REFINERY HYDROGEN NETWORK OPTIMISATION WITH IMPROVED HYDROPROCESSOR MODELLING

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Abstract

Heavier crude oil, tighter environmental regulations and increased heavy-end upgrading in the petroleum industry are leading to the increased demand for hydrogen in oil refineries. Hence, hydrotreating and hydrocracking processes now play increasingly important roles in modern refineries. Refinery hydrogen networks are becoming more and more complicated as well. Therefore, optimisation of overall hydrogen networks is required to improve the hydrogen utilisation in oil refineries.

In previous work for hydrogen management many methodologies have been developed for H2 network optimisation, all with fixed H2/Oil ratio and H2 partial pressure for H2 consumers, which may be too restrictive for H2 network optimisation. In this work, a variable H2/Oil and H2 partial pressure strategy is proposed to enhance the H2 network optimisation, which is verified and integrated into the optimisation methodology. An industrial case study is carried out to demonstrate the necessity and effectiveness of the approach.

Another important issue is that existing binary component H2 network optimisation has a very simplistic assumption that all H2 rich streams consist of H2 and CH4 only, which leads to serious doubts about the solution's validity. To overcome the drawbacks in previous work, an improved modelling and optimisation approach has been developed. Light-hydrocarbon production and integrated flash calculation are incorporated into a hydrogen consumer model. An optimisation framework is developed to solve the resulting NLP problem. Both the CONOPT solver in GAMS and a simulated annealing (SA) algorithm are tested to identify a suitable optimisation engine. In a case study, the CONOPT solver out-performs the SA solver. The pros and cons of both methods are discussed, and in general the choice largely depends on the type of problems to solve.

Declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institution of learning.

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Chapter 1 Introduction

1.1 Basics of Oil Refineries

With the rising crude oil price and the growing transportation fuel market, it is becoming a trend that refineries convert as much crude oil as possible into transportation fuels, such as gasoline, diesel and jet fuel etc. Besides this, crude oil can also be further processed into feed stock for petrochemical plants to produce valuable products such as ethylene, polyethylene and so on. Although this market is increasing rapidly, it is still far behind the transportation fuel production in overall revenue distribution.

Unsurprisingly, refineries all over the world are always looking for new ways or new technology to improve the process performance as well as the quality of products in order to increase their profitability. To achieve the goal of the highest possible conversion from crude oil into transportation fuel, many newly developed methodologies and technologies have adopted advanced hydroprocessing technology. The implementation of hydroprocessing technology also helps refineries to overcome the increasingly stricter specifications of petroleum products.

Refineries vary in capacity and configurations, and the overall flowsheet of a refinery can be very complicated and huge. Figure 1.1 shows a typical modern refinery structure. Basically refineries intake crude oil and then process it through various processes so as to produce different kinds of products.

Crude first gets heated before going into the atmospheric distillation column (Atmospheric Distillation Unit, ADU), where the distillation happens in different stages inside a tower with different temperatures and separates crude oil into wet gas, light straight run naphtha, heavy naphtha, kerosene, atmospheric gas oil and atmospheric residue.

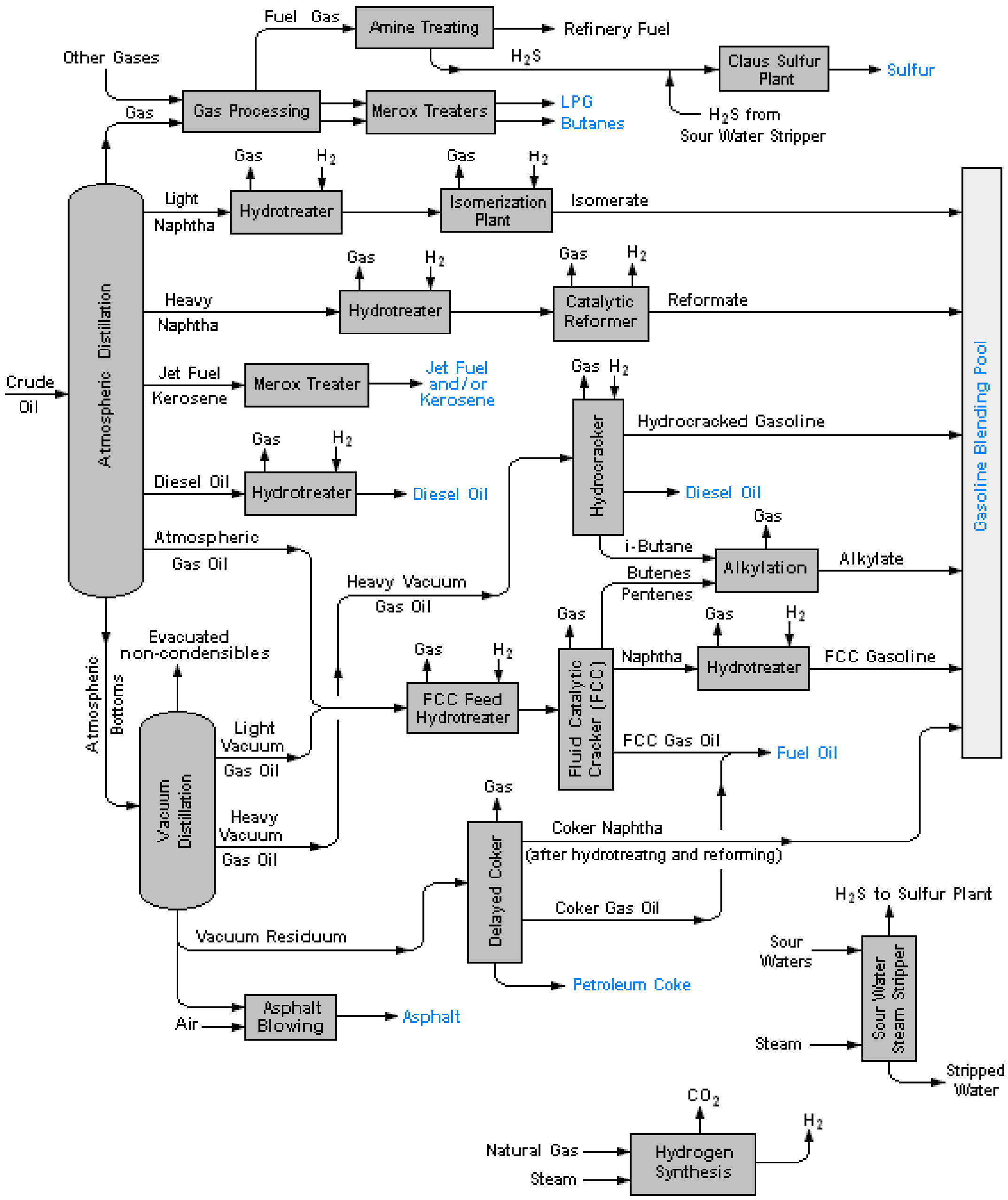

Figure 1.1 A general oil refinery structure (Beychok, 2008)

As an extraction of ADU, light naphtha is hydrotreated and then sent into isomerisation to produce isomerates for gasoline blending. Heavy naphtha is also hydrotreated (NHT) firstly before it goes to catalytic reformer (CCR), where the octane number is improved and the reformate goes to the gasoline blending pool as well. Kerosene comes through a kerosene hydrotreater (KHT) to produce jet fuel. Diesel oil is produced after diesel distillates have been hydrotreated.

Atmospheric residue is further processed in the Vacuum Distillation Unit (VDU) where it is separated into light vacuum gas oil, heavy vacuum gas oil, and vacuum residue. It is generally considered to use light vacuum gas oil as the feed stock of fluid catalytic cracking (FCC) and heavy vacuum gas oil as the feed stock of hydrocracker unit (HCU). Similarly, within FCC and HCU, the heavy petroleum molecules are cracked into lower molecular weight compounds within the boiling ranges of gasoline and distillate fuels. FCC gasoline is hydrodesulphurised and blended into the gasoline pool, as is the hydrocracker naphtha and middle distillates. The alkylation unit produces high-octane alkylate that can be blended into gasoline to improve the octane number of the gasoline pool.

The Vacuum residue (VR) needs to be treated. The Delayed Coker Unit (DCU) is used to process VR, and coker naphtha, coking gas oil and coke is produced. Coker naphtha is hydrotreated and used as petrochemical naphtha or the CCR feedstock, while coke can be sold straight away as one of refinery's products.

Wet gas generated from FCC, DCU, HCU and other units are sent to a gas processing unit, where it can be separated and light naphtha stabilized to produce refinery fuel gas and liquid petroleum gas (LPG). After treating and blending, the refinery can produce gasoline, jet fuel, diesel and lubricating base oil, etc.

1.2 Emerging Trends on the Oil refining Industry

1.2.1 Environmental Concerns on Refinery

It has been a tendency that crude oil is becoming heavier and higher in sulphur. The difficulties of processing heavy oil or high-sulphur crude have been increasing for years and refiners are always perusing better technology to overcome these problems. Table 1.1 gives an overview of U.S. crude characteristics from 1985 to 2009 (U.S. Energy Information

Administration, 2010) including statistics about sulphur content and API gravity. The weight percentage of sulphur rises year by year steadily. The total amount of sulphur content has increased by around 53.8% from 0.91% in 1995 to 1.4% in 2009, which is quite significant.

Table 1.1 U.S. Sulphur content of crude oil

Year	API Gravity	U.S. Sulphur Content of Crude Oil (wt%)
1985	32.46	0.91
1986	32.33	0.96
1987	32.22	0.99
1988	31.93	1.04
1989	32.14	1.06
1990	31.86	1.1
1991	31.64	1.13
1992	31.32	1.16
1993	31.30	1.15
1994	31.39	1.14
1995	31.30	1.13
1996	31.14	1.15
1997	31.07	1.25
1998	30.98	1.31
1999	31.31	1.33
2000	30.99	1.34
2001	30.49	1.42
2002	30.42	1.41
2003	30.61	1.43
2004	30.18	1.43
2005	30.20	1.42
2006	30.44	1.41
2007	30.42	1.43
2008	30.21	1.47
2009	30.37	1.4

(U.S. Energy Information Administration, 2010)

In the meantime, refiners are facing much tighter and stricter transportation fuel specification standards and environmental regulations. Tougher rules have been applied on specifications of gasoline and diesel both in the European Union and United States to reduce smog-forming and other pollutants from vehicle emissions. For instance, the maximum sulphur limit for diesel in the European Union decreased to 10ppm compared with 50ppm in 2005 (Europa.eu, 2007). In the United States a similar thing happened. In 1993 the maximum sulphur limit for diesel was 500ppm and it has been reduced by 10 times in just 12 years to only 15ppm in 2006 (US Environmental Protection Agency, 2006). As can be predicted from these numbers the quality regulations on fuel are becoming stricter and stricter resulting from environmental concerns. Plotting the sulphur content against years, Figure 1.2 indicates the increase trend of sulphur content in the U.S. crude oil.

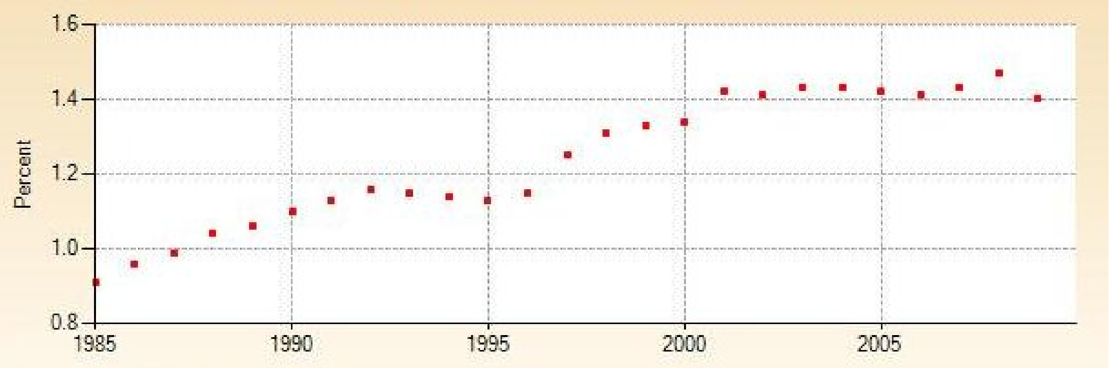

Figure 1.2 U.S. Trend of sulphur content in crude oil (U.S. Energy Information Administration, 2010)

Hence, hydrogen is required considerably more in refineries for desulphurisation, denitrogenation and other usage. Along with the growing transportation fuel market, the hydrogen availability has become a focal point in modern refineries. Lower sulphur fuel would need more hydrogen for hydrotreating processes. Meanwhile as a by-product of catalytic reformer, the amount of hydrogen produced is also affected by milder operation severity resulting from stricter fuel specifications. It is reported that in Europe and US, the hydrogen demand rises from 10MMNm^3/h to 15MMNm^3/h while the rate of by-product hydrogen and recovery from off-gas is decreased from 75% to 35% from 1995 to 2005.

Moreover, hydrogen production is now under pressure as a result of recent rules of cutting down the greenhouse gas emissions. With increased concerns on global warming and controlling of greenhouse gas emissions, it can be predicted that the refinery hydrogen production will become more expensive and face much stringent standards.

1.2.2 Hydroprocessing for Heavy Crude

World's crude oil is estimated to become heavier and contain more sulphur.

Table 1.2 2007 World crude characteristics selection

Crude Type	Total Sulphur (wt %)	Density(kg/m^3)
BOREALIS HEAVY BLEND	3.75	924.9
BOW RIVER	2.92	925.5
COLD LAKE	3.70	927.3
CHRISTINA LAKE SYN-BIT BLEND	3.14	935.2
ECHO SYNTHETIC BLEND	3.35	923.9
FOSTERTON	3.20	932.2
LLOYDMINSTER BLEND	3.46	924.9
LLOYDMINSTER KERROBERT	3.14	928.8
MACKAY RIVER HEAVY	2.73	933.8
SUNCOR-OSH	3.06	932.3
SUNCOR SYNTHETIC SOUR	3.56	923.6
PINE BEND SPECIAL	3.77	939.1
PEACE HEAVY	4.60	926.4
SMILEY COLEVILLE HEAVY	2.95	930.7
BLACK ROCK SEAL HEAVY	4.53	927.6
PORTAL MIDALE	2.21	876.4
U.S.SOUR-CLEARBROOK	2.40	889.7
WESTERN CANADIAN BLEND	3.06	927.5
WESTERN CANADIAN SELECT	3.33	927.3
WABASCA HVY	4.02	929.4

(Crude Oil Characteristics, Enbridge Pipelines Inc., 2007)

With heavier and high-sulphur crude oil and the expanding market for middle distillates such as diesel and jet fuel, the hydrogen-addition technology, hydrocracking and hydrotreating, is widely applied in refineries to process heavy-end or residue, although there are other methods such as catalytic cracking, visbreaking or delay coking, that are capable of heavy-end conversion. Hydroprocessing technology has its advantages in feedstock flexibility, high product yields and also good quality of products. Hydroprocessing units can be integrated into a refinery in order to maximize profits.

Table 1.3 Typical hydrogen consumption data

Process	%wt on feed	%wt on crude
HT Str. Run Naphtha	0.05	0.01
HT FCC/TC Naphtha	1	0.05-1
HT Kerosene	0.1	0.01-0.02
HDS LS Gasoline to 0.2% S	0.1	0.03
HDS HS Gasoline to 0.2% S	0.3	0.04
HDS LS Gasoline to 0.05% S	0.15	0.04
HDS HS Gasoline to 0.05% S	0.35	0.05
HDS FCC/TC Gasoline	1	0.1
Cycle oils hydrogenation	3	0.3
Hydrocracking VGO	2-3	0.5-0.8
Deep residue conversion	2-3.5	1-2

Lamber et al. (1994)

Table 1.3 shows that vacuum distillates and residue hydroprocessing account for most of the hydrogen consumption in refinery processes.

The wide implementation of hydroprocessing technology leads to significantly increased demand for hydrogen. Therefore hydrogen management is focused on making the best use of limited hydrogen resources, and it has become essential for modern refineries to optimise its operation.

1.3 Hydroprocessing Technology

Hydrogen is added into molecules of oil streams by hydroprocessing units. The aims of adding hydrogen by different hydrotreating processes are shown below:

- Removing non-hydrocarbon impurities such as sulphur, nitrogen and metals in order to produce good quality products
  Chemistry:
  - Hydrodesulphurisation
    Ethanethiol + Hydrogen → Ethane + Hydrogen sulphide
    $C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S$

  - Hydrodenitrogenation
    Pyridine + Hydrogen → Pentane + Ammonia
    $C_5H_5N + 5H_2 \rightarrow C_5H_{12} + NH_3$
- Improving the operation of a downstream refining unit
- Saturating olefins and aromatics in order to improve product colour, stability and make premium quality lubricating oils
  Chemistry:
  - Olefins Saturation
    Pentene + Hydrogen → Pentane
    $C_5H_{10} + H_2 \rightarrow C_5H_{12}$
- Cracking heavy, low-value oils into lighter, higher-value products via hydrocracking

Without changing the density and boiling point of oil streams significantly, hydrotreating processes generally remove hazardous materials in the streams. In a hydrocracking process, the main reactions involve hydrogenation, cracking and isomerisation, which change the size and shape of molecules.

1.3.1 Hydrotreating Process

A typical hydrotreating process flowsheet is shown in Figure 1.3.

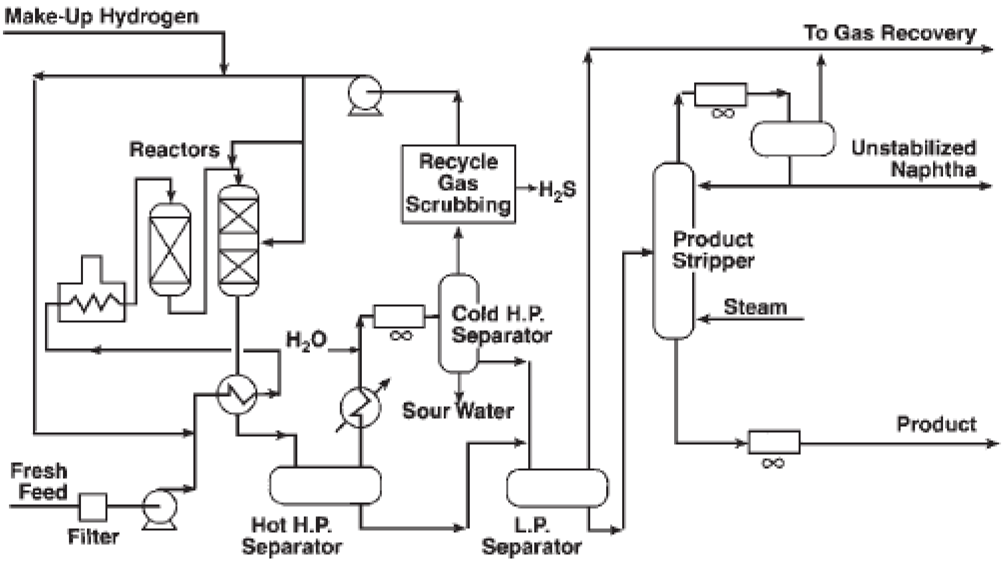

Figure 1.3 A typical hydrotreater flowsheet (Meyers, 2003)

- **Application:** Reduction of the sulphur, nitrogen and metals content of naphtha, kerosene, diesel or gas oil streams.
- **Products:** Low-sulphur products for sale or further processing.
- **Description:** Single or multibed catalytic treatment of hydrocarbon liquids in the presence of hydrogen converts organic sulphur to H_2S and organic nitrogen to ammonia. Naphtha treating normally takes place in the vapour phase, while heavier oils usually operate in mixed-phase.
- **Operating conditions:** 561K to 672K, 2.76MPa to 10.34MPa reactor conditions (Refining Processes Handbook, 2004).

1.3.2 Hydrocracking Process

Figure 1.4 shows a typical hydrocracker flowsheet.

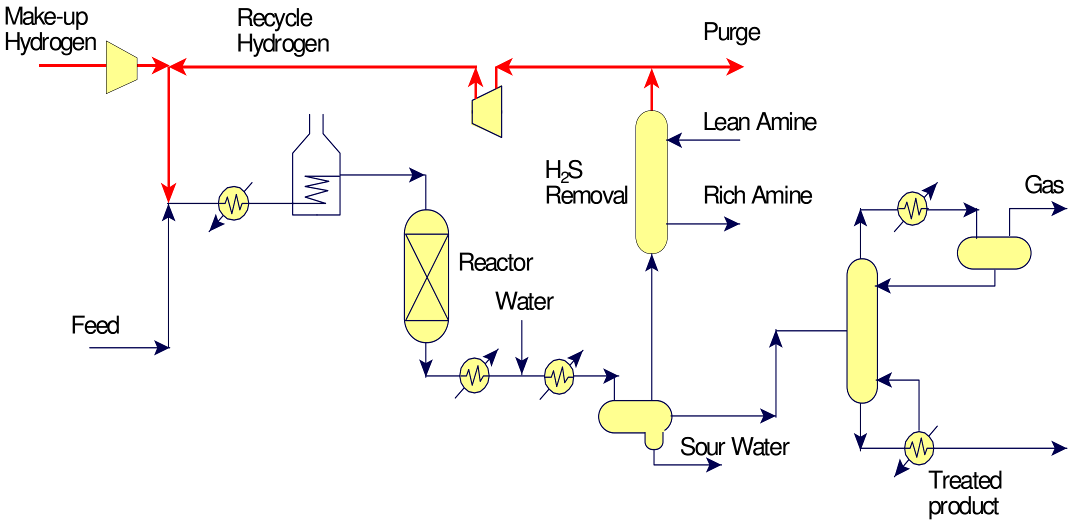

Figure 1.4 A typical hydrocracker flowsheet (Hiller, 1987)

- **Application:** Upgrade vacuum gas oil alone or blended with various feed stocks, light cycle oil, deasphalted oil, and visbreaker or coker-gas oil for instance.
- **Products:** Middle distillates, low-sulphur fuel oil, FCC feed, lube oil base stocks.
- **Description:** By using refining and hydrocracking catalyst, hydrocracker is able to process heavy oil cracking big molecular into smaller ones. The process consists of: reaction section, gas separator, stripper and product fractionator.
- **Operating conditions:**

Reactor temperature, K	658-722
Reactor pressure, MPa	9.66-24.14
H2 partial pressure, MPa	6.89-18.62

(Refining Process Handbook, 2004)

1.3.3 Hydrogen Resources in Refineries

A few hydrogen sources are available in modern refineries such as catalytic reforming, steam reforming and hydrogen recovery from off-gas. Some refineries with high-demand hydrogen also have hydrogen plants to produce hydrogen.

A Catalytic reformer is a very common unit that produces hydrogen. During reforming of hydrocarbon molecules a large amount of hydrogen is produced as a by-product. The off-gas is very rich in hydrogen and can be sent to a hydrotreater or a hydrocracker directly if the purity is high enough. Otherwise the gas will be purified first by a hydrogen purifier such as PSA or membrane and then sent to hydroprocessors.

Table 1.4 Typical hydrogen production data

Process	%wt on feed	%wt on crude
Continuous Regeneration Reformer	0.05	0.01
Semi-regeneration Reformer	1	0.05-1
Residue Gasification	0.1	0.01-0.02
Catalytic Cracking	0.1	0.03
Thermal Cracking	0.3	0.04
Ethylene Cracker	0.15	0.04
Steam Reformer	0.35	0.05

Lamber et al. (1994)

Light distillates, such as LPG or light naphtha can be converted into high purity hydrogen through steam reforming. Table 1.4 summarised typical hydrogen production data.

Off-gas recycle is another important feature of hydrogen utilization in refineries. Apart from an internal recycle built in hydroprocessing units themselves, there are many possible external recycles around refinery processes. Hydrogen is rich in off-gas of many processes such as delayed coking and catalytic cracking. However the purity of off-gas may not be high enough. So sometimes a purifier is introduced to improve the concentration of hydrogen before sending it to a hydrogen consumer. Purifiers can also remove hazards and impurities in hydrogen, which allows hydrogen consumers to use it in a more efficient way.

Although hydrogen resources in refineries look abundant, the rapidly increasing hydrogen demand is causing a hydrogen shortage. Therefore, hydrogen management is aiming to make the best use of hydrogen resources in order to satisfy increased demand and improve profitability.

1.3.4 Hydrogen Network

Obviously, there are many processes in the refinery dealing with hydrogen. If we separate these hydroprocessors and hydrogen plants from other refinery processes, a refinery hydrogen network can be formed. In a hydrogen network, the most common hydrogen consumers are hydrotreaters and hydrocrackers. For hydrogen producers, there can be a hydrogen plant, a catalytic reformer or an ethylene pant. Figure 1.5 gives us an example of a middle-scale refinery hydrogen network with 2 hydrogen producers and 6 hydrogen consumers.

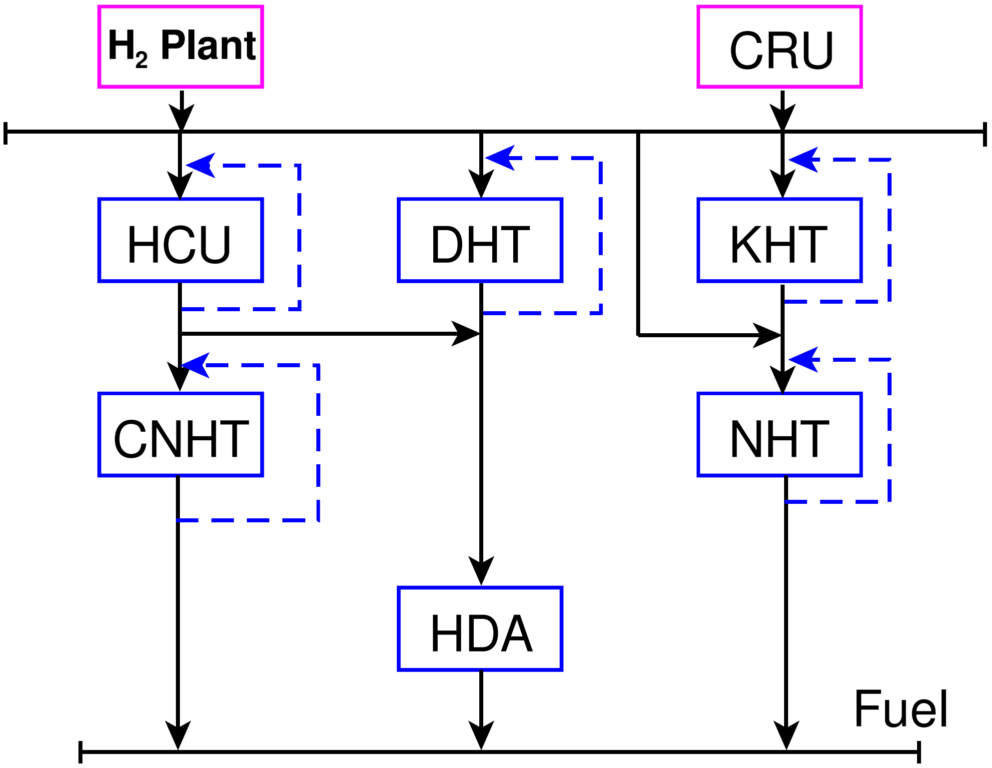

Figure 1.5 A typical refinery structure flowsheet (Singh, 2006)

The processes involved in this hydrogen network can be summarised as follows:

- Hydrogen producers: H2 plant and catalytic reformer (CRU)
- Hydrogen consumers: Hydrocracker (HCU), diesel hydrotreater (DHT), kerosene hydrotreater (KHT), cracked naphtha hydrotreater (CNHT), naphtha hydrotreater (NHT), Hydrodealkylation (HDA)

As can be seen from the flowsheet, two hydrogen producers providing hydrogen to a header, then hydrogen is transported to inlets of these consumers. Both hydrotreaters and hydrocracker have an internal recycle shown by dashed lines. After hydrogen consumption, the purge gas will be sent from hydrogen consumer outlets to a site fuel system.

1.4 Summary and Thesis Structure

Hydrogen is vital for oil refiners to face the trends caused by the clean fuel regulations, increased processing of heavier sour crude and heavy end upgrading. Hydrogen demand is increasing in refineries as more hydrogen is needed for deeper hydrodesulphurisation to reduce the sulphur content in fuels and to achieve high cetane diesel.

Strict environmental rules on pollutant emissions caused a sharp reduction in the fuel oil market. On the other hand, market trends indicate a very large increase in diesel oil and jet fuels production. Hydrocracking can play an important role in heavy end conversion because of its considerable flexibility and high quality of products. This indicates that more hydrogen is needed to satisfy the requirement.

On one hand, hydrogen demand is increasing in refineries. On the other hand, its availability is decreasing. For example, lower aromatic gasoline specification will decrease the operation severity in catalytic reformers thus reducing the by-product hydrogen. A capacity increase or change in product state of an existing refinery is often constrained by the hydrogen availability.

The imbalance between hydrogen availability and demand has to be solved by hydrogen network integration and optimisation, which is the focal point of the developed methods and techniques in this thesis. By optimising hydrogen utilization in a hydrogen network, the hydrogen utility demand can be reduced, and the total operating cost of the network will also be decreased. Nowadays hydrogen network management has become vital for refinery profitability and competitiveness.

The thesis structure is as follows:

- **Chapter 2: Literature Review**

  Review of existing research for refinery hydrogen network design & management

- **Chapter 3: Modified Modelling and Optimisation Methodology for Binary H2 networks**

  Mathematic formulation of a binary H2 network and optimisation methodology with an industrial case study

- **Chapter 4: Detailed Modelling and Validation of H2 consumers**

  Details of individual H2 consumer modelling under multi-component considerations and constant K-values strategy with verification

- **Chapter 5: Multi-component Optimisation for H2 Networks**

  Overall H2 network modelling under multi-component considerations and optimisation methodology for H2 networks with a case study.

- **Chapter 6: Conclusions and Future Work**

Chapter 2 Literature Review

The need for refinery hydrogen network optimisation was first acknowledged by Simpson (1984). Since late 1990s, many methodologies have emerged for refinery hydrogen management. In general, these methodologies can be distinguished into two categories:

- Targeting methods
- Mathematical programming approaches based on network superstructure for design

Targeting methods usually adopt a graphical approach based on thermodynamic principles, while mathematical programming approaches can provide systematic design methods and deal with possible practical constraints. In this chapter, Targeting methods will be addressed first, followed by mathematical programming approaches.

2.1 Hydrogen Management with Thermodynamics Analysis

The research regarding refinery hydrogen management can trace its history back to 1980s. In 1984, Shell Canada decided to commence operation of a refinery designed to process synthetic crude. Due to the high concentrations of nitrogen and aromatics within the synthetic crude, hydrogen became a core for removing these unwanted components to ensure the quality of fuel products and meet the specifications. With a number of involved hydroprocessing units, hydrogen management was considered to be very important in both design and operation.

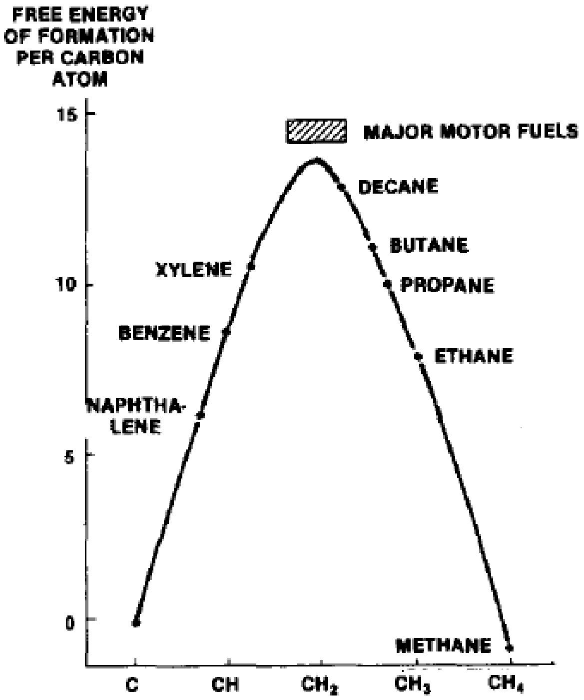

Figure 2.1The thermodynamic mountain (Simpson, 1984)

Simpson (1984) proposed his work over hydrogen management that is based on the analysis of the hydrocarbon thermodynamics. By reviewing the thermodynamics of hydrocarbons, the strategy of using hydrogen resources can be derived.

Figure 2.1 shows the free energy of formation by hydrocarbon types. The higher the curve goes, the more difficult the hydrocarbon to be formed. It can be figured out that the peak point of the thermodynamics mountain is around CH2, which coincidently, also represents the average of our transportation fuels (gasoline or diesel). Hydrogen management is then needed in order to upgrade the synthetic crude to the peak point so as to maximise the fuel production.

The way of doing hydrogen management is mainly about the selection of proper operating conditions and catalytic systems. The availability of hydrogen itself would not be able to upgrade the crude up to the peak point.

With respect to the kinetic and thermodynamic equilibrium of hydroprocessors, they tend to be designed with the lowest possible temperature and pressure conditions while maintaining catalyst activity and stability. A catalytic reformer will need to maximise liquid yield as well as hydrogen production to feed hydrogen consumers. The selection of catalyst used in a hydrocracker is carefully made to ensure the capability of conversion from highly refractive feedstock to high quality naphtha or middle distillates. The catalyst life, quantity to use, and distribution method are all optimised through extensive pilot plant experiments.

Appropriate operating conditions and strategy of using catalyst are two main factors of Simpson's hydrogen management. This raised issues of how to use hydrogen resources in refineries more effectively and intelligently, and led to a great deal of associated research further on.

2.2 Cost and Value Composite Curves for Hydrogen Management

Towler et al. (1996) developed the first systematic approach for hydrogen management. Economics analysis of hydrogen recovery against added values in product by hydrogen is proposed as the main feature in this method.

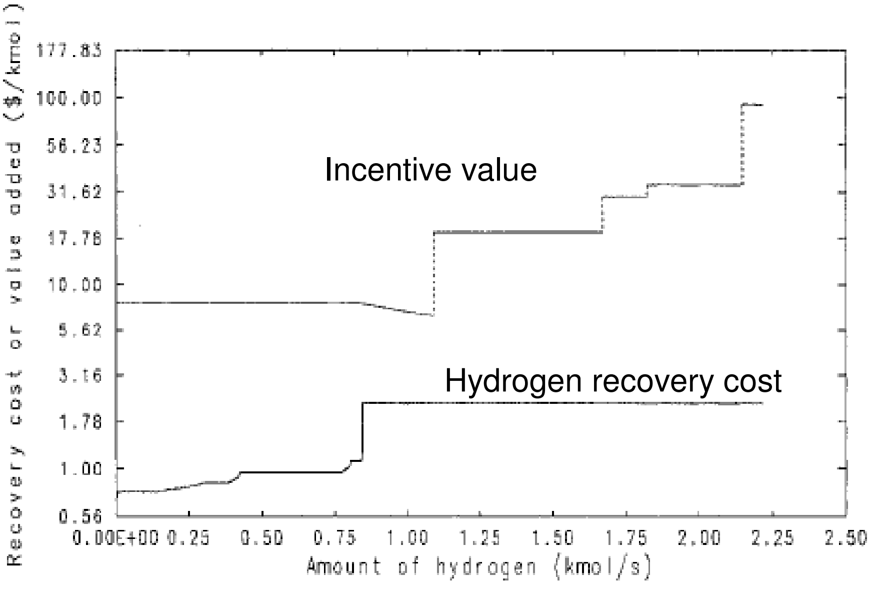

Figure 2.2 An example of value composite curves (Towler et al., 1996)

Hydrogen is recovered for a cost and brings extra value to fuel products. When the extra value brought by hydrogen cannot compensate the cost of hydrogen recovery, it is preferred not to recover hydrogen because no profit can be made. Under this concept, the cost and value composite curves can be plotted for either hydrogen producers or consumers.

The value added to products can be calculated as the value of products minus the summation of the value of feedstock, operating cost and capital cost. The cost of hydrogen recovery is represented by the cost of hydrogen purification units. Figure 2.2 demonstrates the incentive value in hydrogen consumption processes as the result of adding hydrogen. The curve below illustrates the cost of hydrogen recovery. Obviously the incentive value curve positions always above the hydrogen recovery cost curve which means all of the processes are making profit against investments.

The proposed methodology can be used not only for an economic analysis of a refinery hydrogen network, but also for refinery operation management, sensitivity analysis and in examining retrofit design options. However, the essential economic data to the analysis such as the added value by adding hydrogen will not be always available for refineries, bringing difficulties in applying the method. Another limitation of this method is the lack of hydrogen purifier selection and placement strategies.

2.3 Hydrogen Pinch Analysis

Linnhoff et al. (1979) proposed the pinch technology for heat exchanger network synthesis. By plotting cold streams and hot streams data into a composite curve, the overall heat exchanger network's pinch point can be found leading to a theoretical optimal solution. Alves (1999) utilized Linnhoff's work and extended the pinch technology into the hydrogen network field. Hydrogen sinks and sources are introduced similarly to the cold and hot streams in heat exchanger networks. With observation on the balance between hydrogen sinks and sources, hydrogen pinch analysis gives a general overview of the hydrogen usage situation of a specific hydrogen network.

2.3.1 Hydrogen Source and Sink

In order to apply the pinch technology on hydrogen networks, hydrogen sources and sinks must be defined in a simplified hydrogen consumer model (Alves, 1999).

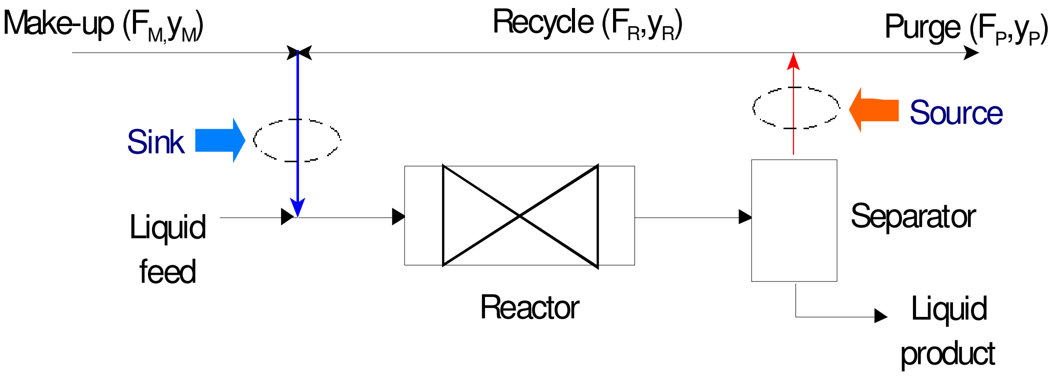

Figure 2.3 A simplified model of a hydrogen consumer

As can be seen in Figure 2.3, the simplified hydrogen consumer model illustrates how hydrogen flows and is used through a process. The hydrogen sink, located at the inlet of the consumer, is defined as the mix of the make-up hydrogen and the recycle stream. The make-up hydrogen mainly comes from a H2 plant or a catalytic reformer. F_{Sink} and Y_{Sink} are used to denote the flowrate and purity of a sink.

On the other hand, a hydrogen source locates at the outlet of a hydrogen consumer, containing a purge stream and a recycle stream. A hydrogen source is a hydrogen-rich stream that can be utilized by hydrogen consumers. It can be off-gas from other hydrogen consumers. In the hydrogen consumer model the hydrogen source would be the mixture of purge and recycle stream. F_{Source} and Y_{Source} are used to denote the flowrate and purity of a source.

Figure 2.3 demonstrates how a hydrogen consumer unit works. Make-up hydrogen will be mixed with liquid hydrocarbon feed. The mixture is then sent into a reactor for reaction under certain operating conditions. The after-reaction stream goes into the flash separation unit and gets stripped into vapour and liquid. The vapour phase portion can be recycled or purged, while the liquid phase becomes a fuel product afterwards.

2.3.2 Hydrogen Composite Curve and Surplus Curve

With defined hydrogen sources and sinks, the mass balance between them in a hydrogen network can now be observed in a hydrogen composite curve. By plotting a hydrogen supply profile and a demand profile against hydrogen flowrate for horizontal axis and purity for vertical axis, a hydrogen composite curve representing an overall hydrogen network hydrogen balance can be obtained (Alves, 1999).

As Figure 2.4 shows, the hydrogen composite curve is plotted by a hydrogen demand profile and a hydrogen supply profile. A few regions have been created by these two curves indicating either hydrogen surplus or deficits in terms of "+" or "-"to indicate advice hydrogen resources in excess or shortage. The area of hydrogen surplus and deficit can be calculated and directly plotted into another diagram, a hydrogen surplus curve, which shows the current situation of hydrogen usage in a hydrogen network (Alves, 1999).

A feasible hydrogen network would require a necessary condition, that no negative hydrogen surplus is allowed anywhere in the hydrogen network. Any negative hydrogen surplus would account for hydrogen shortage resulting in an infeasible network.

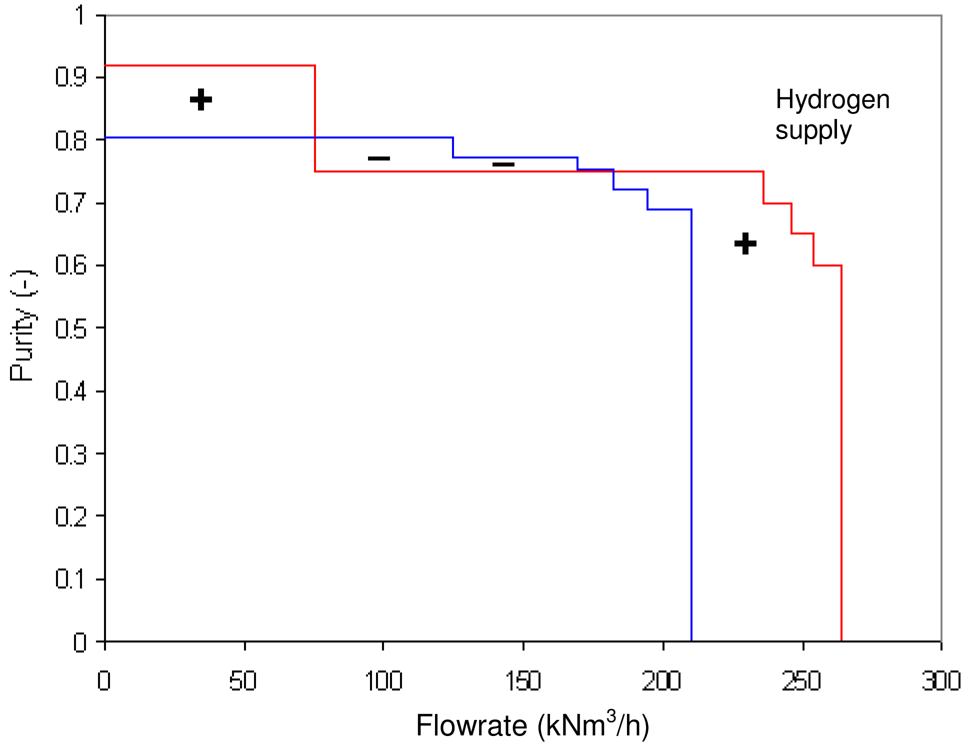

Figure 2.4 Hydrogen composite curve (Alves, 1999)

Figure 2.5 is the hydrogen surplus curve generated using the hydrogen surplus or deficit regions created in Figure 2.4.

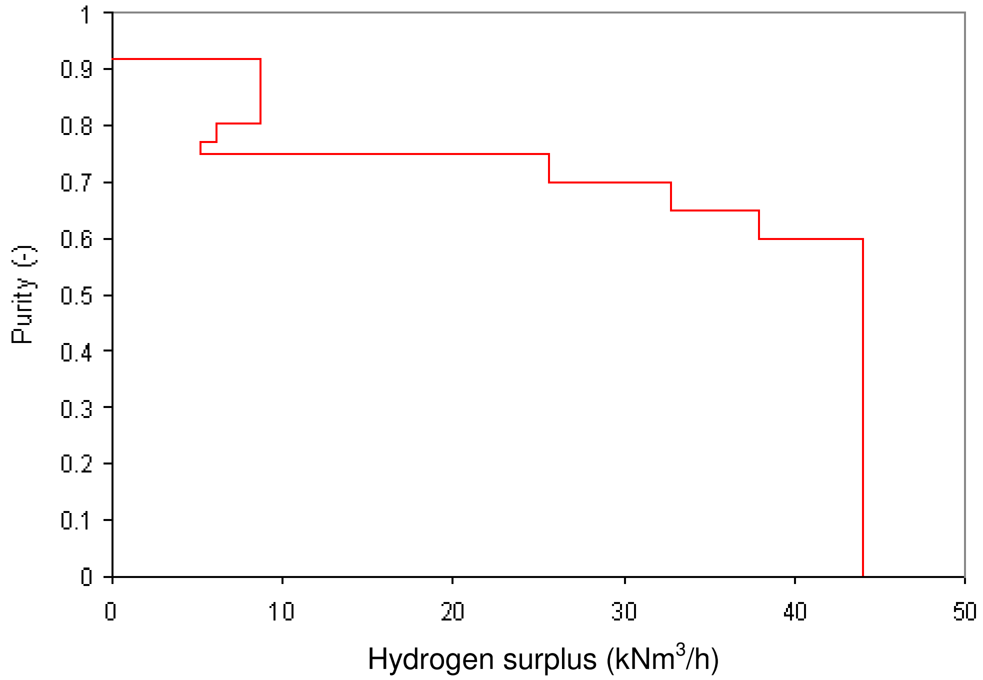

Figure 2.5 Hydrogen surplus curve (Alves, 1999)

The aim of drawing the hydrogen surplus curve is to gain a clear view of the hydrogen utility saving potentials. By moving the curve leftwards until a vertical segment hits the prutiy axis (Figure 2.6), the minimum hydrogen demand in a hydrogen network can be identified, and the target of hydrogen utility saving can be set.

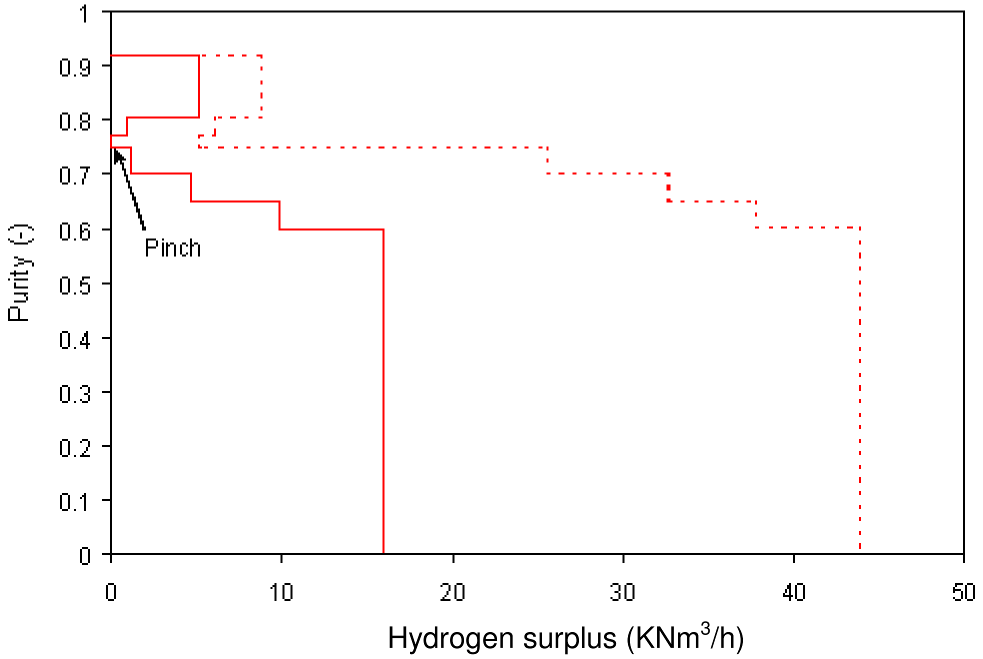

Figure 2.6 Hydrogen pinch point

A hydrogen pinch is then defined as the purity when the curve reaches the purity axis. Theoretically the hydrogen pinch point shows the minimum target for hydorgen utility of a hydrogen network without any constraints such as pressure capability or piping concerns. Therefore, the hydrogen pinch analysis is a simple graphical method to analyze a hydorgen network quickly and clearly. But it may produce infeasible hydrogen saving targets.

The hydrogen pinch point always shows a bottleneck in between sinks and sources, which can be used in network retrofit design. Figure 2.6 shows how to move hydrogen surplus curve in order to find the hydrogen pinch point.

2.3.3 Hydrogen Purity Analysis

Hydrogen utility purity is a very sensitive factor affecting hydrogen networks. In the hydrogen pinch analysis, a possible way to reduce the flowrate of a hydrogen stream is to increase the purity of one or more sources. In fact, a supply stream with higher purity will always produce bigger hydrogen surplus, if the stream has the same flowrate. Therefore, by increasing hydrogen purity, additional hydrogen surplus may be achieved (Alves, 1999).

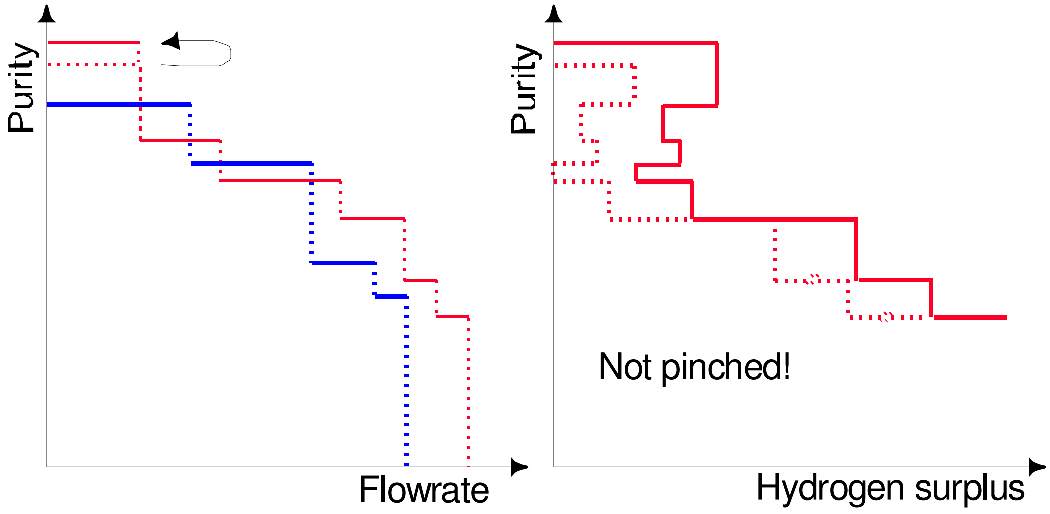

Figure 2.7 Purity increase impace on hydrogen pinch analysis

Figure 2.7 shows how increased purity would affect the hydrogen surplus. The dotted line demonstrates the initial hydrogen network which is already pinched.

Since the purity of hydrogen goes up, the network is unpinched as the solid line shows. As can be seen from the gap between the dotted line and the solid line, the increasing hydrogen purity would give the network extra hydrogen surplus thus the hydrogen pinch will be relaxed and the network will have a new minimum hydrogen utility target.

Consequently, hydrogen purification will need to be introduced for a higher purity of hydrogen which can result in more hydrogen savings. With the installation of hydrogen purification units, a few sinks and sources are also added into the hydrogen network. The inlet a of purifier would be an added sink, while the product and the residue of purifier are treated as the added sources. The whole network would be affected even if a purifier is only attached to a single hydroprocessing unit.

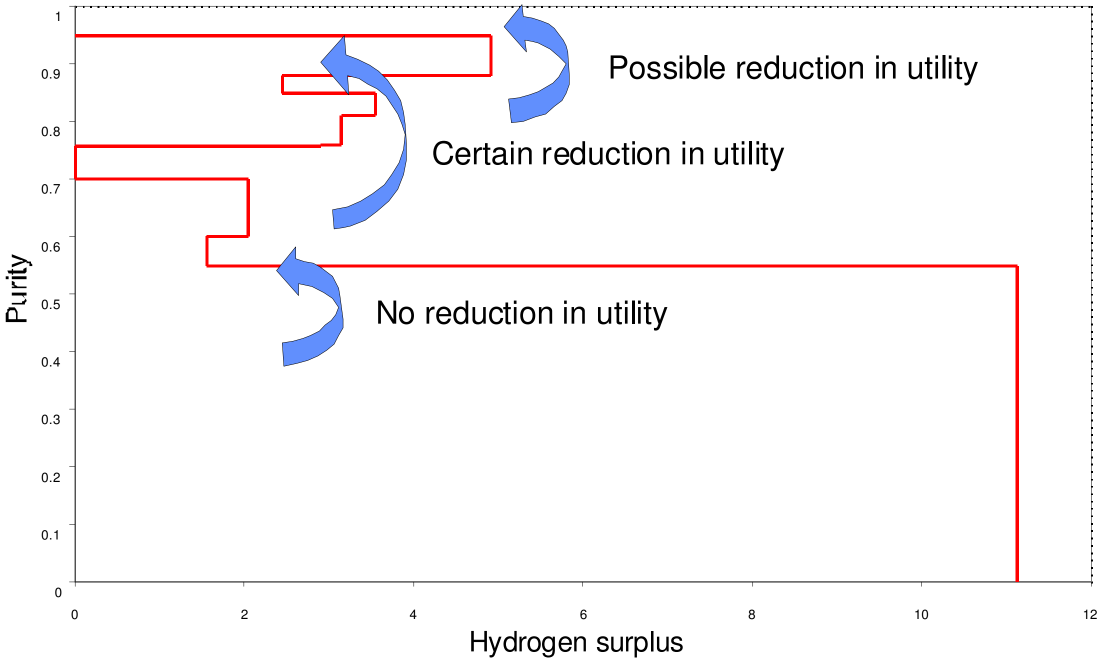

Figure 2.8 Hydrogen purification strategy based on pinch analysis

Basically, placing a hydrogen purifier somewhere in the hydrogen network leads to three possible situations with respect to hydrogen surplus, including above the pinch, across the pinch and below the pinch. Alves(1999) then found out that certain reduction of hydrogen would be achieved when a purifier is placed across the pinch, while no effect when below the pinch and possible savings above the pinch, as Figure 2.8 shows.

2.3.4 Limitation of Hydrogen Pinch Analysis

The hydrogen pinch analysis is a graphical method to analyze a whole hydrogen network. It is simple and easy to access. However, limitations are also obvious and restrict the capability of the method.

The two dimensional pinch analysis is very limited in dealing with practical issues, such as pressure consideration. It assumes that a hydrogen stream can flow from any source to any sink without considering the pressure conditions, which may result in infeasible situations in practical refineries. Thus a saving target given by the hydrogen pinch analysis may be too optimistic and actually impossible to achieve.

Secondly, while the purification units' placement is guided on the basis of across pinch, the detailed selection and design of purifiers are neglected. The hydrogen pinch can give advice for purification before design. However, since the purification is an important design option itself, the trade-offs between capital and H2 saving should be carefully carried out when deciding purification options.

Linear programming proposed by Alves (1999) simplifies the problem and practical constraints in order to ease the problem solving. However, on the other hand, the problem simplification and neglect of necessary practical constraints will definitely bring unrealistic or infeasible solutions.

2.4 Applications and Extensions of Hydrogen Pinch Analysis

As a graphical targeting method, the hydrogen pinch methodology for refinery hydrogen management was quickly accepted by the industry. The approach was then widely used as a basic tool for determining the theoretical target of minimum H2 consumption in a refinery hydrogen network.

Hallale et al. (2002) addressed the hydrogen pinch analysis in his paper and discussed the hydrogen management in a refinery. The hydrogen pinch analysis is used as the targeting approach to get an overview of a whole system for hydrogen utilization and also locate the minimum hydrogen utility target. The main focus of using the hydrogen pinch analysis is to enhance the hydrogen recovery system and improve hydrogen purification in order to save hydrogen utility. A placement strategy of hydrogen purifiers in respect to hydrogen pinch analysis is also proposed.

Furthermore, the hydrogen pinch analysis was highlighted by Kemp (2007) in his book regarding process integration and efficient use of energy, in which he discussed how the pinch analysis can be used for an overall refinery network based on process synthesis. Basically he utilized the concept of pinch analysis and used it for energy targeting, heat exchanger network design, utilities, heat and power system design and processes integration and intensification. The pinch analysis technology has been addressed throughout his methodologies, and explained and applied into practical case studies. It shows practical significance of the general pinch analysis for a refinery, and proves its capability especially in aspects of refinery hydrogen management, heat exchanger network design and utility systems optimisation.

For a wider applicable range of the hydrogen pinch analysis, Foo et al. (2006) develops the theory of gas cascade analysis (GCA). Rather than considering only hydrogen, the GCA method can be used to work out the minimum flowrate target for various utility gas networks such as nitrogen or oxygen network integration.

The conducting procedure of GCA can be summarised in the following steps:

1. Define gas sinks and sources and locate their flowrates at current concentration levels
2. Build the gas surplus/deficit cascade at every single concentration level
3. Set up cumulative impurity load cascade determined by cumulative gas flowrate and concentration across two concentration levels.
4. Calculate the pure gas requirement at each concentration level which is actually the minimum gas target

Following the procedure above, four case studies have been proposed including application of GCA on nitrogen integration, oxygen integration and network design, hydrogen integration with purifier placement and also a multi-pinch problem investigation. The case studies show that the gas cascade analysis technology is able to get minimum utility target (minimum flowrate at specific concentration levels) for various gas utility quickly and precisely. Based on system pinch points, the gas utility network retrofit design for saving utility can be obtained with a systematic methodology of gas purifier selection.

Focusing on hydrogen distribution network utility minimization, Zhao et al. (2007) proposed two systematic methods for targeting minimum utility. The innovation of this work is the impurities pinch analysis. As an analogy to the hydrogen pinch analysis, the impurities pinch analysis can be obtained by plotting impurities' flowrates versus relative purities, and is included in the hydrogen utility minimization methodology (Zhao et al., 2007).

The method proposed by Zhao et al. (2007) takes into account impurities consideration within a hydrogen network, allowing the network minimisation to deal with multiple constraints for multi-components including H2 and various impurities, and figure out the minimised utility target. By using impurities surplus and deficit diagrams, the network pinch point can be located by which the minimum hydrogen consumption target is determined.

Under multi-component consideration, the general targeting procedure can be summarised as follows:

1. Assume flowrate for a given hydrogen network with certain hydrogen purities
2. Defining and arranging sinks and sources in the order of increasing impurity concentration
3. Build impurity composite curves for sinks and sources in terms of concentration versus flowrate
4. Obtain impurity deficit curves
5. If negative deficit happens at any flowrate level, increase hydrogen

flowrate and go back to step 2

6. If positive deficit happens at any flowrate level, decrease hydrogen flowrate and go back to step 2
7. If any place is found with 0 deficit while other places are with deficits larger than 0, the current H2 consumption is the minimum target and pinch point is found

The improved hydrogen utility targeting method incorporates the impact of impurities within a hydrogen network. By taking into account multi-component in streams, the impurity deficits diagram can be achieved which is used for locating the system pinch indicating the utility minimum target.

Another issue in this work is the stream ranking taking into account different impurities. In the proposed targeting procedure, the streams need to be arranged in certain orders. For all impurities, the stream rankings can be the same or different. According to the same or different stream ranking under multiple impurities, hydrogen networks can be classified into two different types. Similarly, a specific targeting procedure has been developed for each type of problems. In addition, the proposed hydrogen pinch targeting technology can be used for water system utility minimisation as well.

In order to obtain more realistic network design, the pressure consideration needs to be incorporated into the hydrogen pinch analysis. Ding et al. (2010) proposed a graphical method for optimising hydrogen networks using hydrogen pinch theory with inclusion of pressure considerations. The authors introduced the concept of average pressure profiles to integrate pressure consideration into the hydrogen pinch analysis.

Unlike the previously proposed hydrogen pinch analysis based methods (Alves, 1999; Hallale et al., 2002; Foo et al., 2006; Zhao et al., 2007), pressure drop is considered when there is hydrogen transportation from a source to a sink. During the transportation, the source pressure is reduced and contributes to the pressure drop. Consequently, the shifted pressure is then defined as the average pressure. On the basis of definition of the average pressure, the average pressure profile can be finalised by analogy to the hydrogen source or sink profiles. The average pressure can be plotted against dropping purities as the same order of hydrogen composite curves. With the average pressure profile, the pressure surplus or deficit can be easily figured out at specific hydrogen purity. For every single hydrogen purity level, if the source curve is above the sink curve, it means the pressure is high enough to feed hydrogen to the sink. Conversely, if the source curve is below the sink, it represents that the pressure requirement is not satisfied and compressors may be needed.

In the case that a source pressure is not enough for a sink to take in hydrogen, two options are available. One is to install a new compressor, while the other choice is swap the source with another one with a higher pressure level. The selection can be determined by cost analysis in order to achieve the most economical solution. In this case, the strategy of whether to add a new compressor or not is proposed with consideration of the capital cost of a compressor. Based on the compressor selection strategy, the complete hydrogen network design taking into account pressure consideration can be obtained by using the enhanced hydrogen pinch analysis.

As discussed, many targeting methods for refinery hydrogen management have been developed. However useful, these graphical methods cannot effectively deal with many practical constraints, which leads to the development of various design methods.

2.5 MINLP H2 Network Optimisation with Purifier Selection Strategy

Based on graphical hydrogen pinch analysis, Alves (1999) proposed a linear programming (LP) approach for optimising H2 network connectivity. As an extension of Alves’s (1999) work, Hallale et al. (2001) and Liu (2002) developed the methodology of automated hydrogen network design using a mixed integer non-linear programming (MINLP) method. To overcome the drawbacks of the hydrogen pinch analysis, Liu has taken the pressure into consideration as well as the hydrogen purifier placement strategy.

2.5.1 Inclusion of Pressure Consideration

Hallale and Liu (2001) developed an MINLP optimisation approach to address the pressure constraints in optimising H2 networks which is based on a hydrogen network superstructure. As shown in Figure 2.9, AM and AR stands for the make-up and recycle compressors for unit A, while BM and BR means the make-up and recycle compressors for unit B. The superstructure shows all the possible connections between sinks and sources. Hydrogen streams go from sources to sinks. As shown in Figure 2.9 Source A is with 1500psi pressure, lower than 2200psi of Sink B. Thus the hydrogen from the purge of unit A cannot be used by unit B directly due to the pressure difference. So, a compressor is needed as shown in the figure. The inlet of a compressor is treated as a sink and the outlet as a source. In this way a superstructure is developed for mathematical formulation and optimisation.

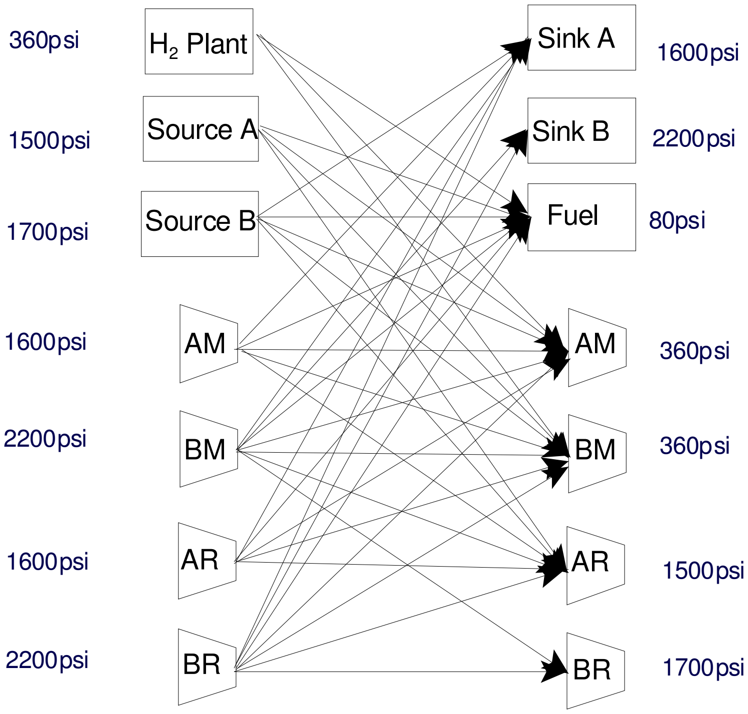

Figure 2.9 Hydrogen network superstucture (Liu, 2002)

The sink requirements and source availability are both formulated in terms of flowrate and purity. In addition, as compressors are also defined as sinks and sources, likely they are formulated in the same way apart from some extra conditions. The overall flowrate and pure hydrogen must be equal between the inlet and the outlet of a compressor.

For an existing compressor, a maximum flowrate must be set according to manufacturer's specifications. Otherwise, unrealistic results may be produced. If needed, the design programme can introduce extra units such as new compressors or purifiers. Sometimes new compressors have to be added in order to meet the minimum utility target and practical restrictions.

As Figure 2.10 shows, one sink and two sources are needed to model a hydrogen purifier into the superstructure. Similar to the formulation of other sinks and sources, the flowrate and purity between feed and product and residue must be balanced. The maximum flowrate limits can also be included if required.

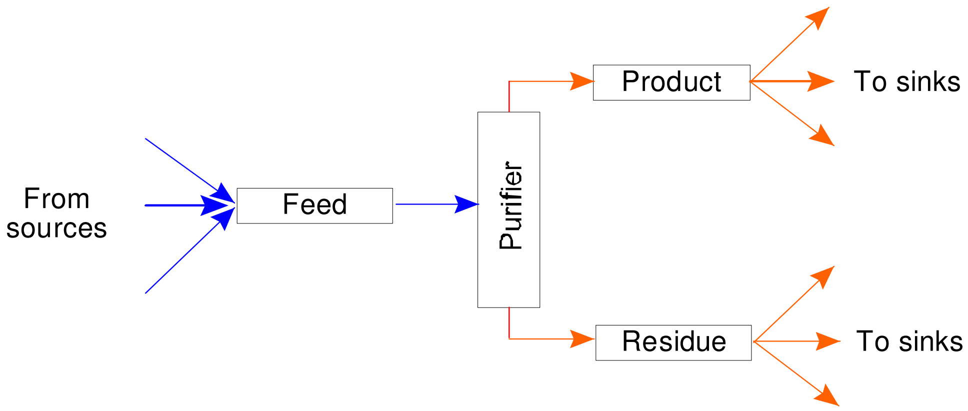

Figure 2.10 Hydrogen purifer involved into superstucture (Liu, 2002)

With a compressor model, the whole hydrogen distribution network is then completed. The objective function is typically set to be the minimum hydrogen utility flowrate.

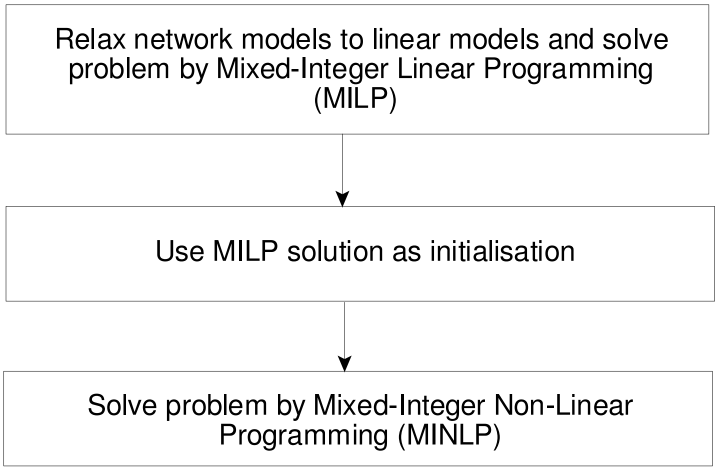

Figure 2.11 MINLP problem relaxation methodology (Liu, 2002)

The hydrogen network with compressor selection is then formulated as a mixed-integer non-linear problem Integer variables are used when there is a need to introduce a new compressor or purifier. Stream flowrate and purity calculation will bring non-linearties. In order to solve this MINLP problem, Liu proposed to relax the non-linear equations into linear inequalities. In this way the whole MINLP problem is first solved as a mixed-integer linear programming (MILP) problem followed by solving the original MINLP problem (Figure 2.11).

2.5.2 Strategy of Purifier Selection

Liu and Zhang (2004) developed an automated design approach to address the selection of purification processes and their integration in hydrogen networks, which again was formulated as an MINLP problem. The selection of hydrogen purifiers depends on process flexibility, reliability as well as economic concerns. Similarly a superstructure was created for options of purifiers, and then an MINLP optimisation procedure is performed to find the optimal solution.

With newly built PSA, membrane and piping cost models, the hydrogen purifier superstructure is subject to optimisation. The objective function is then set to be minimum total annual cost that includes operation cost and annualised capital cost. Minor utility costs, for example hot stream for preheating and instrument air, are neglected in the calculation.

The problem to solve is a mixed integer non-linear programming (MINLP) problem. Hence the linear relaxation method is required again in the exactly same way as used before (Figure 2.11). A few case studies have been carried out and show convincing results of reduced total costs.

In a similar research, Peramanu et al. (1999) proposed economics analysis of hydrogen purifiers dealing with purge gas from hydroprocessors. The authors discussed the economics of three most common types of hydrogen purifiers: pressure swing adsorption (PSA), membrane and cryogenic. For PSAs, the best economics happens at a lower recovery if the purge gas satisfies the fuel gas pressure requirements as the off gas compression is relatively expensive. For a higher feed pressure, membrane can perform better than PSAs. The cryogenic processes are used to recycle hydrogen near feed pressure which has advantages over both PSA and membrane when there is high feed pressure.

A sensitivity analysis case study was also carried out to show the relationship between H2 purifiers, feed gas capacity, purity, and fuel gas value. It shows that higher feed gas flow, higher feed purity, and lower fuel gas value lead to better economics of hydrogen recovery processes.

2.5.3 H2 Plant Integration

Hydrogen production processes are mainly catalytic reforming and steam reforming (hydrogen plant). They both play very important roles on the supply of hydrogen in refineries. In Liu’s work (2002) hydrogen plant process modelling is based on rigorous simulation to derive a simplified model.

The overall hydrogen plant modelling consists of three steps. Firstly a simulation is created in PRO/II to generate process data such as hydrogen production and utility consumption (Figure 2.12). The next step, by using the process data obtained from the first step, a linear hydrogen plant model is developed by regression. The final step is model verification by process simulation and feasibility check.

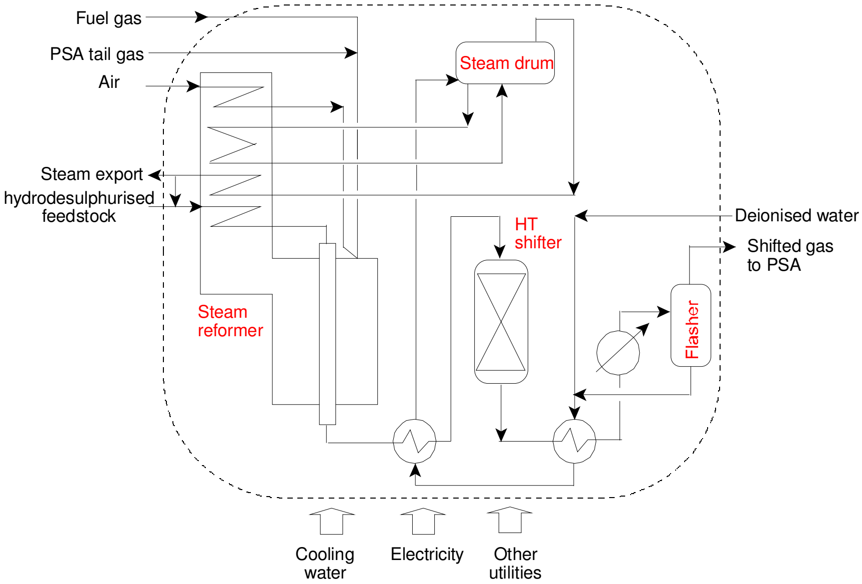

Figure 2.12 Simplified hydrogen model simulation (Liu, 2002)

The objective of process simulation is to figure out the performance hydrogen production with respect to certain feedstock and operating condition, as well as other related utility data such as power, cooling water etc.

The automated hydrogen network design method would require a hydrogen plant model that is capable to describe mass and energy balance of hydrogen plants and relatively simple mathematical expressions to be compatible with the overall optimisation methodology without computation complexity and possible errors. On the basis of the two conditions, a linear hydrogen plant model is then built up.

Figure 2.13 demonstrates the hydrogen plant model and its interface with a hydrogen network model. Utility usage includes fuel, boiler feed water (BFW), cooling water (CW) and electricity. Steam reforming, high-temperature shifting and steam generation processes are included in the hydrogen plant. An individual PSA model can be attached to the outlet of a hydrogen plant in a hydrogen network.

The hydrogen plant model is verified by testing typical bulk feedstock feeding into the model. The results are to be compared for feasibility check. According to Liu's case study, the hydrogen plant model works quite well and fits accurately with the result of simulation.

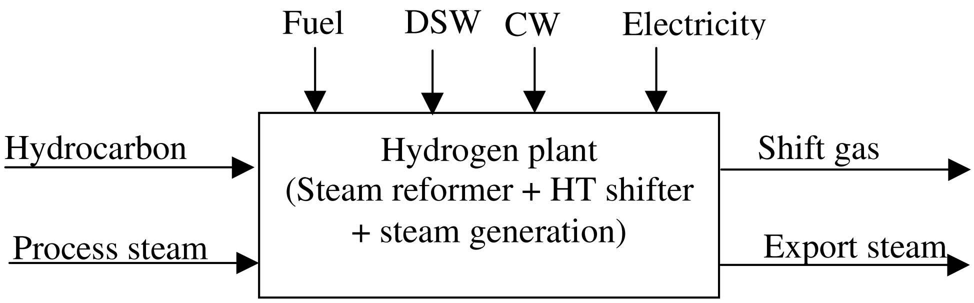

Figure 2.13 Linear hydrogen plant model (Liu, 2002)

The integration of a hydrogen plant starts with building a superstructure as shown in Figure 2.14.

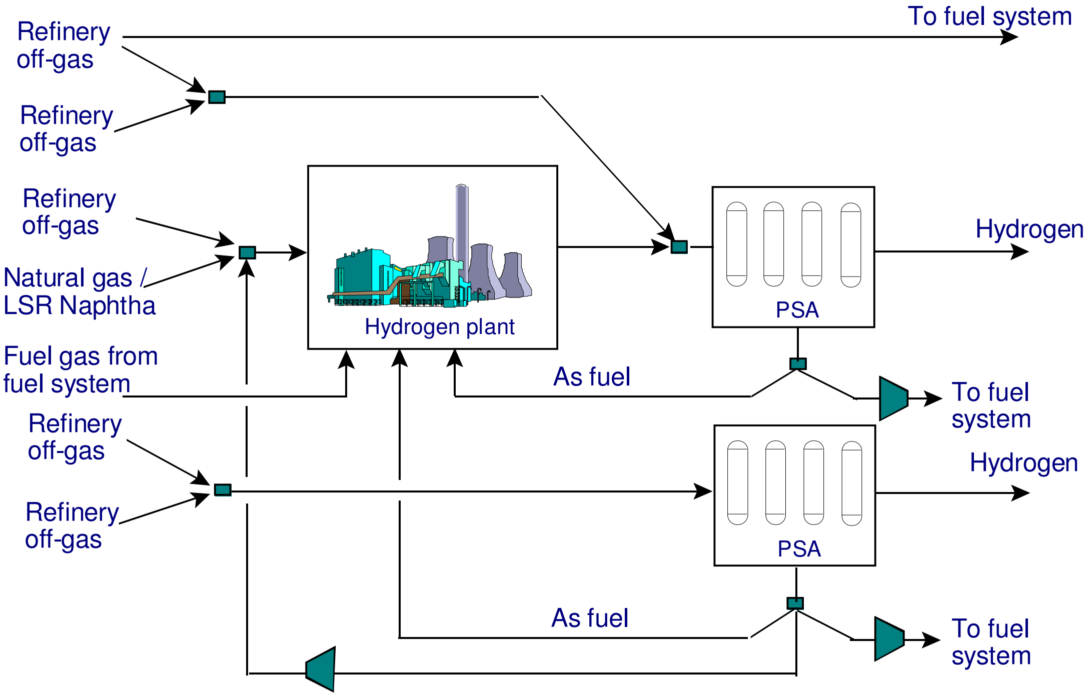

Figure 2.14 Superstructure for integration of hydrogen plant (Liu, 2002)

The integrated hydrogen plant with steam reforming and HT-shifting is treated as a hydrogen generation unit. One PSA unit is attached to the hydrogen plant as the purification process to produce high purity hydrogen utility. The other one purifies the refinery off-gas, which can feed both PSA units, the hydrogen plant or even be sent straight to fuel gas. The feedstock of the hydrogen plant can be hydrocarbons ranging from natural gas to straight-run naphtha. The purge gas from PSAs provides the fuel to the hydrogen plant. Fuel gas from the fuel system can also be used as the fuel of the hydrogen plant. The purge gas from PSAs can also be sent to the refinery fuel system. Due to relatively low pressure level, compressors are necessary to lift the hydrogen utility to relatively high inlet pressure of a hydrogen consumer.

The aim of constructing this superstructure is to find the best way of integrating of hydrogen generation and purification. The superstructure should contain options of feed selection for hydrogen plants, strategies of off-gas recovery and purification. The method can be used to exploit the potentials of both hydrogen plants and purification for existing hydrogen networks.

Based on the superstructure a non-linear formulation is developed. The objective function for operational problems should include all the operating costs relating to a hydrogen plant.

For hydrogen plant modelling, there are also other research developments. Bressan (2010) proposed a new design for H2 plant in refineries based on steam reforming of hydrocarbons. The developed steam reformer design consists of the following key elements:

- Hydrodesulphurisation section
- Pre-reforming section
- Reforming section
- Syngas cooling and shift reaction section
- Pressure Swing Absorption (PSA) section

The new design adopted the Terrace-Wall furnace design developed by Foster Wheeler. According to the author, the developed H2 plant design can offer high flexibility and high reliability for refiners to handle wide range of feedstock securely and stably. The technology is sophisticated and proved its feasibility and applicability in industry with Foster Wheeler.

2.5.4 Other Systematic Optimisation Methodologies

Fonseca et al. (2008) proposed a linear programming (LP) method to solve refinery hydrogen network optimisation problems. The authors utilized the simplified hydrogen consumer model developed by Alves (1999) and constructed an LP formulation in terms of mass balance between sinks and sources under pressure consideration. However, the LP methodology is significantly restricted in problem formulation and is not capable to deal with many network modification options.

Khajehpour et al. (2009) adopted the optimisation methodology by Hallale and Liu (2001), and modified the hydrogen network modelling from MINLP to NLP with a reduced superstructure. Based on industrial experience and engineering judgements, almost a half of the variables proposed by Hallale and Liu (2001) were eliminated. In this way the reduced superstructure is constructed based on which generic algorithm (GA) is applied in optimisation, with an objective function to minimise the total amount of purge hydrogen to the fuel system. However the results generated from this method can only be treated as a theoretical one due to missing critical practical constraints, which may be impractical for a real refinery hydrogen management project.

Kumar et al. (2010) put insights into considering variable inlet and outlet pressure of compressors. With variable pressure configuration of compressors, the previous H2 network modelling proposed by Hallale and Liu (2001) was modified and improved in order to obtain more realistic solutions. The modified compressor formulation takes into account variable inlet and outlet pressure consideration, and both NLP and MINLP modelling and optimisation methodologies are developed. The NLP and MINLP were proved much better than LP when solving complicated hydrogen network optimisation problems as practical constraints such as compressors and piping can be easily incorporated for a more realistic and applicable design.

Liao et al. (2010) proposed a systematic method for refinery hydrogen network retrofit design. The authors proposed an MINLP hydrogen network model based on Hallale and Liu's (2001) hydrogen network superstructure. The proposed optimisation methodology focused on placement of hydrogen purifiers and compressors during retrofit design. The objective was set to be the total annual cost by taking into account H2 production cost, utility cost, and piping costs.

2.6 Molecular Modelling of Hydroprocessors

Sun (2004) tried to improve the integration and optimisation of hydrogen networks by developing kinetic models of hydroprocessors such as hydrotreaters and hydrocrackers at a molecular level. In addition, an interaction analysis between hydrotreating processes and a hydrogen network is proposed using the developed kinetic models seeking for improvements for the hydrogen network.

The kinetic models for hydrotreater and hydrocracker are based on the concept of molecular type homologous series matrix. The matrices are used to describe the chemical components of complicated petroleum mixtures. Feed, reaction, and catalyst deactivation are modelled, allowing monitoring and evaluation of the effects of changes to feed stock or operating conditions.

The hydrogen pinch analysis can only deal with steady-state conditions. Sun (2004) developed a new methodology incorporating a series of systematic procedures to apply the analysis to different operating conditions.

2.7 Rigorous Optimisation of Hydrogen Networks with Impurity Considerations

There is an important assumption of the existing design approaches (Hallale and Liu, 2001; Liu, 2002), which is to maintain constant reaction conditions such as H2/Oil ratio and H2 partial pressure, for all refinery hydroprocessors in a hydrogen network. However, H2 network optimisation will lead to changes in H2 distribution in a network, the impacts of which will result in composition changes of light hydrocarbon compounds in makeup, recycle and purge streams from hydrogen consuming processes.

As demonstrated by Zhang et al. (2008), it is impossible to keep both H2/Oil ratio and H2 partial pressure constant when there is a change of light hydrocarbon composition at the inlet, even if the H2 purity at the inlet remains unchanged, due to the change of vapour-liquid-equilibrium caused by composition changes at downstream separation units. This puts the solutions from the developed design methods in doubts, due to the concerns of feasibility. Therefore, Zhang et al. (2008) developed a systematic approach for H2 network optimisation taking into account the impacts of light hydrocarbons and other impurities on a hydrogen distribution system. By iterating between detailed simulation and simplified optimisation, more accurate optimal solutions can be obtained, which enhances users' confidence in the solution. However, this method has its major drawback of lengthy iteration, which results in expensive computation and sometimes convergence failure.

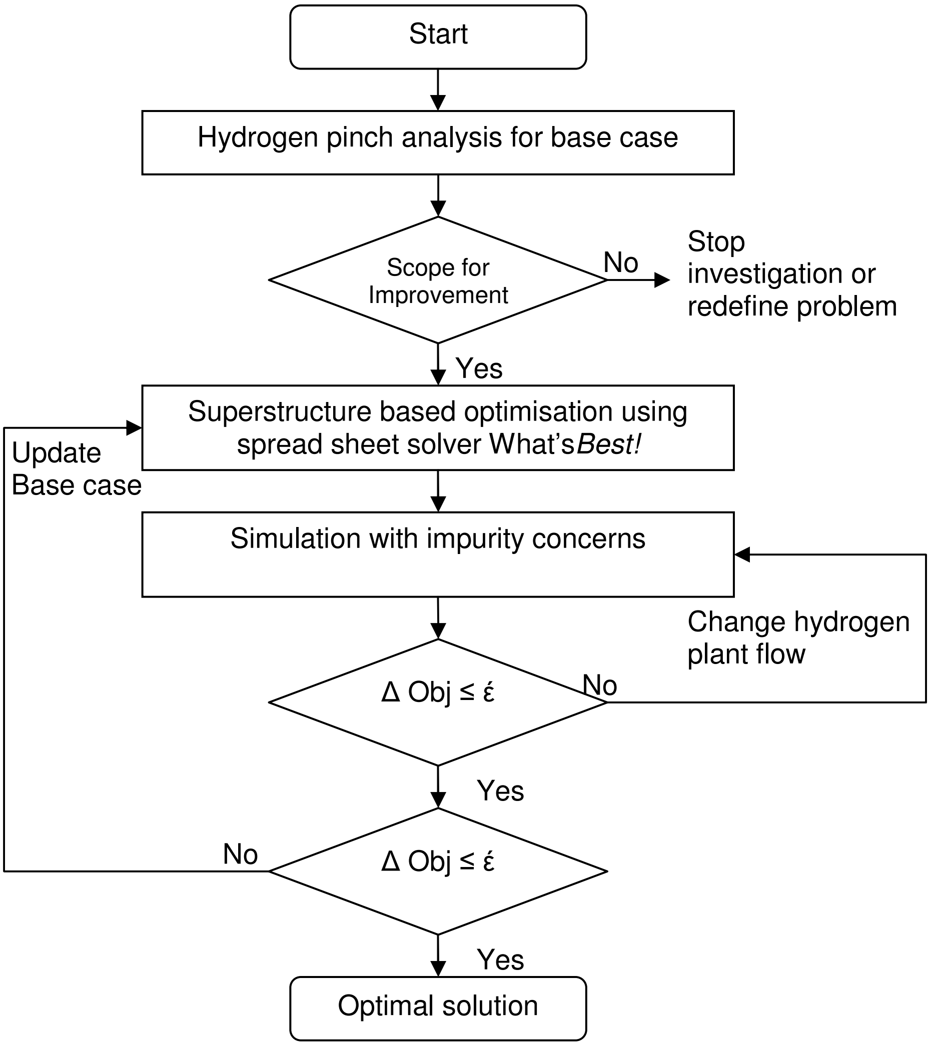

Figure 2.15 Hydrogen network optimisation framework

There are three strict conditions in this optimisation framework as follows:

- Hydrogen-to-oil ratio must be in acceptable range
- Hydrogen partial pressure must be in acceptable range
- Sulphur intake for each consumer must be in acceptable range

Any failure in satisfying the condition listed above may result in infeasible solutions.

The optimisation framework starts out with the hydrogen pinch analysis to scope for any possible potentials or improvements upon an existing network. If there is no improvements detected then the algorithm stops.

Otherwise, proceed to the next step, superstructure based automated design would be called up. The whole hydrogen network modelling and calculations were built in Microsoft Excel environment using VBA programming, including hydrogen producer models, hydrogen consumer models and connections. The detailed modelling of hydrogen consumers contains reaction and separation. The flash separation calculation is done by flash routine proposed by Singh (2006). The optimisation is performed in commercial software What's*Best!*®*.* At this stage, impurities are lumped as methane to boost the optimisation.

The result from optimisation is simulated for feasibility check. The important thing here is that, the simulation takes detailed impurities into consideration. If the difference between simulation and optimisation is too big, the current stream data including flowrates and purities will be sent back to the optimisation step and iterate again, until a pre-specified tolerance is achieved.

The systematic methodology is proven to be capable to incorporate the hydrogen plant model with impurity considerations in hydrogen network management. The overall hydrogen network modelling is more thorough than before with detailed hydrogen network simulation and optimisation.

2.8 Modelling and Optimisation of Hydrogen Networks for Multi-period Operation

In reality, hydrotreating and hydrocracking processes have to operate under dynamic operating conditions to account for catalyst deactiviation. The changes of operating conditions will definitely affect the performance of processes. For example, the changes of feedstock will affect the hydrogen consumption during reactions, so the rector outlet stream would be with different compositions leading to an affected flash separation. Actually, any changes in flowrate, purity, or temperature and pressure conditions would result in different performance of hydrogen consumers.

However, the past research of hydrogen network management are all based on single-period situation, which means only a single set of data are considered without taking into account the possibilities of changing operating conditions.

The methodology for multi-period hydrogen network design was developed by Ahmed et al. (2010). The developed new methodology has taken into account the dynamic operating conditions so that it can cope with flexible multi-period hydrogen network management.

2.8.1 Mathematic Formulation

The formulation is an extension of Liu (2002)'s work by introducing a subscript p indicating a specific period. With the introduction of the subscript, the multi-period hydrogen network optimisation is formulated as an MINLP problem.

The following aspects are included in the formulation:

- Process constraints including overall material and hydrogen balance
- Piping system
- Pressure constraints

The objective function is to minimise the total annualised cost including operating cost and capital cost.

2.8.2 Optimisation Framework

In order to solve the multi-period hydrogen management problem as an MINLP optimisation problem, a systematic optimisation methodology framework is proposed by Ahmed et al. (2010), as shown in Figure 2.16.

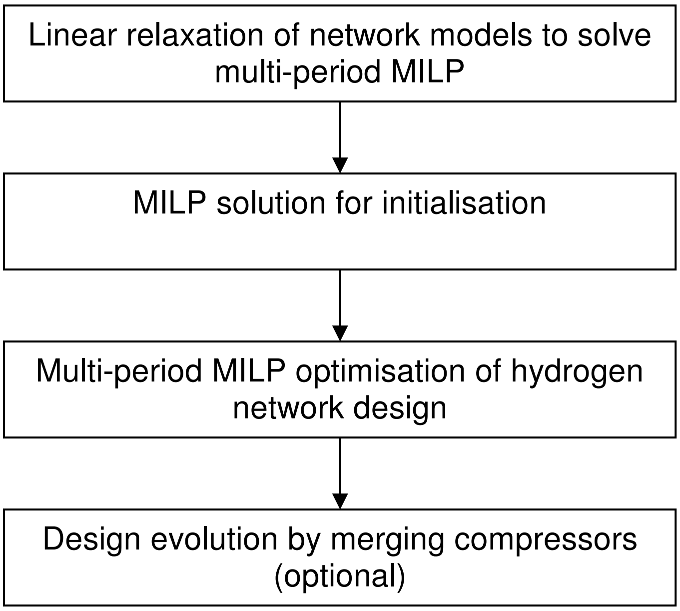

Figure 2.16 Hydrogen network optimisation framework (Ahmed et al., 2010)

A key feature of Ahmed's method is that many variables, for example flowrates and purities of streams, are all assigned with an additional dimension accounting for specific periods. The proposed technology focuses on the extension to multi-period hydrogen management problems on the basis of Liu's methodology (2002), which brings more flexibility and allows it to cope with more practical problems and generate more reliable and reasonable solutions. However, a hydrogen stream is treated as a binary mixture including only hydrogen and methane, which is a major limitation of this method.

2.9 Summary

Since the concept of refinery hydrogen management came out, there has been significant development for refinery hydrogen network management, from the simple graphical hydrogen pinch analysis to systematic computer-aided optimisation strategies.

However, there are still major weaknesses in the existing approaches which can be summarised as follows:

- The assumption of constant H2/Oil ratio and H2 partial pressure in all hydroprocesses makes the optimisation of a H2 network too restricted, especially when dealing with hydrogen manifolds
- There is a need to improve the hydrogen consumer model in order to take into account the impacts of impurities more accurately and effectively
- The computation efficiency of multi-component H2 network optimisation needs to be greatly improved

In order to address these shortcomings, the aim of this work is to develop a more effective modelling and optimisation framework when taking into account detailed composition changes in H2 distribution networks, so that the feasibility of the final optimal solution can be guaranteed with efficient computation effort.

Chapter 3 Modified Modelling and Optimisation Methodology for Binary H2 Networks

3.1 Introduction

There is a key condition for all previous work regarding H2 network optimisation: fixed H2/Oil ratio and H2 partial pressure at the reactor inlet. In a hydrogen consumer, reactor inlet conditions are very sensitive to hydrogen balance in a hydrogen consumer. Therefore, all existing binary hydrogen network optimisation methodologies are completed with fixed reactor inlet H2/Oil ratio and H2 partial pressure.

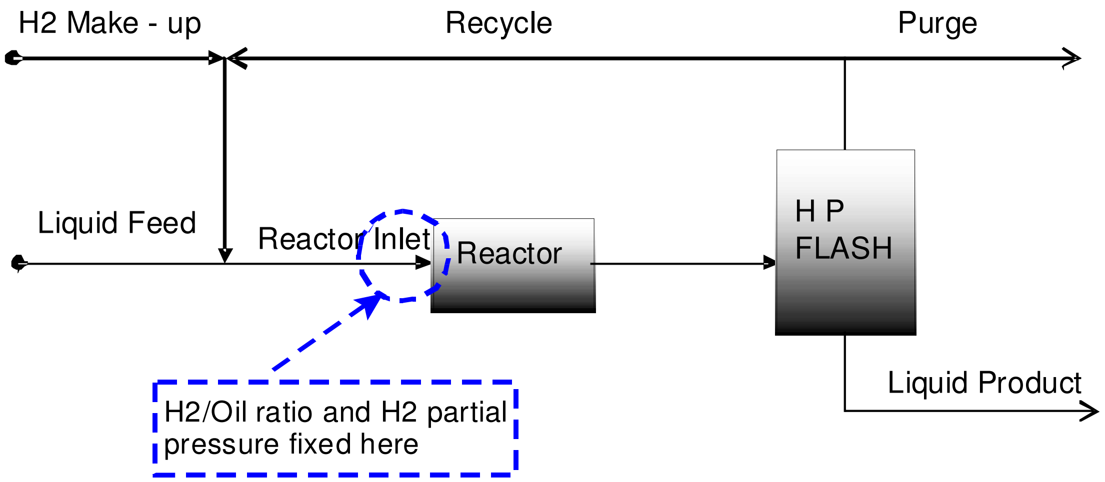

Figure 3.1 Fixed reactor inlet conditions

The reason why H2/Oil ratio and H2 partial pressure are fixed is that refinery hydrogen management uses these conditions as benchmarks when optimising hydrogen network parameters. In this way, the reaction conditions can be maintained when carrying out hydrogen network management activities.

However, this constraint has its own limitations. When we need to deal with a hydrogen network with certain practical constraints and limited freedoms to improve, the scope for optimisation under constant H2/Oil ratio and H2 partial pressure can be very little, which may even prevent optimisation result from reaching any feasible solutions.

Therefore, fixed H2/Oil ratio and H2 partial pressure can be major barriers in hydrogen network optimisation when dealing with large scale complicated refinery hydrogen networks, especially those with many practical constraints. Thus it is necessary to consider reactor inlet conditions relaxation to break out the limitations and improve the performance of optimisation.

Allowing variable H2/Oil ratio and H2 partial pressure can benefit individual hydrogen consumers in a refinery hydrogen network. In a modern refinery, the process flowsheet can be very complex. As for hydroprocessors, they might be supported by hydrogen producers directly or receive hydrogen from headers. Normally in a refinery, there can be a number of hydrotreaters and/or hydrocrackers receiving hydrogen from a specific header. Then all conditions at each reactor inlet can be very sensitive to the changes of hydrogen flowrate or purity provided from the header.

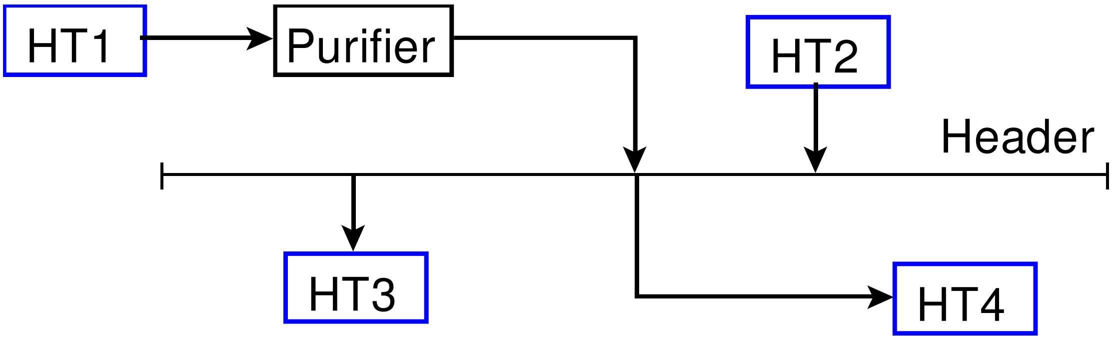

Figure 3.2 An example of a hydrogen network with a header

Figure 3.2 shows an example of how changes in a H2 header affect the H2/Oil ratio or H2 partial pressure of hydrogen consumers at the receiving end. Hydrotreater 1 purges low hydrogen purity off-gas to a purifier where the purged hydrogen is purified into a higher purity and then sent to the header. The purge gas from Hydrotreater 2 is directly sent to the header without any purification. Then the hydrogen of the header is provided to Hydrotreater 3 and Hydrotreater 4. As the header hydrogen is the only source for Hydrotreaters 3 and 4, the hydrogen partial pressures of hydrotreater 3 and 4 will be determined only by the hydrogen purity of the header. It is clear that the hydrogen partial pressure will be affected by the purity change of the header. For example, if we improve the purification performance of the header, the purity of the header will rise, and consequently result in improved hydrogen partial pressure at the inlet of the reactors of Hydrotreaters 3 and 4. However, all these benefits can not happen if we do not allow H2/Oil ratio or H2 partial pressure to vary. If we stick to fixed H2/Oil ratio and H2 partial pressure, there will be no flexibility for HT3 and HT4, and the improved purification would be of no benefit at all.

Nevertheless, what if we relax the H2/Oil ratio and hydrogen partial pressure? For the same hydrogen network example in Figure 3.2, if H2/Oil ratio and H2 partial pressure of Hydrotreaters 3 and 4 are allowed to vary, the change of the hydrogen purity in the header can provide extra potential in hydrogen network management.

3.2 Sensitivity Analysis of Variable H2/Oil Ratio and H2 Partial Pressure on Hydroprocessor Operation

Since the benefits of allowing H2/Oil ratio and H2 partial pressure to vary is obvious, it is important to integrate the idea into the modelling of hydrogen networks. Therefore the first step is to investigate how small changes in H2/Oil ratio and H2 partial pressure affect other operating conditions in a hydrogen processor.

3.2.1 H2/Oil Ratio and H2 Partial Pressure vs Product Yield

Considering the operation of a hydroprocessor, the H2/Oil ratio and H2 partial pressure can be very important parameters. Previous researches (Han, 2001) investigated the variable H2/Oil ratio and H2 partial pressure’s effects on product yield.

The experiment result regarding product yield under different H2 partial pressure for a hydrocracker was proposed by (Han, 2001). The feedstock used in his experiment is vacuum gas oil (VGO) with boiling range 340–530℃. Sulphur content is 2.3wt% while nitrogen content is 0.08wt%. The experiment of the hydrocracker is performed under two different reaction partial pressure levels: 14MPa and 7MPa representing high pressure and intermediate pressure conditions respectively.

Table 3.1 Product yield under different H2 partial pressure

H2 partial pressure	112 (bar)	49 (bar)
Product yield	wt%	wt%
H_2S+NH_3	2.5	2.5
C1+C2	0.5	0.5
C3+C4	3.8	4.1
Naphtha	19.0	20.0
Jet fuel	34.8	34.0
Diesel	41.7	40.6

(Han, 2001)

Table 3.1 shows the experiment results of the comparison of product yield under different H2 partial pressure for a hydrocracker. As can be seen from the table the gas product is exactly the same under different pressure levels and while liquid product varies only slightly.

Another investigation regarding H2 partial pressure's effects in a hydrocracker was done by UOP Company (Han, 2001). The feed stock is chosen as two different pressure levels: 56bar and 91bar. The comparison includes not only the product yield under different pressure levels, but also the product yield at early and late stage of the operation under the same pressure level.

Table 3.2 Product yield under different reaction pressure

H2 partial pressure	91 (bar)	56 (bar)	91(bar)
Operating time (Month)	1	3	8
Product yield	wt%	wt%	wt%
C1-C4	1.2	1.4	1.5
C5-C6	1.1	1.0	1.0
C7-166℃	1.9	2.0	2.0
166-249℃	6.4	6.0	6.2
249-343℃	18.4	18.6	18.5
>343℃	69.2	69.1	69.2

(Han, 2001)

The results and data comparison shown in Table 3.2 show the product yield changes under different reaction pressure. Obviously the H2 partial pressure would vary under different reaction pressure, which is determined by reaction pressure and H2 purity (H2 partial pressure = Reaction pressure * H2 purity). The results show that the product yield is almost the same under high and low pressure. On the other hand, under the same pressure, the product yield after 8 months operating is still the same as that of the first month of operation.

The proposed simulations used different feed stock and operating conditions to test the relative product yield changes for a hydrocracker. All the results show that the product yield is not changed significantly under different pressure levels. Therefore, it is reasonable to assume that product yields of a hydroprocessor will not be affected by marginal changes of its H2 partial pressure.

3.2.2 H2/Oil Ratio and H2 Partial Pressure vs H2 Recycle/Purge

In order to verify the significance of variable H2/Oil ratio and H2 partial pressure, the effects on recycle and purge streams in a hydrogen consumer from varying H2/Oil ratio and H2 partial pressure also need to be investigated. Through monitoring flowrate and purity changes in these two streams, the relevant effects of changing reactor inlet conditions on reactor outlet can be monitored.

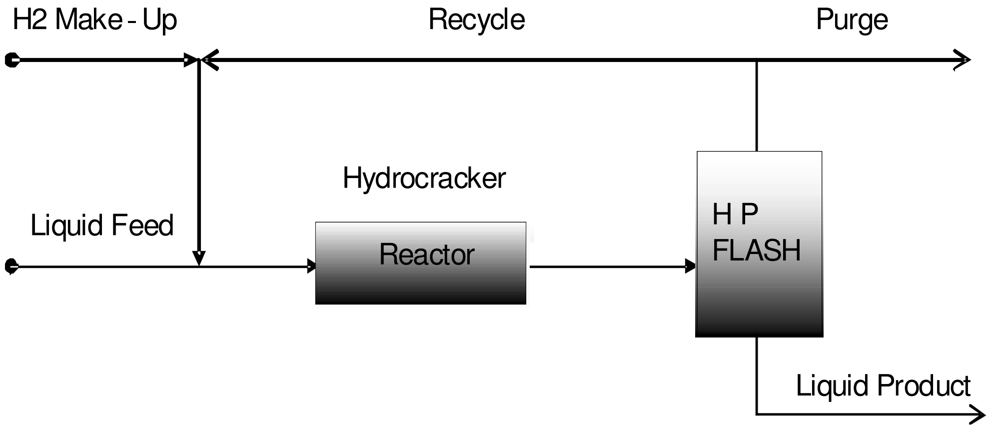

Figure 3.3 The hydrocracker model for verification

A simplified hydrogen consumer (hydrocracker) model (Alves, 1999) is set up with variable H2/Oil ratio and H2 partial pressure consideration by giving small changes to the hydrogen flowrate and purity at the inlet of the reactor model in the mathematical formulation.

On the basis of the hydrocracker model shown in Figure 3.3, a number of simulation scenarios have been run. Firstly, the values of H2 partial pressure is changed both upwards and downwards in a small range, whilst the H2/Oil ratio is maintained the same as the base case.

The simulation with variable H2 partial pressure and constant H2/Oil ratio is configured under the following conditions:

- Base case conditions: H2/Oil ratio (1544.3 Nm^3/m^3), H2 partial pressure (107.6 bar)
- Constant H2/Oil ratio: 1544.3341 Nm^3/m^3
- Varying H2 partial pressure range: 107.1 – 108.1 bar

The hydrocracker model is created In ***ASPEN PLUS*** as shown in Figure 3.4.

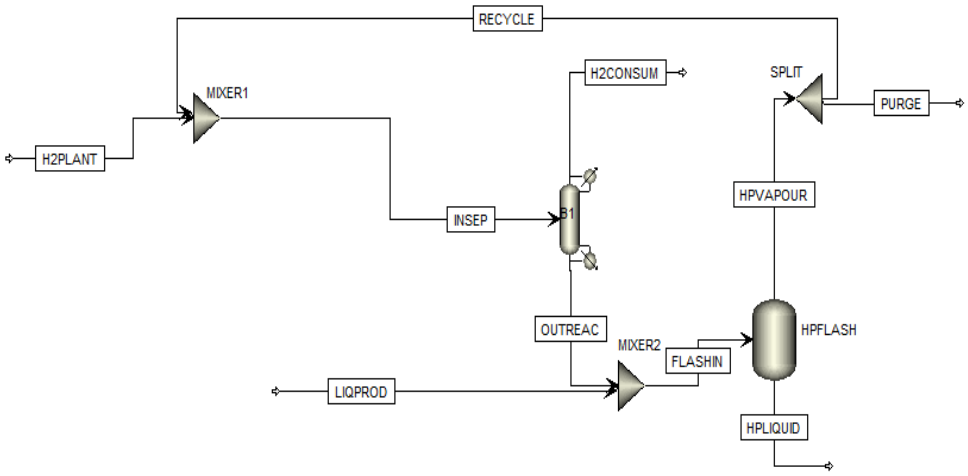

Figure 3.4 The hydrocracker model for verification in ASPEN PLUS

The way H2 purity is changed at the reactor inlet is to change the hydrogen purity in the make-up stream. According to the flowsheet shown in Figure 3.4, when the hydrogen purity in the make-up varies, the hydrogen purity at the reactor inlet will consequently change, leading to variations of the H2 partial pressure.

Table 3.3 Variable H2/Oil ratio and H2 partial pressure strategy simulation scenarios

H_2 PP (bar)	Er%	H_2/Oil Ratio (Nm^3/m^3)	Er%	Recycle/ Purge H_2 Purity (Vol%)	Er%	Recycle (Nm3/h)	Er%	Purge (Nm3/h)	Er%
107.0812	0.4969	1544.3341	0	81.4354	0.3977	127072	0	56.6780	1.2637
107.2951	0.2981	1544.3341	0	81.556	0.2502	127072	0	56.9740	0.7480
107.4555	0.1490	1544.3341	0	81.6756	0.1040	127072	0	57.2067	0.3426
107.6159	0	1544.3341	0	81.7606	0	127072	0	57.4034	0.0000
107.7763	0.1490	1544.3341	0	81.8499	0.1092	127072	0	57.5770	0.3025
107.9367	0.2981	1544.3341	0	81.9212	0.1964	127072	0	57.8077	0.7043
108.0971	0.4471	1544.3341	0	82.011	0.3063	127072	0	58.0376	1.1048

Table 3.3 shows the simulation results of 7 scenarios and each of them are operated at a different pressure level. The shaded row in Table 3.3 is shown in the middle of the table as the base case. The detailed data for H2/Oil ratio and H2 partial pressure at each scenario and the deviations

between them can be found from the table. The flowrate and purity deviations among these scenarios are also shown.

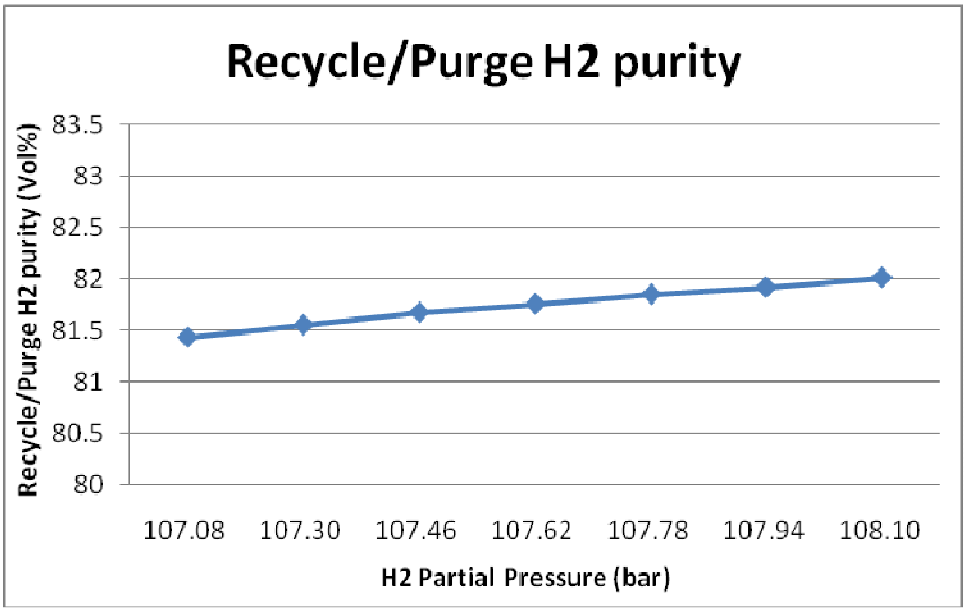

Figure 3.5 The recycle/purge purity vs H2 partial pressure

In order to analyze the changing trends of recycle and purge streams according to the changes of the H2 partial pressure, all the detailed data in Table 3.3 have been plotted into diagrams from Figure 3.5 to Figure 3.7.

Since the recycle and the purge streams both come from the high pressure flash vapour, they have the same hydrogen purity. Hence, the recycle/purge H2 purity is plotted against the varying H2 partial pressure in Figure 3.5. As can be seen from the figure, as the H2 partial pressure increases, the recycle/purge H2 purity increases slightly. The purity is raised from 81.4354 vol% at a H2 partial pressure 107.0812 bar (lowest point) to 82.011 vol% at a H2 partial pressure 108.0971 bar (highest point). With a 0.94% increase of H2 partial pressure in total, the recycle/purge purity has only increased by 0.71%.

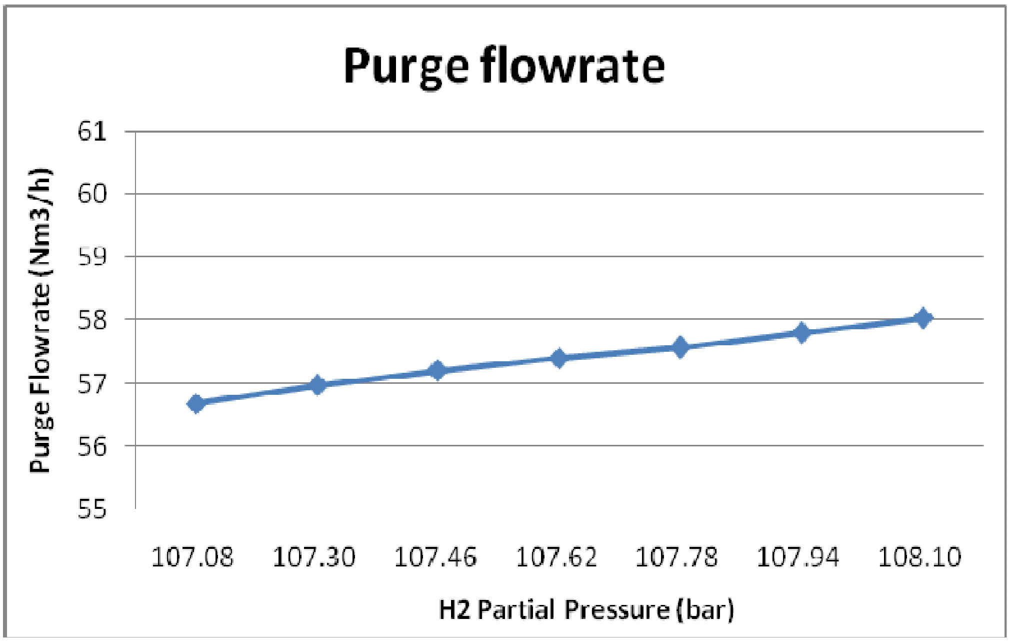

Figure 3.6 The purge flowrate vs H2 partial pressure

Figure 3.6 shows the relationship between the purge flowrate and the H2 partial pressure. As the figure shows, the purge flowrate is increased from 56.6780Nm^3 to 58.0376Nm^3 as a result of the increase of H2 partial pressure from 107.0812 bar to 108.0971 bar. The flowrate of the purge stream is slightly increased by about 1.4Nm^3 in total resulting from the 0.94% increase of H2 partial pressure.

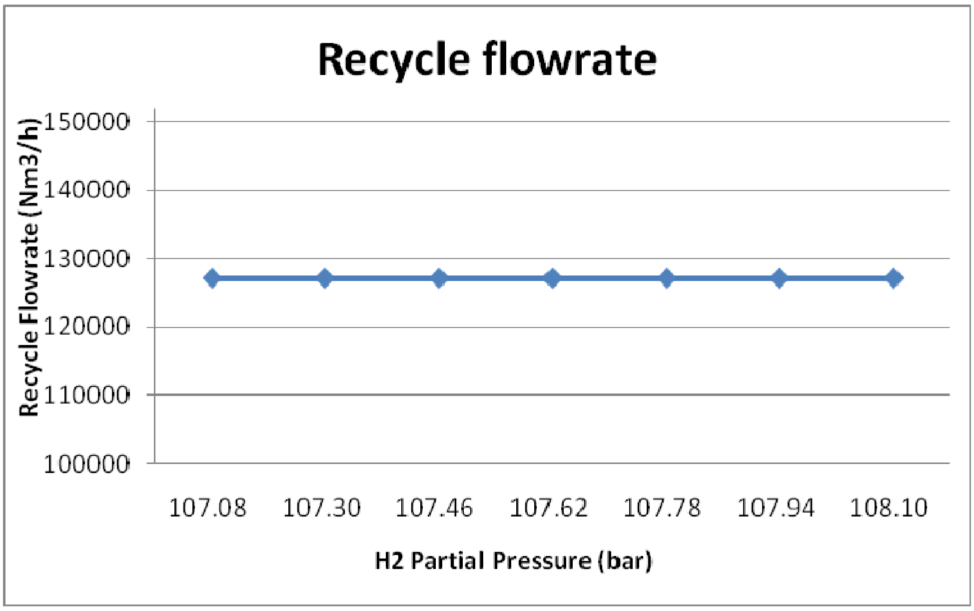

Figure 3.7 The recycle flowrate vs H2 partial pressure*

*All points show the same flowrate value. No error between each other.

On the other hand, as shown in Figure 3.7, the flowrate of the recycle stream shows no change during the change of the H2 partial pressure.

Another investigation is carried out with H2/Oil ratio and H2 partial pressure both varying. The simulation with both variable H2 partial pressure and H2/Oil ratio is configured under the following situations:

- Base case conditions: H2/Oil ratio (1544.3 Nm^3/m^3), H2 partial pressure (107.6 bar)
- Varying H2/Oil ratio range: 1536.66 – 1551.24 Nm^3/m^3
- Varying H2 partial pressure range: 107.1 – 108.1 bar

Table 3.4 Variable H2/Oil ratio and H2 partial pressure strategy verification simulation scenarios

H_2 PP (bar)	Er%	H_2/Oil Ratio (Nm^3/m^3)	Er%	Recycle/ Purge H_2 Purity (Vol%)	Er%	Recycle (Nm3/h)	Er%	Purge (Nm3/h)	Er%
107.08	0.50	1536.66	0.49	81.03	0.88	127072	0	56.29	1.92
107.24	0.35	1538.96	0.34	81.21	0.67	127072	0	56.62	1.35
107.40	0.20	1541.26	0.19	81.44	0.38	127072	0	56.95	0.78
107.62	0	1544.33	0	81.76	0.00	127072	0	57.40	0
107.78	0.15	1546.63	0.14	81.99	0.28	127072	0	57.74	0.59
107.94	0.29	1548.93	0.29	82.23	0.57	127072	0	58.08	1.19
108.10	0.45	1551.23	0.44	82.38	0.76	127072	0	58.43	1.80

The detailed data of the simulation results is shown in Table 3.4. Similarly, the numbers have been plotted into Figures 3.8 to 3.10 to show effects on the downstream flows from variable H2/Oil ratio and H2 partial pressure.

According to Figure 3.8, the recycle/purge H2 purity has increased only slightly during the increase of H2/Oil ratio and H2 partial pressure. The recycle/purge H2 purity rises from 80.9761 vol% at a H2 partial pressure 107.0812 bar and a H2/Oil ratio 1536.662 Nm^3/m^3 (lowest point) to 82.467 vol% at a H2 partial pressure 108.0971 bar and a H2/Oil ratio 1551.237 Nm^3/m^3 (highest point). The recycle/purge H2 purity has only increased by 1.5%.

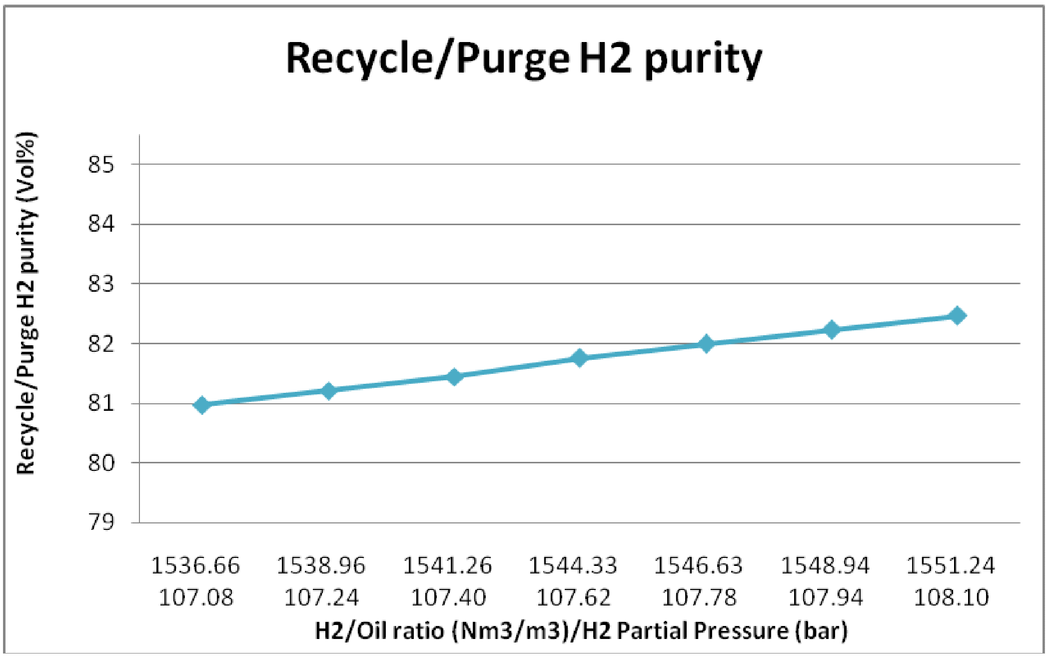

Figure 3.8 The recycle/purge purity vs H2/Oil ratio&H2 partial pressure

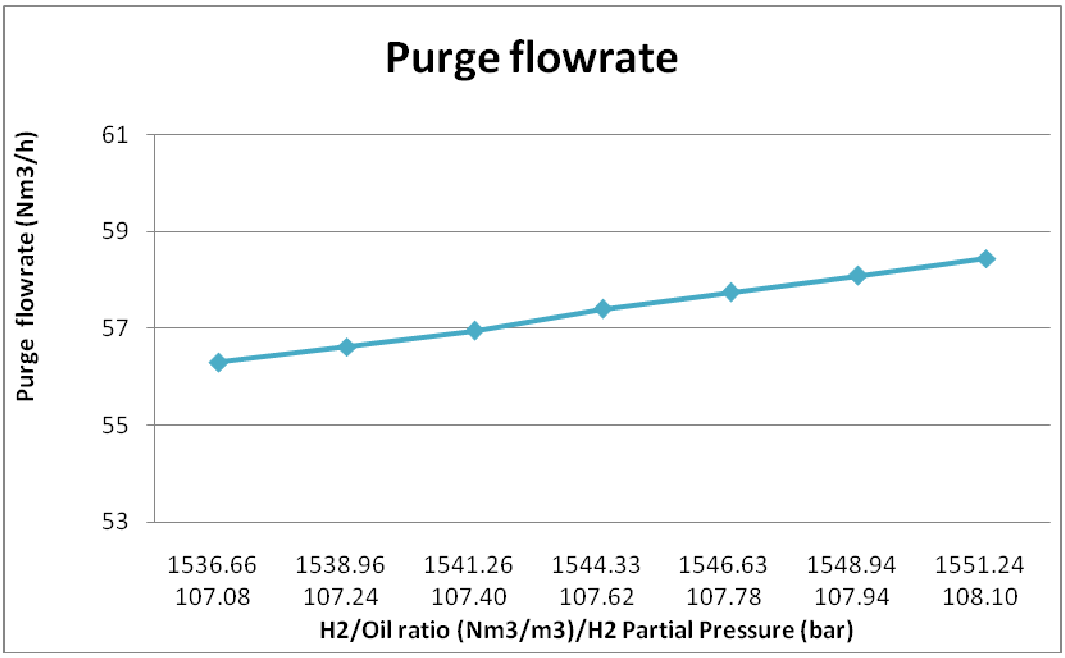

Figure 3.9 The purge flowrate vs H2/Oil ratio&H2 partial pressure

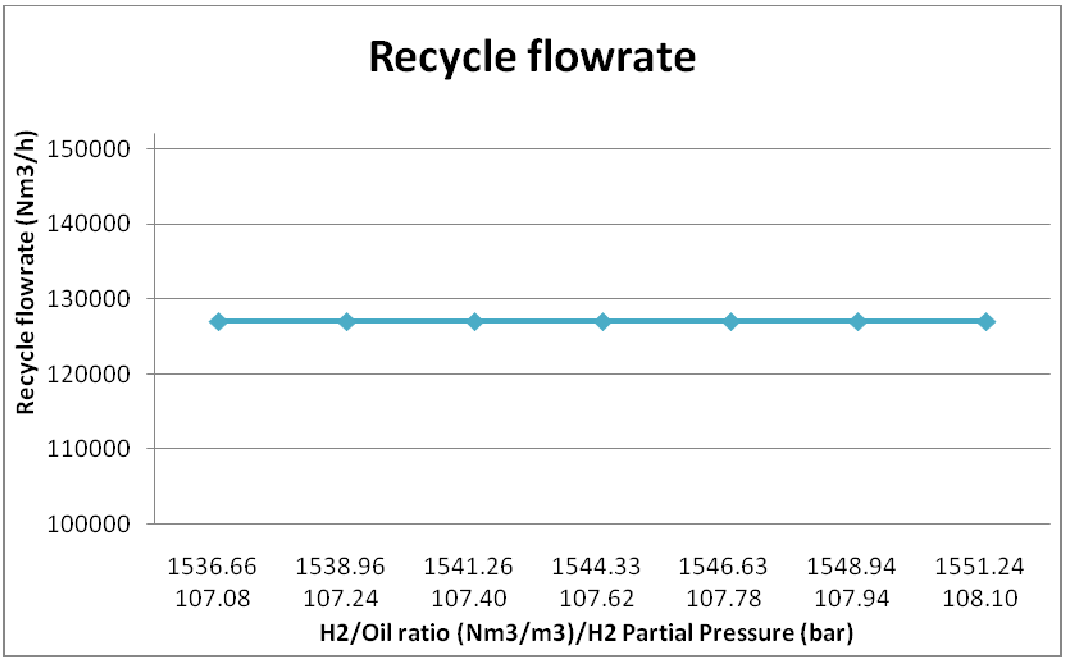

Figure 3.10 The recycle flowrate vs H2/Oil ratio&H2 partial pressure

Figure 3.9 shows how the purge flowrate varied according to the varied H2/Oil ratio and H2 partial pressure. During the increase of reactor inlet conditions, the purge stream flowrate has increased from 56.3 Nm^3/h to 58.4 Nm^3/h, indicating only 2Nm^3/h of purge flowrate increase.

As can be seen from Figure 3.10, although the H2/Oil ratio and H2 partial pressure have been increased by certain amount, the recycle flowrate can be maintained the same as the base case.

3.2.3 Conclusions from the Sensitivity Analysis

From the sensitivity analysis, it is clear that when H2 partial pressure changes marginally, the recycle flowrate can maintain constant. For the purge flowrate and purge/recycle purity, there are only slight changes.

To simplify the model building of hydroprocessors, it is reasonable to assume that marginal variation in H2 partial pressure does not affect the performance of a hydrogen consumer in terms of product yields and operating conditions such as recycle and purge flows/purity. It is important to point out that in practice, such an assumption has to be verified by relevant process engineers, and different criteria may be applied to individual process units.

3.3 Improved Hydrogen Network Formulation and Optimisation Methodology

The relaxation of reactor inlet conditions requires new mathematical formulation of hydrogen networks. Both automated hydrogen network design (Liu, 2002) and multi-component hydrogen network optimisation (Zhang et al., 2008) methods are set up with fixed H2/Oil ratio and H2 partial pressure by fixing H2 flowrate and purity at hydrogen sinks. In this work variable H2/Oil ratio and H2 partial pressure are applied into the new formulation to provide extra freedom for each hydrogen consumer in a hydrogen network.

3.3.1 Mass Balance of Hydrogen Producers

The mass balance of hydrogen producers represents the hydrogen transportation from hydrogen producers to hydrogen consumers, hydrogen headers, and purifiers:

$$FI_i = \sum_j FI_{i,j} + \sum_n FI_{i,n} + \sum_k FI_{i,k} \qquad \forall j \tag{3.1}$$

Where FI represents the total flowrate of hydrogen producers, the subscripts i, j, n and k represent hydrogen producers, consumers, headers and purifiers respectively. In reality, the throughput of a hydrogen producer is normally constrained due to practical limitations, and these limits can be formulated as:

$$FI_{i\min} \leq FI_i \leq FI_{i\max} \qquad \forall j \tag{3.2}$$

With Equation 3.2, each hydrogen producer can be set with a upper limits and lower limits, denoted by $FImax$ and $FImin$ for hydrogen producer i, respectively.

3.3.2 Mass Balance of H2 Headers

In a hydrogen network, hydrogen is produced in hydrogen producers then sent to hydrogen consumers directly or via headers. Hydrogen headers are common and widely used in modern refineries, especially for large scale complicated hydrogen networks. The mass balance of H2 headers is defined as follows:

$$\sum_j FNJ_{n,j} = \sum_i FIN_{i,n} + \sum_j FJN_{j,n} + \sum_j FJNL_{j,n} + \sum_j FKN_{k,n} \tag{3.3}$$

$$\begin{aligned} &\sum_j FNJ_{n,j} \cdot YN_n \\ &= \sum_i (FIN_{i,n} \cdot YI_i) + \sum_j (FJN_{j,n} \cdot YJ_j + FJNL_{j,n} \cdot YJL_j) + \sum_k (FKN_{k,n} \cdot YK_k) \end{aligned} \tag{3.4}$$

$FNJ_{n,j}$ is hydrogen flowrates from header n to consumers j, while $FIN_{i,n}$, $FJN_{j,n}$, $FJNL_{j,n}$ and $FKN_{k,n}$ represent hydrogen from producer i, consumers high pressure flash j, consumer low pressure purge j, and purifier k to header n. YN_n, YI_i, YJ_j, YJL_j and YK_k stand for relevant purities for headers, producers, consumer high pressure flash vapour stream, consumer low pressure flash vapour stream, and hydrogen purifiers. Equation 3.3 is for overall flow balance, while 3.4 is for component balance.

3.3.3 Consumer Reactor Inlets

The H2/Oil ratio and H2 partial pressure are directly determined by the hydrogen flowrate and purity, which are important in consumer modelling. The mass balance at reactor inlets can be expressed as:

$$\sum_j FC_j = \sum_i FIJ_{i,j} + \sum_{j1}(FJ_{j1,j} + FJL_{j1,j}) + \sum_k FKJ_{k,j} + \sum_n FNJ_{n,j} \quad (3.5)$$

$$\begin{aligned} &\sum_j FC_j \cdot YC_j \\ &= \sum_i (FIJ_{i,j} \cdot YI_i) + \sum_{j1}(FJ_{j1,j} \cdot YJ_{j1} + FJL_{j1,j} \cdot YJL_{j1}) + \sum_k (FKJ_{k,j} \cdot YK_k) \\ &+ \sum_n (FNJ_{n,j} \cdot YN_n) \end{aligned} \quad (3.6)$$

Where FC_j denotes the total reactor inlet flowrate of consumer j. Subscript $j1$ is introduced as an alias of j so that flow from $j1$ to j or j to $j1$ can cover recycle and hydrogen transportation between different consumers. $FIJ_{i,j}$, $FKJ_{k,j}$ and $FNJ_{n,j}$ represent flowrate from hydrogen producer i, purifier k and header *n* to consumer j. $FJ_{j1,j}$ and $FJL_{j1,j}$ are used to represent the flowrates of the vapour stream from high pressure flash and low pressure flash. When $j1$ equals to j, the flowrate is the internal recycle of the consumer *j*. When $j1$ is different from j, they are representing different consumers, so the flow between them would be the hydrogen transportation from a hydrogen consumer's high or low pressure flash to another consumer. YC_j stands for hydrogen purities at the reactor inlets of consumer j, while YI_i, YJ_{j1}, YJL_{j1}, YK_k, and YN_n stand for hydrogen purities of hydrogen producer i, vapour stream from high pressure flash of consumer j, vapour stream from low pressure flash of consumer j, purifier k and header n, respectively.

With Equations 3.3 and 3.4 the mass balance and hydrogen balance are calculated. However the reactor inlet modelling is still incomplete without limits on H2/Oil ratio and H2 partial pressure. In the existing hydrogen optimisation methodology (Zhang et al., 2008), the H2/Oil ratio and H2 partial pressure are set as constants through fixing mass flowrates and pure hydrogen flow at inlets of reactors. Considering variable H2/Oil ratio and H2 partial pressure at reactor inlets, the mass flowrates and pure hydrogen at reactor inlets should be given certain freedom to vary. As a result, an upper limit parameter and a lower limit parameter are introduced to enable the varying range for variable reactor inlet conditions. On the basis of Equations 3.4 and 3.5, the reactor inlet conditions relaxation Equation 3.6 and 3.7 are introduced:

$$FC_{j\min} \le FC_j \le FC_{j\max} \qquad \forall j \tag{3.7}$$

$$FC_{j\min} \cdot YC_{j\min} \le FC_j \cdot YC_j \le FC_{j\max} \cdot YC_{j\max} \qquad \forall j \tag{3.8}$$

Parameter FC_{jmax} and FC_{jmin} indicate the upper and lower flowrate limits at the reactor inlet of consumer *j*. YC_{jmax} and YC_{jmin} indicate the relevant hydrogen purity. With the introduced upper bounds and lower bounds, the total flowrate of reactor inlets (FC_j) and the pure hydrogen going into reactor inlets ($FC_j \cdot YC_j$) are allowed certain space to vary instead of fixing them at a constant level. In this way, H2/Oil ratio and H2 partial pressure constraints are relaxed.

Apart from reactor inlets, the make-up hydrogen stream in a hydrogen consumer may be under limits as well due to practical restrictions.

$$FC_j - FJ_{j,j} \le FMUMAX_j \tag{3.9}$$

$FJ_{j,j}$ denotes internal recycle flowrate of consumer j. As an upper limit parameter, $FMUMAX_j$ is set as the maximum value for hydrogen make-up stream flowrate.

3.3.4 Consumer Flash Calculation

The consumer flash calculation is simplified and expressed by hydrogen balance at the hydrogen consumer outlets.

For high pressure flash hydrogen balance:

$$FJ_j = \sum_{j1} FJ_{j,j1} + \sum_k FJK_{j,k} + \sum_n FJN_{j,n} + FJP_j \tag{3.10}$$

FJ_j represents the total flowrate of the vapour stream from high pressure flash of consumer j, while $FJ_{j,j1}$, $FJK_{j,k}$ and $FJN_{j,n}$ represents hydrogen transportation from this high pressure flash to other consumers or recycle, purifiers and headers. FJP_j represents high pressure purge gas sent to the site fuel.

For low pressure flash hydrogen balance:

$$FJL_j = \sum_{j1} FJL_{j,j1} + \sum_k FJLK_{j,k} + \sum_n FJLN_{j,n} + FJLP_j \tag{3.11}$$

FJL_j represents the total flowrate of the vapour stream from low pressure flash of consumer j, while $FJL_{j,j1}$, $FJLK_{j,k}$ and $FJLN_{j,n}$ represent hydrogen transportation from this low pressure flash to other consumers or recycle, purifiers and headers. $FJLP_j$ represents low pressure purge gas sent to the site fuel.

3.3.5 Mass Balance of Purifiers

In a hydrogen network, hydrogen purifiers are used for hydrogen recovery and re-use. Normally a hydrogen purifier intakes tail gas from hydrogen consumers and purifies it then sends it back to consumers. The mass balance of hydrogen purifiers in a hydrogen network can be expressed by hydrogen balance between inlets and outlets of purifiers.

$$\begin{aligned}&\left[\sum_j (FJK_{j,k} \cdot YJ_j + FJLK_{j,k} \cdot YJL_j) + \sum_i (FIK_{i,k} \cdot YI_i)\right] \cdot RECP_k \\ &= \left(\sum_j FKJ_{k,j} + \sum_n FKN_{k,n}\right) \cdot YK_k\end{aligned} \tag{3.12}$$

$FJK_{j,k}$, $FJLK_{j,k}$ and $FIK_{i,k}$ denote the hydrogen flowrate from high pressure flash of consumer j, low pressure flash of consumer j and producer i respectively, while YJ_j, YJL_j and YI_i denote their relevant purity. $FKJ_{k,j}$ and $FKN_{k,n}$ express the hydrogen flowrate from purifier k to consumer j or header n. Parameter $RECP_k$ is used as the rate of hydrogen recovery for purifier $_k$.

The throughput of a hydrogen purifier must have an upper limit in hydrogen network design.

$$\sum_j FKJ_{k,j} + \sum_n FKN_{k,n} \leq FKMAX_k \tag{3.13}$$

$FKJk,j$ stands for the flowrate from purifier k to consumer j and $FKN_{k,n}$

stands for the flowrate from purifier *k* to header *n*. The summation of these flowrates is the total flowrate at the outlet of purifier *k* and this value should always not be higher than the maximum limits of the purifier *k* set by parameter $FKMAX_k$.

3.3.6 Power Consumption of Compressors

In a hydrogen network, there are make-up compressors to increase pressure of hydrogen when it is needed.

For make-up compressors:

$$CMU_j = E_f \cdot PCMU_j \cdot (\sum_i FIJ_{i,j} + \sum_k FKJ_{k,j} + \sum_n FNJ_{n,j} + \sum_{j1} FJ_{j1,j} + \sum_{j1} FJL_{j1,j})$$
$$(j1 \neq j \text{ for } FJ)$$

(3.14)

CMUj represents total power consumption for make-up hydrogen compression of consumer *j*. Two parameters, *Ef* and *PCMUj*, are defined as the efficiency parameter and the power rate (unit compression power duty). When $j1 \neq j$, the flowrate between *j1* and *j* would be between different consumers, where a make-up hydrogen compressor may be needed.

For recycle compressors:

$$CRE_j = E_f \cdot PCRE_j \cdot FJ_{j,j} \qquad (3.15)$$

Similarly, *CREj* denotes total power consumption for the recycle compressor of consumer *j*. *Ef* and *PCREj* are for efficiency and power rate of the recycle compressor of consumer *j*. *FIj,j* is used to represent the flowrate from consumer *j* to itselt, which is actually the recycle flowrate for consumer *j*.

3.3.7 Summary of Binary H2 Network Modelling

With all the proposed equations, an overall binary hydrogen network model is completed. On the basis of the hydrogen network model, the design and optimisation strategy for binary hydrogen network can be developed. For an optimisation problem, a few definitions need to be made beforehand, including:

- Variables

The variables of binary hydrogen network optimisation problems mainly include the stream flowrates and purities around a hydrogen network, for example the flowrate and purity for hydrogen from producers to consumers or from headers or purifiers to consumers. It also includes the flowrates and purities of hydrogen between consumers. Also there are variables for power calculation of compressors.

- Parameters

Many parameters are involved in the formulation equations such as process pressures, hydrogen production unit prices, and upper bound and lower bound values for reactor inlet conditions and hydrogen production for producers, maximum limits for make-up hydrogen of each hydrogen consumer as well as the throughput of purifiers. In addition, for compressors the power rate and efficiency are also set in order to calculate the compression power cost.

- Constraints

The constraints for binary hydrogen network optimisation problems are mainly the mass balance around the network between hydrogen sources and sinks. As expressed with Equation 3.1 to Equation 3.15, the mass balances for hydrogen producers, consumers, headers and purifiers have been formulated. All these equations are to be used as the problem constraints during optimisation.

- Objective function

In this work the optimisation objective can be set as the minimum total operating cost. Therefore on the basis of Equations 3.1 - 3.15, the optimisation objective function can be expressed as:

$$OBJ = MIN(\sum_i FI_i \cdot Unit\,Price_{H2} + UtilityCost - FuelGasValue) \qquad (3.16)$$

As stated in Equation 3.16, the total operating cost includes hydrogen production cost, utility cost and fuel gas value. The production cost is calculated using unit price of hydrogen production times the total production flowrate. On the other hand, the fuel gas value calculation would be based on the heating values of the components contained in the fuel gas. By minimising the result of summation of hydrogen production and utility cost minus the fuel gas value, the total operating cost of a hydrogen network can be minimised.

As discussed before, the improvements of this formulation is mainly the inclusion of variable H2/Oil ratio and H2 partial pressure. In this way, the overall hydrogen network is more flexible than before, which may brings more and better design ideas or solutions in the optimisation.

3.4 Optimisation Methodology

For the optimisation methodology, it is important to point out the key conditions for the assumptions before getting into it.

3.4.1 Key Assumptions

There are two main assumptions in this binary hydrogen network optimisation methodology:

- Binary component based hydrogen network
- Marginal changes in H2/Oil ratio and H2 partial pressure not affecting hydrogen consumer operation

A binary hydrogen network means that, for each stream in the network, all the other component apart from hydrogen is lumped as one impurity component for example CH4. In this case, the mass balance around the network is actually the mass balance of hydrogen. The binary system is applied in order to simplify the optimisation calculation and ease the convergence. Without considering the mass balance of all components in a stream, the amount of computation effort can be dramatically reduced to improve the calculation efficiency.

The other assumption is allowing marginal changes in H2/Oil ratio and H2 partial pressure for a hydrogen consumer. The main reason of this assumption is to provide all reactor inlets in the network with extra degrees of freedom in hydrogen network design. As in both Liu (2002) and Zhang (et al., 2008)'s methods, the reactor inlet conditions are strictly fixed as constants, making it easier to justify hydrogen management decisions. They also reduce the system design flexibility, especially for large scale complicated hydrogen networks that under a number of practical constraints. For those specific hydrogen networks, the space for optimisation can be very limited, and if reactor inlets are still strictly fixed, the hydrogen network optimisation problem can be over-constrained leading to difficulties in solving problems or even no solutions for the problem. Due to these concerns, the variable H2/Oil ratio and H2 partial pressure strategy have been introduced. With Equations 3.7 and 3.8, the hydrogen flowrate and purity at the reactor inlet is allowed in a range to vary. The parameters for upper and lower limits will be carefully set to make sure the feasibility of the reactor and the balance of the hydrogen consumer model.

3.4.2 Optimisation Framework

Based on the proposed binary hydrogen network modelling, the optimisation framework for the binary hydrogen network optimisation is shown in Figure 3.11.

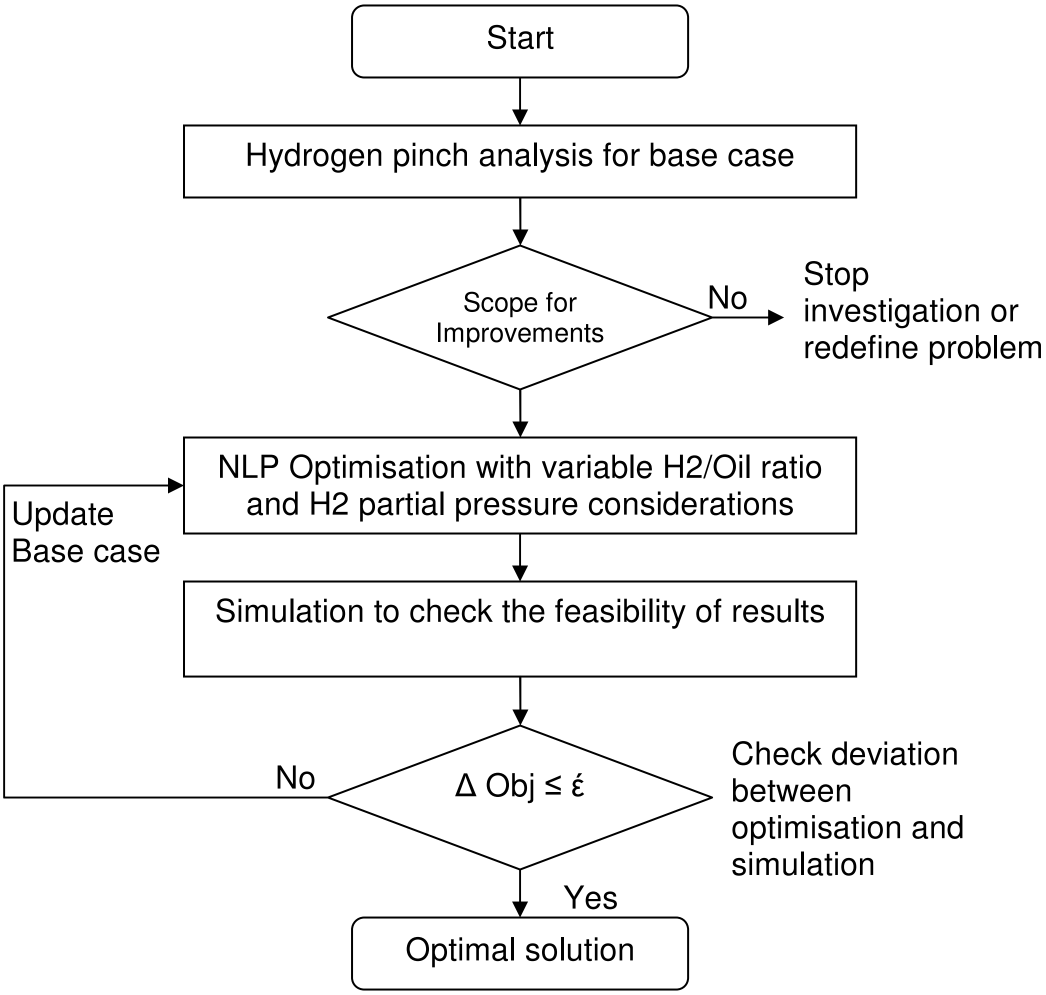

Figure 3.11 Binary hydrogen network optimisation framework

The optimisation methodology can be summarised into a few stages. At the beginning the hydrogen pinch method is used to get hydrogen composite curves and surplus curve to scope for potentials of the network. If there is no potentials found, investigation will be terminated or directed to problem redefinition. The binary hydrogen network optimisation is formulated as a non-linear problem. When an optimisation solution is obtained, it will then be simulated and compared with optimisation results to check deviations between them for feasibility. If the deviation criterion is not met, the base case will be updated with the results and perform the optimisation again from the beginning until the convergence criterion is finally satisfied.

The new mathematical formulation with considerations of variable H2/Oil ratio and H2 partial pressure can be applied with the following steps:

- Set up model for the H2 network

- Initially fix the configuration
- Optimise the system allowing H2/Oil ratio and H2 partial pressure to vary between limits
- In this case only increase in H2/Oil ratio and H2 partial pressure is allowed

In this way a hydrogen network can be incorporated with flexible reactor inlet conditions for each hydrogen consumer, which will open up the degrees of freedom for the network, and reach better optimisation solutions. The variable H2/Oil ratio and H2 partial pressure can be counter-intuitive especially for hydrogen networks under many practical constraints, which will be shown in the forthcoming case study.

3.5 Case study

The case study for the hydrogen network optimisation with variable H2/Oil ratio and H2 partial pressure considerations is taken from an industrial project. A refinery undertakes a retrofit design project that will increase its crude oil through put from 1.35MT/year to 1.8MT/year, which brings in new processes so that the overall hydrogen requirement for the refinery will be hugely increased. As a result, the hydrogen network management is then required to optimise the hydrogen utilization in order to save H2 utility or operating cost of hydrogen consumers or purifiers.

The hydrogen network to be optimised is located within the refinery with a number of hydrogen consumers and producers as well as relatively supporting processes such as purifiers. On the other hand, an ethylene plant also produces hydrogen as a by-product which is sent to the refinery as a hydrogen source. So this part of hydrogen will be considered in the hydrogen network optimisation as well.

3.5.1 Software Tool

GAMS (General Algebraic Modelling System) is used as the modelling and optimisation software in this work. Since the multi-component hydrogen network optimisation is designed to be a NLP problem so CONOPT is chosen as the solver in GAMS.

In this work the version of ***GAMS*** software being used is GAMS IDE 2.0.13.0. The detailed codes of this case study are attached in appendix.

3.5.2 Hydrogen Network Base Case with Pinch Analysis

The hydrogen network base case is set up according to the actual refinery configuration. There are 10 hydrogen consumers and 4 hydrogen producers involved in the hydrogen network base case. The flowsheet is shown in Figure 3.12.

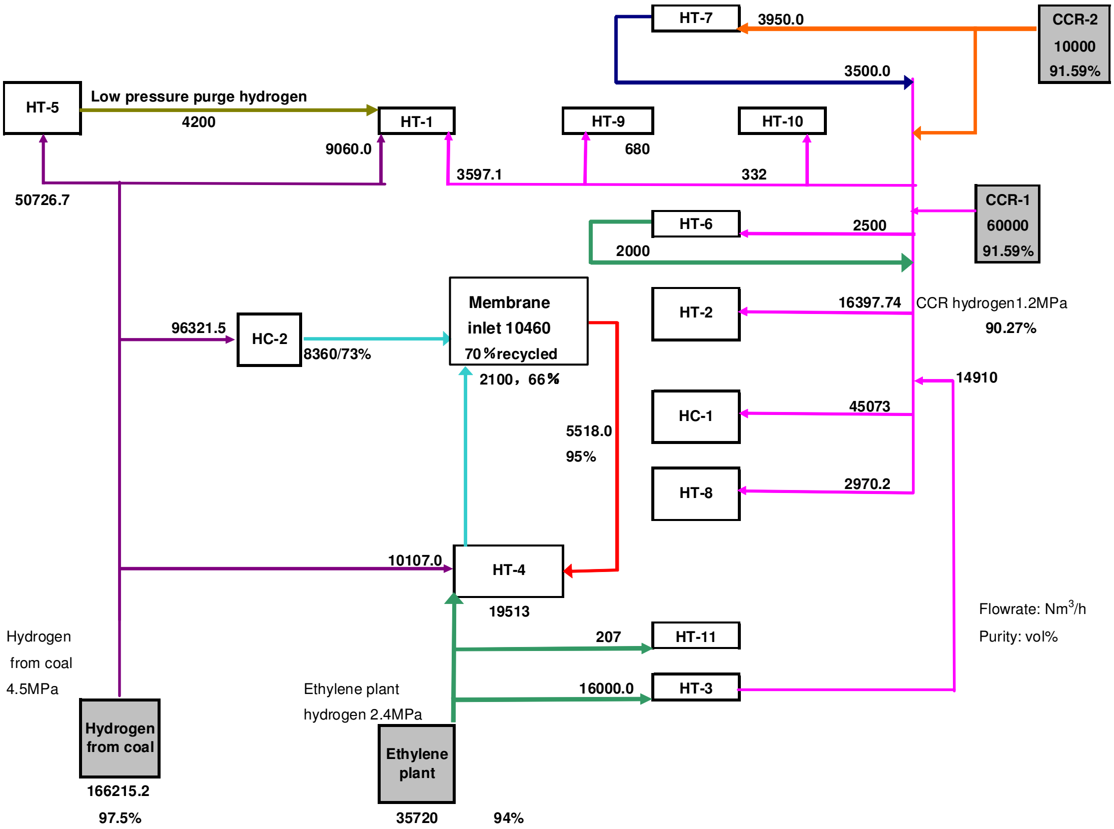

Figure 3.12 The hydrogen network base case*

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* Only make-up hydrogen distribution is shown in flowsheets in this chapter.

The hydrogen producers and hydrogen consumers involved in the base case can be summarised as:

- Hydrogen producers: catalytic reformer 1 (CCR-1), catalytic reformer 2 (CCR-2), ethylene plant, and hydrogen from coal gasification
- Hydrogen consumers: HT-1, HT-2, HT-3, HT-4, HT-5, HT-6, HT-7, HT-8, HT-9, HT-10, HT-11
- Hydrogen purifiers: Membrane

The entire hydrogen network contains of three hydrogen distribution headers under different pressure levels. CCR hydrogen is with 1.2MPa while the ethylene plant and the coal-based hydrogen plant are with relatively higher 2.4MPa and 4.5MPa respectively. From the flowrate point of view, the hydrogen from coal accounts for the biggest portion of hydrogen supply at 166215 Nm^3 per hour, which is more than the total of all other hydrogen sources including hydrogen from the ethylene plant, CCR-1 and CCR-2. Moreover, the purity of hydrogen generated from the coal-hydrogen plant is 97.5%, also higher than 94% of the ethylene plant and 91.59% of CCR-1 and CCR-2.

The utilisation strategy of hydrogen resources has been set under the following considerations:

- All reactor inlet conditions of hydroprocessing units should be no lower than values of the base case.
- 4.5MPa pressure hydrogen is mainly used for process with higher hydrogen partial pressure.
- 2.4MPa pressure hydrogen including membrane purified hydrogen and ethylene hydrogen supports HT-3, HT-4 and HT-11.
- 1.2MPa pressure hydrogen only consisting of two CCR units with purity 91.59% and total 70000Nm^3/h flowrate supplying hydrogen to HC-1, HT-1, HT-2, HT-7, HT-8, HT-9, HT-10.

Table 3.5 Reactor inlet conditions for the base case*

Process	Hydrogen purity v%	Hydrogen flowrate Nm^3/h	Pure hydrogen flowrate Nm^3/h
HC-1	84.22	165346	139254
HC-2	94.45	503921	475953
HT-1	87.02	123102	107123
HT-2	84.46	126554	107261
HT-3	92.00	16000	14720
HT-4	80.39	158572	127803
HT-5	93.91	409977	384998
HT-6	91.00	2484	2260
HT-7	91.00	3950	3600
HT-8	87.03	11732	10210

Table 3.5 shows all detailed data for reactor inlet conditions of all hydrogen consumers in the hydrogen network, including hydrotreaters and hydrocrackers. All the hydrogen purity and flowrate as well as net hydrogen flowrate are shown in the table. These values are listed not only for checking the reactor inlet conditions of the base case, but also for comparison with optimisation solutions.

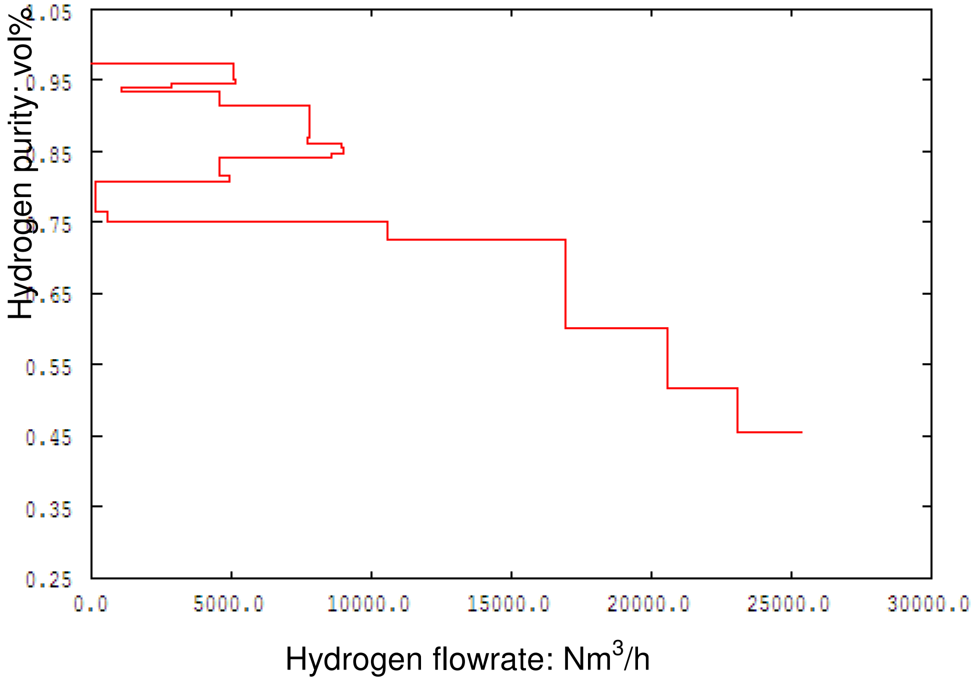

Figure 3.13 Hydrogen surplus curve for the base case

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* Hydrogen listed in tables for reactor inlets in this chapter includes both make-up and recycle hydrogen.

Figure 3.13 shows the hydrogen surplus curve for the current base case. As can be seen from the diagram, on the basis of the existing purification situation, the present hydrogen plant (mainly hydrogen from coal gasification) production is already close to the theoretical minimum of the hydrogen requirement target. The minimum hydrogen target can only be reached by modifications of pipeline distribution and compressors systems which are very costly and sometimes unrealistic. However this does not suggest that there is no saving potential from the hydrogen network. It is also observed that around 25247Nm^3/h hydrogen is not being utilised due to low purity and sent to site fuel system directly.

In the base case HT-3 is currently adopting a hydrogen once-through option in order to save compression work from its own recycle compressor. However, the once-through option of HT-3 reduces the purity of the ethylene hydrogen source from 94% to 93%. To make sure that the reactor inlet conditions of all hydrogen consumers are not deteriorated, more hydrogen production is then required from the coal gasification hydrogen plant leading to an increased hydrogen utility for the overall hydrogen network.

In optimisation there are also practical limitations of the hydrogen network design:

- No continuous high pressure purge is allowed for each hydrogen consumer
- All hydrogen consumers receive hydrogen from headers

These limitations indicate that if hydrogen purity of the header varies, every hydrogen consumer fed by the header will be affected simultaneously.

Looking at the purged low purity hydrogen below the pinch, it is straight forward to think about hydrogen purification and recovery to reduce the hydrogen requirement. However, considering the discussed practical constraints, if we purify and re-use hydrogen we will have to change the reactor inlet conditions unless it has the same purity currently as that of the headers. Therefore, the hydrogen network purification can be improved only if we allow H2/Oil ratio and H2 partial pressure at reactor inlets to vary.

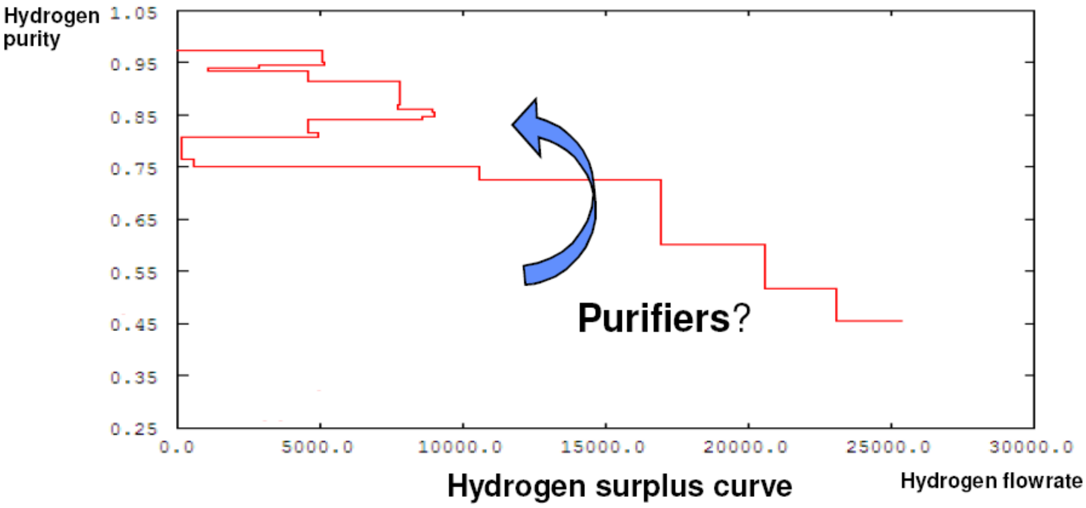

Figure 3.14 Idea of hydrogen purification below the pinch

To summarise the hydrogen pinch analysis, when operating optimisation or selecting optimisation solutions, we should be focusing on how to improve the HT-3 process design or enhance the hydrogen purification, and increase the rate of hydrogen recovery with variable H2/Oil ratio and H2 partial pressure to extract the potentials of the hydrogen network as much as possible.

3.5.3 H2 Network Operating Cost

For both new and revamping design, the total network operating cost is a very important economical factor to consider. In a revamping design, the operating cost saving can affect the pay back period significantly.

$$TotalOperatingCost = H2productionCost + UtilityCost - FuelGasValue \tag{3.17}$$

Normally, the operating cost for a hydrogen network would be the summation of all utility costs including hydrogen production cost, power, water and steam costs. Taking into account the fuel gas value, the total net operating cost for the hydrogen network is the total utility cost minus the fuel gas value. The value of fuel gas includes the heating values of hydrogen and the heating values of impurities. The pricing of hydrogen and impurities depends on their heating values. For example the heating value for hydrogen is 10.7kJ/Nm^3 and for impurities (all impurities lumped as methane) it is 35.8kJ/Nm^3. The unit price of methane is at £0.16/Nm^3, so that as fuel the hydrogen unit price can be calculated as 0.16*10.7/35.8=£0.052/Nm^3. Therefore, the calculation of value of fuel gas can be calculated as:

$$FuelGasValue = \\ F_{FuelGas} \cdot Y_{FuelGas} \cdot Unitprice_{H2} + F_{FuelGas} \cdot (1 - Y_{H2inFuel}) \cdot Unitprice_{\mathrm{Im}\,purity} \quad (3.18)$$

Where $F_{FuelGas}$ and $Y_{FuelGas}$ denote the flowrate and H2 purity of fuel gas, while $Unitprice_{H2}$ and $Unitprice_{\mathrm{Im}\,purity}$ denote the hydrogen unit price and impurity (methane) unit price respectively.

Table 3.6 shows the details of evaluation of hydrogen and impurities as well as the utility costs. By using the data listed in Table 3.6 and Equation 3.18 the economic value of total fuel gas of the hydrogen network can be obtained. Hence, the optimisation objective, minimise total operating cost of a hydrogen network, can be programmed for optimisation based on both hydrogen production cost and price of the fuel gas.

Table 3.6 costs of hydrogen production and utility (Meyers, 2003)

Items	Unit	Price
CCR hydrogen	£/ Nm^3	0.11183
Ethylene plant hydrogen	£/ton	0.11233
Hydrogen from coal gasification	£/Nm^3	0.11600
H2 in fuel gas	£/Nm^3	0.05
CH4 in fuel gas	£/Nm^3	0.16
Electricity	£/(kWh)	0.062
Recycle water	£/ton	0.027
Steam 3.5MPa	£/ton	16
Steam 1.0MPa	£/ton	13.8

3.5.4 Optimisation Solutions Analysis and Comparison

Optimisation solution 1: no new facilities

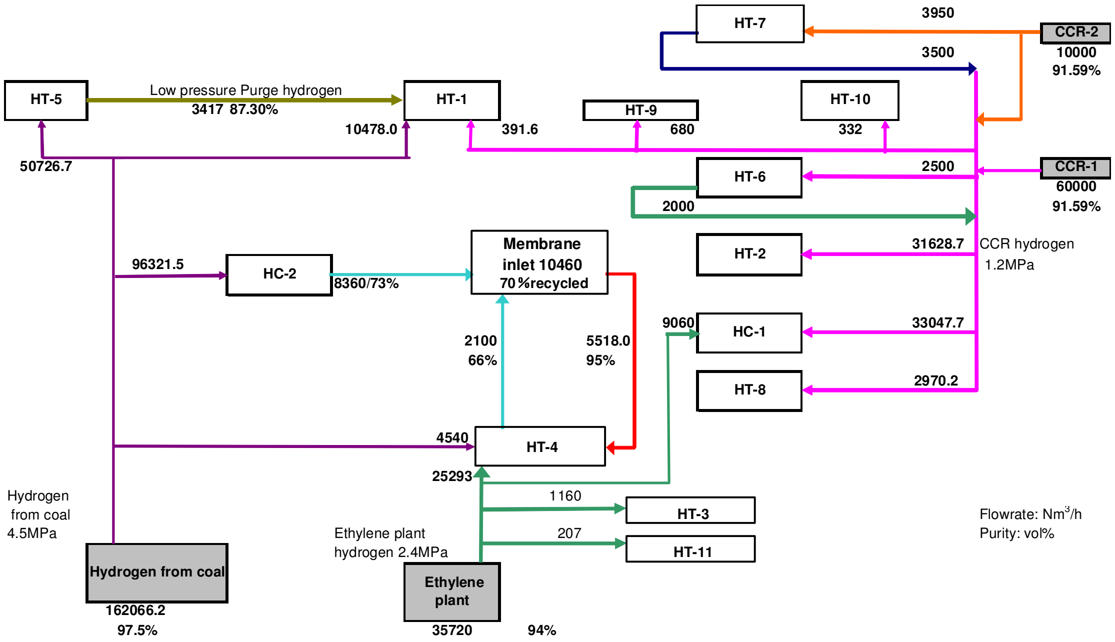

Figure 3.15 The optimised hydrogen network of solution 1

The first solution is mainly about the re-configuration of HT-3. As analyzed in the hydrogen pinch analysis, the once-through operation poses a question mark on the overall network economics. Therefore in this solution, the once-through option is compared with the option of complete recycle operation with no purged hydrogen to improve the hydrogen utilization efficiency.

The optimised modifications of the hydrogen network structure include:

- Some hydrogen is sent from the ethylene plant to HT-4 so as to reduce the hydrogen production of coal gasification hydrogen plant
- Some hydrogen from ethylene plant feeds HC-1 as well
- No hydrogen purged from HT-3 to header

Table 3.7 compares the reactor inlet conditions between the base case and the solution to ensure feasibility.

Table 3.7 Reactor inlet conditions comparison for Solution 1

Process	Hydrogen purity v%		Hydrogen flowrate Nm^3/h		Pure hydrogen flowrate Nm^3/h	
	Base case	Solution1	Base case	Solution1	Base case	Solution1
HC-1	84.22	84.22	165346	167462	139254	141036
HC-2	94.45	94.45	503921	503921	475953	475956
HT-1	87.02	87.02	123102	124638	107123	108460
HT-2	84.46	84.54	126554	126875	107261	107261
HT-3	92.00	92.10	16000	16000	14720	14736
HT-4	80.39	80.49	158572	158785	127803	127809
HT-5	93.91	93.91	409977	409977	384998	384998
HT-6	91.00	91.59	2484	2500	2260	2290
HT-7	91.00	91.59	3950	3950	3600	3618
HT-8	87.03	87.03	11732	11732	10210	10210

It is clear that all the hydrogen purities and flowrates in Solutions 1 are either higher than or equal to those in the base case. The results have confirmed that the hydrogen consumer reactor inlet conditions are either maintained or improved with a higher hydrogen purity or flowrate.

With the recycle hydrogen compressor for HT-3 in operation, the required power has increased by 357.6kWh. However, hydrogen from the coal gasification requirement and the total amount of purged hydrogen of the whole network were both reduced by 4,149Nm^3/h. Meanwhile, the total network operating cost was saved by 2.27 million pounds per year. However, this solution still has an amount of 21,202Nm^3 hydrogen being purged, which could be further recovered, therefore, it should be investigated further.

Optimisation solution 2: additional purification

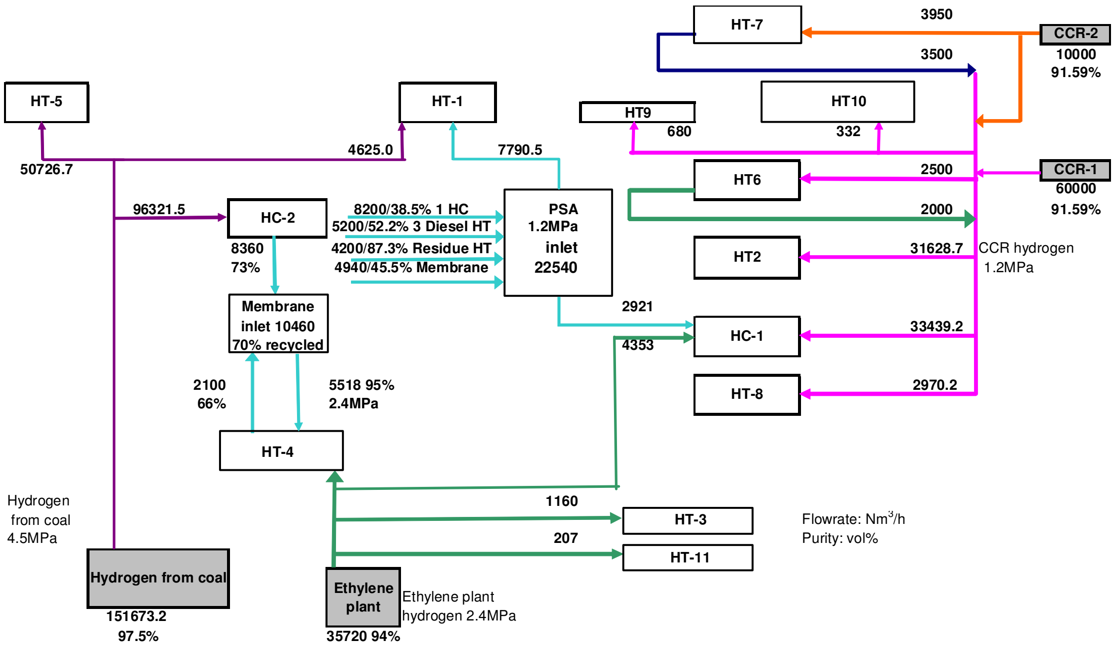

Figure 3.16 The optimised hydrogen network of solution 2

Considering enhancing the capability of hydrogen recovery, since the current membrane unit is already on full load, a new purifier needs to be installed. In this solution a PSA is planned, which will be working along with the existing membrane. With the capacity of 10000Nm^3/h, the PSA can be used to recover the purged gases from HC-1, HT-2 and the membrane. As a result, the hydrogen production of hydrogen from coal gasification is reduced by 14500Nm^3 compared with the base case.

The main features of this solution are:

- HT-3 is changed from hydrogen once-through process into complete H2 recycle process
- Purge gases from HT-5, HC-1, HT-2 and the membrane are sent to PSA for purification and recovery.
- PSA product to feed HC-1 and HT-1
- HC-1 supported by three hydrogen sources including the ethylene plant , PSA, and CCR.
- HT-1 fed by hydrogen from the coal gasification and PSA
- HT-4 now receives hydrogen from the ethylene plant only.

Table 3.8 Reactor inlet conditions comparison for Solution 2

Process	Hydrogen purity v%		Hydrogen flowrate Nm^3/h		Pure hydrogen flowrate Nm^3/h	
	Base case	Solution2	Base case	Solution2	Base case	Solution2
HC-1	84.22	84.22	165346	166065	139254	139860
HC-2	94.45	94.45	503921	503921	475953	475956
HT-1	87.02	87.26	123102	122767	107123	107124
HT-2	84.46	84.54	126554	126875	107261	107261
HT-3	92.00	92.10	16000	16000	14720	14736
HT-4	80.39	80.41	158572	158954	127803	127809
HT-5	93.91	93.91	409977	409977	384998	384998
HT-6	91.00	91.59	2484	2500	2260	2290
HT-7	91.00	91.59	3950	3950	3600	3618
HT-8	87.03	87.03	11732	11732	10210	10210

Again the hydrogen purities and flowrates for each hydrogen consumer are compared with the base case to show the how these conditions have been changed. The overall network purged hydrogen is reduced to about 11,069Nm^3/h, leading to considerably reduced network operating cost with a saving of 6.62 million pounds per year. The investment of the new installed PSA unit is estimated at 3.2 million pounds. Taking into account both PSA investment and reduced operating cost, the simple payback period is only 0.48 year.

Optimisation solution 3: simplified purification scheme

In order to simplify the hydrogen purification system as well as saving operating cost, this solution considers installing a large scale PSA unit and meanwhile shutting down the membrane unit. The new PSA is designed at a capacity of 16,000Nm^3/h which is much larger than that of Solution 2, so that the associated product volume and the capacity of tail gas compressor would increase. Compared with Solution 2, the modifications made in this solution are:

- Purge gases from HT-5, HC-1, HT-2, HC-2 and HT-4 are sent to the new large capacity PSA

- HT-4 supported by hydrogen from the ethylene plant and the coal gasification
- HC-1 fed by PSA and CCR

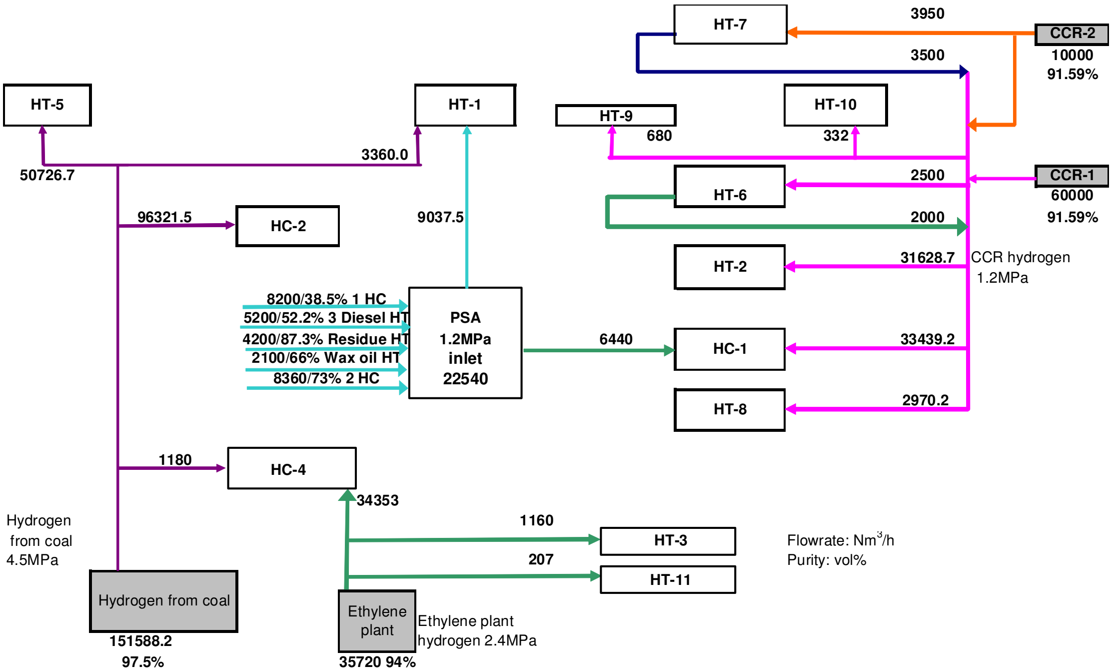

Figure 3.17 The optimised hydrogen network of solution 3

Figure 3.17 shows the flowsheet of Solution 3, while Table 3.9 lists all reactor inlet conditions of hydroprocesses. Similarly, all reactor inlet conditions are either maintained or improved. So far the results from the three different optimisation solutions have shown that saving H2 and improving certain reaction conditions may not be contradictory with each other.

Table 3.9 Reactor inlet conditions comparison for solution 3

Process	Hydrogen purity v%		Hydrogen flowrate Nm^3/h		Pure hydrogen flowrate Nm^3/h	
	Base case	Solution3	Base case	Solution3	Base case	Solution3
HC-1	84.22	84.28	165346	165233	139254	139254
HC-2	94.45	94.45	503921	503921	475953	475956
HT-1	87.02	87.27	123102	122749	107123	107125
HT-2	84.46	84.54	126554	126875	107261	107261
HT-3	92.00	92.10	16000	16000	14720	14736
HT-4	80.39	80.40	158572	158967	127803	127808
HT-5	93.91	93.91	409977	409977	384998	384998
HT-6	91.00	91.59	2484	2500	2260	2290
HT-7	91.00	91.59	3950	3950	3600	3618
HT-8	87.03	87.03	11732	11732	10210	10210

With simplified hydrogen purification scheme, the purged hydrogen of the whole hydrogen network has been reduced down to 10,986Nm^3/h and operating cost is also saved by 6.73 million pounds. The installation of the new large capacity PSA costs 4.6 million pounds and the simple payback period is calculated as 0.69 year. Again Solution 3 indicates great economic benefits. When comparing with Solution 2, this solution requires higher investment for the capital cost of the PSA in order to simplify the configuration and operation of the hydrogen network.

3.5.5 Solutions Comparison

From Table 3.10 it can be found that all three solutions reduce total hydrogen requirement as well as total operating cost for the overall hydrogen network comparing with the base case.

Table 3.10 Reactor inlet conditions comparison for solution 3

	Base case	Solution 1	Solution 2	Solution 3
H2 Consumption (Nm^3/h)	271,935	267,786	257,393	257,308
H2 Reduction (%)	_	1.5	5.3	5.4
H2 Cost Reduction (£million/y)	_	3.85	13.49	13.57
Compression Costs (£million/y)	27.01	26.76	27.46	27.39
Fuel Value (£million/y)	26.55	24.72	20.13	20.09
Total operating cost reduction (£million/y)	_	2.27	6.62	6.73

In the table, Solution 3 achieves the biggest hydrogen utility reduction and the biggest saving on the total operating cost for the hydrogen network. Solution 2 is actually close to Solution 3 with slightly smaller utility cost reduction. However, Solution 2 only requires 3.2 million pounds for the investment, while Solution 3 needs a much higher 4.6 million pounds investment. As for Solution 1, although there is no need for investment, the result still has a lot of purged hydrogen and limited reduced operating cost.

All in all, Solution 1 shows limited improvements, and Solution 3 has to pay higher investment and requires a longer pay back period with a more or less a similar result as Solution 2. By taking into account all of these considerations, Solution 2 has been considered as the best solutions for this hydrogen network optimisation case.

3.6 Summary

The most important advantage of the hydrogen network methodology proposed in this chapter is the introduction of variable H2/Oil ratio and H2 partial pressure strategy. Allowing variable H2/Oil ratio and H2 partial pressure is extremely important in the hydrogen network optimisation, especially dealing with over-constrained network optimisation problems. For those complicated hydrogen network with many practical constraints, varying H2/Oil ratio and H2 partial pressure rather than fixing them to obtain improvements can be counter-intuitive.

An industrial case study has been demonstrated. A number of productive thoughts derived from hydrogen network design and optimisation are as follows:

- In hydrogen network design, it is important to analyze how capacity, feed and process operation of the hydrogen plants or purifiers would affect the hydrogen production, purity and consumption as well as the process investment
- Proper applications of applying purged hydrogen recovery process can save hydrogen network operating cost effectively.
- As a graphical method, the hydrogen pinch analysis can be used for targeting bottlenecks and indicating the optimisation direction
- When applying hydrogen network optimisation, practical constraints must be considered to ensure the feasibility of the optimised design.

With this case study, the optimisation with variable H2/Oil ratio and H2 partial pressure is shown to be capable of dealing with large scale complicated refinery hydrogen networks. It provides extra flexibilities for network design. In addition, this strategy can be applied to both new network design and retrofit design.

Chapter 4 Detailed Modelling and Validation of H2 Consumers

4.1 Introduction

Chapter 3 illustrates the optimisation methodology for binary H2 networks, in which the hydrogen network modelling and optimisation is simplified with binary component configuration. However, considering only H_2 and CH_4 rather than full components analysis will definitely affect the accuracy of optimisation calculation especially for the mass balance calculation. The neglect of other impurities except CH_4 could lead to inaccuracy and even generate unrealistic solutions. Considering building a detailed hydrogen network model to overcome this drawback mentioned, all components in a stream should be considered. Furthermore, the binary optimisation methodology only focuses on mass balance between hydrogen sinks and sources in the network without considering the detailed internal balance of an individual hydrogen consumer. For more accurate hydrogen network optimisation, a detailed model for individual hydrogen consumers is necessary. In this chapter, a detailed modelling approach for hydrogen consumers with multi-component considerations is developed.

Hydrogen consumer models are important to the overall hydrogen network modelling, since the hydrogen balance would be dependent on the mass balance between hydrogen producers and hydrogen consumers. Hence, the performance of hydrogen consumers would affect a hydrogen network directly. A detailed hydrogen consumer model is essential to the quality of the hydrogen network simulation and optimisation. As stated in the previous chapters, significant progress in hydrogen-addition process modelling has been made. From a simplified hydrotreater model to a large scale hydrogen network model, great improvements have been achieved in this field. However, there are still a few drawbacks lying in existing models (Zhang et al., 2008), which affect the accuracy and practicality of modelling, which can be summarised as follows:

- Ignore of light hydrocarbon production in reaction stage
- Time consuming and slow convergence without integrated flash calculation when considering multi-component
- Fixed H2/Oil ratio and H2 partial pressure can be too restrictive leading to inferior solutions or even infeasibility

All of these drawbacks need to be improved with a new hydrogen consumer model. The consideration of detailed light hydrocarbon production in the reaction is integrated into the reactor model, while reactor inlet conditions are relaxed as well. Along with the improved reaction modelling, the integrated flash calculation strategy has also been incorporated in order to improve the convergence rate of the optimisation framework.

4.2 Improved Hydrogen Consumer Model

A simplified model of an individual hydrotreater was developed by Alves (1999) in order to define hydrogen sinks and sources. However the main purpose of this model is to figure out hydrogen surplus in the pinch analysis, thus the application of the model is very limited and not suitable for accurate simulation. Therefore, in order to improve the accuracy of H2 network modelling and optimisation, a more detailed hydrogen consumer model needs to be developed. Figure 4.1 shows the structure of the developed detailed hydrogen consumer model with integrated flash calculation, which incorporates detailed vapour-liquid equilibrium calculation for the flash separation.

The make-up hydrogen, produced from a hydrogen plant or other hydrogen producers like catalytic reformers, is sent to the inlet of a hydrogen consumer, where it is mixed with recycle hydrogen and liquid feedstock. The mixture is then processed through the reactor, and during the reaction a certain amount of hydrogen is consumed and a number of light hydrocarbons are generated, which is considered in the improved hydrogen consumer model.

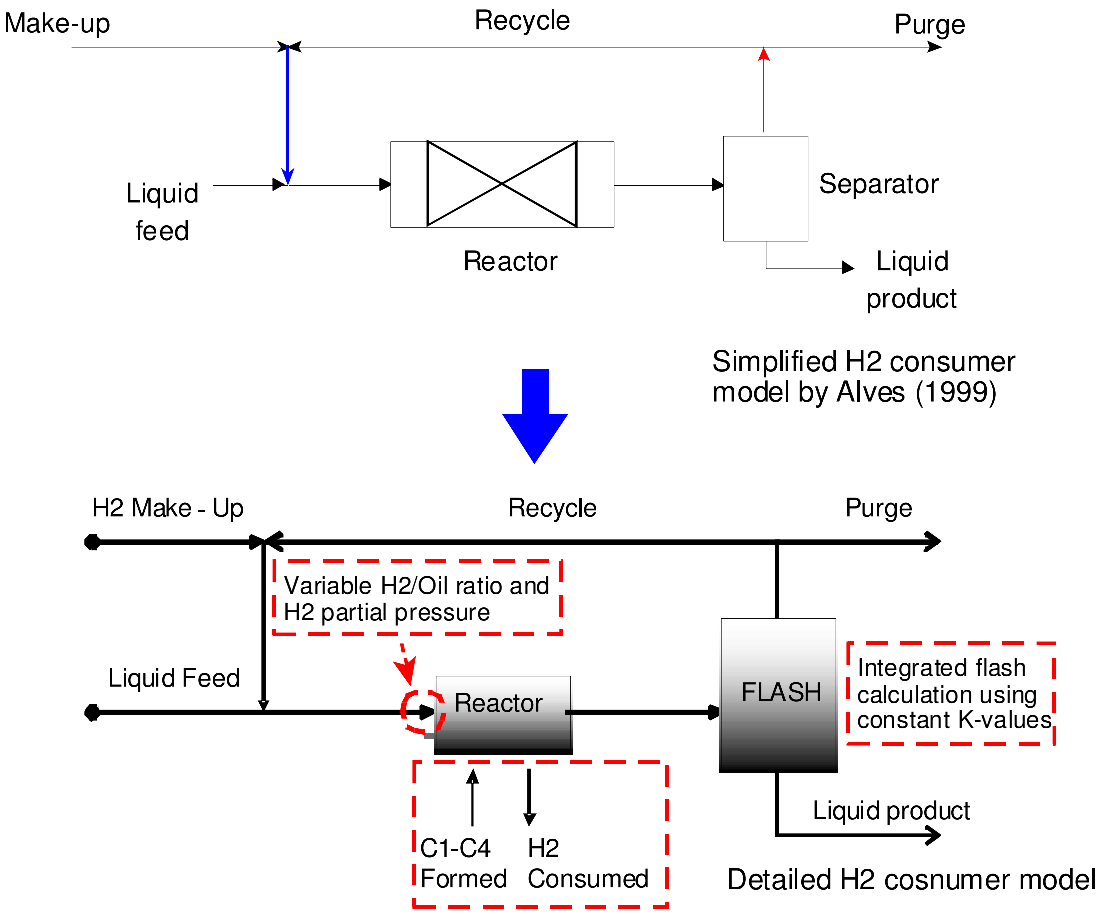

Figure 4.1 The improved hydrogen consumer model

The reactor is modelled by taking into account detailed light hydrocarbon production under appropriate H2/Oil ratio as well as H2 partial pressure, which are very important to the performance of the reactor. In the reactor model certain amount of hydrogen is consumed depending on the quality of the feedstock and operating conditions. In addition, there is also a production of light hydrocarbon such as CH_4, C_2H_6, C_3H_8, and C_4H_{10}. The reactor outlet stream needs to be further separated before it can be sent for other applications or ready for sale.

As Figure 4.1 explains, the simplified H2 consumer model (Alves, 1999) has been featured with new developments and improved into a detailed H2 consumer model. With considerations of variable reactor inlet conditions, light hydrocarbons production during reaction and detailed flash calculation, the newly developed multi-component hydrogen consumer model is able to be used for hydroprocessing unit modelling and simulation or integrated into a hydrogen network for optimisation.

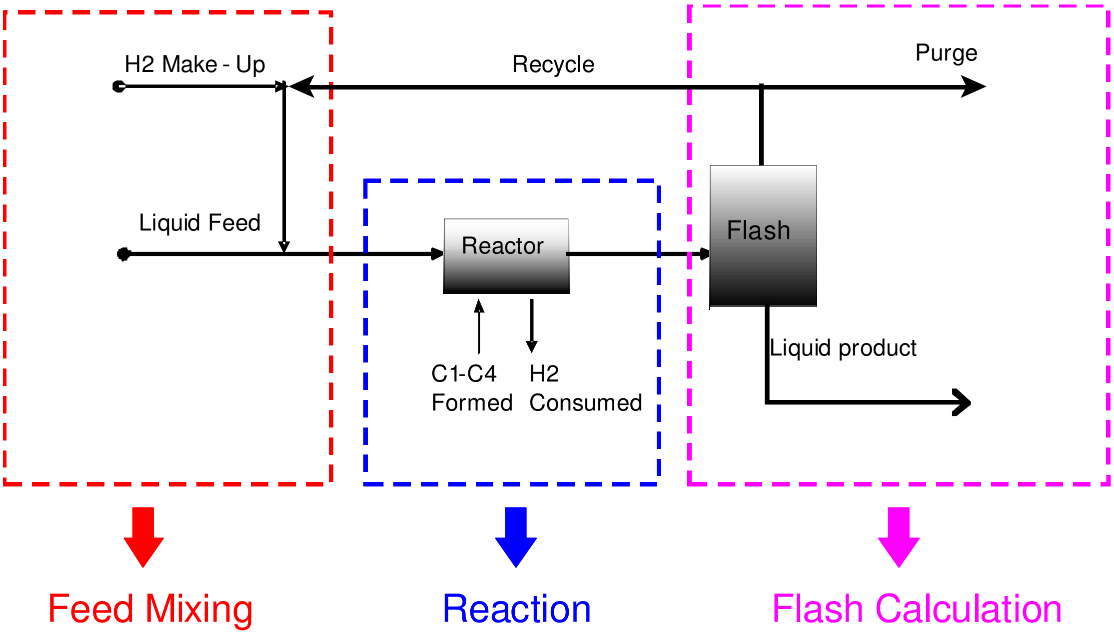

Figure 4.2 Model construction of a H2 consuemr

The structure of the improved hydrogen consumer model can be found in Figure 4.2 which can be divided into three different sections for detailed modelling:

- Feed mixing
- Reaction (hydrotreating or hydrocracking)
- Flash separation

Each section is modelled under multi-component considerations. The formulation is mainly based on mass balance. Practical constants have been included. The detailed formulation equations are shown in following sections.

4.2.1 Feed Mixing

The feed mixing model is used to calculate the mass balance at the inlet of a hydrotreater. Basically there are three streams involved, including:

- Make-up hydrogen
- Liquid feedstock
- Recycle hydrogen

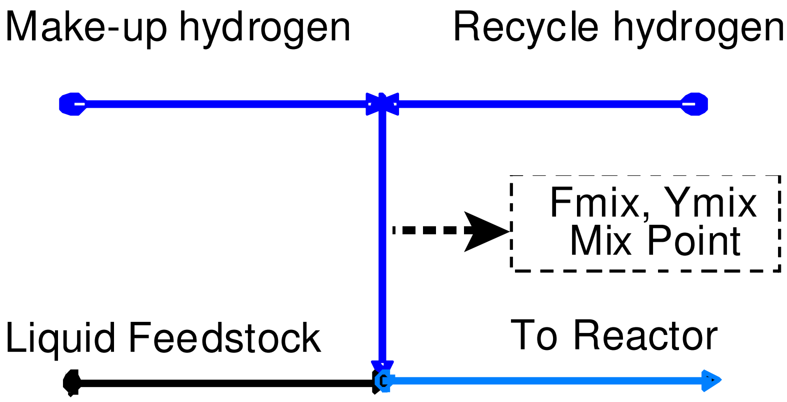

Figure 4.3 Sink mass balances

The balance among these streams can be demonstrated in Figure 4.3. The mathematical formulation can be expressed as follows:

$$F_{mix,j} = F_{mu,j} + F_{re,j} \qquad \forall j \qquad (4.1)$$

$$F_{mix,j} \cdot Y_{mix,i,j} = F_{mu,j} \cdot Y_{mu,i,j} + F_{re,j} \cdot Y_{re,i,j} \qquad \forall i \qquad \forall j \qquad (4.2)$$

$$F_{ri,j} = F_{mu,j} + F_{re,j} + F_{feed,j} \qquad \forall j \qquad (4.3)$$

$$F_{ri,j} \cdot Y_{ri,i,j} = F_{mu,j} \cdot Y_{mu,i,j} + F_{re,j} \cdot Y_{re,i,j} + F_{feed,j} \cdot Y_{feed,i,j} \qquad \forall i \qquad \forall j \quad (4.4)$$

Where $F_{feed,j}$, $F_{mu,j}$, $F_{re,j}$ and $F_{mix,j}$ represent the flowrates of liquid feedstock, make-up stream, recycle stream and the mix stream (mixture of make-up and recycle streams) of consumer j respectively, while $Y_{feed,i,j}$, $Y_{mu,i,j}$, $Y_{re,i,j}$ and $Y_{mix,i,j}$ stand for the purity of component i in feedstock, make-up stream, recycle stream and mix stream of consumer j. Subscripts i is used to indicate each component such as H2 or impurities in a stream. The subscripts j indicates different hydrogen consumers. In this way hydrogen and all impurity components are considered to accomplish the multi-component hydrogen consumer modelling for each H2 consumer in a H2 network. With Equations 4.1 to 4.4, the mass balance including hydrogen balance and impurity balance for the three streams around the hydrogen consumer inlet are maintained.

As Figure 4.3 shows, the mixing point is defined as the mixture of make-up hydrogen and recycled hydrogen at the inlet of the reactor. The mixing point represents the amount of hydrogen and its purity going into the reactor along with the liquid feed. When considering a H2 network, a hydrogen consumer can also receive hydrogen from other hydrogen consumer's purge gas, which may be rich in hydrogen. Details of hydrogen network modelling can be found in Chapter 5.

4.2.2 Hydroprocessing Reaction

The reactor model is essential to the overall hydrotreater model. The liquid feedstock is mixed with hydrogen and then sent through the hydroprocessing reactor. The hydrogen-consuming reaction removes sulphur, nitrogen and metals content and meanwhile saturates olefins and some aromatics.

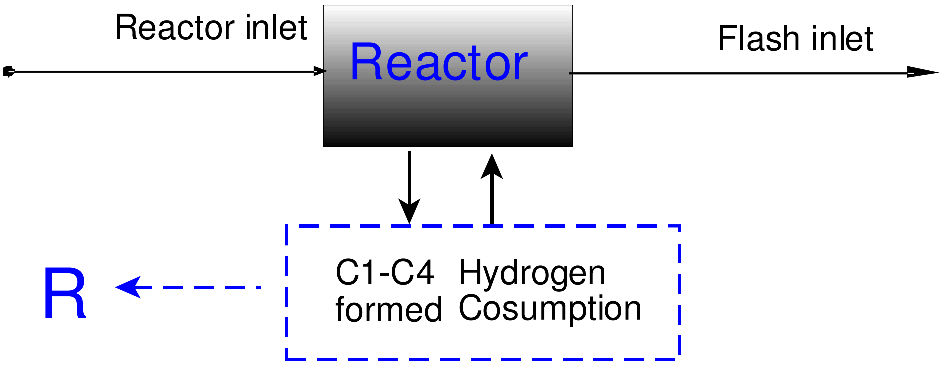

Figure 4.4 Reactor model

One of the key improvements within this new model is the inclusion of light hydrocarbon production, which is defined as R. For a specific case R is involved in the calculation as a constant matrix depending on different hydroprocessing units in the network. R can be used to express hydrogen consumption and light hydrocarbon production simultaneously. The light hydrocarbon production in the hydrotreating reaction is typically 1wt% to 4wt%. The importance of taking into account the light hydrocarbon production can be:

- Formed light hydrocarbons affect vapour-liquid equilibrium in flash separation, leading to composition changes in recycle and purge streams
- Ignoring such aspects will affect downstream flash separation leading to inaccuracy of the overall H2 consumer modelling

To overcome these drawbacks, the mass balance equations for modelling of hydroprocessing reaction have taken into account light hydrocarbons production as follows.

$$F_{fi,j} \cdot Y_{fi,i,j} = F_{ri,j} \cdot Y_{ri,i,j} - R_{i,j} \qquad \forall i \qquad \forall j \tag{4.5}$$

$$F_{fi,j} = F_{ri,j} - \sum_i R_{i,j} \qquad \forall j \tag{4.6}$$

The inclusion of light hydrocarbons production during the reaction stage is essential to the accurate modelling of a hydrogen consumer reactor. Equations 4.6 and 4.7 show how the light hydrocarbon production is considered in the improved formulation. $F_{fi,j}$, $Y_{fi,i,,j}$, $F_{ri,j}$, $Y_{ri,i,j}$ stand for flowrate and composition for component *i* of the flash inlet stream and reactor inlet stream of hydrogen consumer *j*. Parameter R is defined as the amount of reacted content including consumed H2 and formed light hydrocarbons. Normally in a hydrotreating or a hydrocracking the formed light hydrocarbons includes CH4, C2H6, C3H8 and C4H10. Other components setting into the vapour stream are small, which is neglected. Parameter $R_{i,j}$ can be used to describe the reacted amount in consumer *j*. In Equation 4.7 hydrogen consumption (R_{H2}) should be a positive value, while formed light hydrocarbons (R_{C1}, R_{C2}, R_{C3} and R_{C4}) should be negative values in equations above.

$$F_{fi,j} \cdot Y_{fi,i,j}{}^{L} \le F_{fi,j} \cdot Y_{fi,i,j} \le F_{fi,j} \cdot Y_{fi,i,j}{}^{U} \qquad i = H2 \tag{4.7}$$

$$Y_{fi,i,j}{}^{L} \le Y_{fi,i,j} \le Y_{fi,i,j}{}^{U} \qquad i = H2 \qquad (4.8)$$

For a hydrogen consumer reactor, practical constraints for reactor inlet conditions need to be considered. Rather than maintaining reactor inlet conditions, by unfixing the H2/Oil ratio and H2 partial pressure at reactor inlets (Zhang et al., 2008), they can be relaxed and also constrained in an acceptable range in order to expand optimisation searching space and help convergence. H2/Oil can be controlled by setting upper and lower bound parameters for the amount of pure hydrogen going into reactor, whilst the H2 partial pressure can be controlled by setting upper bound and lower bound parameters for the hydrogen purity at the reactor inlet. With Equations 4.8 and 4.9, the variable H2/Oil ratio and H2 partial pressure strategy is implemented into the hydrogen consumer model.

4.2.3 Flash Separation

The reactor outlet needs to be separated into liquid and vapour. The liquid phase will be further processed or blended into products before selling, whilst the vapour will be either recycled for reuse or purged to a site fuel system.

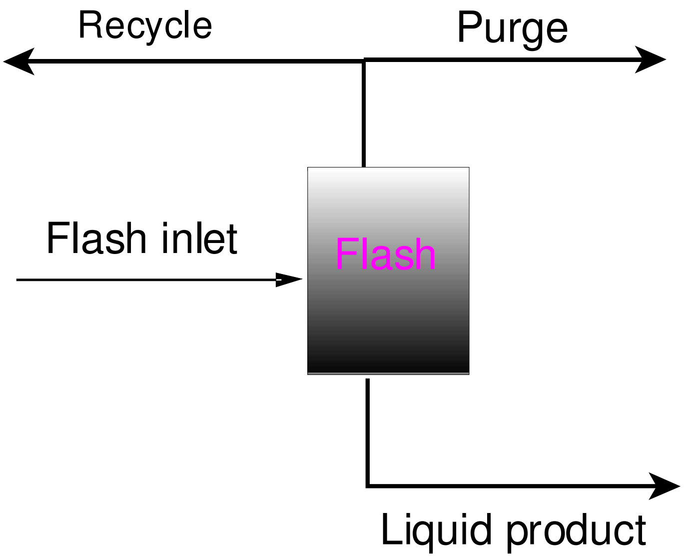

Figure 4.5 Flash separation model

In the newly developed flash model as shown in Figure 4.5, the flash inlet stream is sent from the reactor outlet and is separated into vapour and liquid. To reflect the flash separation, a general method for flash calculation is to make use of vapour-liquid equilibrium constants, commonly known as the K-values, to describe the situation of flash separation. Basically the separation can be expressed in terms of K-values in a general equation:

$$Y_{vap,i,j} = Y_{liq,i,j} \cdot K_{i,j} \qquad \forall i \qquad \forall j \tag{4.9}$$

Where $Y_{vap,i,j}$ and $Y_{liq,i,j}$ stand for the composition of component i in vapour or liquid from the flash unit of consumer j. The vapour-liquid equilibrium constant, $K_{i,j}$, is used to represent the K-value for component i used for flash calculation in consumer j. Combining the flash separation equation with other mass balance equations, the whole hydrogen consumer flash model can be expressed as:

$$F_{fi,j} = F_{re,j} + F_{liq,j} + F_{pu,j} \qquad \forall j \tag{4.10}$$

$$F_{fi,j} \cdot Y_{fi,i,j} = F_{re,j} \cdot Y_{re,i,j} + F_{liq,j} \cdot Y_{liq,i,j} + F_{pu,j} \cdot Y_{pu,i,j} \qquad \forall i \qquad \forall j \tag{4.11}$$

$$F_{fi,j} = F_{vap,j} + F_{liq,j} \qquad \forall j \tag{4.12}$$

$$F_{vap,j} = F_{re,j} + F_{pu,j} \qquad \forall j \tag{4.13}$$

$$Y_{vap,i,j} = Y_{re,i,j} \qquad \forall i \qquad \forall j \tag{4.14}$$

$$\sum_i Y_{vap,i,j} = 1 \qquad \forall j \tag{4.15}$$

$$\sum_i Y_{liq,i,j} = 1 \qquad \forall j \tag{4.16}$$

$$F_{re,j} = F_{H2C,j,j} \qquad \forall j \tag{4.17}$$

$F_{fi,j}$, $F_{re,j}$, $F_{pu,j}$, $F_{vap,j}$ and $F_{liq,j}$ denote the flowrate of flash inlet stream, recycle, purge, flash outlet vapour and flash outlet liquid of consumer j, while $Y_{fi,i,j}$, $Y_{re,i,j}$, $Y_{pu,i,j,}$, $Y_{vap,i,j}$ and $Y_{liq,i,jj}$ represent the relative composition of component i in each stream mentioned above. Equations 4.11 to 4.13 express the mass balance for the flash separation. The recycle hydrogen has the same purity as the flash vapour as shown in Equation 4.14. To make sure the feasibility of the flash calculation, the summation of compositions for all components in vapour or liquid stream is forced to be equal to 1 to maintain the components balance. Variable $F_{H2C,j,j}$ is defined as the hydrogen flowrate from hydrogen consumer j to j which is actually the internal recycle hydrogen of consumer j. For modelling of a hydrogen network, the hydrogen transportation between hydrogen consumers will be shown in terms of this variable with different subscripts.

As for the previous optimisation method (Zhang et al., 2008), the K-values need to be calculated at every iteration for an accurate separation result. It brought excessive amount of calculation into the optimisation steps and considerably time-consuming. Meanwhile, convergence problems could occur during the large number of iterations, which is another drawback.

To overcome the drawbacks, the constant K-values strategy is introduced. By using constant K-values for all iterations rather than calculating it every time, it not only speeds up the optimisation procedure but also prevents it from major convergence issues. The constant K-values strategy will be discussed in more details with a complete verification procedure followed in the next section.

Another issue with the flash modelling is the selection of the property package. For a hydrocarbon-rich process there are mainly three popular property packages to choose from:

- Peng-Robinson
- Soave-Redlich-Kwong (SRK)
- Grayson Streed

Grayson Streed is featured with special treatment on hydrogen content. Therefore it is widely acknowledged as the most suitable property package for simulating a stream with heavy hydrocarbons and high hydrogen content, such as hydrotreating or hydrocracking process.

4.2.4 Detailed H2 Consumer Modelling Summary

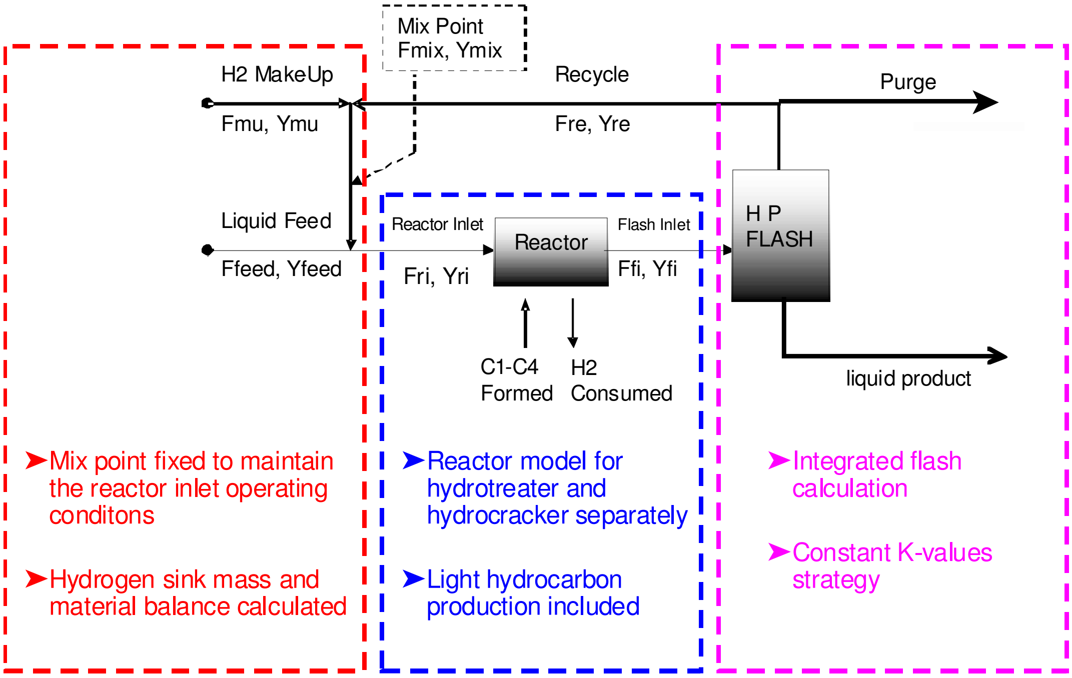

Figure 4.6 The improved hydrocracker model

As shown in Figure 4.6, the detailed hydrogen consumer model is completed by connecting up the three main sections: feed mixing, reaction and flash separation, which have been discussed in details with all relevant formulation equations. As one of the major improvements, the reaction modelling takes into account the light hydrocarbon production. In addition, the flash separation is incorporated with constant K-values for flash calculation. The details of integrated flash calculation with constant K-values are discussed in the next section.

4.3 Integrated Flash Calculation with Constant K-values

4.3.1 Introduction of Integrated Flash Calculation

One of the major improvements over the previous hydrogen network optimisation methodology (Zhang et al., 2008) is the integrated flash calculation with constant K-values strategy. In the existing optimisation methodology (Zhang et al., 2008), the hydrogen network optimisation is based on binary component systems while simulation is required to update the hydrogen purity and flowrate variations for different iterations. A built-in flash routine receives detailed information of the compositions of flash inlet stream and generate K-values that used in the flash calculation.

However, calculating K-values at every iteration can be extremely time consuming, especially for a multi-component system. A large number of K-values will need to be calculated during flash calculation, which will definitely slow down the optimisation procedure and may bring difficulties in convergence. To overcome these drawbacks, the assumption of constant K-values used in flash calculation can be considered.

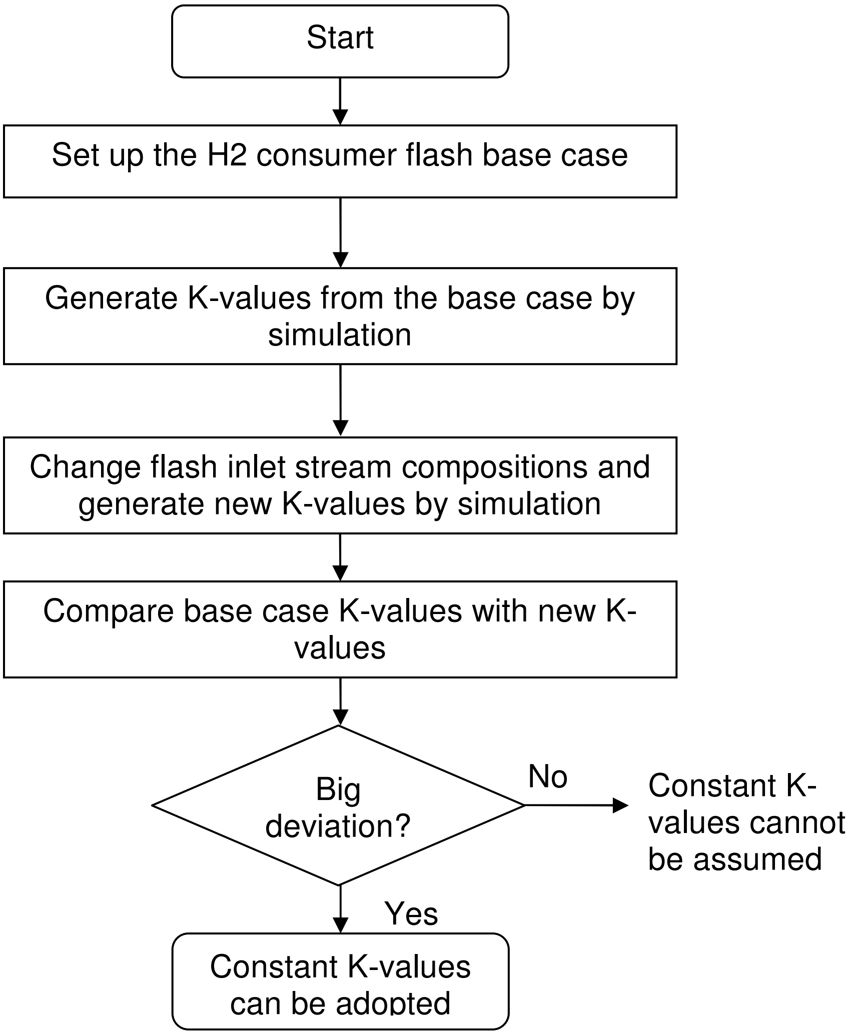

Figure 4.7 Constant K-values verification procedure

As stated in Section 4.2.3, the K-values of a flash process depend on the operating conditions including temperature and pressure. In addition, K-values are also affected by compositions of the flash inlet stream to a very small extent. Normally in refineries, the operating conditions of a flash unit in a hydrogen consumer stay stable with very negligible change. Considering the stable operating conditions, K-values are only related to the flash inlet stream compositions. Since the influence of different compositions on variation of K-values is very limited, there is a possibility that K-values can be treated as constants.

The Constant K-values strategy allows us to integrate the flash calculation into optimisation step without calculating K-values by simulation at every iteration. However, it is needed to prove that whether the impact of flash inlet stream composition on K-values is negligible or not.

As Figure 4.7 shows, the verification procedure of constant k-values starts with the base case for a flash unit in a hydrogen consumer. The base case model involves a stream going into the flash unit where it gets separated into vapour and liquid. After building up the base case, simulation runs to generate the K-values for the base case under specified operating conditions. Then the flash inlet stream compositions are changed and the flash unit will be simulated for each of them to generate new K-values for each set of compositions. Note that in this procedure the operating conditions including temperature and pressure are remained exactly the same as those of the base case. The new K-values are compared with the base case K-values, and the deviations between them will be checked to see whether the constant K-value strategy is appropriate or not.

4.3.2 Results of Constant K-values Verification

In this work, ***ASPEN HYSYS*** (version 2006.5) software suite is used for the verification. It is widely used and accepted as a simulation tool in chemical engineering for modelling and simulation of refining or petrochemical processes.

A general standard flash separation unit can be found in the HYSYS library. The feed stream can be defined using one of the HYSYS built-in property packages, Grayson-Streed, as it is designed to model streams with high hydrogen content.

As for the base case, the flowrate and compositions of the feed stream is set to be a sample of a naphtha hydrotreater reactor outlet stream. The operating temperature and pressure for the flash unit has been set to common flash conditions.

Table 4.1 Typical operating temperature and pressure for a hydrotreater

Flash operating conditions settings	
Temperature (^{o}C)	50
Pressure (bara)	18

The specified operating conditions are shown in Table 4.1. As the simulation is completed, the flowrate and compositions of each flash outlet stream will be available and the k-values for the flash calculation can be generated.

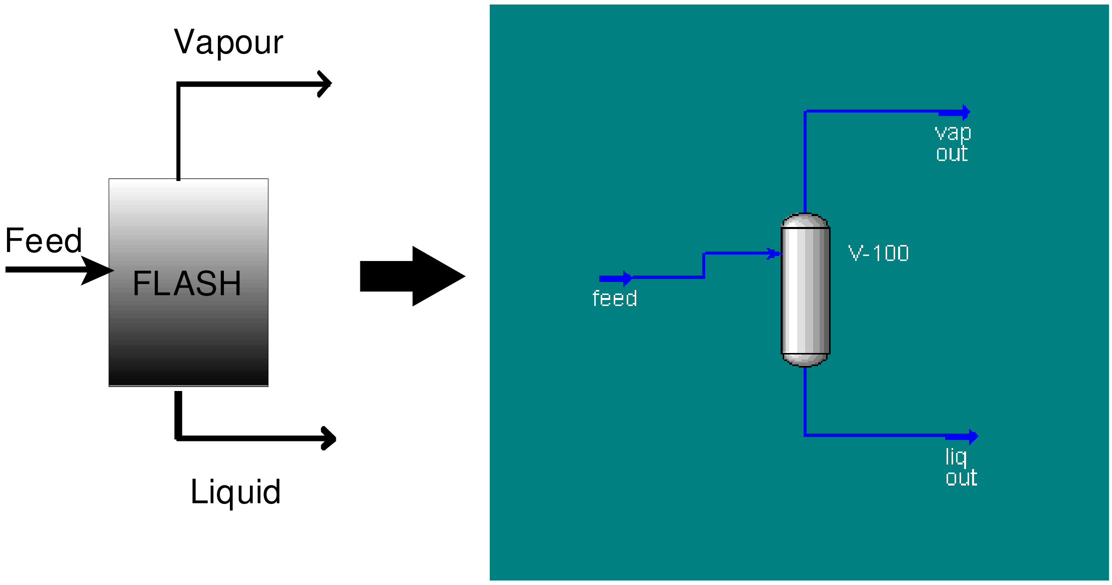

Figure 4.8 Constant K-values verification

The flash unit base case is modelled in ***HYSYS*** as Figure 4.8 shows. A feed stream is sent into the flash unit, and separated into a vapour phase going out from the top and a liquid phase going out from the bottom.

The detailed data for the base case is shown in Table 4.2.

Table 4.2 Constant K-values verification base case

Flowrates	Ffeed (MMscfd*)	Fliq (MMscfd)	Fvap (MMscfd)	
	86.04	33.45	52.59	
Compositions	Yfeed (vol%)	Yliq (vol%)	Yvap	K-values
H2	47.05	1.05	75.88	72.0203
CH4	9.29	1.71	14.03	8.1959
C2H6	1.29	0.42	1.84	4.3970
C3H8	1.69	1.15	2.02	1.7614
i-C4H10	0.51	0.4	0.57	1.4133
n-C4H10	0.54	0.69	0.45	0.6551
H2S	1.76	0.46	2.53	5.4879

Ffeed, Fliq and Fvap are the flowrates of the feed stream, the liquid from the flash, and the vapour from the flash, respectively. The stream compositions of H2 and other main impurities are also listed below the flowrates. Note that not all components in a stream are shown in the table and the detailed data for the entire Grayson-Streed property package definition can be found in Appendix B. The feed stream is pre-defined and the liquid and vapour stream are the results from the ***HYSYS*** as well as the K-values which is used for flash calculation. The target of this case study is to figure out how K-values are affected by composition changes.

Therefore, three simulation runs are carried out with different compositions of flash feed streams. The detailed data for the simulation results are shown in Table 4.3. Note that for all the simulation scenarios the flowrate of the feed stream is not changed, while the compositions are varied.

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*1MMscfd = 1.12kNm^3

Table 4.3 Flash model simulation results

	Scenario1			
	Yfeed (vol%)	Yliq (vol%)	Yvap (vol%)	K-values
H2	51.05	1.11	82.35	73.9495
CH4	7.95	1.67	11.88	7.1032
C2H6	1.19	0.41	1.68	4.1215
C3H8	1.68	1.51	1.78	1.1787
i-C4H10	0.63	0.52	0.69	1.3166
n-C4H10	0.58	0.69	0.51	0.7301
H2S	1.76	0.61	2.47	4.0561

	Scenario2			
	Yfeed (vol%)	Yliq (vol%)	Yvap (vol%)	K-values
H2	49.05	1.08	79.12	73.0116
CH4	8.01	1.70	11.95	7.0208
C2H6	1.24	0.44	1.74	3.9813
C3H8	1.70	1.52	1.80	1.1882
i-C4H10	0.62	0.51	0.69	1.3388
n-C4H10	0.56	0.69	0.47	0.6833
H2S	1.77	0.56	2.52	4.5042

	Scenario3			
	Yfeed (vol%)	Yliq (vol%)	Yvap (vol%)	K -values
H2	45.05	1.02	72.64	71.2198
CH4	11.00	2.00	16.62	8.3037
C2H6	2.30	1.02	3.10	3.0445
C3H8	1.73	1.16	2.07	1.7803
i-C4H10	0.71	0.65	0.74	1.1359
n-C4H10	0.69	0.8	0.62	0.7658
H2S	1.95	0.56	2.82	5.0231

The detailed composition data for the three different feed streams can be found in Table 4.3. The hydrogen purity for each stream is different, ranging from 45vol% to 51vol% (47vol% H2 purity for the base case). The listed impurities also varied in a small range. Resulting from different flash inlet streams, the flash outlet vapour and liquid both experience variations in compositions. Similarly, three different sets of K-values are obtained as shown in Table 4.4. As discussed before, these K-values need to be compared with the base case K-values to check out the deviations. Table 4.4 shows the deviation between each of them is calculated. The deviations between new generated K-values and the base case K-values are very limited. In Scenario 1, the biggest deviation is +1.9292 for H_2 component, while all other deviations are within +/-1.1. Similarly for Scenario 2, all deviations are within +/-1.2. For Scenario 3, the biggest deviation for K-values comparison happens to C_2H_6 component, which is however, only -1.35. Again, all other K-values deviations appear no more than +/-1.

To summarise comparison, it shows some but very limited deviations for the K-values of all components, which indicates that using constant K-values is a reasonable assumption to deal with different flash inlet stream with varying compositions in optimisation. However, after obtaining the optimisation result, re-simulation is necessary to correct certain deviations caused by the assumption of constant K-values.

Table 4.4 Flash model base case and simulations comparison

	Base case K-values	K-values of scenario 1	Deviation
H_2	72.0203	73.9495	1.9292
CH_4	8.1959	7.1032	-1.0927
C_2H_6	4.3970	4.1215	-0.2755
C_3H_8	1.7614	1.1787	-0.5828
i-C_4H_{10}	1.4133	1.3166	-0.0966
n-C_4H_{10}	0.6551	0.7301	0.0751
H_2S	4.8685	4.0561	-0.8125
	Base case K	K of scenario 2	Deviation
H_2	72.0203	73.0116	0.9913
CH_4	8.1959	7.0208	-1.1751
C_2H_6	4.3970	3.9813	-0.4157
C_3H_8	1.7614	1.1882	-0.5733
i-C_4H_{10}	1.4133	1.3388	-0.0745
n-C_4H_{10}	0.6551	0.6833	0.0282
H_2S	4.8685	4.5042	-0.3643
	Base case K	K of scenario 3	Deviation
H_2	72.0203	71.2198	-0.8005
CH_4	8.1959	8.3037	0.1078
C_2H_6	4.3970	3.0445	-1.3525
C_3H_8	1.7614	1.7803	0.0188
i-C_4H_{10}	1.4133	1.1359	-0.2774
n-C_4H_{10}	0.6551	0.7658	0.1107
H_2S	4.8685	5.0231	0.1546

Therefore, for a hydrogen network optimisation problem, the integrated flash calculation with constant K-values can be incorporated in the optimisation procedure with 2 steps:

1. K-values are initially obtained from rigorous flash calculation in simulation
2. Then K-values will be checked by using simulation when optimisation results are obtained.

The main advantages of integrated flash calculation using constant K-values in optimisation include:

- More accurate optimisation methodology
- More reliable and efficient flash calculation
- Huge time and computing resource saving compared with the existing approach by (Zhang et al., 2008)

Although the integrated flash calculation with the constant K-values strategy has been verified, it has to be careful when incorporating it into the optimisation of a hydrogen network, due to the complexity and uncertainty of a complicated hydrogen network. As a result, for each optimisation procedure, the K-values for flash calculation in each hydrogen consumer model will be initialised and assumed as constant from the base case simulation. When the optimisation result is obtained, the K-values generated from the optimisation solutions will need to be verified in order to ensure the feasibility of the optimisation results. Detailed discussion and application of the optimisation framework with constant K-values can be found with a case study in Chapter 5.

4.4 Summary

A detailed general hydrogen consumer model has been proposed under multi-component consideration. The main features and advantages for the detailed hydrogen consumer model are as follows:

- Inclusion of light hydrocarbon production
- Variable H2/Oil ratio and H2 partial pressure
- Integrated flash calculation

These improvements are developed based on the existing hydrogen consumer model (Zhang et al., 2008). Firstly, light hydrocarbon production during hydroprocessing reaction is now considered and represented by mass balance calculations in reactor modelling. Furthermore, the reaction inlet conditions are allowed to vary slightly instead of strictly fixed, in order to open up the degrees of freedom for the hydrogen network optimisation. Also, the flash calculation is incorporated to take into account vapour-liquid equilibrium under multi-components.

It is the most detailed hydrogen consumer model for H2 network management so far, and will be used in the detailed hydrogen network modelling and optimisation, which will be discussed in Chapter 5.

Another major improvement over the previous work by (Zhang et al., 2008) is the introduction of integrated flash calculation using constant K-values, in the optimisation model.

By using the constant K-values, the flash calculation for each hydrogen consumer can be integrated into optimisation without the need of iterative simulation. The constant K-values assumption has been verified for its feasibility. The integrated flash calculation can simplify the whole optimisation procedure with significantly reduced computation time and much more improved calculation efficiency.

Chapter 5 Multi-component Optimisation for H2 networks

5.1 Overall Hydrogen Network Modelling and Optimisation

In Chapter 4, the detailed hydrogen consumer model with multiple components has been developed. However, to complete an overall hydrogen network, we still need to involve models of hydrogen producers and site fuel systems. Considering hydrogen consumers as a core of a hydrogen network, they need to receive hydrogen from hydrogen producers and may purge hydrogen to a site fuel system. Therefore, to complete a hydrogen network model, the balance among hydrogen consumers, producers and fuel system needs to be modelled.

5.1.1 Hydrogen Producer Model

In this work, a shortcut model for a general hydrogen producer is developed, which simply provides make-up hydrogen to hydrogen consumers with a flowrate and composition.

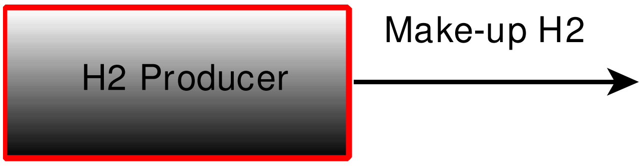

Figure 5.1 Short-cut hydrogen producer model

In refineries, the make-up hydrogen mainly comes from hydrogen producers including hydrogen plants and/or other purified by-product hydrogen, for example catalytic reformers or ethylene plants. The H2 purity of different hydrogen producers may vary. Therefore, with different flowrate and H2 purity specifications, the general hydrogen producer model can be adjusted to a various hydrogen producer models. The relationship between hydrogen producers and consumers can be represented by mass balance.

$$\sum_{k} F_{H2P,k,j} + \sum_{j1} F_{H2C,j1,j} = F_{mix,j} \qquad \forall j \tag{5.1}$$

$$\sum_{k} (F_{H2P,k,j} \cdot Y_{H2P,i,k}) + \sum_{j1} (F_{H2C,j1,j} \cdot Y_{H2C,i,j1}) = F_{mix,j} \cdot Y_{mix,i,j} \qquad \forall j \tag{5.2}$$

$F_{H2P,k,j}$ denotes the flowrates of hydrogen production from producer *k* to hydrogen consumer *j*. Subscript $j1$ is introduced as an alias of subscript j to represent different consumers. Using subscripts $j1$ and j, $F_{H2C,j1,j}$ represents the hydrogen transportation from consumer $j1$ to consumer j. When $j1$ equals j, it represents the internal recycle of consumer j (or $j1$). When $j1$ is not equal to j, it represents the hydrogen flowrate from the purge gas of consumer $j1$ to consumer j. $Y_{H2P,i,k}$ and $Y_{H2C,i,j1}$ represent composition of component i of hydrogen producer k and composition of component i of hydrogen stream between consumers, respectively.

According to Equation 5.1 the summation of hydrogen production from various hydrogen producers to consumer j plus recycle and hydrogen from other consumers equals to the flowrate at the mixing point of consumer j, which is a hydrogen sink. Combined with Equation 5.2 which represents component balance between sinks and sources, the complete mass balance between hydrogen producers and consumers is modelled.

5.1.2 Site Fuel Balance

In a hydrogen network, a site fuel system is used to collect the purge gas from various hydrogen consumers. Normally the purge gas comes from the flash vapour in a hydrogen consumer. Figure 5.2 shows an example of a site fuel system. Four hydrotreaters purge gas from their high pressure flash to the site fuel. The site fuel system is important to a hydrogen network, as it maintains the overall hydrogen network mass balance.

The purge gas flowrate and purities can be obtained from the flash model proposed in Chapter 4. Note that the compositions of a purge stream are exactly the same as the recycle, as they are both generated from the high pressure flash.

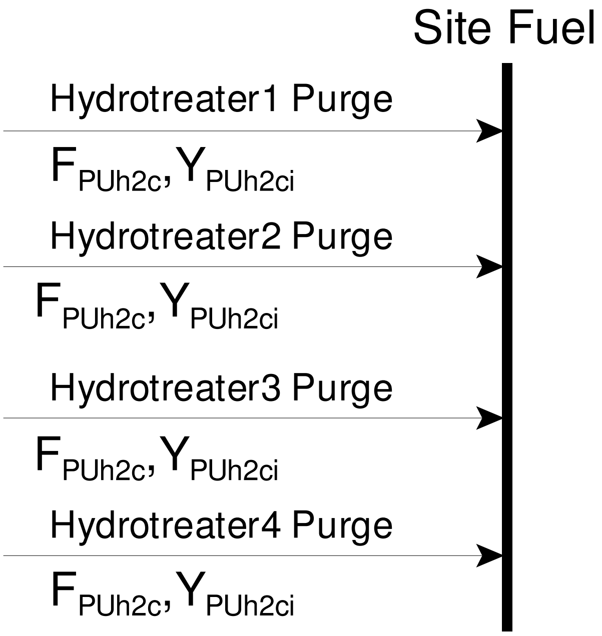

Figure 5.2 An example of site fuel model for a hydrogen network

The hydrogen producer model is connected to the inlets of hydrogen consumers, and the site fuel model needs to be connected to the outlets of hydrogen consumers. The relationship between hydrogen consumers and a site fuel system is represented as follows:

$$F_{pu,j} = F_{SF,j} + \sum\nolimits_{j1} F_{H2C,j,j1} \qquad j \neq j1 \qquad \forall j \tag{5.3}$$

$$F_{pu,j} \cdot Y_{pu,i,j} = F_{SF,j} \cdot Y_{SF,i,j} + \sum\nolimits_{j1} (F_{H2C,j,j1} \cdot Y_{H2C,i,j}) \qquad j \neq j1 \qquad \forall j \tag{5.4}$$

$$Y_{pu,i,j} = Y_{SF,i,j} = Y_{H2C,i,j} \qquad \forall i \qquad \forall j \tag{5.5}$$

$F_{pu,j}$ and $F_{SF,j}$ represent the flowrate of the total purge gas of consumer j and the amount sent to the site fuel system. When $j \neq j1$, $F_{H2C,j,j1}$ excludes the internal recycle of consumer j, and represents the hydrogen flowrate from the purge gas of consumer j to consumer $j1$. Equation 5.3 explains the possible destination of purge gas from a hydrogen consumer. Normally the purge gas is generated from the flash separation and can be sent to a site fuel system or feed other consumers if it contains rich enough hydrogen. As shown in Equation 5.3, the total amount of purge gas from consumer j

equals to the site fuel contribution from consumer j plus the summation of hydrogen sent to other consumers from consumer j.

$Y_{pu,i,j}$, $Y_{SF,i,j}$, and $Y_{H2C,i,j}$ represent compositions of purge, purge to site fuel and recycle streams, which are actually the same because they are all from the same source, the flash vapour phase.

Together with Equations 4.1-4.17 for detailed hydrogen consumer models, a hydrogen network is modelled by incorporating Equations 5.1 to 5.5, which represent mass balance among hydrogen producers, consumers and a site fuel system.

5.1.3 Overall Multi-component H2 Network Modelling

The H2 network optimisation problem can be formulated by using a few groups of definitions including variables, parameters, constraints, and objectives.

- **Variables:**

  Flowrates and purities of hydrogen streams around a hydrogen network including hydrogen make-up, recycle, purge stream of each hydrogen consumer and connections consumers and hydrogen plant. Some of them are independent variables such as hydrogen production of hydrogen producers, while others are dependent such as recycle flowrate and purities, as these are calculated from flash calculations. Details of variable declarations can be found in Appendix C.

- **Parameters:**

  - Liquid feed stock properties
  - reactor parameter R (hydrogen consumption and light hydrocarbon production)
  - K-values used for flash calculation

  - Range of variable H2/Oil ratio and H2 partial pressure for hydrogen consumer inlets

- **Constraints:**

All proposed equations in chapter 4 and chapter 5 are used as constraints for the optimisation. Constraints for individual detailed hydrogen consumer include Equations 4.1 to 4.17, 5.1 to 5.5 are used as hydrogen network balance constraints.

- **Objective function:** minimise total required hydrogen production

$$Obj = MIN\left\lfloor \sum_k (F_{H2P,k} \cdot Y_{H2P,i,k}) \right\rfloor \qquad i = H2 \qquad (5.6)$$

Where Obj stands for the optimisation objective; $F_{H2P,K}$ represents the flowrate of hydrogen production for each hydrogen producer and $Y_{H2P,i,k}$ denotes relative hydrogen production purity for each hydrogen producer. As the objective function shows, the optimisation target is to minimise the summation of all hydrogen production from all hydrogen utility producers involved in hydrogen network.

For economic concerns, the objective function can be extended to minimise the total operating cost for a hydrogen network by taking into account the hydrogen production cost and fuel gas value.

$$Obj = MIN\left\lfloor \sum_k (F_{H2P,k} \cdot U_{H2}) - \sum_j (F_{SF,j} \cdot U_{SF,j}) \right\rfloor \qquad i = H2 \qquad (5.7)$$

The total operating cost should involve both hydrogen production cost and fuel gas value in the site fuel system. In Equation 5.7 the total operating cost is represented by total hydrogen production cost minus total fuel gas value, where U_{H2} and $U_{SF,j}$ represent the unit price for hydrogen and fuel gas respectively. It is suggested to calculate both unit prices based on heating value contributions.

5.1.4 H2 Network Superstructure

The H2 network optimisation is based on a H2 network superstructure. When considering optimisation for a hydrogen network, a couple of questions must be considered beforehand.

For each hydrogen consumer:

- Make-up hydrogen: where and how much?
- Recycle hydrogen: how much?

Considering the make-up hydrogen at the inlet of each hydrogen consumer, it is defined as a variable which can be obtained from various H2 producers such as a hydrogen plant, CCR, an ethylene plant, etc. Meanwhile, the purge gas from other consumers may contribute to the make-up hydrogen as well. When dealing with a large and complicated hydrogen network with many hydrogen consumers involved, the possibilities of sources for make-up hydrogen can be plenty.

As for recycle hydrogen, each hydrogen consumer should decide the flowrate of recycle hydrogen. As discussed before, the recycle is taken from flash vapour and sent back to the consumer inlet, mixing with make-up hydrogen. Therefore it is very sensitive to the overall H2 balance of the consumer, and will affect the make-up hydrogen requirement due to the reactor inlet conditions constraints.

To answer these questions systematically and quantitatively, we will need to introduce a H2 network superstructure for optimisation. In a H2 network superstructure, all hydrogen producers and consumers will be defined as hydrogen sinks and sources. Hydrogen producers are defined as hydrogen sources clearly. Hydrogen consumers are defined as sinks and sources at the same time, as it can receive hydrogen from sources, meanwhile provide hydrogen to other sinks (from its high pressure flash vapour). In this way the H2 superstructure allows flexibility for the balance between hydrogen sinks and sources, based on which the optimisation can exploit the best solutions for a hydrogen network under constraints.

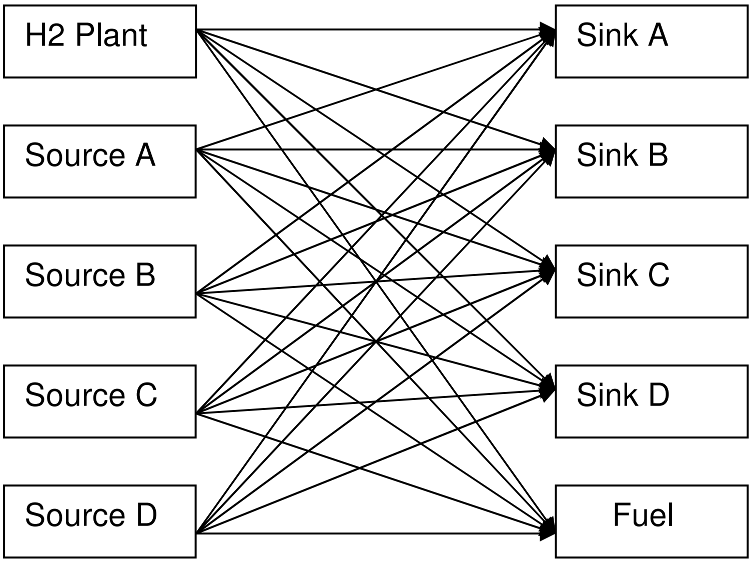

Figure 5.3 An example of hydrogen network superstructure

An example of hydrogen network superstructure is shown in Figure 5.3, the network consists of five hydrogen sources, including a hydrogen plant and sources A to D, and five hydrogen sinks including fuel and sinks A to D. Typically, most of the hydrogen consumers would act as both sinks and sources.

As Figure 5.3 shows, hydrogen can be transported from any source to any sink. This is to give the maximum potential in the hydrogen network superstructure to provide a large searching space for optimisation. On the basis of this superstructure, an optimisation algorithm can search from these possibilities and figure out the best solution. Therefore the hydrogen superstructure is essential to the hydrogen network optimisation in this work.

5.1.5 H2 Network Optimisation Framework

The optimisation framework for a multi-component H2 network is illustrated in Figure 5.4. Starting with the hydrogen pinch analysis, the super-structure based optimisation will be performed based on the proposed multi-component hydrogen network model. The obtained optimisation result needs to be verified by simulation for its feasibility.

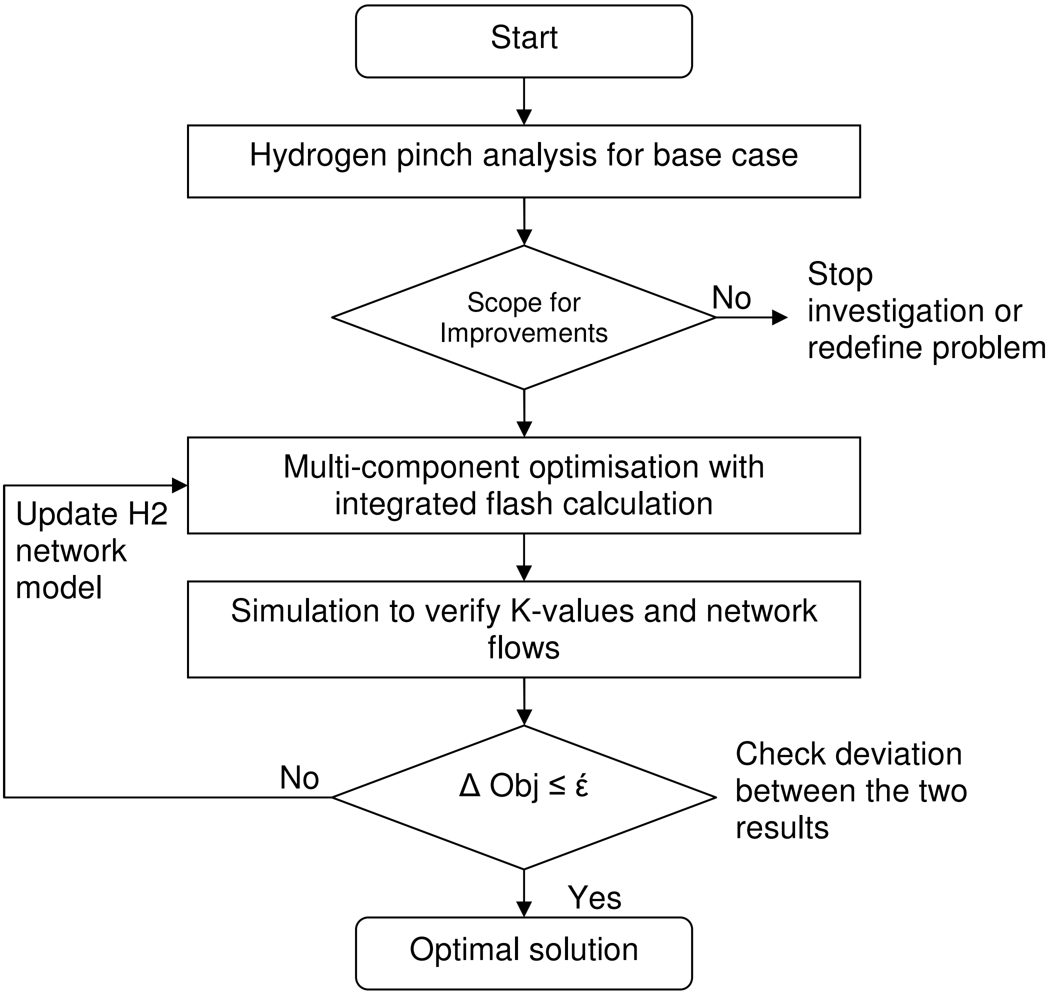

Figure 5.4 The Multi-component hydrogen network optimisation framework

The overall optimisation procedure can be summarised into 4 steps:

Step1: Hydrogen pinch analysis for base case

First, the base case is simulated and relevant data are extracted. Then the hydrogen pinch analysis (Alves, 1999) is applied to check for system potentials and scope for improvement, by comparing the current H2 consumption against the theoretical minimum H2 target. If there is a big gap between current H2 utility flow and the target, the procedure continues. Otherwise the optimisation stops or requires problem redefinition.

Step 2: Integrated hydrogen network optimisation

The overall H2 network model is optimised, in which the integrated flash calculation is included in order to improve calculation efficiency and accuracy, as discussed in Chapter 4.

Step 3: Network simulation

During the optimisation there is a key assumption that the K-values used for flash calculation is considered as constants. However, changes in network connections may result in slight variations in K-values, which may affect the accuracy of the optimisation results. Therefore, network simulation is carried out based on the updated network connections from the optimisation result to retain feasibility.

Step 4: Optimality check

After retaining feasibility from the network simulation, all flowrates and purities from simulation are compared the optimisation results. Only when the tolerance between them is met, the optimisation results can be approved. Otherwise the model is updated and optimised all over again.

5.1.6 Pseudo-components

For multi-component hydrogen network optimisation, all chemical components in each stream around the hydrogen network need to be specified with physical property information. Since the exact component information would not be available due to petroleum mixture’s complexity, the definition of components is in terms of both real and pseudo-components.

Table 5.1 Properties of pseudo components

Pseudo-Components	TB (K)	API Gravity	Specific gravity	MW	TC (K)	PC (bar)
PC1-NHT	344.30	68.4914	0.7075	89.92	523.70	33.69
PC2-NHT	368.50	67.9645	0.7094	102.9	545.57	28.97
PC3-NHT	390.00	65.6453	0.7177	114.8	566.46	26.11
PC4-NHT	412.80	62.1456	0.7307	127.9	589.51	23.86
PC5-NHT	434.00	58.5494	0.7445	140.7	611.25	22.20
PC1-CNHT	349.70	68.6665	0.7069	92.8	528.35	32.43
PC2-CNHT	376.40	67.4160	0.7114	107.3	552.97	27.76
PC3-CNHT	409.40	61.7406	0.7322	125.3	587.09	24.44
PC4-CNHT	436.60	58.0798	0.7464	142.3	613.95	22.02
PC5-CNHT	477.30	51.3646	0.7738	169.3	655.45	19.48
PC1-DHT	499.80	48.0363	0.7881	185.8	677.93	18.28
PC2-DHT	536.20	43.1501	0.8102	215	713.61	16.56
PC3-DHT	579.10	37.8757	0.8354	253.2	754.95	14.88
PC4-DHT	600.80	35.3928	0.8478	274.1	775.58	14.15
PC5-DHT	640.40	31.0198	0.8707	314.6	812.99	12.98
HC-GA1	287.10	76.9630	0.6788	67.36	463.63	46.57
HC-GA2	304.40	72.0910	0.6950	72.75	483.97	42.97
HC-GA3	320.20	67.8959	0.7096	78.11	502.34	40.12
HC-GA4	336.70	63.2102	0.7267	84.18	521.86	37.74
HC-GA5	353.90	68.6862	0.7068	95.05	532.06	31.54
HC-NAP1	349.00	68.6385	0.7070	92.42	527.75	32.59
HC-NAP2	374.10	67.5696	0.7108	106	550.83	28.10
HC-NAP3	399.30	64.3468	0.7225	120.1	575.74	25.10
HC-NAP4	421.10	60.7085	0.7362	132.8	598.06	23.19
HC-NAP5	446.30	56.3756	0.7532	148.4	623.96	21.37
HC-DIE1	438.00	57.8706	0.7472	143.2	615.35	21.91
HC-DIE2	484.90	50.2637	0.7785	174.8	663.01	19.05
HC-DIE3	529.90	43.9419	0.8065	209.7	707.51	16.84
HC-DIE4	575.20	38.3582	0.8330	249.6	751.18	15.02
HC-DIE5	618.40	33.4522	0.8578	291.8	792.19	13.60

The lighter components such as methane, propane, i-butane, n-butane can be found from ***ASPEN HYSYS*** components library as real components. The heavier part of the mixture can be calculated by using ***ASPEN HYSYS*** internal components estimation function on the basis of true boiling point and API gravity. Table 5.1 lists all of the pseudo-components included in the multi-component model and their properties.

The liquid fractions can be classified into a number of groups based on true boiling point (TBP). In addition, each group of components can be used to represent a fuel product from a hydroprocessor such as gasoline or diesel. All properties information for each pseudo-component can be found in Table 5.1. These pseudo-components are used for modelling each stream in a hydrogen network.

5.1.7 Selection of Optimisation Solvers

A variety of optimisation engines are available for multi-component hydrogen network optimisation problems. Different specifications of optimisation problems would require accordingly different optimisation methodologies. Basically the optimisation algorithms to choose from can be classified into two main groups:

- Deterministic method : Linear programming (LP), Non-Linear programming (NLP) or Mixed Integer Non-Linear programming (MINLP)
- Stochastic method: Simulated Annealing (SA), Genetic Algorithm (GA), Tabu search, etc.

The deterministic methods are mainly gradient based approaches. They are always fast in searching for solutions. However they do not perform well when dealing with large scale mixed integer non-linear programming problems and may be trapped in local optimum, if a problem is non-convex.

On the other hand, stochastic methods are random search methods with relatively slow searching speed, but with great capability to solve mix integer non-linear programming problems and converge to near-global optimum solutions.

Both methodologies have got obvious advantages and disadvantages. In this work the non-linear programming (NLP) approach is first chosen for the multi-component H2 network optimisation method. In the following case study ***GAMS*** (Version GAMS IDE 2.0.13.0.) is selected as the modelling and optimisation tool with its built-in NLP solver.

5.2 Case Study

Based on the proposed multi-component H2 network modelling and optimisation methodology, a case study is carried out using NLP algorithm.

5.2.1 Base Case

The base case carried out in this case study is originally from the hydrogen consumer and hydrogen network model by (Singh, 2006). Figure 5.5 shows the flowsheet of the hydrogen network base case. There are two hydrogen producers undertaking hydrogen production and supply hydrogen to the hydrogen network. As the main hydrogen source, the hydrogen plant produces 109.6 MMscfd of hydrogen with high purity of 99 vol%. The supporting hydrogen source is CCR which provides 14.63 MMscfd of hydrogen with a relatively lower purity of 83 vol%.

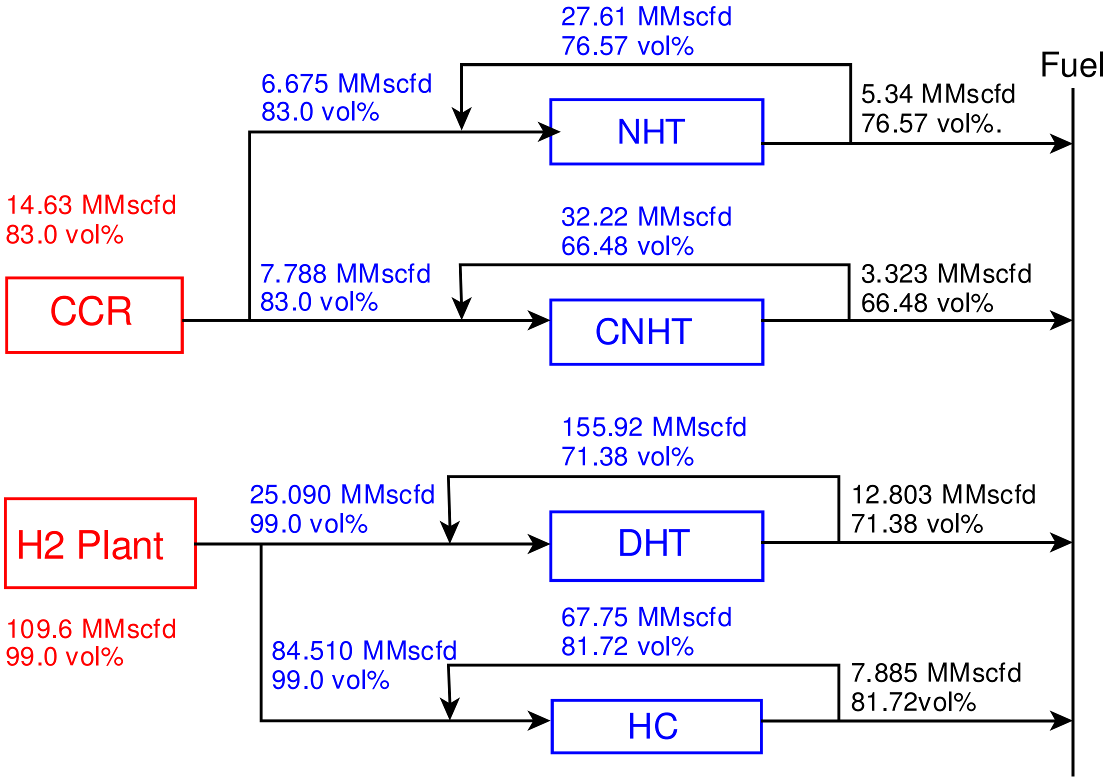

Figure 5.5 Multi-component hydrogen network base case

As for hydrogen consumers, there are three different hydrotreaters and one hydrocracker in the hydrogen network. Each of them is modelled with certain amount of hydrogen consumption, and the hydrocracker is with the largest hydrogen consumption. All hydrogen consumers are configured with an internal recycle. All the purged gases from these hydrogen consumers are collected in fuel gas system. In the current network there is no hydrogen transportation between hydrogen consumers. Tables 5.2 and 5.3 shows network connections and the detailed data for each unit in the hydrogen network.

Table 5.2 Details of network connections for each H2 consumer

	NHT	CNHT	DHT	HC	FUEL
CCR	6.675	7.788	0.000	0.000	0.000
H2PLANT	0.000	0.000	25.090	84.510	0.000
NHT	76.57	0.000	0.000	0.000	5.34
CNHT	0.000	32.22	0.000	0.000	3.323
DHT	0.000	0.000	155.92	0.000	12.803

An overview of the hydrogen network distribution is summarised in Table 5.2. The flowrate of hydrogen from hydrogen producers to consumers are shown. Also the flowrate of hydrogen between consumers are listed. The hydrogen flowrate between the same consumers is used to indicate its internal recycle hydrogen. Table 5.3 gives operating conditions for flash units of each hydrogen consumer.

Table 5.3 Flash Operating conditions for each hydrogen consumer

High pressure flash	Temperature (^oC)	Pressure (bara)
NHT	50	18
CNHT	50	20
DHT	50	20
HC	50	160

For the four different H2 consumers, each of them is supposed to process feedstock with different properties in order to produce relevant products. For the hydrotreaters the feedstock is relatively light, while the hydrocracker can take much heavier feedstock. Table 5.4 gives detailed information of the feedstock for each hydrogen consumer including flowrates and compositions for all components in the system. Note that the liquid feedstock contains no hydrogen, and it will be mixed with make-up and recycle hydrogen at the reactor inlet. For each individual hydrogen consumer, the flowrate and complete compositions of hydrogen make-up, recycle and purge are all provided.

Table 5.4 Detailed data of liquid feedstock for each H2 consumer

Feedstock	NHT	CNHT	DHT	HC
Flowrate(MMScfd)	32.79	12.95	36.15	37.62
Compositions (vol%)				
H2	0.00	0.00	0.00	0.00
CH4	1.47	1.63	6.53	1.45
C2H6	0.62	1.30	2.74	1.35
C3H8	1.33	2.07	5.94	5.23
i-C4H10	0.43	0.67	1.93	8.31
n-C4H10	0.72	1.12	3.22	5.09
H2S	0.67	3.09	4.88	5.69
NH3	0.00	0.18	0.30	2.86
PC1-NHT	19.40	0.00	0.03	0.00
PC2-NHT	21.35	0.00	0.03	0.00
PC3-NHT	22.51	0.00	0.03	0.00
PC4-NHT	10.89	0.00	0.04	0.00
PC5-NHT	20.00	0.00	0.02	0.00
PC1-CNHT	0.14	11.61	0.00	0.00
PC2-CNHT	0.29	18.37	0.00	0.00
PC3-CNHT	0.18	22.63	0.00	0.00
PC4-CNHT	0.00	16.79	0.00	0.00
PC5-CNHT	0.00	20.54	0.00	0.00
PC1-DHT	0.00	0.00	7.52	0.00
PC2-DHT	0.00	0.00	15.20	0.00
PC3-DHT	0.00	0.00	19.47	0.00
PC4-DHT	0.00	0.00	23.95	0.00
PC5-DHT	0.00	0.00	8.17	0.00
HC-GA1	0.00	0.00	0.00	1.02
HC-GA2	0.00	0.00	0.00	2.03
HC-GA3	0.00	0.00	0.00	4.01
HC-GA4	0.00	0.00	0.00	2.54
HC-GA5	0.00	0.00	0.00	1.64
HC-NAP1	0.00	0.00	0.00	2.57
HC-NAP2	0.00	0.00	0.00	3.76
HC-NAP3	0.00	0.00	0.00	7.66
HC-NAP4	0.00	0.00	0.00	6.20
HC-NAP5	0.00	0.00	0.00	2.96
HC-DIE1	0.00	0.00	0.00	5.89
HC-DIE2	0.00	0.00	0.00	7.92
HC-DIE3	0.00	0.00	0.00	9.95
HC-DIE4	0.00	0.00	0.00	8.18
HC-DIE5	0.00	0.00	0.00	3.68

Table 5.5 Detailed data of H2 consumers for base case

	NHT			CNHT			DHT			HC		
Flowrate	Make-up	Recycle	Purge	Make-up	Recycle	Purge	Make-up	Recycle	Purge	Make-up	Recycle	Purge
(MMScfd)	6.675	27.61	5.34	7.788	32.22	3.32	25.09	155.92	12.8	84.51	67.75	7.89
	Compositions (vol%)			Compositions (vol%)			Compositions (vol%)			Compositions (vol%)		
H2	83.00	75.87	75.87	83.00	65.49	65.49	99.00	71.44	71.44	99.00	82.19	82.19
CH4	17.00	19.34	19.34	17.00	28.30	28.30	1.00	15.34	15.34	1.00	6.66	6.66
C2H6	0.00	1.20	1.20	0.00	1.57	1.57	0.00	3.43	3.43	0.00	0.96	0.96
C3H8	0.00	1.11	1.11	0.00	1.10	1.10	0.00	3.64	3.64	0.00	1.57	1.57
i-C4H10	0.00	0.17	0.17	0.00	0.17	0.17	0.00	0.57	0.57	0.00	1.20	1.20
n-C4H10	0.00	0.17	0.17	0.00	0.21	0.21	0.00	0.75	0.75	0.00	0.56	0.56
H2S	0.00	0.21	0.21	0.00	2.47	2.47	0.00	4.28	4.28	0.00	2.48	2.48
NH3	0.00	0.91	0.91	0.00	0.34	0.34	0.00	0.55	0.55	0.00	3.95	3.95
PC1-NHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC2-NHT	0.00	0.46	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC3-NHT	0.00	0.32	0.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC4-NHT	0.00	0.15	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC5-NHT	0.00	0.07	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC1-CNHT	0.00	0.02	0.02	0.00	0.21	0.21	0.00	0.00	0.00	0.00	0.00	0.00
PC2-CNHT	0.00	0.00	0.00	0.00	0.14	0.14	0.00	0.00	0.00	0.00	0.00	0.00
PC3-CNHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC4-CNHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC5-CNHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC1-DHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC2-DHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC3-DHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC4-DHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC5-DHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-GA1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.07
HC-GA2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.09

Table 5.5 Detailed data of H2 consumers for base case (Continued)

	NHT			CNHT			DHT			HC		
Flowrate (MMScfd)	Make-up 6.675	Recycle 27.61	Purge 5.34	Make-up 7.788	Recycle 32.22	Purge 3.32	Make-up 25.09	Recycle 155.92	Purge 12.8	Make-up 84.51	Recycle 67.75	Purge 7.89
	Compositions (vol%)			Compositions (vol%)			Compositions (vol%)			Compositions (vol%)		
HC-GA3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.12
HC-GA4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.05
HC-GA5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02
HC-NAP1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.03
HC-NAP2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02
HC-NAP3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02
HC-NAP4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-NAP5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-DIE1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-DIE2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-DIE3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-DIE4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-DIE5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Before optimising the base case, it is important to verify the whole hydrogen network base case. The way to do this is to simulate the base case and compare the simulation result with the base case to check any deviations. If the deviation meets the allowed tolerance, then the base case is verified for optimisation. Otherwise the base case needs to be redefined.

Table 5.6 Base case data verification in HYSYS

Hydrogen consumers		**NHT**			**CNHT**		
Itmes		**Base case**	**Simulation**	**E_R%**	**Base case**	**Simulation**	**E_R%**
Sink Stream	Flowrate(MMscfd)	34.29	35.00	**2.07**	40.00	40.10	**0.00**
		Compositions (vol%)					
	H2 (Vol %)	76.79	76.18	**0.08**	68.34	69.05	**1.03**
	CH4 (Vol %)	19.02	19.07	**0.00**	26.44	25.88	**2.10**
Source Stream	Flowrate(MMscfd)	32.95	33.00	**0.00**	45.23	45.23	**0.00**
		Compositions (vol%)					
	H2 (Vol %)	75.87	75.19	**1.20**	65.49	65.28	**0.03**
	CH4 (Vol %)	19.34	19.34	**0.00**	28.30	28.30	**0.00**
Liquid product Stream	Flowrate(MMscfd)	32.96	32.96	**0.00**	13.27	13.27	**0.00**
		Compositions (vol%)					
	H2 (Vol %)	1.05	1.05	**0.00**	1.54	1.54	**0.00**
	CH4 (Vol %)	1.71	1.69	**0.00**	4.09	4.00	**2.25**
		DHT			**HC**		
		Base case	Simulation	**E_R%**	Base case	Simulation	**E_R%**
Sink Stream	Flowrate(MMscfd)	181.01	182.35	**0.07**	152.60	153.30	**0.08**
		Compositions (vol%)					
	H2 (Vol %)	74.51	74.50	**0.00**	89.68	89.70	**0.00**
	CH4 (Vol %)	13.74	13.80	**0.04**	4.14	4.20	**1.69**
Source Stream	Flowrate(MMscfd)	168.72	168.56	**0.01**	113.03	114.00	**0.09**
		Compositions (vol%)					
	H2 (Vol %)	71.45	71.44	**0.00**	75.64	77.21	**0.05**
	CH4 (Vol %)	15.34	15.32	**0.01**	6.66	6.70	**0.05**
Liquid product Stream	Flowrate(MMscfd)	33.21	33.12	**0.03**	39.25	39.85	**1.50**
		Compositions (vol%)					
	H2 (Vol %)	1.44	1.47	**2.08**	6.87	6.61	**3.78**
	CH4 (Vol %)	1.92	2.11	**1.00**	2.21	2.25	**2.00**

The simulation is undertaken by using ***ASPEN HYSYS***. In Table 5.6 the flowrate and key compositions are listed for comparison. Er% is calculated as the deviation between the base case and simulation results. It is clear that the simulation data are almost the same as the base case data with only slight deviations. The high consistency between the base case and HYSYS simulation is an indication that the base case model is well verified and ready for optimisation.

5.2.2 Hydrogen Pinch Analysis

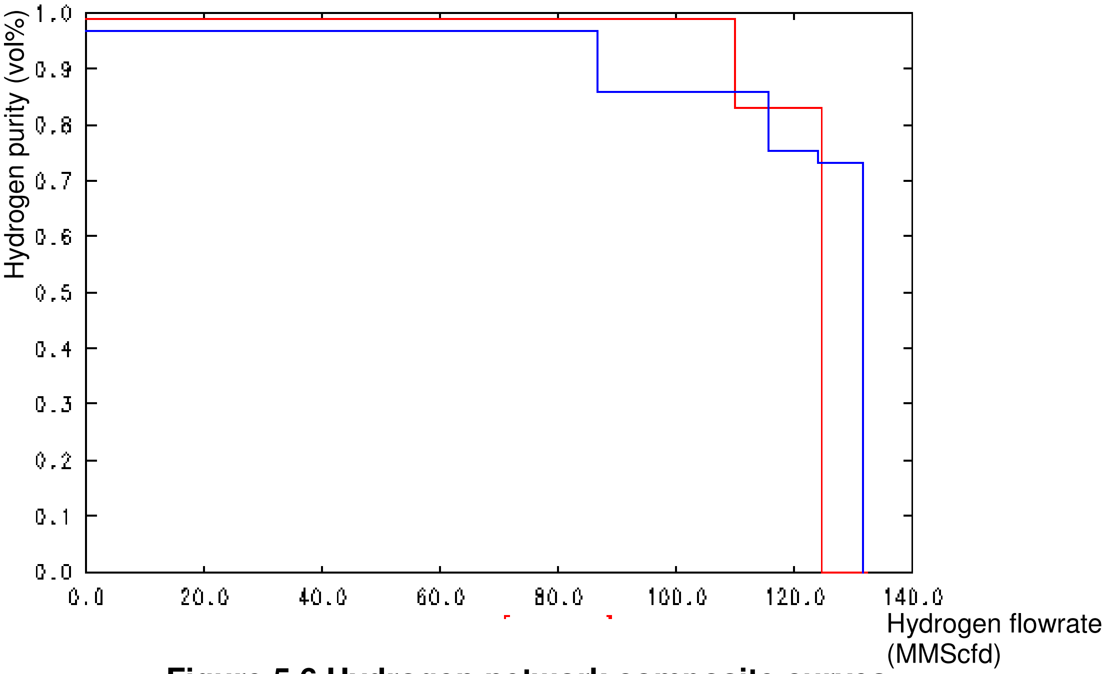

Figure 5.6 Hydrogen network composite curves

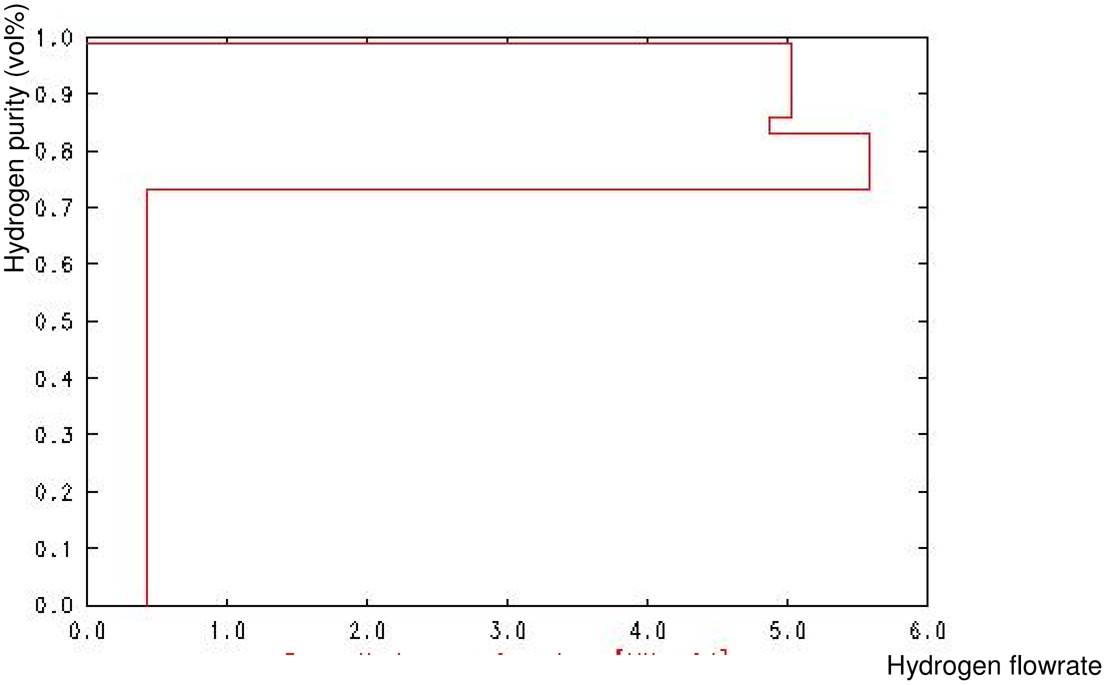

Figure 5.7 Hydrogen network surplus curve

According to the hydrogen pinch analysis (Figures 5.6 and 5.7), the minimum hydrogen requirement for hydrogen plant is 102.4MMscfd. Compared with the base case, the current hydrogen production from hydrogen plant is 109.6MMscfd. Therefore there is a considerable gap of 7.48MMscfd hydrogen of 99vol% purity, which indicates the possible hydrogen saving potentials.

5.2.3 Optimisation and Solution Analysis

The optimisation model is coded in *GAMS* (detailed codes can be found in Appendix C). NLP solver CONOPT is selected to solve the multi-component H2 network optimisation problem. The whole optimisation procedure only takes no more than 1 minute in ***GAMS*** to reach a optimisation solution. Before we can analyze the optimisation solution, it needs to be verified for its feasibility with simulations due to the assumption of constant K-values. The pre-defined constant K-values need to be compared with the generated K-values in the optimisation result. As discussed in Section 4.3, the K-values for flash separation calculation should have minimum changes during optimisation procedure.

Table 5.7 Constant K-values strategy verification

	NHT			**CNHT**		
	Base case	**Opt solution**	**Deviation**	**Base case**	**Opt solution**	**Deviation**
H2	72.0140	72.0575	**0.0435**	42.6469	42.7927	**0.1458**
CH4	11.2857	11.2860	**0.0003**	6.9179	6.8374	**-0.0805**
C2H6	2.8654	2.8642	**-0.0012**	1.8184	1.6784	**-0.1400**
C3H8	0.9741	0.9734	**-0.0007**	0.6346	0.5836	**-0.0510**
i-C4H10	0.4130	0.4125	**-0.0005**	0.2743	0.2527	**-0.0216**
n-C4H10	0.3101	0.3096	**-0.0005**	0.2058	0.1899	**-0.0159**
H2S	1.7641	1.7625	**-0.0016**	1.0100	1.1231	**0.1131**
H3N	7.4751	7.4652	**-0.0099**	3.9462	4.4127	**0.4665**
	DHT			**HC**		
H2	49.2106	49.1038	**-0.1068**	14.7690	14.6079	**-0.1610**
CH4	7.9403	7.8784	**-0.0619**	3.0112	2.9469	**-0.0643**
C2H6	2.0714	1.9366	**-0.1348**	0.9698	1.0531	**0.0834**
C3H8	0.7185	0.6693	**-0.0492**	0.3345	0.2497	**-0.0848**
i-C4H10	0.3090	0.2882	**-0.0208**	0.1560	0.1109	**-0.0451**
n-C4H10	0.2320	0.2165	**-0.0154**	0.1184	0.0826	**-0.0359**
H2S	1.1713	1.2591	**0.0878**	0.5004	0.4610	**-0.0394**
H3N	4.9353	5.0744	**0.1391**	2.0233	1.9277	**-0.0956**

As Table 5.7 shows, the K-values in optimal solution are compared with the ones in base case and the deviation is shown as well. As can be observed from Table 5.7, all of the deviations are very small, which indicates good accuracy of the optimisation solution.

GAMS is able to generate the solution for an NLP optimisation problem in such scale in seconds. As the Figure 5.8 shows, the optimisation did not make big changes to the original hydrogen network but successfully reduced the hydrogen plant production down to 103. 69MMscfd. Although this is still higher than the theoretical minimum target 102.4MMscfd given by pinch, the gap is even no more than 1MMscfd and the theoretical minimum target may never be reached due to the system constraints therefore the result for reduced hydrogen production can be considered as a good one. The hydrogen saving result is similar to the result Singh (2006) has managed to achieve with the existing method, which means that, for the newly developed methodology proposed in this work, the optimisation quality is not affected while the model stability and optimisation calculation efficiency is significantly improved.

The solution given by ***GAMS*** suggests very little network configuration modification, which can be very cost-effective for a refinery hydrogen network retrofit design. Meanwhile, a considerable amount of hydrogen is saved with small network modifications including:

- CCR hydrogen now to feed DHT as well as NHT and CNHT
- H2 Plant now supplying hydrogen to DHT, HC and NHT

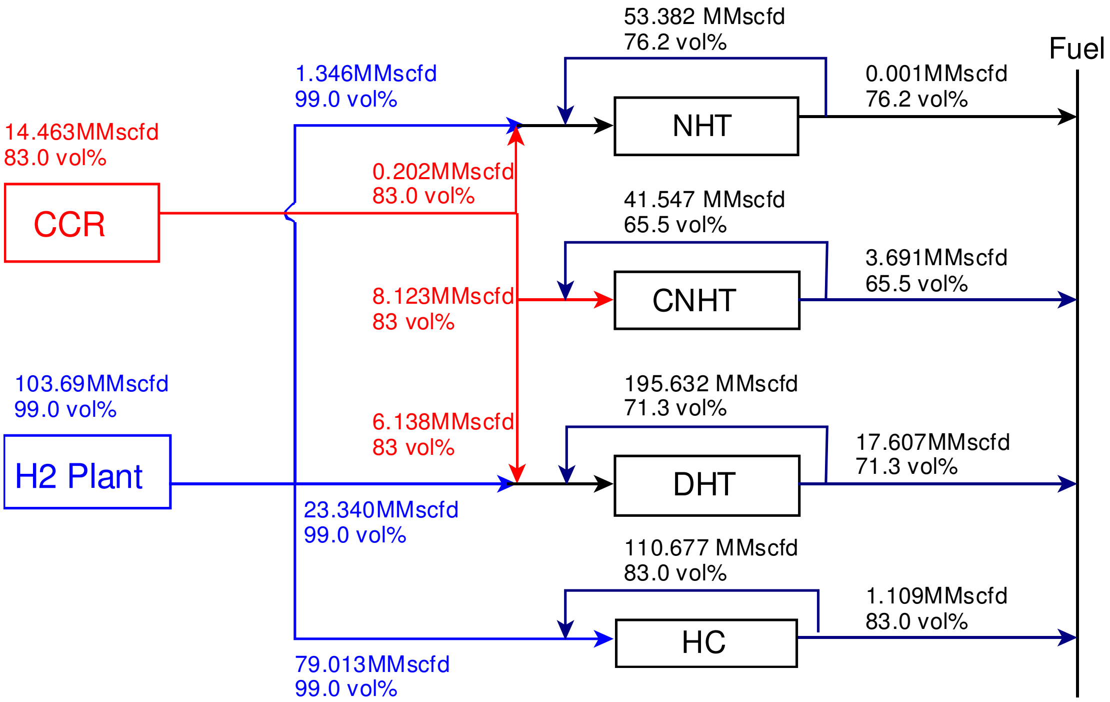

Figure 5.8 The optimal solution for multi-component optimisation

Only two new connections are added, the hydrogen sources from CCR and hydrogen plant are re-distributed in the system. Since the hydrogen production of CCR is fixed, all the hydrogen consumption reduction leads to hydrogen production reduction in the hydrogen plant. As a result, the total production from the hydrogen plant is reduced from 109.6MMscfd in the base case down to 103.69MMscfd in the optimal design.

Table 5.8 Connections overview for the optimal solution

	NHT	CNHT	DHT	HC	FUEL
CCR	6.675	7.788	0.000	0.000	0.000
H2PLANT	0.000	0.000	25.090	84.510	0.000
NHT	76.57	0.000	0.000	0.000	5.34
CNHT	0.000	32.22	0.000	0.000	3.323
DHT	0.000	0.000	155.92	0.000	12.803
HC	0.000	0.000	0.000	67.75	7.885

The information of system connections of the optimal design is shown in Table 5.8, which focuses on the hydrogen flowrate between hydrogen producers and consumers. Refer to Table 5.9 for the detailed data of each hydrogen consumer in the optimised network, including flowrate and full compositions for make-up, recycle and purge streams for all consumers.

Table 5.9 Detailed data of H2 consumers for optimal solution

	NHT			CNHT			DHT			HC		
Flowrate	Make-up	Recycle	Purge	Make-up	Recycle	Purge	Make-up	Recycle	Purge	Make-up	Recycle	Purge
(MMScfd)	1.548	53.382	0.001	8.123	41.547	3.691	29.478	195.63	17.61	79.013	110.68	1.109
	Compositions (vol%)			Compositions (vol%)			Compositions (vol%)			Compositions (vol%)		
H2	96.91	76.20	76.20	83.00	65.50	65.50	95.67	71.30	71.30	99.00	83.00	83.00
CH4	3.09	18.00	18.00	17.00	28.40	28.40	4.33	16.70	16.70	1.00	9.20	9.20
C2H6	0.00	1.80	1.80	0.00	1.50	1.50	0.00	3.00	3.00	0.00	1.10	1.10
C3H8	0.00	1.30	1.30	0.00	1.10	1.10	0.00	3.40	3.40	0.00	0.00	0.00
i-C4H10	0.00	0.20	0.20	0.00	0.20	0.20	0.00	0.60	0.60	0.00	0.00	0.00
n-C4H10	0.00	0.20	0.20	0.00	0.60	0.60	0.00	0.70	0.70	0.00	0.00	0.00
H2S	0.00	1.20	1.20	0.00	0.47	0.47	0.00	3.90	3.90	0.00	1.60	1.60
NH3	0.00	0.60	0.60	0.00	2.00	2.00	0.00	0.40	0.40	0.00	5.10	5.10
PC1-NHT	0.00	0.30	0.30	0.00	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.00
PC2-NHT	0.00	0.10	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC3-NHT	0.00	0.10	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC4-NHT	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
PC5-NHT	0.00	0.00	0.00	0.00	0.05	0.05	0.00	0.00	0.00	0.00	0.00	0.00
PC1-CNHT	0.00	0.00	0.00	0.00	0.14	0.14	0.00	0.00	0.00	0.00	0.00	0.00
PC2-CNHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC3-CNHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC4-CNHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC5-CNHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC1-DHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC2-DHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC3-DHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC4-DHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PC5-DHT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-GA1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-GA2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 5.9 Detailed data of H2 consumers for base case (Continued)

	NHT			CNHT			DHT			HC		
Flowrate	Make-up	Recycle	Purge	Make-up	Recycle	Purge	Make-up	Recycle	Purge	Make-up	Recycle	Purge
(MMScfd)	6.675	27.61	5.34	7.788	32.22	3.32	25.09	155.92	12.8	84.51	67.75	7.89
	Compositions (vol%)			Compositions (vol%)			Compositions (vol%)			Compositions (vol%)		
HC-GA3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-GA4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-GA5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-NAP1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-NAP2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-NAP3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-NAP4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-NAP5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-DIE1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-DIE2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-DIE3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-DIE4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HC-DIE5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 5.10 Data comparison between base case and optimisation results

		Make-up		Recycle		Purge	
		Flowrate (MMScfd)	H2 Purity (vol%)	Flowrate (MMScfd)	H2 Purity (vol%)	Flowrate (MMScfd)	H2 Purity (vol%)
NHT	Base case	6.675	83%	27.61	76.57	5.34	76.57
	Optimal result	1.548	96.91	53.382	76.2	0.001	76.2
	Deviation	-5.127	N/A	25.772	-0.37	-5.339	-0.37
CNHT	Base case	7.79	83	32.22	66.48	3.32	66.48
	Optimal result	8.123	83	41.55	65.5	3.691	65.5
	Deviation	0.333	0	9.33	-0.98	0.371	-0.98
DHT	Base case	25.09	99	155.92	71.38	12.8	71.38
	Optimal result	29.478	95.67	195.632	71.3	17.61	71.3
	Deviation	4.388	-3.33	39.712	-0.08	4.81	-0.08
HC	Base case	84.51	99	67.75	81.72	7.89	81.72
	Optimal result	79.013	99	110.68	83	1.109	83
	Deviation	-5.497	0	42.93	1.28	-6.781	1.28

Compared with the base case, NHT recycle is increased from 27.61MMscfd to 53.382MMscfd in the optimised network while CNHT recycle increased from 32.22MMscfd to 41.55MMscfd, DHT recycle increased from 155.92MMscfd to 195.632MMscfd, and HC recycle increased from 67.75MMscfd to 110.677MMscfd. The purity of the recycles remains almost the same, so the flowrate can represent the improvements made on recycles. The make-up hydrogen requirement of NHT and HC are considerably reduced, while CNHT and DHT are similar to the base case.

In the meantime, the purged gas from NHT and HC has also been significantly reduced in order to reduce the hydrogen loss to the site fuel system. Note that the purge gas is not reduced for all hydrogen consumers, because the overall hydrogen network mass balance must be maintained.

Reactor inlet conditions for a hydrogen consumer include H2/Oil ratio and H2 partial pressure which are very sensitive to the performance of a hydrogen consumer. The H2/Oil ratio and H2 partial pressure have to be maintained in the optimal design in order to fulfil the reactor operation requirements. In this work the liquid feedstock is considered as constant so that H2/Oil ratio would be determined only by the pure H2 flowrate going into the reactor. On the other hand, H2 partial pressure will be determined by the H2 purity at reactor inlets.

Table 5.11 Reactor inlet conditions comparison

	Reactor Inlets	Base case	Optimal result	Deviation	Er%
NHT	H2 purity	0.47	0.48	0.01	1.70
	Pure H2 flowrate	40.27	41.45	1.18	2.94
CNHT	H2 purity	0.52	0.54	0.02	3.63
	Pure H2 flowrate	32.89	33.94	1.05	3.19
DHT	H2 purity	0.63	0.64	0.02	2.39
	Pure H2 flowrate	162.85	167.73	4.87	2.99
HC	H2 purity	0.73	0.75	0.02	2.47
	Pure H2 flowrate	142.98	147.59	4.61	3.22

Table 5.11 shows the reactor inlet conditions for both the base case and the optimised H2 network design with detailed information about H2 purities and pure H2 flowrates at reactor inlets of all hydrogen consumers. The absolute and relative deviations of H2/Oil ratio and H2 purity between the optimal result and the base case (optimal result – base case) are shown in Table 5.11.

In the reactor inlet conditions comparison it is clear that the hydrogen purity and H2/Oil ratio at each consumer's reactor inlet in the optimised hydrogen network are all slightly improved by 1-3% which will not have negative effects on the operation of the hydrogen consumers. Therefore both H2/Oil ratio and H2 partial pressure are well maintained, which indicates the optimisation result is feasible and reliable under practical constraints. In this case study, it is suggested to maintain the H2 partial pressures while increase the H2/Oil ratios at reactor inlets to optimise a hydrogen consumer leading to better hydrogen utilization for the whole hydrogen network.

5.3 Methodology Comparison with Simulated Annealing

Apart from gradient-based deterministic methods such as NLP or MINLP approaches, there are also other optimisation methods that can deal with hydrogen network optimisation problems, for example stochastic methods, especially the simulated annealing (SA).

SA has been applied to solve optimisation problems such as heat exchanger network design (Chen, 2007). Since the successful history has proven the capability of SA in solving various optimisation problem, In 2009, Loughrey has tried to use SA to optimise a refinery hydrogen network. In this section, the SA hydrogen network optimisation is compared with NLP hydrogen network optimisation to check for the performance differences of these two methods when dealing with detailed hydrogen network optimisation problems.

5.3.1 Brief Introduction of Simulated Annealing

The simulated annealing algorithm is known as a generic probabilistic meta-algorithm for global optimisation problems. It is famous for its ability to locate global or near-global optimum solution within large searching space. Typically the simulated annealing method is used to solve non-convex, integer involved or discrete optimisation problems to which gradient-based methods such as NLP or MINLP are not effective. For most of integer involved discrete optimisation problem, simulated annealing has proven its considerable advantages compared with gradient-based approaches.

The name of SA comes from theory of annealing metallurgy, a technical process that melts metal into crystal by using high initial temperature and slow cooling procedure. During the melting process, atoms system would become a disorder through all states of energy because of the heat. In the following, controlled cooling method is required to slow down the cooling procedure so that the system configuration with lower internal energy than initial would be able to be achieved.The relationship between energy states and temperatures can be expressed as the Boltzmann-Gibbs distribution:

$$P_{energy} = C_T \exp\left(\frac{x}{c_B T_a}\right) \tag{5.8}$$

Where P_{energy} is the probability that a system is in a state x, C_T is partition function, x is energy state, C_B is Boltzmann's constant and T_a is temperature.

As can be seen from Equation 5.8, the temperature would change with energy states accordingly. In addition, at a higher temperature there will be much higher probability for the system to be with a higher energy state, resulting in higher mobility for atoms. Conversely, when the temperature starts to decrease, the probability of the system with a high energy state will be consistently reduced and if the cooling process is controlled slow enough allowing the whole system to be in thermodynamic equilibrium at any time approximately, the metal can be crystallized with minimum internal energy. However, this kind of annealing technique requires rigorous conditions for initial temperature and sufficiently slow cooling. Therefore, failure of satisfying either condition can allow metal to be formed as glassy meta-stable structure rather than wanted crystalline state.

By exploiting the metal annealing process, the idea of connecting this to mathematical optimisation was first investigated by Kirkpatrick who proposed analogies between physical annealing process and an optimisation problem (Kirkpatrick, 1983). Then it was Spall that introduced the general algorithm of SA as the first systematic SA method for optimisation problems (Spall, 2003). By making use of a global parameter to take control of the whole optimisation procedure, the proposed algorithm is able to locate global optimum or near-global optimum solutions, which has been convinced as the most advantages for SA against gradient-based approaches. By taking not only improved objective values but also worse objective values into account, the SA optimisation is able to overcome local optimums with additional freedom to exploit a solution space.

5.3.2 SA Parameters

SA parameters are important because it will affect the problem solving procedure sensitively. The selection of parameters can vary from problem to problem. The most important parameters to be used in the hydrogen network design problem are:

- Acceptance criteria

- Initial annealing temperature
- Cooling schedule
- Markov chain length
- Termination criteria

5.3.3 SA Moves

In the superstructure based optimisation algorithm, SA moves can be extremely important as it will determine the scale of the searching space. In the SA optimisation procedure, each move will introduce a new design and the system will be changed therefore the moves for SA is very sensitive to the optimisation and defining moves is quite important.

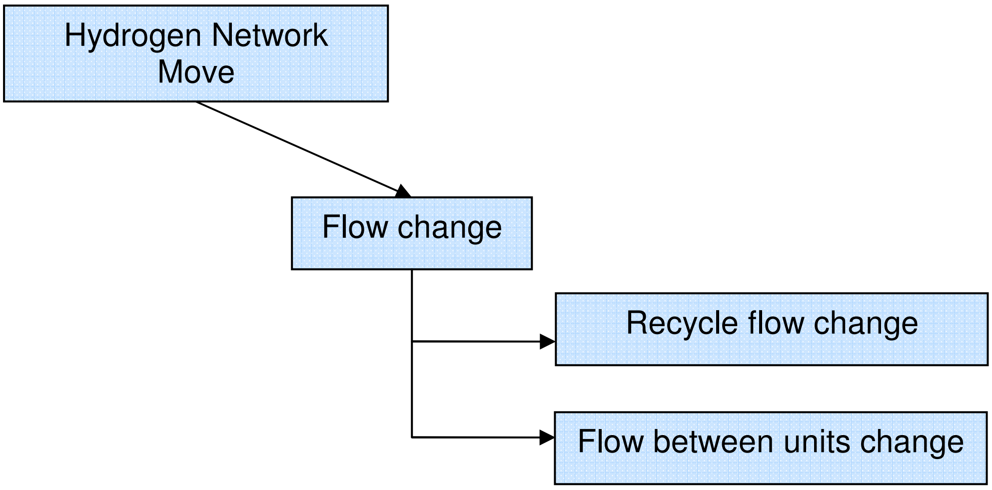

Figure 5.9 SA moves for hydrogen network optimisation

For a hydrogen network optimisation problem, the key consideration of moves would be changes in flow which can be classified into two groups: recycle flow change and flow between units change. The moves are made based on random number generated and also affected by the probability for each particular move. The move probabilities depend on the influence factor of the variables. The higher the variable's influence, the higher probability of the move.

According to the complexity of the hydrogen network optimisation problem, the move tree shown in Figure 5.9 can be extended to cover more variables. For example, to take into account pressure consideration or piping, we could possibly add in more relevant variables into the move tree.

5.3.4 Modelling Comparison with NLP Methodology

Although most of the hydrogen network model are exploit the same idea as that of the NLP methodology, there is a key difference for the individual hydrogen consumer model in SA.

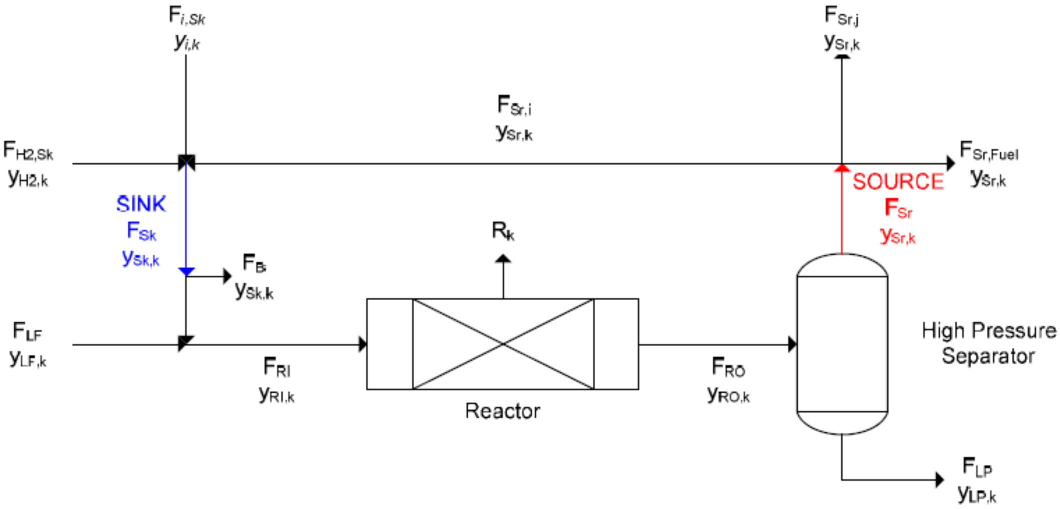

Figure 5.10 SA moves for hydrogen network optimisation

Unlike the hydrogen consumer model in NLP method, the SA model has incorporated two new variables at the mix point of the make-up and recycle stream before merging with the liquid feed. The two new added variables, F_B and Ysk, are used to act as slack variables to help convergence at the inlet of the reactor. Since the model is based on multi-component configuration, the convergence can be difficult due to too many mass balance and material balance requirements.

Sometimes SA fails to generate moves leading to no feasible solution only because of tiny errors in mass balance calculations which actually can be tolerated. Therefore, to improve the optimisation calculation efficiency and overcome unnecessary constraints, these two slack variables are introduced to balance the calculation at the inlet of reactors at any time when required. To obtain a feasible solution, in the SA objective functions all slack variables will be involved and minimized until the preset tolerance is met. The hydrogen network distribution balance model and the super-structure model adopted in SA are similar to the modelling used in the NLP method.

5.3.5 Case Study Comparison

The base case that carried out for SA optimisation is exactly the same as the one used in the NLP method as shown in Figure 5.5. In this four-consumer hydrogen network system, 20 continuous manipulated variables are involved with implementation of SA. The modelling and optimisation are completed in ***MATLAB***.

SA parameters have been set for optimisation. Table 5.12 shows all the information about the SA parameters used in this hydrogen network optimisation. The parameters for cooling rate and penalty are adjusted slightly lower due to the problem complexity.

Table 5.12 SA parameters selection

Parameter	Value
Initial temperature	1,000,000
Cooling rate	0.01
Markov chain length	30
Final temperature	0.0001
Move probability	50%
Penalty	0.001

As a stochastic algorithm, SA works much slower than NLP algorithms. For this four-consumer hydrogen network optimisation problem, it normally takes 10 – 11 hours to finish a scenario. Some key features are included in this SA optimisation:

- Hydrogen pinch analysis
- Integrated Flash calculation
- Constant K-values strategy

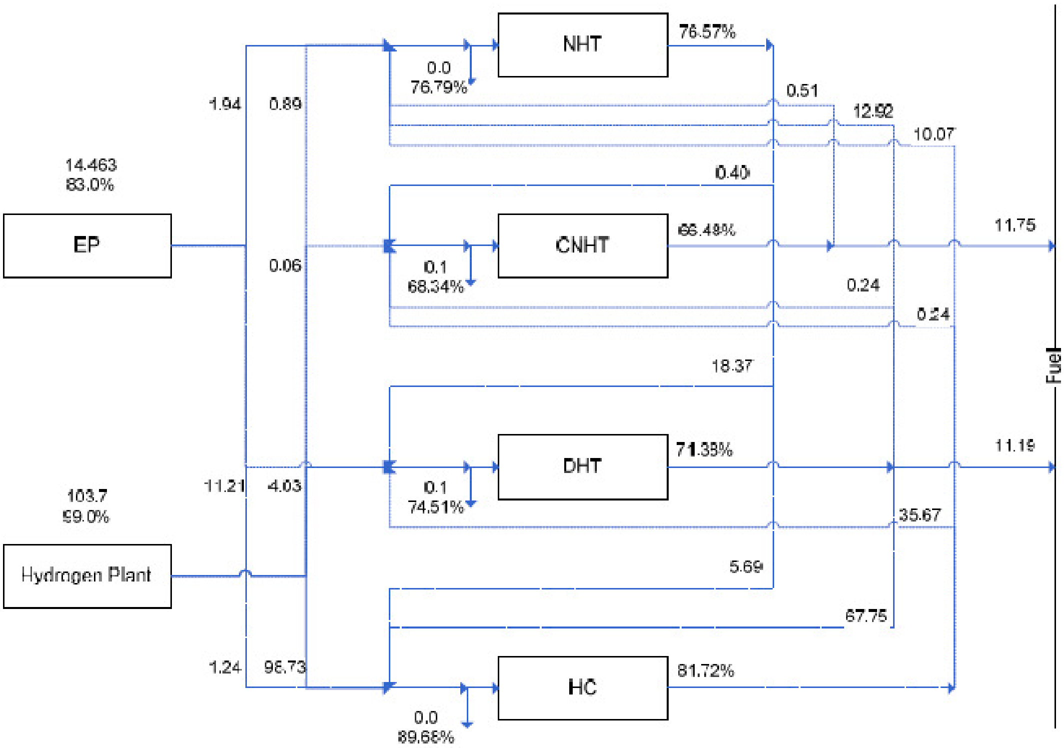

Figure 5.11 SA optimisation solution

SA generates an optimised hydrogen network as shown in Figure 5.11. Compared with the base case flowsheet, the optimisation result flowsheet shows a much complicated configuration with 11 new connections between hydrogen consumers.

Table 5.13 Network connections summary

	NHT	CNHT	DHT	HC	Fuel
NHT	0	0	18.37	5.69	0
CNHT	0.51	0	0	0	11.75
DHT	12.92	0.24	0	67.75	11.19
HC	10.07	0.24	35.67	0	0

Table 5.13 gives a summary of the optimised hydrogen network connections between processing units. The detailed data can be found in table 5.14.

Table 5.14 Detailed data for SA optimal solution

		NHT	**CNHT**	**DHT**	**HC**
Hydrogen Plant	FH2 (MMscfd)	0.89	0.06	4.03	98.73
	YH2 (vol%)	99.00	99.00	99.00	99.00
CCR	FH2 (MMscfd)	1.94	0.05	11.21	1.24
	YH2 (vol%)	83.00	83.00	83.00	83.00
Make-up	F_M (MMscfd)	26.33	17.52	69.31	121.95
	Y_M (vol%)	76.51	74.26	78.13	94.31
Recycle	F_r (MMscfd)	27.61	32.22	155.92	67.75
	Y_r (vol%)	76.57	66.48	71.38	81.72
Purge	F_P (MMscfd)	24.51	12.31	57.15	46.00
	Y_P (vol%)	76.57	66.48	71.38	81.72
Sink	F_{Sk} (MMscfd)	53.93	49.67	225.11	189.69
	Y_{Sk} (vol%)	76.79	68.34	74.51	89.68
Source	F_{Sr} (MMscfd)	52.12	44.53	213.07	113.74
	Y_{Sr} (vol%)	76.57	66.48	71.38	81.72

In the optimum solution from SA, 6.18MMscfd hydrogen from the H2 plant has been saved. The minimum hydrogen plant requirement is reduced from 109.6MMscfd to 103.7MMscfd. The SA hydrogen saving is almost the same as the NLP optimisation.

Similarly as the NLP method, the optimisation result is compatible with the minimum hydrogen target 102.4MMscfd given by the hydrogen pinch analysis. This confirms that SA is able to optimise a multi-component hydrogen network.

5.3.6 Methodology Comparisons

Taking into account all of the discussed aspects, we can summarise the methodology comparisons between NLP and SA into Table 5.15.

From the result point of view, the two methods both performed well and with almost the same optimum output. The NLP optimisation solution introduced 2 new connections, while SA uses 11 new connections, bringing in more complexity to the design.

Table 5.15 Detailed data for optimal solution

Methodology	NLP	Simulated Annealing
Minimum hydrogen generated	103.69	103.7
New connections introduced	2	11
CPU run time	10 - 20s	10 - 11 hours
Solution complexity	easy	difficult
Extension to mixed integer problems	limited	flexible

The NLP methodology has huge advantage on CPU run time, which only needs a few seconds to reach an optimum solution. Conversely, each scenario in SA will require around 10 to 11 hours to be completed.

Nevertheless, SA is more flexible than NLP and is more adaptable to different types of problems especially for MINLP problems. Currently the hydrogen network is optimised without integer variables. However in the future, when pressure or piping consideration needs to be included, then there must be binary variables required. Therefore the problem would be an MINLP problem. In this case, SA can be easily extended by introducing more new moves while deterministic methods may struggle to converge for an MINLP problem.

5.4 Summary

By incorporating the detailed hydrogen consumer model, overall hydrogen network modelling is developed under multi-component considerations, with integrated flash calculation and variable H2/Oil ratio and H2 partial pressure configuration.

The proposed NLP methodology for the multi-component H2 network works well, and generates good results which is fully verified by simulation to confirm the feasibility of reactor performance and network configuration.

In addition, the NLP is compared with SA as an optional optimisation engine for the same case study. SA and NLP both work well with the multi-component cases and generate good results. NLP optimisation is faster in speed but with limited ability to cope with complicated problems, for example MINLP problems. However, simulated annealing is much slower, but with great flexibility for all kinds of problems and tends to produce near-global optimum solutions. It can be concluded that the solver selection should be dependent on the types of problems.

Chapter 6 Conclusions and Future work

6.1 Conclusions

In this thesis a few key improvements have been made to overcome the drawbacks in existing methods. Firstly, a binary hydrogen network optimisation methodology with variable H2 partial pressure and H2/Oil ratio is proposed. Secondly, a detailed hydrogen consumer model is developed under multi-component consideration. Finally, based on the proposed detailed hydrogen consumer model, a multi-component hydrogen network optimisation methodology is proposed.

For a binary component hydrogen network optimisation problem, H2/Oil ratio and H2 partial pressure of each hydroprocessor can be slightly relaxed to obtain extra flexibility. The variable H2/Oil ratio and H2 partial pressure strategy has been proposed, verified, and tested with a industrial case study in Chapter 3. This method is effective when dealing with over-constrained network optimisation problems.

For hydroprocessor modelling, a detailed hydrogen consumer model has been developed. To overcome the drawbacks of existing models, the reaction modelling has incorporated light hydrocarbon production to obtain a better reflection of the reality. Integrated flash calculation has been introduced into a flash separator model for more efficient computation. By combining the improved detailed hydrogen consumer models with a hydrogen plant model and site fuel system, an overall hydrogen network model can be constructed. By taking into account all of the improvements discussed above, this model can be considered as the most detailed model for hydrogen network optimisation so far.

On the basis of the detailed hydrogen network model, a multi-component hydrogen network optimisation methodology is developed. A gradient-based deterministic NLP solver is able to solve the network optimisation problem and produce solutions efficiently. As another option, stochastic simulated annealing was also tried to solve the same optimisation problem. By comparing the two optimisation methods it is found out that each of them has its advantages and disadvantages, and the methodology selection should be dependent on the types of problems. Generally deterministic methods are faster in computation, while stochastic methods can be more effective when dealing with problems that contain many discrete decisions.

6.2 Future Work

The current hydrogen network optimisation methodology is based on single-period operation. However in a realistic refinery the operation is always changing. Therefore the developed methodology should be extended to multi-period hydrogen network operation.

Currently the performance of an individual hydrogen consumer model is fixed by fixing the hydrogen consumption in reactors to simplify the H2 network optimisation problem. However the performance of a hydrogen consumer can be improved by optimising the reactor inlet conditions. For example, if the H2/Oil ratio or H2 partial pressure is increased the hydrogen consumer could have better yield, better hydrodesulphurisation and hydrodenitrogenation performance and also better olefins and aromatics saturation, at the expense of more H2 consumption. Such trade-offs are not included in the current hydrogen network optimisation technology.

Using hydrogen more effectively rather than just saving H2 is the ultimate goal of refinery hydrogen management, which can only be achieved by proper integration between hydroprocessing reactions and hydrogen networks.

Nomenclature

CMU	Total power consumption of make-up hydrogen compression of a consumer
CRE	Power consumption of compressors of a consumer
E_f	Compression efficiency
PCMU	Power rate of make-up compressors of a consumer
PCRE	Power rate of recycle compressors of a consumer
F	Flowrates of a stream
Y	compositions of a stream
FC	Total reactor inlet flowrate of a consumer
FI	Total flowrate of hydrogen producers
FIK	Hydrogen flowrate from a producer to a purifier
FIJ	Hydrogen flowrate from a producer to a consumer
FIN	Hydrogen flowrate from a producer to a header
FJ	Hydrogen flowrate from a consumer high pressure purge to a consumer
FJK	Hydrogen flowrate from a consumer high pressure purge to a purifier
FJP	Hydrogen flowrate from a consumer high pressure purge to site fuel
FJL	Hydrogen flowrate from a consumer low pressure purge to a consumer
FJLK	Hydrogen flowrate from a consumer low pressure purge to a purifier
FJLN	Hydrogen flowrate from a consumer low pressure purge to a header
FJLP	Hydrogen flowrate from a consumer low pressure purge to site fuel
FJN	Hydrogen flowrate from a consumer high pressure purge to a header
FKJ	Hydrogen flowrate from a purifier to a consumer
FKMAX	Maximum limit of a purifier

FKN	Hydrogen flowrate from a purifier to a header
$FMUMAX$	Maximum limit of hydrogen make-up stream flowrate
FNJ	Hydrogen flowrate from a header to a consumer
K	Vapour liquid equilibrium (K-values)
YC	Hydrogen purity at the reactor inlet of a consumer
YI	Hydrogen purity of hydrogen produced from a hydrogen producer
YJ	Hydrogen purity of high pressure purge hydrogen of a consumer
$RECP$	Hydrogen recovery rate of a purifier
YJL	Hydrogen purity of low pressure purge hydrogen of a a consumer
YN	Hydrogen purity of a header
YK	Hydrogen purity of a purifier

Subscripts

$feed$	Liquid feedstock
fi	Flash inlet
$H2C$	Hydrogen consumer
$H2P$	Hydrogen producer
i	A hydrogen producer (Chapter 3); a component (Chapter 4 and 5)
$imin$	Hydrogen production minimum limit of a producer
$imax$	Hydrogen production maximum limit of a producer
j	A hydrogen consumer
$j1$	Alias of subscript j
$jmin$	Reactor inlet hydrogen minimum limit of a consumer
$jmax$	Reactor inlet hydrogen maximum limit of a consumer
k	A purifier (Chapter 3); A producer (Chapter 5)
Liq	Liquid
mix	Mix point
mu	Make-up
n	A header

pu	Purge
re	Recycle
ri	Reactor inlet
SF	Site fuel
U	Unit price
vap	Vapour

Superscripts

L	Lower bound
U	Upper bound

Abbreviations

ADU	Atmospheric distillation unit
BFW	Boiler feed water
CCR	Catalytic reformer
CNHT	Cracked naphtha hydrotreater
CRU	Catalytic reformer unit
CW	Cooling water
DCU	Delayed coker unit
FCC	Fluid catalytic cracker
GA	Generic algorithm
HC	Hydrocracker
HCU	Hydrocracker unit
HDA	Hydrodealkylation
HT	Hydrotreater
LP	Linear programming
KHT	Kerosene hydrotreater
LPG	Liquid petroleum gas
MILP	Mixed integer linear programming
MINLP	Mixed integer non-linear programming
NHT	Naphtha hydrotreater
NLP	Non-linear programming
OBJ	Objective function

PSA	Pressure swing adsorption
SA	Simulated Annealing
VDU	Vacuum distillation unit
VR	Vacuum residue

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Appendix A Binary H2 network optimisation program codes (GAMS)

```
option NLP=minos5;

Set
i       H2 producers/HP1, HP2, HP3, HP4 /
j       H2 consumers/HC1, HC2, HT1, HT2, HT3, HT4, HT5, HT6, HT7/
k       Purifiers/PSA, MEM/
n       H2 mains/12Bar, 24Bar/
;

Alias (j, j1);

Parameters
FH2S(i)  H2 producer flow Nm3h-1/
HP1     60000
HP2     10000
HP3     167391
HP4     35720
/

YH2S(i)  H2 producer purity/
HP1     91.59
HP2     91.59
HP3     99.9
HP4     92
/

PH2S(i)  H2 producer pressure MPa/
HP1     1.3
HP2     1.7
HP3     2.4
HP4     2.8
/


CH2S(i)  H2 producer price RMB.Nm3-1/
HP1     1.118297505
HP2     1.118289637
HP3     1.220978826
HP4     1.123301936
/

FH2C(j)  H2 consumer reactor inlet flow Nm3h-1/
HC1     158931
```

```
HC2      501616
HT1     109728
HT2     126995
HT3     3237
HT4     298
HT5     408747
HT6     154944
HT7     11733
/

YH2C(j)  H2 consumer reactor inlet purity/
HC1     84.22
HC2     94.89
HT1     87.11
HT2     84.46
HT3     92
HT4     91
HT5     94.19
HT6     81.22
HT7     88.29

/

PH2C(j)  H2 consumer reactor inlet pressure MPa/
HC1    17.5
HC2    17.5
HT1     4.6
HT2     7
HT3     2.5
HT4     5.3
HT5     16.4
HT6     11.5
HT7     6.5

/

FH2V(j)  H2 consumer high pressure flash vapor flow Nm3h-1/
HC1     125354
HC2     407628
HT1     96609
HT2     95246
HT3     0
HT4     0
HT5     359250
HT6     123433
HT7     8762
/

YH2V(j)  H2 consumer high pressure flash vapor purity/
HC1      81.57
```

```
HC2    93.73
HT1    85.5
HT2    82.2
HT3    91
HT4    91
HT5    93.4
HT6    76.45
HT7    85.4u

/

PH2V(j)  H2 consumer high pressure flash vapor pressure MPa/
HC1     15.6
HC2     15.6
HT1      3.9
HT2      6.5
HT3      1.5
HT4      5.3
HT5      15.6
HT6      10
HT7      6

/

FH2L(j)  H2 consumer low pressure purge flow Nm3h-1/
HC1    2462
HC2    7440
HT1    954
HT2    4445
HT3    0
HT4    0
HT5    7000
HT6    2165
HT7    686

/

YH2L(j)  H2 consumer low pressure purge purity/
HC1    70.0
HC2    85.32
HT1    67.25
HT2    56.58
HT3    70
HT4    70
HT5    90.0
HT6    66.29
HT7    68

/
```

```
PH2L(j)  H2 consumer low pressure purge pressure MPa/
HC1    1.95
HC2    1.95
HT1    1.2
HT2    1.5
HT3    0
HT4    0.45
HT5    2.1
HT6    2.5
HT7    1.4

/

PCMUI(j) Inlet pressure of make-up compressors of hydrogen consumers/
HC1    1.1
HC2    1.1
HT1    1.15
HT2    1.2
HT3    2.5
HT4    1.2
HT5    2.2
HT6    2.2
HT7    1.2

/

PCMUO(j) Outlet pressure of make-up compressors of hydrogen
consumers/
HC1    18.1
HC2    18.1
HT1    5.8
HT2    7.8
HT3    2.5
HT4    6.5
HT5    17.35
HT6    11.9
HT7    7.3

/

PCREI(j) Inlet pressure of recycle compressors of hydrogen consumers/
HC1    15.6
HC2    15.6
HT1    3.9
HT2    6.5
HT3    0
HT4    0
HT5    15.5
HT6    9.9
HT7    5.8
```

```
/

PCREO(j) Outlet pressure of recycle compressors of hydrogen consumers/
HC1    18.1
HC2    18.1
HT1    5.8
HT2    7.8
HT3    0
HT4    0
HT5    17.35
HT6    11.9
HT7    7

/

PPO(k)   Purification outlet pressure MPa/
PSA      2.4
MEM      1.2
/

RECP(k)  Purification recovery/
PSA      0.9
MEM      0.9
/

YH2P(k)  Purity of H2 purification/
PSA      99.9
MEM      89
/

Pmax(k)  Purification max flow/
PSA      60000
MEM      10000
/

FH2Smax(i)  H2 producer max flow Nm3h-1/
HP1      50700
HP2      15000
HP3      60000
HP4      29500
/

FH2Smin(i)  H2 producer min flow Nm3h-1/
HP1      50700
HP2      15000
HP3      0
HP4      29500
/
```

```
CMUmax(j) Maximum make-up flow of hydrogen consumers Nm3/
HC1    48000
HC2    110000
HT1    16000
HT2    42017
HT3    7000
HT4    4000
HT5    60602
HT6    44000
HT7    9001

/

PPCMU(j) Power rate of make-up compressors of hydrogen consumers
kW.Nm3-1/
HC1    0.1333
HC2    0.1149
HT1    0.07
HT2    0.09524
HT3    0
HT4    0.0875
HT5    0.1096
HT6    0.0971
HT7    0.1111

/

PPCRE(j) Power rate of recycle compressors of hydrogen consumers
kW.Nm3-1/
HC1    0.0103
HC2    0.01003
HT1    0.019
HT2    0.0117
HT3    0
HT4    0
HT5    0.0129
HT6    0.01043
HT7    0.0154

/

PH2M(n)  Pressure of H2 mains MPa/
12Bar   1.2
24Bar   2.4
/
;

Variables
FH2    Total H2 production Nm3.hr-1
Cost   Total H2 production cost RMB
```

```
;

Positive variables
FI(i)          Total flowrate of producer i Nm3.h-1
FIJ(i,j)       Flowrate from producer i to consumer j Nm3.h-1
FIK(i,k)       Flowrate from producer i to purifier k Nm3.h-1
FIN(i,n)       Flowrate from producer i to H2 main n Nm3.h-1
FNJ(n,j)       Flowrate from H2 main n to consumer j Nm3.h-1
FJ(j,j1)       Flowrate from consumer j to consumer j1 Nm3.h-1
FJN(j,n)       Flowrate from consumer j to H2 main n Nm3.h-1
FJK(j,k)       Flowrate from consumer j to purifier k Nm3.h-1
FJL(j,j1)      Flowrate from low pressure flash of consumer j to consumer
j1 Nm3.h-1
FJNL(j,n)      Flowrate from low pressure flash of consumer j to H2 main n
Nm3.h-1
FJKL(j,k)      Flowrate from low pressure flash of consumer j to purifier k
Nm3.h-1
FKJ(k,j)       Flowrate of purifier k to consumer j Nm3.h-1
FKN(k,n)       Flowrate of purifier k to H2 main n Nm3.h-1
FPH(j)         Flowrate of high pressure H2 purge from consumer j Nm3.h-1
FPL(j)         Flowrate of low pressure H2 purge from consumer j Nm3.h-1
YN(n)          Purity of H2 main n
CMU(j)         Power cost of make-up compressors
CRE(j)         Power cost of recycle compressors
;

Equations
MFI(i)         Mass balance of H2 producer i
MaxFI(i)       Maximum flow of producer i
MinFI(i)       Minimum flow of producer i
MFN(n)         Mass balance of H2 main n
MHN(n)         H2 balance of H2 main n
*MFJR(j)       Mass balance of consumer j reactor inlet
MHJR(j)        H2 balance of consumer j reactor inlet
MFJF(j)        Mass balance of consumer j high pressure flash
MFJL(j)        Mass balance of consumer j low pressure purge
MFK(k)         Mass balance of purifier k
FPmax(k)       Max. flowrate of purifier products
FMUmax(j)      Max. flowrate of make-up flows
CCMU(j)        Power cost of make-up compressors
CCRE(j)        Power cost of recycle compressors

OBJ      Objective function
;

MFI(i)..       FI(i) =e= sum(j, FIJ(i,j))+sum(n, FIN(i,n))+sum(k, FIK(i,k));
MaxFI(i)..     FI(i) =l= FH2Smax(i);
MinFI(i)..     FI(i) =g= FH2Smin(i);
MFN(n)..       sum(i, FIN(i,n))+sum(j, FJN(j,n)+FJNL(j,n))+sum(k, FKN(k,n))
=e= sum(j, FNJ(n,j));
```

```
MHN(n)..      sum(i,FIN(i,n)*YH2S(i))+sum(j,FJN(j,n)*YH2V(j)
+FJNL(j,n)*YH2L(j))+sum(k, FKN(k,n)*YH2P(k)) =e= sum(j, FNJ(n,j)*YN(n));

MHJR(j)..     FH2C(j)*YH2C(j) =e= sum(i, FIJ(i,j)*YH2S(i))+sum(j1,
FJ(j1,j)*YH2V(j1)+FJL(j1,j)*YH2L(j1))+sum(k, FKJ(k,j)*YH2P(k)) + sum(n,
FNJ(n,j)*YN(n));

MFJF(j)..      FH2V(j) =e= sum(j1, FJ(j,j1))+sum(k, FJK(j,k))+sum(n,
FJN(j,n))+FPH(j);

MFJL(j)..      FH2L(j) =e= sum(j1, FJL(j,j1))+sum(k, FJKL(j,k))+sum(n,
FJNL(j,n))+FPL(j);

MFK(k)..       (sum(j, FJK(j,k)*YH2V(j)+FJKL(j,k)*YH2L(j))+sum(i,
FIK(i,k)*YH2S(i)))*RECP(k) =e= (sum(j, FKJ(k,j))+sum(n,
FKN(k,n)))*YH2P(k);

FPmax(k)..    (sum(j, FKJ(k,j))+sum(n, FKN(k,n))) =l= Pmax(k);
FMUmax(j)..  FH2C(j) - FJ(j,j) =l= CMUmax(j);

CCMU(j)..     CMU(j) =e= 0.6*PPCMU(j)*(sum(i, FIJ(i,j))+sum(j1$(ord(j1) ne
ord(j)), FJ(j1,j))+sum(k, FKJ(k,j))+sum(n, FNJ(n,j))+sum(j1, FJL(j1,j)));

CCRE(j)..     CRE(j) =e= 0.6*PPCRE(j)*FJ(j,j);

OBJ..           FH2 =e= sum(i, FI(i)*CH2S(i))-sum(j,
FPH(j)*(0.5720631*YH2V(j)+1.78571232*(100-YH2V(j)))
       +FPL(j)*(0.5720631*YH2L(j)+1.78571232*(100-YH2L(j))))/100 -
sum(k, sum(j,(FJK(j,k)*YH2V(j)+FJKL(j,k)*YH2L(j))
       +sum(i, FIK(i,k)*YH2S(i)))*(1-RECP(k))*0.5720631/100)
       - (sum((j,k),FJK(j,k)+FJKL(j,k))+sum((i,k), FIK(i,k))- (sum((i,k),
FIK(i,k)*YH2S(i)/100)
       +sum((j,k), (FJK(j,k)*YH2V(j)+FJKL(j,k)*YH2L(j))/100)))*1.78571232
       + sum(j, CMU(j)+CRE(j));

model M /all/;

FIJ.fx('HP3',j) =0;
FIJ.fx('HP1',j) =0;
FIJ.fx(' HP2',j) =0;

FIN.fx('HP3','12Bar') =0;

FIN.fx(' HP4','12Bar') =0;
FIJ.fx(' HP4',j) =0;

FJ.fx(j,j1)$(ord(j) ne ord(j1)) = 0;

FNJ.fx('12Bar',' HT6 ') =0;
FNJ.fx('12Bar',' HT5') =0;
```

```
FNJ.fx('12Bar','HC2') =0;
FNJ.fx('24Bar','HC1') =0;
FNJ.fx('24Bar','HT7') =0;
FNJ.fx('24Bar','HT1') =0;
FNJ.fx('24Bar','HT2') =0;
FNJ.fx('24Bar','HT4') =0;

FNJ.fx('24Bar','HT7') =0;


FJK.fx(j,k) =0;
FJKL.fx(j,'MEM') =0;
FJN.fx(j,'24Bar') =0;

FIN.fx('HP1','24Bar') =0;
FIN.fx(' HP2','24Bar') =0;

FJNL.fx(j,'24Bar') =0;

FPH.fx(j) =0;

FJL.fx(j,j1) =0;

FKJ.fx('PSA','HC2') =0;
FKJ.fx('PSA',' HT6 ') =0;
FKJ.fx('PSA',' HT5') =0;

FKN.fx('PSA','12Bar') =0;
FIK.fx(i,k)$(ord(i) ne 6) =0;
*FIK.fx(i,k) =0;

*FI.fx('HP3') = 22800;

Solve M using NLP minimizing FH2;
Solve M using NLP minimizing FH2;
*Solve M using NLP minimizing FH2;
*Solve M using NLP minimizing FH2;
*Solve M using NLP minimizing FH2;
*Solve M using NLP minimizing FH2;

display FI.l, FIJ.l, FIK.l, FIN.l, FJ.l, FJL.l, FNJ.l, FJK.l, FJKL.l, FKN.l, YN.l,
        FKJ.l, FJN.l, FJNL.l, FPH.l, FPL.l;

parameter YH2CC(j) Calculated reactor inlet purities;

YH2CC(j) = (sum(i, FIJ.l(i,j)*YH2S(i))+sum(j1, FJ.l(j1,j)*YH2V(j1)+
          FJL.l(j1,j)*YH2L(j1))+sum(k, FKJ.l(k,j)*YH2P(k)) + sum(n,
FNJ.l(n,j)*YN.l(n)))/
          (sum(i, FIJ.l(i,j))+sum(j1, FJ.l(j1,j)+FJL.l(j1,j))+sum(k, FKJ.l(k,j)) +
sum(n, FNJ.l(n,j)));
```

```
parameter FH2CC(j) Calculated reactor inlet flows;

FH2CC(j) =  sum(i, FIJ.l(i,j))+sum(j1, FJ.l(j1,j)+FJL.l(j1,j))+sum(k, FKJ.l(k,j))
+
          sum(n, FNJ.l(n,j));

parameter FPSA   PSA feed flowrate;

FPSA = sum(j, FJK.l(j,'PSA'))+ sum(j,FJKL.l(j,'PSA'))+sum(i, FIK.l(i,'PSA'));

parameter YRPSA PSA residue purity;

YRPSA = (sum(j, FJK.l(j,'PSA')*YH2V(j))+
sum(j,FJKL.l(j,'PSA')*YH2L(j))+sum(i, FIK.l(i,'PSA')*YH2S(i))
       -sum(j, FKJ.l('PSA',j)*99.9))/(FPSA-sum(j, FKJ.l('PSA',j)));

parameter CPC    Compression cost;

CPC = sum(j, CMU.l(j)+CRE.l(j))

display YH2CC, YH2C, FH2C, FH2CC, FPSA, YRPSA, CPC, FH2.l;
```

Appendix B Constant K-values simulation for verification

Base case K-values

	Yfeed (vol%)	Yliq (vol%)	Yvap (vol%)	K
H2	47.0500	1.0536	75.8800	72.0203
CH4	9.2900	1.7118	14.0300	8.1959
C2H6	1.2900	0.4185	1.8400	4.3970
C3H8	1.6900	1.1468	2.0200	1.7614
i-C4H10	0.5100	0.4033	0.5700	1.4133
n-C4H10	0.5400	0.6869	0.4500	0.6551
H2S	1.7600	0.4610	2.5300	5.4879
PC1-NHT	2.1900	19.2888	0.6400	0.0332
PC2-NHT	7.0400	21.1423	0.3200	0.0151
PC3-NHT	0.5000	2.0548	0.1500	0.0730
PC4-NHT	1.5000	20.4367	0.0667	0.0033
PC5-NHT	0.1000	0.4000	0.0200	0.0500
PC1-CNHT	1.0000	1.2903	0.1000	0.0775
PC2-CNHT	0.0000	0.0000	0.0000	0.0000
PC3-CNHT	0.0000	0.0000	0.0000	0.0000
PC4-CNHT	0.1000	0.5882	0.0100	0.0170
PC5-CNHT	0.0000	0.0000	0.0000	0.0000
PC1-DHT	0.0000	0.0000	0.0000	0.0000
PC2-DHT	0.0000	0.0000	0.0000	0.0000
PC3-DHT	0.0000	0.0000	0.0000	0.0000
PC4-DHT	0.0000	0.0000	0.0000	0.0000
PC5-DHT	0.0000	0.0000	0.0000	0.0000
HC-GA1	8.0000	1.0000	0.2000	0.2000
HC-GA2	0.4000	0.4858	0.0500	0.1029
HC-GA3	4.5000	4.5714	0.4000	0.0875
HC-GA4	2.5800	2.8124	0.1000	0.0356
HC-GA5	5.2000	6.1306	0.1200	0.0196
HC-NAP1	1.0000	1.5487	0.0700	0.0452
HC-NAP2	3.2000	3.4077	0.0316	0.0093
HC-NAP3	0.5600	9.0286	0.4063	0.0450
HC-NAP4	0.0000	0.0000	0.0000	0.0000
HC-NAP5	0.0000	0.0000	0.0000	0.0000
HC-DIE1	0.0000	0.0000	0.0000	0.0000
HC-DIE2	0.0000	0.0000	0.0000	0.0000
HC-DIE3	0.0000	0.0000	0.0000	0.0000
HC-DIE4	0.0000	0.0000	0.0000	0.0000
HC-DIE5	0.0000	0.0000	0.0000	0.0000

Simulation Scenario 1

	Yfeed (vol%)	Yliq (vol%)	Yvap (vol%)	K
H2	51.0500	1.1100	82.3500	73.9495
CH4	7.9500	1.6700	11.8800	7.1032
C2H6	1.1900	0.4100	1.6800	4.1215
C3H8	1.6800	1.5100	1.7800	1.1787
i-C4H10	0.6300	0.5200	0.6900	1.3166
n-C4H10	0.5800	0.6900	0.5100	0.7301
H2S	1.7600	0.6100	2.4700	4.0561
PC1-NHT	2.4500	25.6800	0.7004	0.0273
PC2-NHT	12.0000	15.2300	0.1747	0.0115
PC3-NHT	1.1000	12.0000	0.0611	0.0051
PC4-NHT	0.4500	0.5000	0.0010	0.0020
PC5-NHT	0.5000	5.6900	0.0048	0.0008
PC1-CNHT	0.2000	1.0000	0.0225	0.0225
PC2-CNHT	0.0000	0.0000	0.0000	0.0000
PC3-CNHT	0.0000	0.0000	0.0000	0.0000
PC4-CNHT	0.3700	0.5000	0.0004	0.0007
PC5-CNHT	0.0000	0.0000	0.0000	0.0000
PC1-DHT	0.0000	1.1100	82.3500	0.0000
PC2-DHT	0.0000	1.1100	82.3500	0.0000
PC3-DHT	0.0000	1.1100	82.3500	0.0000
PC4-DHT	0.0000	1.1100	82.3500	0.0000
PC5-DHT	0.0000	1.1100	82.3500	0.0000
HC-GA1	5.1500	10.0000	1.7734	0.1773
HC-GA2	3.5600	5.6800	0.5845	0.1029
HC-GA3	0.3200	0.5600	0.0346	0.0617
HC-GA4	2.2000	5.1200	0.1821	0.0356
HC-GA5	3.1200	5.5100	0.1079	0.0196
HC-NAP1	3.0400	4.2500	0.0981	0.0231
HC-NAP2	0.5800	1.2000	0.0111	0.0093
HC-NAP3	0.1200	0.5600	0.0020	0.0035
HC-NAP4	0.0000	0.0000	0.0000	0.0000
HC-NAP5	0.0000	0.0000	0.0000	0.0000
HC-DIE1	0.0000	0.0000	0.0000	0.0000
HC-DIE2	0.0000	0.0000	0.0000	0.0000
HC-DIE3	0.0000	0.0000	0.0000	0.0000
HC-DIE4	0.0000	0.0000	0.0000	0.0000
HC-DIE5	0.0000	0.0000	0.0000	0.0000

Simulation Scenario 2

	Yfeed (vol%)	Yliq (vol%)	Yvap (vol%)	K
H2	49.0500	1.0800	79.1200	73.0116
CH4	8.0100	1.7000	11.9500	7.0208
C2H6	1.2400	0.4400	1.7400	3.9813
C3H8	1.7000	1.5200	1.8000	1.1882
i-C4H10	0.6200	0.5100	0.6900	1.3388
n-C4H10	0.5600	0.6900	0.4700	0.6833
H2S	1.7700	0.5600	2.5200	4.5042
PC1-NHT	11.5100	25.6800	1.9993	0.0779
PC2-NHT	11.1800	24.4500	2.0428	0.0835
PC3-NHT	11.6200	23.5400	1.8770	0.0797
PC4-NHT	2.0000	8.5600	0.7417	0.0867
PC5-NHT	0.7400	11.3700	0.4755	0.0418
PC1-CNHT	0.0000	0.0000	0.0000	0.0000
PC2-CNHT	0.0000	0.0000	0.0000	0.0000
PC3-CNHT	0.0000	0.0000	0.0000	0.0000
PC4-CNHT	0.0000	0.0000	0.0000	0.0000
PC5-CNHT	0.0000	0.0000	0.0000	0.0000
PC1-DHT	0.0000	0.0000	0.0000	0.0000
PC2-DHT	0.0000	0.0000	0.0000	0.0000
PC3-DHT	0.0000	0.0000	0.0000	0.0000
PC4-DHT	0.0000	0.0000	0.0000	0.0000
PC5-DHT	0.0000	1.0800	79.1200	0.0000
HC-GA1	0.0000	0.0000	0.0000	0.0000
HC-GA2	0.0000	0.0000	0.0000	0.0000
HC-GA3	0.0000	0.0000	0.0000	0.0000
HC-GA4	0.0000	0.0000	0.0000	0.0000
HC-GA5	0.0000	0.0000	0.0000	0.0000
HC-NAP1	0.0000	0.0000	0.0000	0.0000
HC-NAP2	0.0000	0.0000	0.0000	0.0000
HC-NAP3	0.0000	0.0000	0.0000	0.0000
HC-NAP4	0.0000	0.0000	0.0000	0.0000
HC-NAP5	0.0000	0.0000	0.0000	0.0000
HC-DIE1	0.0000	0.0000	0.0000	0.0000
HC-DIE2	0.0000	0.0000	0.0000	0.0000
HC-DIE3	0.0000	0.0000	0.0000	0.0000
HC-DIE4	0.0000	0.0000	0.0000	0.0000
HC-DIE5	0.0000	0.0000	0.0000	0.0000

Simulation Scenario 3

	Yfeed (vol%)	Yliq (vol%)	Yvap (vol%)	K
H2	45.0500	1.0200	72.6400	71.2198
CH4	11.0000	2.0000	16.6200	8.3037
C2H6	2.3000	1.0200	3.1000	3.0445
C3H8	1.7300	1.1600	2.0700	1.7803
i-C4H10	0.7100	0.6500	0.7400	1.1359
n-C4H10	0.6900	0.8000	0.6200	0.7658
H2S	1.1200	2.5600	2.8200	5.0231
PC1-NHT	1.4500	2.5800	0.0856	0.0332
PC2-NHT	5.6900	15.2000	0.2301	0.0151
PC3-NHT	0.0900	0.5000	0.0037	0.0073
PC4-NHT	3.2600	10.9900	0.0359	0.0033
PC5-NHT	2.5600	9.2300	0.0138	0.0015
PC1-CNHT	5.4200	8.2400	0.1855	0.0225
PC2-CNHT	5.5500	7.5600	0.0645	0.0085
PC3-CNHT	0.5700	1.0700	0.0025	0.0023
PC4-CNHT	0.6200	1.2300	0.0009	0.0007
PC5-CNHT	0.0000	0.0000	0.0000	0.0000
PC1-DHT	0.0000	1.0200	72.6400	0.0000
PC2-DHT	0.0000	1.0200	72.6400	0.0000
PC3-DHT	0.0000	1.0200	72.6400	0.0000
PC4-DHT	0.0000	1.0200	72.6400	0.0000
PC5-DHT	0.0000	1.0200	72.6400	0.0000
HC-GA1	0.5900	10.0000	1.7734	0.1773
HC-GA2	4.3500	8.7700	0.9025	0.1029
HC-GA3	0.2500	0.3400	0.0210	0.0617
HC-GA4	0.1000	0.4500	0.0160	0.0356
HC-GA5	0.9800	1.2800	0.0251	0.0196
HC-NAP1	1.2400	2.4600	0.0568	0.0231
HC-NAP2	2.5600	3.6800	0.0342	0.0093
HC-NAP3	0.2100	0.8900	0.0031	0.0035
HC-NAP4	1.1000	3.5900	0.0052	0.0014
HC-NAP5	0.7700	2.4500	0.0037	0.0015
HC-DIE1	0.0400	0.2800	0.0002	0.0007
HC-DIE2	0.0000	0.0000	0.0000	0.0000
HC-DIE3	0.0000	0.0000	0.0000	0.0000
HC-DIE4	0.0000	0.0000	0.0000	0.0000
HC-DIE5	0.0000	0.0000	0.0000	0.0000

Appendix C Multi-component H2 network optimisation program codes (GAMS)

```
option nlp=conopt;

 Sets
    Sink   all sinks
      /NHT,CNHT,DHT,HC,Fuel/
    Source     all sources
      /NHT,CNHT,DHT,HC/
    H2Sr  H2plant and CCR
     /H2Plant,CCR/
    Flash   fixed sources to be separated by flash routine
     /NHT,CNHT, DHT,HC/
    C all components in the hydrogen stream
/H2,C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,C11,C12,C13,C14,C15,C16,C17,
C18,C19,C20,C21,C22,C23,C24,C25,C26,C27,C28,C29,C30,C31,C32,C3
3,C34,C35,C36,C37/;
Table
R(Flash, C)       Reacted amount

            H2      C1        C2       C3       C4        C5
    NHT    1.1520  0.0189  0.0050  0.0074  0.0009   0.0000
    CNHT   4.1220  0.0525  0.0324  0.0458  0.0056   0.0000
    DHT    15.170  0.1786  0.1245  0.0287  0.0100   0.0000
    HC     75.030  0.8458  0.4821  0.1698  0.1457   0.0000

            C6       C7       C8       C9      C10       C11
    NHT    0.0000  0.0000  0.0000  0.0000  0.0000   0.0000
    CNHT   0.0000  0.0000  0.0000  0.0000  0.0000   0.0000
    DHT    0.0000  0.0000  0.0000  0.0000  0.0000   0.0000
    HC     0.0000  0.0000  0.0000  0.0000  0.0000   0.0000

            C12     C13     C14       C15      C16      C17
    NHT    0.0000  0.0000 0.0000   0.0000  0.0000  0.0000
    CNHT   0.0000  0.0000 0.0000   0.0000  0.0000  0.0000
    DHT    0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
    HC     0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
```

```
          C18     C19     C20     C21     C22     C23
NHT     0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
CNHT    0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
DHT     0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
HC      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000

          C24     C25     C26     C27     C28     C29

NHT     0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
CNHT    0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
DHT     0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
HC      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000

          C30     C31     C32     C33     C34     C35

NHT     0.0000  0.0000   0.0000  0.0000  0.0000   0.0000
CNHT    0.0000  0.0000   0.0000  0.0000  0.0000   0.0000
DHT     0.0000  0.0000   0.0000  0.0000  0.0000   0.0000
HC      0.0000  0.0000   0.0000  0.0000  0.0000   0.0000

          C36     C37

NHT     0.0000  0.0000
CNHT    0.0000  0.0000
DHT     0.0000  0.0000
HC      0.0000  0.0000;

Table
Flowrate1Initial(H2Sr,Flash)    Initial Flowrate of H2plant and CCR

               NHT     CNHT    DHT     HC
   H2plant     0        0      25.090  84.51
   CCR       6.675     7.788    0        0;


Table
Flowrate2Initial(Source,Flash)    Initial Flowrate of Fpr

               NHT     CNHT    DHT     HC
   NHT       0         0.4     18.37    5.69
   CNHT       0.51    0        0        0
   DHT       12.92     0.24    0       67.75
   HC        10.07     0.24    35.67    0;
```

```
Table
Yfeed(Flash,C)    Feed stream compositon

              H2      C1       C2       C3       C4       C5
      NHT     0.0000  0.0147  0.0062  0.0133  0.0043  0.0072
      CNHT    0.0000  0.0163  0.0130  0.0207  0.0067  0.0112
      DHT     0.0000  0.0653  0.0274  0.0594  0.0193  0.0322
      HC      0.0000  0.0145  0.0135  0.0523  0.0831  0.0509

              C6      C7       C8       C9       C10      C11
      NHT     0.0067  0.0000  0.1940  0.2135  0.2060  0.2251
      CNHT    0.0309  0.0018  0.0000  0.0000  0.0000  0.0000
      DHT     0.0488  0.0030  0.0003  0.0003  0.0003  0.0004
      HC      0.0569  0.0286  0.0000  0.0000  0.0000  0.0000

              C12     C13      C14      C15      C16     C17
      NHT     0.1089  0.0000  0.0000  0.0000  0.0000  0.0000
      CNHT    0.0000  0.1161  0.1837  0.2263  0.1679  0.2054
      DHT     0.0002  0.0000  0.0000  0.0000  0.0000  0.0000
      HC      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000

              C18     C19      C20      C21      C22      C23
      NHT     0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      CNHT    0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      DHT     0.0752  0.1520  0.1947  0.2395  0.0817  0.0000
      HC      0.0000  0.0000  0.0000  0.0000  0.0000  0.0102

              C24     C25      C26      C27      C28      C29
      NHT     0.0000   0.0000  0.0000  0.0000  0.0000  0.0000
      CNHT    0.0000   0.0000  0.0000  0.0000  0.0000  0.0000
      DHT     0.0000   0.0000  0.0000  0.0000  0.0000  0.0000
      HC      0.0203   0.0401  0.0254  0.0164  0.0257  0.0376

              C30     C31      C32      C33      C34      C35
      NHT     0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      CNHT    0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      DHT     0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      HC      0.0766  0.0620  0.0296  0.0589  0.0792  0.0995

             C36      C37

      NHT     0.0000   0.0000
      CNHT    0.0000   0.0000
      DHT     0.0000   0.0000
      HC      0.0818   0.0368;
```

```
Table
KValue(Flash, C)     K values foir the streams from the sources before flash
calculation

           H2        C1        C2       C3       C4       C5
NHT      72.0140  11.2857   2.8654   0.9741   0.4130   0.3101
CNHT     42.6469   6.9179   1.8184   0.6346   0.2743   0.2058
DHT      49.5106   7.9403   2.0714   0.7185   0.3090   0.2320
HC       14.7690   3.0112   0.8698   0.3345   0.1560   0.1184

           C6       C7        C8       C9       C10      C11
NHT      1.7641   7.4751   0.0332   0.0151   0.0073   0.0033
CNHT     1.0100   3.9462   0.0219   0.0102   0.0050   0.0023
DHT      1.1713   4.6353   0.0246   0.0114   0.0056   0.0025
HC       0.5004   2.0233   0.0147   0.0072   0.0014   0.0006

           C12      C13      C14      C15      C16      C17
NHT      0.0015   0.0225   0.0085   0.0023   0.0007   0.0001
CNHT     0.0010   0.0184   0.0078   0.0026   0.0010   0.0002
DHT      0.0012   0.0145   0.0055   0.0015   0.0005   0.0001
HC       0.0002   0.0057   0.0022   0.0006   0.0002   0.0000

           C18      C19      C20      C21      C22      C23
NHT      0.0000   0.0000   0.0000   0.0000   0.0000   0.1773
CNHT     0.0000   0.0000   0.0000   0.0000   0.0000   0.0967
DHT      0.0001   0.0000   0.0000   0.0000   0.0000   0.1357
HC       0.0000   0.0000   0.0000   0.0000   0.0000   0.0723

           C24      C25      C26      C27      C28      C29
NHT      0.1029   0.0617   0.0356   0.0196   0.0231   0.0093
CNHT     0.0561   0.0337   0.0194   0.0107   0.0126   0.0051
DHT      0.0831   0.0528   0.0323   0.0190   0.0212   0.0095
HC       0.0460   0.0302   0.0191   0.0116   0.0128   0.0060

           C30      C31      C32      C33      C34      C35
NHT      0.0035   0.0014   0.0005   0.0007   0.0001   0.0000
CNHT     0.0019   0.0008   0.0003   0.0004   0.0000   0.0000
DHT      0.0041   0.0019   0.0008   0.0010   0.0002   0.0000
HC       0.0027   0.0013   0.0006   0.0007   0.0001   0.0000

           C36       C37

NHT      0.0000    0.0000
CNHT     0.0000    0.0000
DHT      0.0000    0.0000
HC       0.0000    0.0000;
```

Table
Initial1(Flash, C) Purities of the components in the source streams before flash separation

	H2	C1	C2	C3	C4	C5
NHT	0.7587	0.1932	0.0120	0.0112	0.0017	0.0021
CNHT	0.6562	0.2788	0.0175	0.0122	0.0018	0.0022
DHT	0.7070	0.1500	0.0312	0.0356	0.0066	0.0076
HC	0.8122	0.0820	0.0091	0.0154	0.0120	0.0056

	C6	C7	C8	C9	C10	C11
NHT	0.0092	5.e-11	0.0064	0.0032	0.0015	0.0007
CNHT	0.0241	0.0030	0.0001	0.0000	0.0000	0.0000
DHT	0.0429	0.0192	8.1E-6	4.2E-6	1.9E-6	9.8E-7
HC	0.0240	0.0355	0.0000	0.0000	0.0000	0.0000

	C12	C13	C14	C15	C16	C17
NHT	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000
CNHT	0.0000	0.0021	0.0014	0.0006	0.0002	4.1E-5
DHT	2.2E-7	0.0000	0.0000	0.0000	0.0000	0.0000
HC	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

	C18	C19	C20	C21	C22	C23
NHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CNHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HC	0.0000	0.0000	0.0000	0.0000	0.0000	0.0007

	C24	C25	C26	C27	C28	C29
NHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CNHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HC	0.0009	0.0012	0.0005	0.0002	0.0003	0.0002

	C30	C31	C32	C33	C34	C35
NHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CNHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HC	0.0002	7.9E-5	1.6E-5	4.2E-5	1.0E-5	2.1E-6

	C36	C37
NHT	0.0000	0.0000
CNHT	0.0000	0.0000
DHT	0.0000	0.0000
HC	2.5E-7	1.5E-08;

```
Table
Initial2(Flash, C)      Purities of the mix point

             H2      C1      C2      C3      C4      C5
      NHT    0.7663  0.1937  0.0097  0.0091  0.0014  0.0018
      CNHT   0.7049  0.2424  0.0140  0.0105  0.0015  0.0019
      DHT    0.7542  0.1154  0.0223  0.0282  0.0092  0.0071
      HC     0.9059  0.0458  0.0073  0.0095  0.0043  0.0027

             C6      C7      C8      C9      C10     C11
      NHT    0.0080  0.0002  0.0053  0.0027  0.0012  0.0006
      CNHT   0.0180  0.0018  0.0010  0.0005  0.0002  0.0001
      DHT    0.0366  0.0258  0.0000  0.0000  0.0000  0.0000
      HC     0.0129  0.0105  0.0000  0.0000  0.0000  0.0000

             C12     C13     C14     C15     C16     C17
      NHT    0.0001  0.0000  0.0000  0.0000  0.0000  0.0000
      CNHT   0.0000  0.0015  0.0010  0.0004  0.0001  0.0000
      DHT    0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      HC     0.0000  0.0000  0.0000  0.0000  0.0000  0.0000

             C18     C19     C20     C21     C22     C23
      NHT    0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      CNHT   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      DHT    0.0000  0.0000  0.0000  0.0000  0.0000  0.0003
      HC     0.0000  0.0000  0.0000  0.0000  0.0000  0.0002

             C24     C25     C26     C27     C28     C29
      NHT    0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      CNHT   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      DHT    0.0003  0.0004  0.0001  0.0001  0.0001  0.0001
      HC     0.0002  0.0003  0.0001  0.0000  0.0001  0.0001

             C30     C31     C32     C33     C34     C35
      NHT    0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      CNHT   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      DHT    0.0001  0.0000  0.0000  0.0000  0.0000  0.0000
      HC     0.0001  0.0000  0.0000  0.0000  0.0000  0.0000

             C36     C37
      NHT    0.0000  0.0000
      CNHT   0.0000  0.0000
      DHT    0.0000  0.0000
      HC     0.0000  0.0000;
```

Table
YreInitial(Flash, C)   Purities of recycle

	H2	C1	C2	C3	C4	C5
NHT	0.7587	0.1934	0.0120	0.0111	0.0017	0.0021
CNHT	0.6549	0.2830	0.0157	0.0110	0.0017	0.0021
DHT	0.7144	0.1534	0.0343	0.0364	0.0058	0.0075
HC	0.8219	0.0666	0.0096	0.0157	0.0120	0.0056

	C6	C7	C8	C9	C10	C11
NHT	0.0091	0.0000	0.0064	0.0032	0.0015	0.0007
CNHT	0.0241	0.0034	0.0000	0.0000	0.0000	0.0000
DHT	0.0428	0.0055	0.0000	0.0000	0.0000	0.0000
HC	0.0248	0.0395	0.0000	0.0000	0.0000	0.0000

	C12	C13	C14	C15	C16	C17
NHT	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000
CNHT	0.0000	0.0021	0.0014	0.0006	0.0002	0.0000
DHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HC	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

	C18	C19	C20	C21	C22	C23
NHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CNHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HC	0.0000	0.0000	0.0000	0.0000	0.0000	0.0007

	C24	C25	C26	C27	C28	C29
NHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CNHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DHT	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
HC	0.0009	0.0012	0.0005	0.0002	0.0003	0.0002

	C30	C31	C32	C33	C34	C35
NHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CNHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DHT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HC	0.0002	0.0001	0.0000	0.0000	0.0000	0.0000

	C36	C37
NHT	0.0000	0.0000
CNHT	0.0000	0.0000
DHT	0.0000	0.0000
HC	0.0000	0.0000;

```
Table
YH2Source(H2Sr,C)      Purity of the sources from hydrogen producers

                H2      C1       C2       C3       C4       C5
      H2Plant 0.9900  0.0100  0.0000  0.0000  0.0000  0.0000
      CCR     0.8300  0.1700  0.0000  0.0000  0.0000  0.0000

               C6       C7       C8       C9       C10      C11
      H2Plant  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      CCR      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000


               C12      C13      C14      C15      C16      C17
      H2Plant  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      CCR      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000


               C18      C19     C20       C21      C22      C23
      H2Plant  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      CCR      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000


               C24      C25      C26      C27      C28      C29
      H2Plant  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      CCR      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000


                C30      C31      C32      C33      C34      C35
      H2Plant  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      CCR      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000


                C36      C37
      NHT      0.0000  0.0000
      CNHT     0.0000  0.0000;




Parameter
Ffeed(Flash)       flowrate of Feed
          /NHT        32.79
           CNHT       12.95
           DHT        36.15
           HC         37.62/
```

```
Variables

z;


Positive Variables

Flowrate1(H2Sr,Flash)
Flowrate2(Source,Flash)


Fuel(Source)

Slack1(Flash,C)

Slack2(Flash,C)

Slack3(Flash)

Slack4(Flash)

Slack5(Flash)

Slack6(Flash)

Slack7(Flash)

Slack8(Flash)

Slack9(Flash)

Slack10(Flash)

Slack11(Flash)

Slack12(Flash)

Slack13(Flash)

Slack14(Flash)

Fuel(Source)        Purge to fuel

Fpr(Flash)          Flowrate of H2 between consumers
Ypr(Flash,C)        Compositions of H2 between consumers

Fri(Flash)          Flowrate of reactor inlet
Yri(Flash,C)        Compositions of reactor inlet

Fre(Flash)          Flowrate of recycle
```

```
Yre(Flash,C)          Compositions of recycle


Fmu(Flash)            Flowrate of H2 makeup
Ymu(Flash,C)          Compositions of H2 makeup

Fmix(Flash)           Flowrate of mixture of recycle and makeup
Ymix(Flash,C)         Compositions of mixture of recycyel and makeup


Ffi(Flash)            Flowrate of flash inlet
Yfi(Flash,C)          Compositions of flash inlet


Fliq(Flash)           Flowrate of flash liquid
Yliq(Flash,C)         Compositions of flash liquid

Fpu(Flash)            Flowrate of Purge

Yri.up(Flash,C)=0.9999;
Yri.lo(Flash,C)=0;
Yre.up(Flash,C)=0.9999;
Yre.lo(Flash,C)=0;
Ymu.up(Flash,C)=0.9999;
Ymu.lo(Flash,C)=0;
Ymix.up(Flash,C)=0.9999;
Ymix.lo(Flash,C)=0;
Yliq.up(Flash,C)=0.9999;
Yliq.lo(Flash,C)=0;

Fri.lo(Flash)=1e-3;
Fre.lo(Flash)=1e-3;
Fmu.lo(Flash)=1e-3;
Fmix.lo(Flash)=1e-3;
Fliq.lo(Flash)=1e-3;
Fpu.lo(Flash)=1e-3;
Ypr.up(Flash,C)=0.9999;
Ypr.lo(Flash,C)=0;


Ymix.up('NHT','H2')=0.8;
Ymix.up('CNHT','H2')=0.8;
Ymix.up('DHT','H2')=0.8;
Ymix.up('HC','H2')=0.9;

Ymix.lo('NHT','H2')=0.7;
Ymix.lo('CNHT','H2')=0.6;
Ymix.lo('DHT','H2')=0.7;
Ymix.lo('HC','H2')=0.8;
```

```
Fmix.fx('NHT')= 53.93;
Fmix.fx('CNHT')=49.67;
Fmix.fx('DHT')=225.11;
Fmix.fx('HC')=189.69;

Fmix.up('NHT')= 60;
Fmix.up('CNHT')=60;
Fmix.up('DHT')=250;
Fmix.up('HC')=220;

Fmix.lo('NHT')= 45;
Fmix.lo('CNHT')=40;
Fmix.lo('DHT')=180;
Fmix.lo('HC')=150;


Fre.l('NHT')=47.28;
Fre.l('CNHT')=42.04;
Fre.l('DHT')=200.17;
Fre.l('HC')=105.16;

Equations

equ1            Reactor inlet flowrate balance
equ2            Reactor inlet composition balance
equ3            Flash inlet flowrate balance
equ4            Flash inlet composition balance
*equ5           Flash calculation
equ6            Flash inlet flowrate = outlet flowrate
equ7            Flash outlet split composition balance
equ8            Sum Yri to 1
equ9            Sum Yre to 1
equ10           Sum Ymu to 1
equ11           Sum Ymix to 1
equ12           Sum Yfi to 1
equ13           Sum Yliq to 1
*const1(Flash)


equ14            mix point flowrate balance
equ15            mix point composition balance
equ16            Flash component balance

equ17            H2Sr Flowrate balance
equ18            H2Sr Component balance

equ19            Define Fpr
equ20            Define Ypr
```

```
equu21          Sum Ypr to 1
```

```
equ21           Sum Ypr to 1
equ22           Fuel=Fpu-Fpr
equ23
*equ24
*equ25
*equ26

obj             objective function;


*Flash calculation and network mass balance

equ1(Flash)..       Fri(Flash) =e=
Fmix(Flash)+Ffeed(Flash)+Slack11(Flash)-Slack12(Flash);

equ2(Flash,C)..     Fri(Flash)*Yri(Flash,C) =e=
Fmix(Flash)*Ymix(Flash,C)+Ffeed(Flash)*Yfeed(Flash,C)+Slack13(Flash,C
)-Slack14(Flash,C);

equ3(Flash)..       Ffi(Flash) =e= Fri(Flash) - sum(C, R(Flash,C));

equ4(Flash,C)..     Yfi(Flash,C)*Ffi(Flash) =e= Fri(Flash)*Yri(Flash,C)-
R(Flash,C);

*equ5(Flash,C)..    Yfi(Flash,C) =e= Yre(Flash,C)*(1-
f(Flash))+f(Flash)*Yliq(Flash,C)+Slack1(Flash,C);

equ16(Flash,C)..    Ffi(Flash)*Yfi(Flash,C)
=e=Fre(Flash)*Yre(Flash,C)+Fpu(Flash)*Yre(Flash,C)+Fliq(Flash)*Yliq(Fla
sh,C);

equ6(Flash)..       Fre(Flash)+Fpu(Flash)+Fliq(Flash) =e= Ffi(Flash);

equ7(Flash,C)..     Yre(Flash,C)=e=
Yliq(Flash,C)*KValue(Flash,C)+Slack1(Flash,C)-Slack2(Flash,C);

equ8(Flash)..       sum(C,Yri(Flash,C))+Slack3(Flash)-Slack4(Flash)  =e=
1;

equ9(Flash)..       sum(C,Yre(Flash,C)) =e= 1;

equ10(Flash)..      sum(C,Ymu(Flash,C)) +Slack7(Flash)-Slack8(Flash)
=e= 1;

equ11(Flash)..      sum(C,Ymix(Flash,C)) +Slack9(Flash)-Slack10(Flash)
=e= 1;

equ12(Flash)..      sum(C,Yfi(Flash,C))+Slack5(Flash)-Slack6(Flash) =e=
1;
```

```
equ13(Flash)..        sum(C,Yliq(Flash,C)) =e= 1;


equ14(Flash)..        Fmix(Flash)=e= Fmu(Flash)+Fre(Flash)+Fpr(Flash);

equ15(Flash,C)..     Fmix(Flash)*Ymix(Flash,C)=e=
Fmu(Flash)*Ymu(Flash,C)+Fre(Flash)*Yre(Flash,C)+Fpr(Flash)*Ypr(Flash,
C);

equ17(Flash)..        Fmu(Flash)=e=sum(H2Sr,Flowrate1(H2Sr,Flash));

equ18(Flash,C)..
Fmu(Flash)*Ymu(Flash,C)=e=sum(H2Sr,Flowrate1(H2Sr,Flash)*YH2Sourc
e(H2Sr,C));


equ19(Flash)..        Fpr(Flash)=e= sum(Source$(ord(source) ne
ord(flash)),Flowrate2(Source,Flash));

equ20(Flash,C)..
Fpr(Flash)*Ypr(Flash,C)=e=sum(Source$(ord(source) ne
ord(flash)),Flowrate2(Source,Flash)*Yre(Flash,C));

equ21(Flash)..        sum(C,Ypr(Flash,C))=e=1;

equ22..               sum(Flash,Flowrate1('CCR',Flash)) =e= 14.463;

equ23..               sum(Flash,Flowrate1('H2plant',Flash)) =e= 103.7;


obj..                 z =e=sum((Flash),Flowrate1('H2Plant',Flash))
+sum((Flash,C),Slack1(Flash,C)

+Slack2(Flash,C)+Slack13(Flash,C)+Slack14(Flash,C))*10000+sum(Flash,
Slack3(Flash)+Slack4(Flash)

+Slack5(Flash)+Slack6(Flash)+Slack7(Flash)+Slack8(Flash)+Slack9(Flash)

+Slack10(Flash)+Slack11(Flash)+Slack12(Flash))*10000;



option reslim = 1e20;
option domlim = 10;
option iterlim = 2e5;


 Model  Basecase /all/ ;

 Basecase.workspace = 100;
```

```
 Basecase.optfile =1;
 Basecase.scaleopt = 1;
 Basecase.iterlim = 2e5;

 Solve Basecase using nlp minimizing z;

display Fri.l,Yri.l,Fre.l,Fmu.l,Ymu.l,Fmix.l,Ymix.l,Ffi.l,Yfi.l,Fliq.l,Yliq.l,Fpu.l,
Slack1.l,
Slack2.l,
Slack3.l,
Slack4.l,
Slack5.l,
Slack6.l,
Slack7.l,
Slack8.l
Slack9.l,
Slack10.l,
Slack11.l,
Slack12.l,
Slack13.l,
Slack14.l,
display Flowrate1.l, Flowrate2.l,Fpr.l, z.l, yre.l;

parameter H2con;
H2con = sum((Flash),Flowrate1.l('H2Plant',Flash));
display H2con;
```