

# Retrofit of Refinery Hydrogen Network Integrated with Light Hydrocarbon Recovery

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The processing ratio of inferior and heavy oil has been increasing. With the much more stringent environmental regulations, hydrogenation process in the modern refinery has been more widely used. Hydrogen as necessary utility in the modern refinery, accounted for a very high ratio in the cost of refining. How to achieve optimal design or retrofit of the refinery hydrogen network is one of the important problems faced by modern refineries. The refinery off-gas streams are typical hydrogen-rich gas streams and they are important hydrogen sources. In addition, certain refinery off-gas streams are rich in light hydrocarbons, which are highly valuable raw materials for downstream chemical processes, such as ethylene cracking. Worthy to mention, once the light hydrocarbons in the refinery off-gas streams are recovered, the hydrogen in the remaining gas stream is enriched as new hydrogen source with higher hydrogen purity. Thus, the design or retrofit of refinery hydrogen network integrated with light hydrocarbons recovery offers much more possibilities for maximum usage of hydrogen. This paper aims to investigate the systematic approach for the optimal retrofit of refinery hydrogen network integrated with light hydrocarbon recovery. The retrofit of an industrial refinery hydrogen network is applied to illustrate the approach in detail. The results show that the benefit of the retrofit scheme with light hydrocarbons recovery reaches 6.24 M/y, and the investment payback period is merely 8 months.

## 1. Introduction

With the depletion of conventional crude oil resources, the world's supplied crude oil showed a trend of heavy, inferior quality. Moreover, inferior crude oil's price is relatively cheap. In order to reduce costs, refineries imported a great amount of heavy crude oil. At the same time, environmental regulations on the quality of product oil became more stringent. For increased demand in light oil, refineries have been increasing the processing ratio of hydrotreating and hydrocracking processes, which consume a large amount of hydrogen. As one of the necessary utility of refineries, how to optimize hydrogen networks, improving the utilization ratio of hydrogen is an important problem faced by current refineries.

At present, there are two main methodologies for the synthesis of refinery hydrogen networks: Pinch analysis such as, Hydrogen Surplus Diagram (Alves and Towler, 2002), Material Recovery Pinch Diagram (El-Hawalgi, 2003), Gas Cascade Analysis (Foo and Manan, 2006), Improved Limiting Composite Curve and Composite Table Algorithm (Agrawal and Shenoy, 2006) and Improved Problem Table (Deng et al., 2014a), and optimization-based mathematical programming approaches. The latest progress for the synthesis of hydrogen network can be referred to the review article (Marques et al., 2017).

Hydrogen integration has been an effective tool to recover hydrogen and reduce the capacity of hydrogen plant. However, the conventional pinch analysis method does not take into account the recovery of light hydrocarbons contained in streams. Light hydrocarbons, especially C<sub>3+</sub> hydrocarbons, are valuable industrial raw material. They can be applied in various fields, especially being raw material of ethylene process. Zhou et al. (2012) embedded the light hydrocarbon recovery module in the hydrogen network optimization, calculated the light hydrocarbon recovery ratio and the product hydrogen purity according to the material balance. Wu et al. (2014) proposed a model of hydrogen purification units involved light hydrocarbon recovery, and put C<sub>3+</sub> hydrocarbons as an impurity required to remove, but the light hydrocarbon recovery process was not described in detail, and

the specific case study was not analysed. Zhang et al. (2015) compared the economic benefits of recycling hydrogen only with the benefit of comprehensive recovery of hydrogen and light hydrocarbons. It is proposed that hydrogen network integrated light hydrocarbon recovery can be reached more profits. However, how to integrate light hydrocarbon recovery in hydrogen network is not presented clearly. Therefore, it is necessary to investigate the systematic approach for the optimal retrofit of refinery hydrogen network integrated with light hydrocarbon recovery, and the recovery process should be modelled and simulated via process simulation software to accurately determine the composition of light hydrocarbons and hydrogen stream.

## 2. Problem statement

The problem can be expressed as follows. Given a refinery hydrogen network, there is a set of hydrogen consuming processes. Their outlet streams are treated as a set of process hydrogen sources ( $i \in NSR$ ) while their inlet treated as a set of process hydrogen sinks ( $j \in NSK$ ). Each process hydrogen source is specified by its outlet flow rate ( $F_{SRi}$ ) and hydrogen purity ( $y_{SRi}$ ). Each process hydrogen sink has inlet flow rate ( $F_{SRj}$ ) and the lower bound of hydrogen purity ( $y_{SRj}$ ). In addition, a set of hydrogen utilities are needed for supplementary. The surplus hydrogen sources would be allocated to fuel networks or purifiers (i.e. pressure swing absorption, membrane) for upgrading for further utilization. In most cases, these kinds of hydrogen sources contain rich light hydrocarbon components, which will cause huge waste if they are released into fuel system. The purpose of this paper is to explore the systematic approach for the optimal retrofit of refinery hydrogen network integrated with light hydrocarbon recovery.

## 3. Retrofit procedure for hydrogen network integrated with light hydrocarbon recovery

The retrofit procedure for hydrogen network integrated with light hydrocarbon recovery is illustrated in Figure 1.

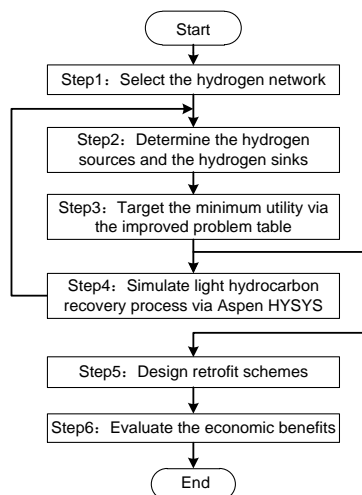


Figure 1: Schematic procedure for the retrofit of hydrogen networks integrated with light hydrocarbon recovery

Step 1: Select the hydrogen system. Given a refinery plant, the hydrogen-consuming processes (such as hydrocracking, hydrotreating, etc.) need to be selected. So do the hydrogen generation processes (such as hydrogen production unit, continuous catalytic reforming, ethylene plant, fertilizer plant, etc.) and hydrogen purification units (such as pressure swing adsorption, membrane separation, desulfurization units, light hydrocarbon recovery units, etc.), and hydrogen pipelines.

Step 2: Determine hydrogen sources and hydrogen sinks. The outlet streams of hydrogen-consuming processes are treated as a set of process hydrogen sources while inlet streams treated as a set of process hydrogen sinks. The flowrates, hydrogen purities, outlet pressures and other parameters of hydrogen sources and sinks for each process need to be extracted. Hydrogen plants, ethylene plants, and fertilizer plants, generally are considered as an external hydrogen sources, their available maximum flowrates, hydrogen purities and outlet pressures also need to be extracted.

Step 3: Target the minimum flowrate of hydrogen utility via the improved problem table (IPT) proposed by Deng et al. (2015). The flowrates and impurities of waste hydrogen streams can be determined accordingly.

Step 4: Simulate the light hydrocarbon recovery process. In order to determine the recovered streams, compositions of waste streams obtained in the third step require to be analyzed and those made up with rich light hydrocarbons will be selected to the light hydrocarbon recovery units. Modelling and simulation for the process of light hydrocarbon recovery can be achieved via simulation software Aspen HYSYS. The hydrogen rich stream will be obtained and accurate amount of recovered light hydrocarbons could be calculated.

Go back to steps 2 and 3: After the last step, a few of the hydrogen source streams are allocated to light hydrocarbon recovery units, at the same time, it produces the hydrogen-rich stream, which causes changes in the number of hydrogen sources. Hence, after light hydrocarbon recovery, the hydrogen sources and sinks need to be re-determined. Then the improved problem table is used once again to locate the new minimum hydrogen utility of integrated hydrogen network. Next, go straight to step 5.

Step 5: Design the network for retrofit schemes. Considering the pressure constraints and compressor arrangement, the retrofit schemes of integrated hydrogen network could be designed via nearest neighbours algorithm (Agrawal and Shenoy, 2006) or manual matching.

Step 6: Evaluate the economic performance. By performing the technical feasibility analysis and economic evaluations of different schemes, the final retrofit scheme can be figured out.

#### 4. Case study

On the basis of the systematic procedure of retrofitting proposed in section 3, a refinery in the northern of China is used as a retrofit example to illustrate its feasibility and applicability. The detailed procedure is presented as follows.

Step 1: The refinery hydrogen network includes hydrocracking (HC), diesel hydrogenation (DHT), gasoline hydrogenation (GOHT), naphtha hydrogenation (NHT) and kerosene hydrogenation (KHT), as shown in Figure 3. Hydrogen-rich gas produced by the styrene plant is sent to the PSA (Pressure Swing Adsorption) in hydrogen plant. After purification, it is distributed to the hydrogen header. In addition, the ethylene plant supplies hydrogen to the hydrogen header. Current flowrate of hydrogen utility provided by hydrogen plant is 32,000 Nm<sup>3</sup>/h with the H<sub>2</sub> purity of 99.98 % and the pressure of 2.2 MPa.

Table 1: Data for hydrogen sources

Number	Hydrogen sources	Flowrate (Nm <sup>3</sup> /h)	Purity (v%)	Pressure (MPa)
HP	Hydrogen plant	32,000	99.98	2.2
EP	Ethylene plant	22,000	95	3.2
SR1	GOHT recycle	61,000	93.65	2.173
SR2	HC high gas	328,000	93.65	14.298
SR3	DHT high gas	74,000	91.5	8.17
SR4	KHT recycle	16,000	89.65	4.5
SR5	NHT recycle	90,000	75.5	3.6
SR6	HC high gas	950	72	0.575
SR7	KHT dry gas	130	35.8	0.301
SR8	NHT dry gas	1,550	32.5	0.279

Step 2: The hydrogen sources and hydrogen sinks are determined. The corresponding data are extracted as shown in Table 1 and Table 2.

Step 3: The minimum flowrate of hydrogen utility is determined by means of the improved problem table. The results show that the impurity concentration of pinch point is 24.5 %, that is, the hydrogen purity is 75.5 %, corresponding to the hydrogen source SR5 (NHT recycle). The minimum hydrogen utility is 31,800 Nm<sup>3</sup>/h, while current hydrogen utility is 32,000 Nm<sup>3</sup>/h, thus the hydrogen reduction potential is 200 Nm<sup>3</sup>/h.

Step 4: By analysing the components of waste hydrogen sources (shown in Table 3) attained in step3, it was noticed that SR6, SR7 and SR8 are rich in C<sub>3</sub>+ hydrocarbons. The mixed low gas stream (second column in Table 3) which was directly sent to the purification device is also rich in light hydrocarbons. The four streams can be allocated to the light hydrocarbon recovery unit, avoiding the valuable hydrocarbon emissions discharged to the fuel system directly.

Table 2: Data for hydrogen sinks

Number	Hydrogen sinks	Flowrate (Nm <sup>3</sup> /h)	Purity (v%)	Pressure (MPa)
SK1	HC	368,000	94.25	16.6
SK2	NHT	63,000	93.8	2.6
SK3	DHT	78,000	91.8	8.2
SK4	KHT	17,000	90	5
SK5	GOHT	97,000	76.6	5

Table 3: Data of the streams for recovery

	Mixed low gas	HC high gas	KHT dry gas	GHT dry gas
Flowrate (Nm <sup>3</sup> /h)	7,200	950	130	1,550
Temperature (°C)	13.62	27	35	33.5
Pressure (MPa)	2.5	0.58	0.3	0.3
Components (v%)				
H <sub>2</sub>	86.6	72	35.8	32.5
C1	4.85	12.3	20.35	5.8
C2	2.12	10.16	1.5	0.7
C3+	5.8	1.85	6.45	51.5
NH <sub>3</sub>	0	0.15	0.01	0.04
O <sub>2</sub>	0.05	0.82	2.15	1.82
N <sub>2</sub>	0.57	1.9	33.6	7.72
H <sub>2</sub> S (mg/m <sup>3</sup> )	0	16,000	6,000	5,000

Based on Table 3, modelling and simulation for the process of light hydrocarbon recovery is accomplished via Aspen HYSYS. Figure 2 is the simulation flow chart which includes the processes of desulfurization and light hydrocarbon recovery. The mixed stream flows into the desulfurization tower, and then the purified gas is delivered to oil absorption tower to remove light hydrocarbons, finally the rich diesel after absorbing the light hydrocarbons is conveyed to the light hydrocarbons separation device.

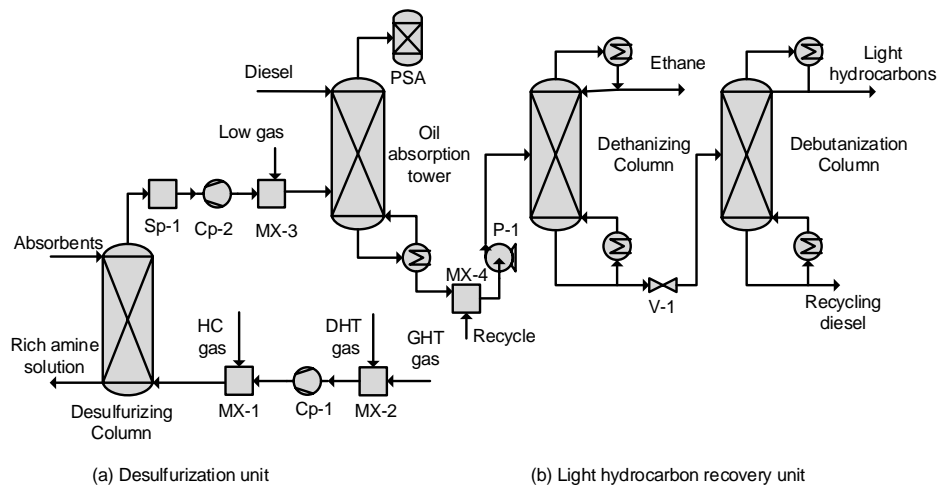


Figure 2: Simulation process of light hydrocarbon recovery: (a) Desulfurization unit; (b) Light hydrocarbon recovery unit

After recovery, two major streams have been obtained shown in Table 4, one stream is rich in hydrogen, and the other is recovered light hydrocarbons that can be sold as products to the feed of ethylene plant.

Table 4: The simulation results of light hydrocarbon recovery

Streams	Volume flowrate (Nm <sup>3</sup> /h)	Pressure (MPa)	Components (v%)	
Hydrogen-rich stream	8,541	1.05	H <sub>2</sub>	87.15
			C1	6.04
			C2	1.43
			C3+	0.01
Light hydrocarbons	1,116	1.21	C3	0.35
			C4	0.41
			C5+	0.15

Go back to step 2 and step 3: After recovery of light hydrocarbons, the hydrogen sources as well as hydrogen sinks need to be re-determined, and then the improved problem table is used again to determine the pinch and the minimum hydrogen utility. The results show that the impurity concentration of pinch in the integrated hydrogen network is 6.35 %, that is, the hydrogen purity is 93.65 %. It can be seen that the impurity concentration of the pinch decreases and the hydrogen purity increases. The minimum hydrogen utility is 31,682 Nm<sup>3</sup>/h, which is less than 31,800 Nm<sup>3</sup>/h that calculated in step 3. The hydrogen-rich stream obtained by recovery can be treated as a new hydrogen source to fulfill hydrogen sinks. The new minimum hydrogen utility can be located by the improved problem table for integrated hydrogen network. However, the plant engineers suggest that it is practical that the rich hydrogen stream is directly sent to PSA unit.

Go straight to Step 5: According to the simulation results and their advice, a balance diagram of retrofitted hydrogen network is designed, as shown in Figure 3. The blue solid lines represent the retrofitted allocation and blue dashed lines represent the current allocation. The current flowrate of feed natural gas is 9,600 Nm<sup>3</sup>/h. After retrofitted, the 8,541 Nm<sup>3</sup>/h of hydrogen rich stream with the hydrogen purity of 87.15 % is feed to PSA unit. The flowrate of natural gas is reduced to be 9,236 Nm<sup>3</sup>/h with the reduction of 364 Nm<sup>3</sup>/h.

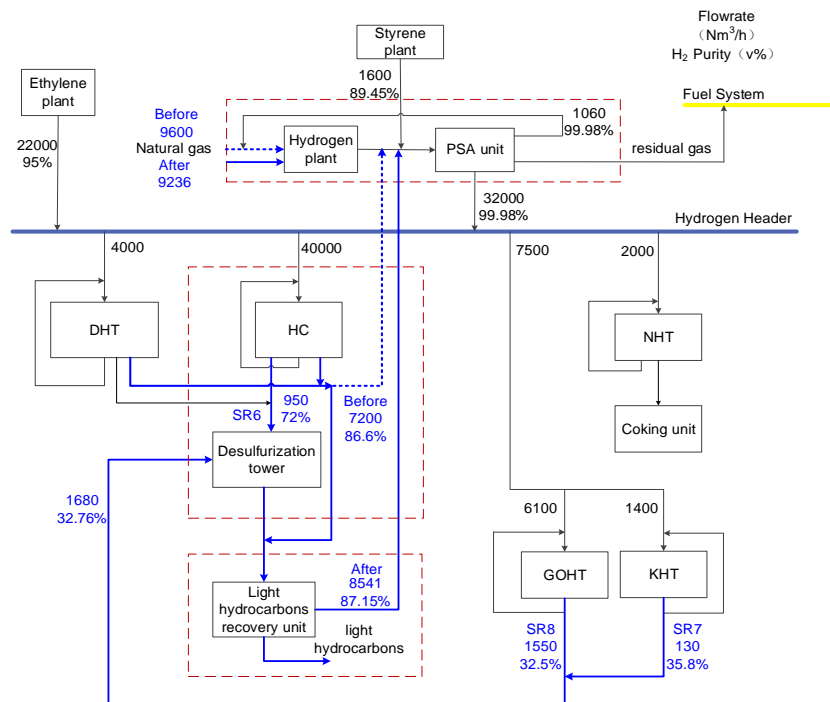


Figure 3: Balance diagram of the new hydrogen network with integrated light hydrocarbon recovery.

Step 6: At last, the economic benefits for retrofitted hydrogen network is evaluated, include recovery benefits, equipment investment, and payback period, as shown in Table 5. The economic benefit of light hydrocarbons recovery is 5.19 M/y. The cost of equipment investment is accounted by newly installed three compressors for

pressure lifting, which is estimated as 1.05 M. The payback period of the integrated network is calculated as 8 months.

Table 5: Comparison of economic benefits

Savings (M/y)	Non-integrated	Integrated
Light hydrocarbon benefits	0	5.19
Natural gas cost reduction	0.88	1.05
Total benefit	0.88	6.24
Equipment investment	0	1.05
* Total investment	0	4.2
Payback period (months)	0	8

\* The total investment is calculated via equipment investment times four, including civil engineering, labour and other engineering cost.

## 5. Conclusions

In this paper, the pinch analysis has been combined with Aspen HYSYS for modelling and simulation, and the retrofit procedure of refinery hydrogen network integrated with light hydrocarbons recovery has been proposed. In the procedure, the pinch analysis and Aspen HYSYS are combined for modelling and simulation. The hydrogen network of one real refinery plant is retrofitted according to the proposed procedure. Results show that, the reduction of natural gas cost achieves 1.05 M/y. The total benefit of recovered light hydrocarbons reaches 6.24 M/y. The investment payback period is only 8 months. It shows remarkable economic performance. The hydrogen network integrated with hydrocarbon recovery not only improves the utilization of hydrogen, but also reduces the light hydrocarbon in the refinery gas and facilitates the subsequent treatment, such as feeding to the PSA (pressure swing adsorption) device. It is conducive to the realization of sustainable energy-saving society and has a wide application prospects in the optimization of refinery hydrogen network.

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