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Hydrogen Integration in Petroleum Refining

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There is a worldwide trend towards the production of cleaner gasoline and diesel. Legislation is placing increasingly tight limits on the sulphur content of fuels. There is also a worldwide trend towards processing heavier crude oils This requires increased levels of hydroprocessing, which places increased demands on hydrogen supply in refineries. At the same time, reduction in the aromatics content of fuels in constraining catalytic reformer operation and removing some of the traditional sources of hydrogen available to refineries. In addition, there is also a worldwide trend towards processing heavier crude oils that contain more long chain hydrocarbons and organic sulphur. To obtain the best value from these heavy crudes, refiners must be able to convert heavy end compounds to lighter fractions that can be blended with gasoline or diesel. All these trends point in the same direction of placing increasing demands on the hydrogen systems of refineries. Meeting the increased demands for hydrogen can require significant investment in, for example, steam reformers and compression equipment. Yet, most refinery hydrogen systems are inefficient and have significant room for improvement. By modifying the hydrogen network, perhaps with recovery of hydrogen from tail gas, refiners can often satisfy the increased demands for hydrogen with much significantly reduced operating cost and investment. In recent years, systematic methods for the analysis of hydrogen systems have been developed and are now practiced worldwide. The assessment of hydrogen processes can be presented in a simple, graphical manner, which gives the engineer insight into process design, sensitivity analysis and operations planning. Targets can be set for hydrogen recovery and hydrogen plant production. Targets also give insights into the effective use of hydrogen purification units. However, these simple methods that are now widely practiced neglect many issues that can be important in the study of the hydrogen network. Importantly, impurities in the hydrogen are all lumped together as methane. However, small amounts of certain impurities can prevent what would otherwise be very useful recovery. In addition, pressure constraints need to be considered explicitly. These cannot be included in the targeting methods. Other issues that need to be considered are recycle of hydrogen to steam reformers. Recent developments in the field have allowed systematic ways to address these complexities. This paper will review the background and recent developments and present an industrial case study.

1. Introduction

The worldwide trend towards processing heavier crude oils and producing cleaner fuels is placing new demands on refinery hydrogen networks. To obtain the best value from these heavy crude oils, refiners must be able to convert heavy-end compounds to lighter fractions that can be blended with gasoline or diesel. In order to achieve this, refineries are using more ‘hydrogen-addition’ than the conventional ‘carbon-rejection’, for better production yield. The reason for such selection is not only to produce better quality transportation fuels, but also because of processing more lower quality of crude oil, which

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becomes heavier and contains more sulphur and nitrogen contents. All these facts are driving refineries to increase the levels of hydroprocessing, which places increasing demands on hydrogen supply in refineries. As energy price goes higher and higher, the cost for hydrogen production is also increasing. Currently, all major hydrogen production processes cost a significant amount of energy and generate a large mount of greenhouse gases. Therefore, better hydrogen management through hydrogen network optimisation is needed for energy saving and hydrogen generation cost reduction

2. Existing methodologies

2.1 Hydrogen pinch analysis

Generally speaking, refinery hydrogen network consists of three parts: hydrogen production, hydrogen consumption and hydrogen recovery through purification. Hydrogen producers generate hydrogen, such as continuous catalyst regeneration reformers (CCR), steam reformer and partial oxidation reformer etc. Hydrogen consumers include hydrocracker, hydrotreater, hydroprocesser and isomer etc. Hydrogen purifiers convert lower purity hydrogen containing gases into higher purity product, which can then be reused in processes. Typical hydrogen purifiers include membrane, pressure swing adsorption (PSA) and cryogenic separation. The interaction among hydrogen producers, consumers and purifiers determines the hydrogen network in a refinery, as well as the hydrogen demand.

Alves (1999) presented hydrogen network pinch analysis and hydrogen network optimisation methods. The hydrogen network pinch analysis method is based on the heat exchanger network pinch analysis technology (Linnhoff and Mason, 1979). This method can determine the bottleneck of the whole hydrogen network, and analyse hydrogen utilisation at different purification level systematically.

To carry out hydrogen network pinch analysis, firstly it is to identify sources and sinks of hydrogen, which can be analogous to hot and cold streams in heat exchanger networks. Hydrogen sources are streams containing hydrogen, which can be used to provide hydrogen to the system. Hydrogen sinks are processes that consume hydrogen. A hydrogen consumer is a hydrogen source and also a hydrogen sink, as illustrated in Figure 1. Recycle hydrogen, high pressure purge, low pressure purge and other purge gases can be regarded as hydrogen sources, and the reactor inlet should be regarded as hydrogen sink. With hydrogen pinch analysis, all conditions for hydrogen sources and sinks are fixed.

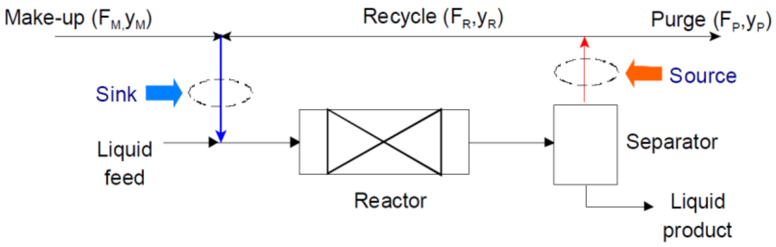

Figure 1: Simplified diagram of a hydrogen consumer showing hydrogen source and sink

Once the conditions for all hydrogen sources and sinks are determined, the next step is to draw the hydrogen surplus curve, as illustrated in Figure 2.

For any existing network, the surplus curve is always on the right side of the vertical axis.

For an existing network, all parts of the surplus curve are always positive. The hydrogen utility can be reduced through moving the curve towards the vertical axis until a vertical segment between the purity of the sink and the source overlaps with the zero axes (Figure 2). The purity at which this occurs is defined as the “hydrogen pinch” and is the theoretical bottleneck on how much hydrogen can be used from the sources to the sinks. The hydrogen utility flowrate that results in a pinch is the minimum target and is determined before any network design.

With hydrogen pinch technology, the minimum hydrogen demand of a hydrogen network can be determined with very basic information and simple data collection. Hydrogen pinch analysis technology also provides certain principles for hydrogen network design:

1. No cross-pinch match between hydrogen sources and sinks
2. Effective hydrogen purification should bring hydrogen from below the pinch to above the pinch

Alves (1999) also presented a mathematical method using Linear Programming (LP) to design hydrogen distribution network. Mass balance for sinks and sources is imposed through equality constraints. The objective function is to minimise the total cost in hydrogen network.

The hydrogen pinch analysis is a graphical approach to find the minimum hydrogen utility in distribution networks. It can provide insights to hydrogen distribution and is easy to access, therefore was quickly adopted for industrial applications. However, it also has some significant drawbacks.

The first is that the targets are set based only on the flowrate and purity requirements and pressure is ignored. The targeting method assumes that any streams containing hydrogen can be sent to any consumers, regardless of the stream pressure. In reality, a source can only feed a sink if it is at a sufficient pressure level. Thus the targets generated may be too optimistic and unachievable in a real design (Hallale and Liu, 2001).

Another drawback is that the selection of hydrogen purification process is simply based on the purities of the product and the feedstock. In practice, purification process selection relates to many practical conditions, such as recovery, pressure conditions, payback rate, and network structure, etc. (Liu and Zhang, 2004).

One more drawback for the hydrogen pinch technology is to lump all impurities as methane. In fact, for a hydrotreating process, even though the purity and flowrate for makeup hydrogen are fixed, the flowrate and purity of recycle hydrogen and purges will vary if the composition of impurities changes. Therefore the minimum hydrogen demand target would be affected (Zhang et al., 2008).

To overcome the drawbacks of the hydrogen pinch analysis, many researchers have presented different mathematical programming approaches for hydrogen network design and optimisation.

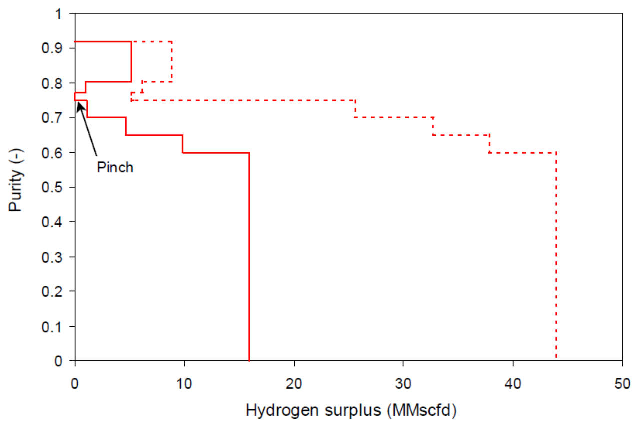

Figure 2: Targeting minimum hydrogen utility flowrate

2.2 Detailed mathematical programming approaches

An automated design approach for hydrogen network management has been developed by Hallale and Liu (2001), which is based on the optimisation of a reducible superstructure. With the superstructure, all possible connections within a network can be included, so that optimisation algorithm could select among all possible design scenarios. The pressure constraints are also included in design. Compressors are considered both as hydrogen sinks and sources: a compressor inlet as a sink and an outlet as a source.

Efficient utilisation of hydrogen in refineries relies on hydrogen recovery. Most hydrogen resources with lower purity can not be directly used in processes. Therefore, hydrogen purifiers (PSA, membrane and cryogenic separation process) need to be in the right place. The selection of hydrogen purifier, type and scale, can be crucial to hydrogen utilisation efficiency (Miller and Stoecker, 1989, Spillmann, 1989, Winston and Sirkar, 1992; Ruthven et al., 1994; Peramanu et al. 1999). Liu and Zhang (2004) presented simplified models for membrane and PSA. When integrated with mixed integer non-linear programming (MINLP) approach, the selection of hydrogen purifier can be considered in the hydrogen network superstructure optimisation. Ahmad et al. (2010) improved this method by considering typical operating conditions for hydrogen consumers in various operating periods, and applying it with multiple operating cases.

For all mathematical programming approaches discussed above, there has been one common assumption: that there are only hydrogen and methane components within the system. All impurities have been lumped as methane. However, hydrocarbon impurities compositions could vary in practical hydrogen sources in any refineries. Under fixed hydrogen to oil ratio and hydrogen partial pressure at the reactor inlet of a hydrogen consumer, if hydrocarbon impurities composition changes in the make-up stream, the vapour to liquid equilibrium in the downstream flash separation will be affected, hence, the flowrate and composition for recycle and purge hydrogen will also change. Therefore, impurities could affect the results of the pinch analysis. Zhang et al. (2008) presented a more detailed modelling approach for hydrogen network simulation and optimisation, which uses a detailed model for high pressure separator of hydrogen consumer. Because of the scale of this detailed model, an iterative approach between simulation and optimisation is used in solving the model.

In summary, there are two major categories for refinery hydrogen network optimisation techniques. One is based on graphical analysis, and the other is based on mathematical programming. The pinch analysis can quickly determine the bottleneck of a hydrogen system and the minimum hydrogen demand. Various mathematical programming approaches can help in designing a practical hydrogen network. Both approaches have certain advantages and disadvantages. Therefore, it is necessary to integrate the two approaches in practical hydrogen network design and retrofit.

On the other hand, for all the approaches discussed above, there is a common constraint, which is the fixed hydrogen flowrate and purity (or hydrogen to oil ratio and hydrogen partial pressure) at the reactor inlet of each hydrogen consumer. This constraint is to make sure that operating conditions of hydrogen consumers will not be affected while the network is optimised. However, for new design or retrofit of a hydrogen network, because of the uncertainties of new processes, such a constraint could be a barrier in determining optimisation scenarios, which will be discussed in this paper.

3. Case study - an industrial application

In this project, Luoyang Petrochemical Engineering Corporation (LPEC) collaborated with Process Integration LTD (PIL) for a hydrogen network design optimisation project in Sinopec M Refinery. Sinopec M Refinery consists of a refinery and an petrochemical complex. Currently, the refinery has a capacity of processing 13.5 Mt/y of crude oil, and the ethylene production is 1 Mt/y. In 2009, Sinopec M Refinery decided to implement a de-bottlenecking project to increase the crude oil processing capacity to 18 Mt/y. Many new processes will be installed, including a crude distillation unit (CDU), fluid catalytic cracker (FCC), hydrocracker (HC) and sulphur recovery etc. The hydrogen network design and optimisation project is to improve the hydrogen utilisation under the new refining configuration.

Currently, the hydrogen mains in M refinery have two pressure levels: 1.2 MPa(G) and 2.4 MPa(G).

1.2 MPa(G) hydrogen main

There are two CCR units and one membrane unit attached to the 1.2 MPa(G) hydrogen main. The overall hydrogen generation from two CCRs is about 70,000 Nm^3/h, with hydrogen purity of about 91.59 v%. In 2005, M Refinery installed a membrane process to recover hydrogen from the feedstock of a steam reformer (hydrogen plant). The feedstock of the membrane unit has a flowrate of around 10200 Nm^3/h and a purity of about 62.62 v%. Product hydrogen has a flowrate of about 4782 Nm^3/h and a purity of about 94.84 v%. The overall recovery is over 71 %. Membrane inlet and outlet pressures are 3.4 and 1.2 MPa(G). The hydrogen concentration in the 1.2 MPa(G) hydrogen main is about 91.80 v%.

2.4 MPa(G) hydrogen main

There are two sources of hydrogen to the 2.4 MPa(G) hydrogen main: the ethylene plant and the hydrogen plant. The ethylene plant provides hydrogen at a flowrate of 35,720 Nm^3/h, and the hydrogen concentration is about 94.00 v%. The hydrogen plant generates 99.9 v% purity hydrogen at a flowrate of 43,500 Nm^3/h. There is a reciprocating compressor to compress steam reformer feedstock from 0.4 to 3.7 MPa(G). The hydrogen concentration in 2.4 MPa hydrogen main is about 97.24 v%.

3.1 Base case for the new hydrogen network in M Refinery

A basic hydrogen network design has been produced for the new M Refinery at the feasibility study stage for the de-bottlenecking project, which is therefore used as the base case for optimisation design.

3.1.1 Hydrogen providers

The hydrogen demand for M Refinery after de-bottlenecking will be significantly increased. As estimated in the feasibility study, the overall hydrogen usage would reach 270,000 Nm^3/h. Meanwhile, the hydrogen production in M Refinery is facing new limitations. According to the local environmental legislation, heavy fuel oil is no longer allowed to be used as fuel in furnaces and fired heaters, and desulphurised fuel gas is considered as the substitution. Therefore, there will be a shortage of fuel gas to be used as raw material for hydrogen production. Moreover, the local natural gas and naphtha prices are high, so that hydrogen production based on them would be uneconomical.

After many investigations, Sinopec decided to install a coal-gasification based hydrogen plant, with a design capacity of 200,000 Nm^3/h. The existing hydrogen plant based on fuel gas will be used as a stand-by. The cost of hydrogen generated from coal-gasification based hydrogen plant is estimated to be around RMB1.16/ Nm^3. The hydrogen pressure from the new hydrogen plant is 4.5 MPa(G). Hence, there will be three hydrogen mains (4.5, 2.4 and 1.2 MPa(G)) in the M Refinery. This introduces new complexity to the design of the hydrogen network.

3.1.2 Hydrogen network

The hydrogen supply is very close to the minimum target based on the current hydrogen purifying strategy. However, it is also indicated in this diagram that there is large amount of hydrogen (over 25000 Nm^3/h pure hydrogen) lost to the fuel gas system. Therefore, hydrogen recovery through additional hydrogen purification could be an economical variable option, which was investigated further. These streams have lower hydrogen concentration, and can not be re-used directly.

The objective for the hydrogen network design is to set minimise the total operating cost:

• Total operating cost = H_2 generation cost + Total compression cost - Fuel gas value

• Fuel gas flowrate = Total supply from all H_2 providers – Net H_2 consumption in all H_2 consumers

• H_2 concentration in fuel gas = Pure H_2 supply from all providers – Net H_2 consumption in all H_2 consumers) / Fuel gas flowrate

The net H_2 consumption in each H_2 consumer is assumed to be fixed. The impurities are lumped as methane, so the net heating value of fuel gas can be calculated based on H_2 concentration and fuel gas flowrate.

Table 1: Results comparison

	Base case	Optimisation scenario 1	Optimisation scenario 2	Optimisation scenario 3
	Hydrogen supply			
Total H_2 supply, Nm^3/h	271,935	267,786	257,393	257,308
Total pure H_2 supply, Nm^3/h	259,749	255,704	245,571	245,488
Total H_2 consumption, Nm^3/h	234,502	234,502	234,502	234,502
Net H_2 loss, Nm3/h	25,247	21,202	11,069	10,986
Effective H_2 usage, %	90.23	91.71	95.49	95.53
Total operating cost: MMRMB/y	**2,494.3**	**2471.6**	**2428.1**	**2427**
(H_2 generation cost+Total compression cost-Fuel gas value)	**Base**	**Base-22.7**	**Base-66.2**	**Base-67.3**
Capital investment: MMRMB/y			32	46
Pay back time: y			0.48	0.69

Note: 1 RMB is about 0.15 USD

The first optimisation scenario aims to optimise the hydrogen network design without introducing any new hydrogen purification process. With the second scenario, a new PSA process is introduced into the hydrogen network, and the exiting membrane unit is still used. With the third scenario, a larger PSA process is introduced into the hydrogen network, and the exiting membrane is turned off.

3.2 Results comparison

Chapter 1 The results comparison for the base case and three optimisation scenarios are presented in Table 1. The improvement for optimisation scenario 1 is limited by the hydrogen purification capacity. Both scenarios 2 and 3 show great improvement with relatively small capital investment. Eventually, optimisation scenario 2 was chosen for implementation.

4. Conclusions

• After hydrogen network design optimisation, the total operating cost for M Refinery has been reduced by 66.2 MMRMB/y, comparing with the base case design
• The selection of type and scale of hydrogen purifiers can be crucial to hydrogen utilisation efficiency
• Fully understanding practical constraints is very important in refinery hydrogen network design or retrofit. The pinch analysis can quickly determine the bottleneck of a hydrogen system and the minimum hydrogen demand, and identify a direction for improvement. Mathematical programming approaches can then help in designing a practical hydrogen network. It is necessary to integrate the two approaches in practical hydrogen network design and retrofit.

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