790</td>
</tr>
</tbody>
</table>

**Figure 2: (a) Efficiency$1$ based on different $X_j$**

**Figure 2: (b) Efficiency$2$ based on different $X_j$**
Figure 3 (a) is HUE data with the same FSRH. The main reason of why $\text{Efficiency}_1$ is so close to $\text{Efficiency}_2$ based RC basis is, RC basis has almost reached the limit of hydrogen savings potential. With the data of HTO, Figure 3 (b) shows the relationship among current, optimized and minimum HTOs in blue triangle, red round and black square curves in sk3. From Table 2 we can see that compared with absolute concentration basis, the RC model consumes less fresh hydrogen and it can increase HUE ($\text{Efficiency}_2$) by about 5%. So, RC constraint is more economical. Also in Figure 3 (a), we can see that with the same FSRH, efficiency of RC model is the highest. However, $\text{Efficiency}_1$ is higher than $\text{Efficiency}_2$ based on the same AC constraints. And Figure 2 (a) shows that for $\text{Efficiency}_1$, RC basis is smaller than AC basis. Consequently, $\text{Efficiency}_2$ is more logical. Figure 3 (b) explains the origin of fresh hydrogen conservation, that is lowering HTO within feasible region. Specifically, for the same sink, the HTO curve based on RC is below absolute concentration basis while above the lower limit. This means that absolute concentration constraint always provides more hydrogen than that of RC constraint. HTO can make us easily know that how much the fresh hydrogen savings potential is.

Figure 3: (a) Different efficiency based on the same FSRH

Figure 3: (b) The HTO data of sink 3
4. Conclusions

Through the analysis of the results we summarize that the NLP model proposed in this paper is superior to all absolute concentration based methods; Efficiency$_2$ calculated by the actual hydrogen demand is more reasonable; HTO is the primary reason to both amount and efficiency of fresh hydrogen consumption. Besides, the gap between current HTO and its lower bound represents the hydrogen saving potential of synthesis methods of hydrogen networks.

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References


