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Integration of a Hydrogen Network with the Vacuum Gas Oil Hydrocracking Reaction

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The hydrogen network of a refinery is integrated with the hydrogen consumption of Vacuum Gas Oil (VGO) hydro-cracking reactor considered. The effect of the inlet raw material and hydrogen of the VGO hydro-cracking reactor are analyzed; the quantitative equation among the hydrogen utility consumption, sulphur content of the feed oil of VGO reactor and the inlet hydrogen is deduced and analyzed. Based on this, the quantitative relationship diagram is constructed, and the quantitative effect of the raw material oil's sulphur content and the inlet hydrogen flow rate of the VGO hydro-cracking reactor to the Pinch location and the utility consumption are identified.

1. Introduction

Nowadays, there is a worldwide trend towards processing heavier and high-sulphur crude oil. Refiners are being compelled to increase their levels of hydroprocessing to upgrade these crudes and keep up with market demand and environment regulations. Therefore, hydrogen is critical to convert poor quality crude oil into desired products, and its consumption is demonstrating a significant growth. Therefore, better hydrogen management through hydrogen network integration is needed for energy savings and hydrogen generation cost reduction.

Vacuum Gas Oil (VGO) hydro-cracking is one of the main hydroprocessing processes to facilitate the control of the products' sulphur content and convert low precious vacuum gas oil to valuable transportation fuels such as diesel and gasoline. As the crude oil of the refinery changes, the raw material oil fed to the VGO hydro-cracking unit changes. To guarantee the product quality and flow rate, the inlet hydrogen, hydrogen consumption and outlet hydrogen of the hydro-cracking reactor will change correspondingly. This affects the integration of the hydrogen network. To decrease the hydrogen consumption, the variation of the hydrogen streams connecting to the VGO hydro-cracking reactor should be considered in the integration of a hydrogen network.

Alves and Towler (2002) found that the Pinch exists in the hydrogen network and developed an iterative hydrogen surplus method. Zhao et al. (2006) proposed a graphical method based on the hydrogen load versus flow rate diagram. Agrawal and Shenoy (2006) proposed a unified conceptual approach for water and hydrogen networks with the composite curve constructed in the contaminant concentration versus contaminant mass load diagram. Based on the surplus diagram, Saw et al. (2011) developed the Material Surplus Composite Curve (MSCC) method with the interval fresh material flow rate introduced. These methods can identify the Pinch point and the minimum hydrogen utility consumption without repetitive computations. Furthermore, purification has been considered in a lot of research. Foo and Manan (2006) improved PCA to Gas Cascade Analysis (GCA) to solve the gas integration problem with purification. Ng et al. (2009a) proposed the Pinch based automated approach to target the minimum utility consumption of the property and purity based conservation networks without regeneration/purification reuse, and later extended this method to the system with purification reuse (2009b). Liu et al. (2013) developed a quantitative diagram method to analyze the effect of the PFFR to the minimum hydrogen utility consumption and the Pinch point and identify the optimal and limiting PFFR. Later, they (2014) extended this method to optimize the purified product purity and purification feed purity. Mao et al. (2015) developed an integration method for the hydrogen network with the coupling of sink and source streams considered.

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Besides the Pinch-based method, scholars developed different mathematical programming methods. However, this kind of methods cannot give clear insights about the integration process, as the mathematical model is generally solved by the black–box solver. To the best of our knowledge, there is no report on the network integration with the VGO reactor considered.

Most of the methods introduced above can optimize the hydrogen network with the hydrogen sources and hydrogen sinks taken as fixed streams. The method proposed by Mao et al. (2015) takes the coupled sink and source as streams with unfixed flow rates and compositions, and hence can be applied to integrate the hydrogen network and consider the variation of the hydrogen streams connecting to the VGO hydro-cracking reactor, simultaneously.

This work aims to integrate the hydrogen network of a refinery with the hydrogen consumption of VGO hydro-cracking reactor considered. The method proposed by Mao et al. (2015) is applied to determine the quantitative equations among the hydrogen utility consumption, the composition of VGO and the inlet hydrogen. Based on this, the quantitative relationship diagram is constructed for analyzing the quantitative effects of the VGO composition and the inlet hydrogen, and targeting the minimum hydrogen consumption, Pinch location and the optimal the inlet hydrogen.

2. The integration method

In this work, Hydrogen Utility Adjustment (HUA) is applied to denote the variation of the hydrogen utility consumption. When the Pinch appears at different sink-tie-lines, the quantitative relationships between HUA and the coupled streams are different. This depends on their relative location to the coupled streams.

A pair of coupled sink and source streams, SKq and SRp, are connected by a hydrogen consuming reactor, and their hydrogen content satisfies the mass balance shown by Eq(1). For sink-tie-lines lying below, between and above the coupled sink and source, their HUA can be calculated by Eq(2), Eq(3) and Eq(4). In the hydrogen processing units, hydrogen is mainly consumed by the chemical reactions. Given the product requirement, higher sulfur feed oil results in higher hydrogen consumption. As the catalyst, reactor and its operating temperature and pressure are fixed, the relation between the hydrogen consumption and the feed oil composition has been explored by Liang et al. (2012) and is shown by Eq(5).

$$F_{SK_q}c_{SK_q} - F_{SR_p}c_{SR_p} = H_r \tag{1}$$

$$\Delta F_u = F_u^{'} - F_u = -\frac{H_i - (\Delta F_{SK_q} - \Delta F_{SR_p})c_{SR_i} - \Delta(F_{SK_q}c_{SK_q}) + \Delta(F_{SR_p}c_{SR_p})}{c_u - c_{SR_i}} \tag{2}$$

$$\Delta F_u = F_u^{'} - F_u = -\frac{H_i + \Delta F_{SK_q}c_{SR_i} - \Delta(F_{SK_q}c_{SK_q})}{c_u - c_{SR_i}} \tag{3}$$

$$\Delta F_u = -\frac{H_i}{c_u - c_{SR_i}} \tag{4}$$

$$H_{chem} = a\Delta S + b\Delta N + c\Delta C + d\Delta A + e \tag{5}$$

Where, ΔS is the variation of the sulfur content of the feed oil, ΔN , ΔC and ΔA are the weight percent variation of the nitrogen, bromine and aromatic hydrocarbon of the feed oil. This equation shows that the hydrogen consumption is linearly proportional to the sulfur content of the feed oil.

The variation of the feed oil and the hydrogen consumption of the reactor also affect the coupled source. As the separator can separate the outlet streams to accommodate the feed fluctuation, the purity of the coupled source can be kept unchanged, while the flow rate of the coupled source will change. Based on this, Eq(2) can be simplified into Eq(6), while Eq(3) can be simplified into Eq(4).

$$\Delta F_u = \frac{c_{SRp} - c_{SRi}}{(c_u - c_{SRi})c_{SRp}}\Delta H_r - \frac{1}{c_u - c_{SRi}}H_i \tag{6}$$

Except the feed oil of the reactor, the variation of the inlet hydrogen stream, which is a sink, also affect the integration of the hydrogen network. If the inlet hydrogen purity and the hydrogen to oil ratio vary in the appropriate region, the chemical hydrogen consumption of the reactor will not change to produce the desired product. With the dissolved hydrogen neglected, the variation of the pure hydrogen of a source equals that of the coupled sink.

When the product of the flow rate and purity of the coupled sink is constant, considering that the purity of the coupled source keeps to be fixed, both Eq(2) and Eq(3) can be simplified into Eq(7). As the composition of the feed oil changes, the quantitative diagram between the HUA and the varying parameter can be plotted according to Eq(6) and (4). The feed oil parameter versus ΔF_u can be obtained with the line corresponding to each source plotted in the same diagram. Taken the product of flow rate and purity of the sink as fixed value, the effect of the inlet hydrogen can be analyzed by constructing the ΔF_{SKq} versus ΔF_u diagram according to Eq(7) and Eq(4).

$$\Delta F_u = -\frac{H_i + \Delta F_{SK_q} c_{SR_i}}{c_u - c_{SR_i}} \tag{7}$$

3. The hydrogen network of a refinery

In a refinery of China, whose annual processing ability is 3.5 Mt of crude oil, there are 10 hydrogen sources (hydrogen utility included) and 9 hydrogen sinks, as shown in Table 1. By the hydrogen surplus method, the initial Pinch purity is identified to be 0.74, and the corresponding minimum hydrogen utility flow rate is 391.52 mol/s. The hydrogen surplus of each sink-tie-line and the source that can intersect them are shown in Table 2. The hydrogen network with the initial Pinch is taken as the initial state to analyze the effects of the feed oil and inlet hydrogen.

Table 1: Data of current hydrogen system network

Sources	Purity, %	Flow rate, mol/s	Sinks	Purity, %	Flow rate, mol/s
SR_0	99.99	400	SK_1	91.33	318.09
SR_1	93.61	156	SK_2	90.80	154.12
SR_2	90.80	371.45	SK_3	90.00	102.24
SR_3	86.63	4.54	SK_4	86.51	2,523.52
SR_4	84.91	1,204.19	SK_5	84.91	1,136.02
SR_5	84.19	456.68	SK_6	84.19	454.41
SR_6	84.00	2,165.36	SK_7	83.31	51.12
SR_7	74.00	900	SK_8	80.00	45.44
SR_8	68.72	109.74	SK_9	72.11	908.82
SR_9	55.72	12.5			

Table 2: Data of sink-tie-line when the initial Pinch point exists

Sink-tie-line	The sinks connected by it	The source intersecting it	Other sources can intersect it	Hydrogen surplus, mol/s
1	SK_1, SK_2	\	\	27.55
2	SK_2, SK_3	\	SR_2	36.56
3	SK_3, SK_4	\	SR_3	39.50
4	SK_4, SK_5	\	SR_4	11.53
5	SK_5, SK_6	\	SR_4	1.19
6	SK_6, SK_7	SR_6	SR_5	0.33
7	SK_7, SK_8	\	\	1.70
8	SK_8, SK_9	SR_7	\	0
9	SK_9, horizontal axis	SR_8	SR_9	14.85

Note: "\" indicates that there is no corresponding stream.

In this system, SK_4 and SR_6 are coupled. The former is the inlet hydrogen stream of the VGO reactor, the latter is separated from the outlet stream of the same reactor, as shown by Figure 1. For the VGO reactor, the inlet flow rate of feed oil is 2,523.52 mol/s. At the present state, the sulfur content of the feed stream is 1 %, and it may change in the region of 0~6 % (weight percent) as the crude oil changes. This variation affects the hydrogen consumption of the VGO reactor and the integration of the hydrogen network. The purity of SK_4 can be varied in the region [84.91 %, 90.00 %], and this variation also affects the hydrogen network. Note, to be constant with the industry, the sulfur content is given in weight percent, while the hydrogen purity is given in mole fraction in this work.

4. Effect of sulfur content

With the dissolved hydrogen ignored, the mass balance between SK_4 and SR_6 is shown by Eq(8).

$$F_{SK4} c_{SK4} - F_{SR6} c_{SR6} = H_r \qquad \bullet \qquad (8)$$

Where, F represents the flow rate, c represents the hydrogen concentration, H_r represents the hydrogen consumed by the reactor, and equals 364.195 mol/s according to the data of Table 1.

As the sulphur content of feed oil changes, the hydrogen consumption of this VGO reactor changes correspondingly, as shown by Table 3. Based on Eq(5), the relationship between the chemical hydrogen consumption and the feed oil composition of this reactor can be regressed, and is shown by Eq(9).

$$H_{Chem} = 100.5S_f + 5.193 \quad \bullet \tag{9}$$

Where, H_{Chem} represents the chemical hydrogen consumption, kg/t, S_f represents the sulfur content of feed oil.

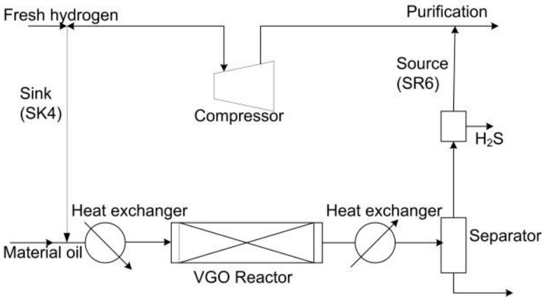


Figure 1: The coupled source and sink

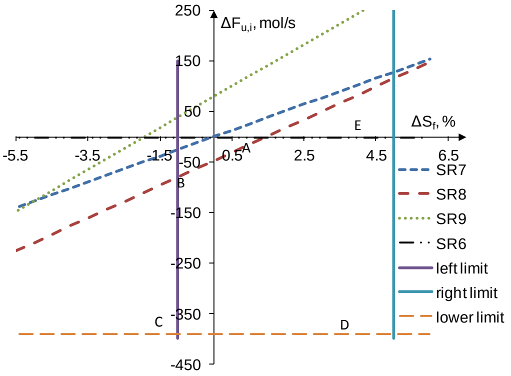


Figure 2: The content of S versus ΔF_u diagram

Table 3: The chemical hydrogen consumption of the VGO reactor when the sulphur content of feed oil changes

Samples	Sulphur content of feed oil, % (weight percent)	Chemical Hydrogen consumption, kg/t	Sulphur content of product, % (weight percent)
1	0.720	4.22	0.154
2	0.748	5.88	0.157
3	0.821	6.09	0.156
4	0.932	6.15	0.157
5	1.062	6.25	0.158
6	1.097	6.28	0.149

According to the annual processing of this device and Eq(9), the equation for calculating ΔH_r can be derived, as shown by Eq(10).

$$\Delta H_r = m\Delta H_{Chem} = 5577.75\Delta S_f (mol/s) \tag{10}$$

Where, m is the flow rate of feed oil.

Sources SR$_8$, SR$_9$ and SR$_{10}$ lay below the coupled sink and source, their quantitative equations can be deduced from Eq(6), and are shown by Eqs(11), (12) and (13).

$$\Delta F_u = 2555.01\Delta S_f \tag{11}$$

$$\Delta F_u = 3245.06\Delta S_f - 47.4993 \tag{12}$$

$$\Delta F_u = 4128.47\Delta S_f + 79.1804 \tag{13}$$

Sources SR$_4$, SR$_5$ and SR$_6$ lie between SK$_4$ and SR$_6$, and their quantitative relationship can be calculated by Eq(4) and are shown by Eqs(14), (15) and (16).

$$\Delta F_u = -4389.58 \tag{14}$$

$$\Delta F_u = -3326.07 \tag{15}$$

$$\Delta F_u = -2.052 \tag{16}$$

Sources SR$_1$, SR$_2$ and SR$_3$ lie above the coupled streams. As SR$_1$ cannot intersect any sink-tie-line, the corresponding equations should be neglected. While the relationships for SR$_2$ and SR$_3$ are shown by Eqs(17) and (18).

$$\Delta F_{u,i} = -485 mol/s \tag{17}$$

$$\Delta F_{u,i} = -403.171 mol/s \tag{18}$$

As the initial hydrogen utility flow rate is 391.52 mol/s, constraint shown by Eq(19) can be added. The constraints shown by Eqs(14), (15), (17) and (18) can be neglected. In addition, the variation scope of ΔS_f can be determined according to the initial sulphur content of the feed oil and its region, and is shown by Eq(20). The final constraint equations are shown by Eqs(11), (12), (13), (16), (19) and (20). According to this, the quantitative relationship diagram can be plotted, as shown by Figure 2.

In this figure, the feasible region is surrounded by ABCDE. As ΔS_f changes in region [-1 %, 5 %], the minimum HUA changes along the broken line ABC. Point B (1.40 %, -2.05) is the intersection point of the $\Delta S_f \sim \Delta F_u$ lines of SR_8 and SR_6. When ΔS_f is less than 1.40 %, the Pinch locates at the intersection point of sink-tie-line 9 and SR_8. Otherwise, the Pinch appears at the intersection point of sink-tie-line 6 and SR_6. There are two Pinches when ΔS_f equals to that of point B. One is the intersection point of sink-tie-line 9 and SR_8, the other is the intersection point of sink-tie-line 6 and SR_6. Point A is the intersection point of the ΔS_f versus ΔF_u line of SR_6 and the upper bound line of ΔS_f , while point C is the intersection point of the ΔS_f versus ΔF_u line of SR_8 and the lower bound line of ΔS_f .

$$\Delta F_u > -391.52 mol/s \tag{19}$$

$$5\% > \Delta S > -1\% \tag{20}$$

5. The effect of the inlet hydrogen stream

When the inlet hydrogen stream of the VGO reactor changes, the quantitative relationship between HUA and SK_4 can be determined according to Eqs(4) and (7). Sources SR_7, SR_8 and SR_9 lie below SK_4 and SR_6, their quantitative relationships are determined by Eq(7) and shown by Eqs(21), (22) and (23).

$$\Delta F_{SKq} = -0.3512 \Delta F_u \tag{21}$$

$$\Delta F_{SKq} = -0.4550 \Delta F_u - 21.6112 \tag{22}$$

$$\Delta F_{SKq} = -0.7323 \Delta F_u + 57.9838 \tag{23}$$

Sources SR_4, SR_5 and SR_6 lie between SK_4 and SR_6, and their quantitative relationship can also be calculated by Eq. (7) and are shown by Eqs(24), (25) and (26).

$$\Delta F_{SKq} = -0.1776 \Delta F_{u,i} - 779.59 \tag{24}$$

$$\Delta F_{SKq} = -0.1877 \Delta F_{u,i} - 624.303 \tag{25}$$

$$\Delta F_{SK_q} = -0.1904 \Delta F_{u,i} - 0.3907 \tag{26}$$

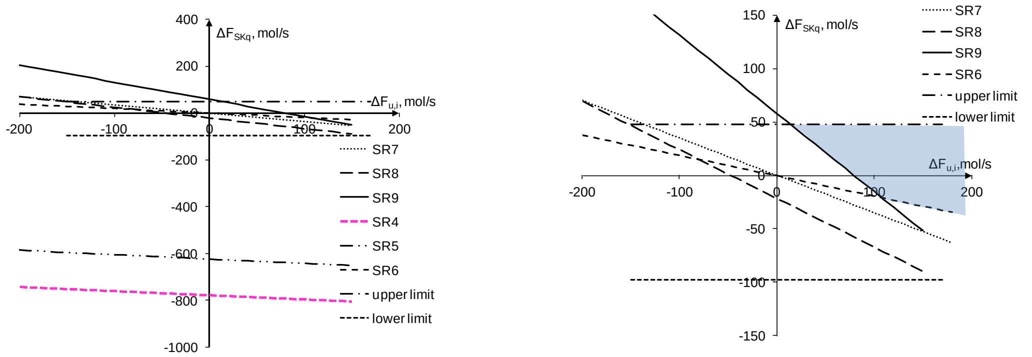
SR_2 and SR_3 lie above SK_4 and SR_6, and the corresponding relationships are shown by Eqs(17) and (18). Similarly, as the initial hydrogen utility is 391.52 mol/s, Eqs(17) and (18) can be neglected, while Eq(19) should be considered. Furthermore, as the purity of SK_4 lies between 90.00 % and 84.91 %, it is easy to determine the flow rate region of SK_4 (the hydrogen load of SK_4 is fixed), as shown by Eq(27).

$$47.55 mol/s > \Delta F_{SKq} > -97.86 mol/s \tag{27}$$

Based on the above analysis, quantitative relationship diagram can be plotted according to Eqs(19) and (21)-(27), as shown by Figure 3(a), the feasible region is denoted by the shadowed region. To show the feasible region clearly, the lines corresponding to SR_4 and SR_5 are neglected, as shown by Figure 3(b).

6. Conclusions

In this work, the hydrogen network of a refinery is optimized with the feed oil and inlet hydrogen variation of VGO hydro-cracking reactor considered. The quantitative relationships between the hydrogen utility adjustment and the coupled sink and source connecting to the VGO reactor are determined and applied to construct the quantitative relationship diagram, and analyze the effect of the feed oil's sulfur content, inlet hydrogen flow rate and purity. The results show that, for any given feed oil and inlet hydrogen, the minimum hydrogen utility adjustment and the location of the Pinch can be easily identified from the far right broken line; the hydrogen consumption increases as the sulfur content increases; it decreases as the inlet pure hydrogen kept constant and the flow rate of inlet hydrogen stream increases. The linear relation between them and the Pinch location changes at the inflection point, and there are two Pinches at each inflextion point.



(a) *(b)*

Figure 3: ΔF_{SKq} *versus* ΔF_u *diagram when the pure hydrogen load of the coupled sink is fixed*

For a given hydrogen network, as long as the corresponding quantitative relationship diagrams are plotted, the effect of the operating parameters, such as the sulphur content, can be analyzed intuitively, and tedious calculation can be avoided. The proposed method can be extended to analyze the effect of other parameters, such as operating temperature and pressure of the hydrogen consuming reactor.

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References

Agrawal V., Shenoy U.V., 2006, Unified conceptual approach to targeting and design of water and hydrogen networks, AIChE Journal, 52, 1071–1082.

Alves J.J., Towler G.P., 2002, Analysis of refinery hydrogen distribution systems, Industrial & Engineering Chemistry Research, 41, 5759–5769.

Foo D.C.Y., Manan Z.A., 2006, Setting the minimum utility gas flow rate targets using cascade analysis technique, Industrial & Engineering Chemistry Research, 45, 5986–5995.

Liang X., Liu Y.Z., 2012, Simulation of a wax oil hydrotreating unit and calculation of hydrogen consumption at off-design conditions, Journal of East China University of Science and Technology (Natural Science Edition), 38, 728-723.

Liu G., Li H., Feng X., Deng C., 2013, Novel method for identifying the optimal purification feed flow rate of the hydrogen network with purification reuse, AIChE Journal, 59, 1964-1980.

Liu G., Zheng M., Li L., Jia X., Dou W., Feng X., 2014, Effect of Purification Feed and Product Purities on the Hydrogen Network Integration, Industrial & Engineering Chemistry Research, 53, 6433–6449.

Mao J.B, Shen R.J, Wang Y.J, Liu G.L.,2015, An integration method for the refinery hydrogen network with coupling sink and source, International Journal of Hydrogen Energy, 40, 8989-9005..

Ng D.K.S., Foo D.C.Y., Tan R.R., 2009a, Automated targeting technique for single-impurity resource conservation networks. Part 1: Direct reuse/recycle, Industrial & Engineering Chemistry Research, 48, 7637–7646.

Ng D.K.S., Foo D.C.Y., Tan R.R., 2009b, Automated targeting technique for single-impurity resource conservation networks. Part 2: Single-pass and partitioning waste-interception systems, Industrial & Engineering Chemistry Research, 48, 7647–7661.

Saw S.Y., Lee L., Lim M.H., Foo D.C.Y., Chew I.M.L., Tan R.R., Klemes J.J., 2011, An extended graphical targeting technique for direct reuse/recycle in concentration and property-based resource conservation networks, Clean Technologies and Environmental Policy, 13, 347–357.

Zhao Z., Liu G., Feng X., 2006, New graphical method for the integration of hydrogen distribution systems, Industrial & Engineering Chemistry Research, 45, 6512–6517.