# Part 1
# Industrial Utilization of Hydrogen

*Hydrogen Science and Engineering: Materials, Processes, Systems and Technology,* First Edition.
Edited by Detlef Stolten and Bernd Emonts.

# 1
# Hydrogen in Refineries

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## 1.1
## Introduction

A critical issue facing the world's refiners today is the changing landscape in processing petroleum crude into refined transportation fuels under an environment of increasingly more stringent clean fuel regulations, decreasing heavy fuel oil demand, and increasing supply of heavy, sour crude. Hydrogen network optimization is at the forefront of world refineries options to address clean fuel trends, to meet growing transportation fuel demands and to continue to make a profit from their crudes [1]. A key element of a hydrogen network analysis in a refinery involves the capture of hydrogen in its fuel streams and extending its flexibility and processing options. Thus, innovative hydrogen network optimization will be a critical factor influencing future refinery operating flexibility and profitability in a shifting world of crude feedstock supplies and ultra-low-sulfur (ULS) gasoline and diesel fuel.

The chemical nature of the crude oil used as the refinery feedstock has always played the major role in determining the hydrogen requirements of that refinery. For example, the lighter, more paraffinic crude oils will require somewhat less hydrogen for upgrading to, say, a gasoline product than a heavier more asphaltic crude oil. It follows that the hydrodesulfurization of heavy oils and residua (which, by definition, is a hydrogen-dependent process) needs substantial amounts of hydrogen as part of the processing requirements.

In fact, the refining industry has been the subject of the four major forces that affect most industries and which have hastened the development of new petroleum refining processes: (i) the demand for products such as gasoline, diesel, fuel oil, and jet fuel, (ii) feedstock supply, specifically the changing quality of crude oil and geopolitics between different countries and the emergence of alternate feed supplies such as bitumen from tar sand (*oil sand*), natural gas, and coal, (iii) technology development such as new catalysts and processes, especially processes involving the use of hydrogen, and (iv) environmental regulations that include more stringent regulations in relation to sulfur in gasoline and diesel [2–6].

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Categories (i), (ii), and (iv) are directly affected by the third category (i.e., the use of hydrogen in refineries) and it is this category that will be the subject of this chapter. This chapter presents an introduction to the use and need for hydrogen petroleum refineries in order for the reader to place the use of hydrogen in the correct context of the refinery. In fact, hydrogen is key in allowing refineries to comply with the latest product specifications and environmental requirements for fuel production being mandated by market and governments and helping to reduce the carbon footprint of refinery operations.

The history and evolution petroleum refining has been well described elsewhere [6,7] and there is little need to repeat that work here except to note that it is not the intent of this chapter to ignore the myriad of processes in modern refineries that do not use hydrogen but may be dependent upon hydrogenated products in one way or another.

## 1.2
## Hydroprocesses

The use of hydrogen in thermal processes is perhaps the single most significant advance in refining technology during the twentieth century and is now an inclusion in most refineries (Figure 1.1). Hydrogenation processes for the conversion

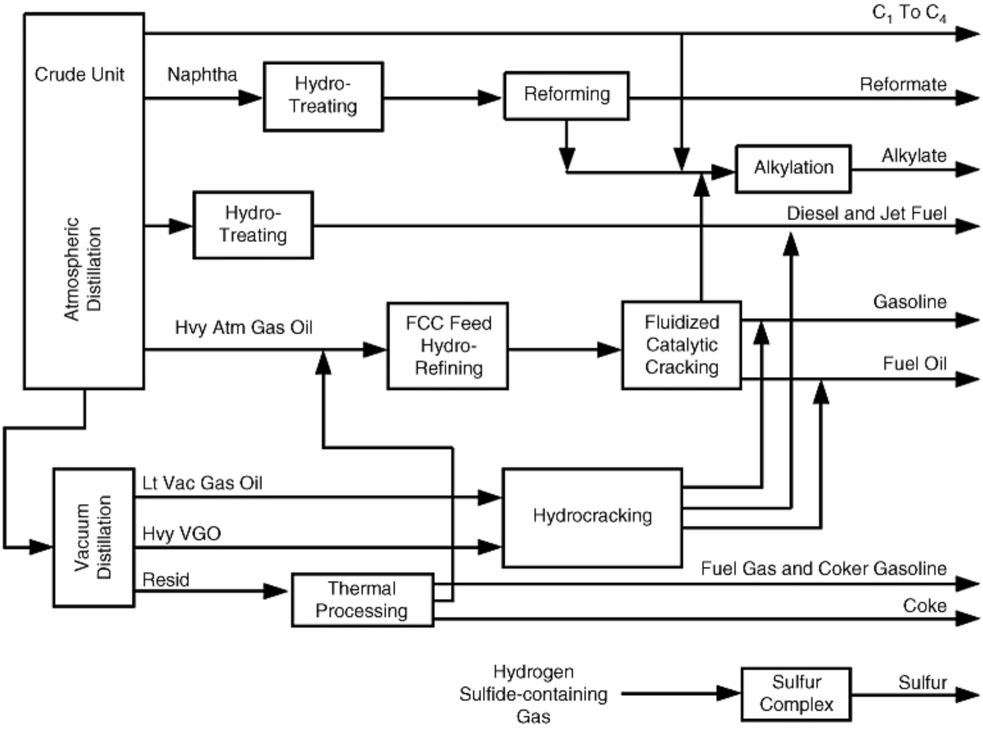

**Figure 1.1** Example of the relative placement of hydroprocesses in a refinery.

of petroleum fractions and petroleum products may be classified as *destructive hydrogenation* and *nondestructive hydrogenation*.

Nondestructive hydrogenation (hydrotreating, simple hydrogenation) is generally used for the purpose of improving product quality without appreciable alteration of the boiling range. Mild processing conditions are employed so that only the more unstable materials are attacked. Nitrogen, sulfur, and oxygen compounds undergo reaction with the hydrogen to remove ammonia, hydrogen sulfide, and water, respectively. Unstable compounds that might lead to the formation of gums, or insoluble materials, are converted into more stable compounds.

On the other hand, destructive hydrogenation (hydrogenolysis, hydrocracking) is characterized by the conversion of feedstock higher molecular weight constituents into lower-boiling value-added products. Such treatment requires severe processing conditions and the use of high hydrogen pressures to minimize polymerization and condensation reactions that lead to coke formation.

The process uses the principle that the presence of hydrogen during a thermal reaction of a petroleum feedstock will terminate many of the coke-forming reactions and enhance the yields of the lower boiling components such as gasoline, kerosene, and jet fuel; processing parameters vary depending upon the character and properties of the feedstock (Tables 1.1 and 1.2).

**Table 1.1** Summary of typical hydrogen applications and production processes in a refinery.

| Hydrogen application | Hydrogen production process |
|---|---|
| **Naphtha hydrotreater:** uses hydrogen to desulfurize naphtha from atmospheric distillation; must hydrotreat the naphtha before sending to a catalytic reformer unit. | **Catalytic reformer:** used to convert the naphtha-boiling range molecules into higher octane reformate; hydrogen is a byproduct |
| **Distillate hydrotreater:** desulfurizes distillates after atmospheric or vacuum distillation; in some units aromatics are hydrogenated to cycloparaffins or alkanes | **Steam–methane reformer:** produces hydrogen for the hydrotreaters or hydrocracker |
| **Hydrodesulfurization:** sulfur compounds are hydrogenated to hydrogen sulfide as feed for Claus plants | **Steam reforming of higher molecular weight hydrocarbons:** produces hydrogen from low-boiling hydrocarbons other than methane |
| **Hydroisomerization:** normal (straight-chain) paraffins are converted into iso-paraffins to improve the product properties (e.g., octane number) | **Recovery from refinery off-gases: p**rocess gas often contains hydrogen in the range up to 50% v/v |
| **Hydrocracker:** uses hydrogen to upgrade heavier fractions into lighter, more valuable products | **Gasification of petroleum residua:** recovery from synthesis gas (syngas) produced in gasification units |
| | **Gasification of petroleum coke:** recovery from synthesis gas (syngas) produced in gasification units |
| | **Partial oxidation processes:** analogous to gasification process; produce synthesis gas from which hydrogen can be isolated |

**Table 1.2** Hydroprocessing parameters.

| Parameter | | | |
|---|---|---|---|
| **Conditions** | **Feedstocks** | **Products** | **Variations** |
| Solid acid catalyst (silica-alumina with rare earth metals, various other options) | Distillates | Lower molecular weight paraffins | Fixed bed (suitable for liquid feedstocks) |
| Temperature: 260–450 °C (500–845 °F) (solid/liquid contact) | Refractory (aromatic) streams | Some methane, ethane, propane, and butane | Ebullating bed (suitable for heavy feedstocks) |
| Pressure: 1000–6000 psi hydrogen | Coker oils | Hydrocarbon distillates (full range depending on the feedstock) | |
| Frequent catalysts renewal for heavier feedstocks | Cycle oils | Residual tar (recycle) | |
| Gas oil: catalyst life up to three years | Gas oils | Contaminants (asphaltic constituents) deposited on the catalyst as coke or metals | |
| Heavy oil/tar sand bitumen: catalyst life less than one year | Residua (as a full hydrocracking or hydrotreating option). In some cases, asphaltic constituents (S, N, and metals) removed by deasphalting | | |

### 1.2.1
### Hydrotreating Processes

The commercial processes for treating, or finishing, petroleum fractions with hydrogen all operate in essentially the same manner. The feedstock is heated and passed with hydrogen gas through a tower or reactor filled with catalyst pellets. The reactor is maintained at a temperature of 260–425 °C (500–800 °F) at pressures of 100–1000 psi, depending on the particular process, the nature of the feedstock, and the degree of hydrogenation required. After leaving the reactor, excess hydrogen is separated from the treated product and recycled through the reactor after removal of hydrogen sulfide. The liquid product is passed into a stripping tower where steam removes dissolved hydrogen and hydrogen sulfide and, after cooling, the product is taken to product storage or, in the case of feedstock preparation, pumped to the next processing unit.

Thus, in a typical catalytic hydrodesulfurization unit, the feedstock is deaerated and mixed with hydrogen, preheated in a fired heater (315–425 °F; 600–800 °F), and then charged under pressure (up to 1000 psi) through a fixed-bed catalytic reactor. In the reactor, the sulfur and nitrogen compounds in the feedstock are converted into hydrogen sulfide and ammonia. The reaction products leave the reactor and after cooling to a low temperature enter a liquid/gas separator. The hydrogen-rich gas from the high-pressure separation is recycled to combine with the feedstock, and the low-pressure gas stream rich in hydrogen sulfide is sent to a gas treating unit where the hydrogen sulfide is removed. The clean gas is then suitable as fuel for the refinery furnaces. The liquid stream is the product from hydrotreating and is normally sent to a stripping column for removal of hydrogen sulfide and other undesirable components. In cases where steam is used for stripping, the product is sent to a vacuum drier for removal of water. Hydrodesulfurized products are blended or used as catalytic reforming feedstock.

*Hydrofining* is a process that first went on-stream in the 1950s and is one example of the many hydroprocesses available. It can be applied to lubricating oils, naphtha, and gas oils. The feedstock is heated in a furnace and passed with hydrogen through a reactor containing a suitable metal oxide catalyst, such as cobalt and molybdenum oxides on alumina. Reactor operating conditions range from 205 to 425 °C (400–800 °F) and from 50 to 800 psi, and depend on the kind of feedstock and the degree of treating required. Higher-boiling feedstocks, high sulfur content, and maximum sulfur removal require higher temperatures and pressures.

After passing through the reactor, the treated oil is cooled and separated from the excess hydrogen, which is recycled through the reactor. The treated oil is pumped to a stripper tower where hydrogen sulfide, formed by the hydrogenation reaction, is removed by steam, vacuum, or flue gas, and the finished product leaves the bottom of the stripper tower. The catalyst is not usually regenerated; it is replaced after about one year’s use.

*Distillate hydrotreating* (Figure 1.2) is carried out by charging the feed to the reactor, together with hydrogen in the presence of catalysts such as tungsten-nickel sulfide, cobalt-molybdenum-alumina, nickel oxide-silica-alumina, and platinum-alumina. Most processes employ cobalt-molybdenum catalysts, which generally contain about 10% of molybdenum oxide and less than 1% of cobalt oxide supported on alumina. The temperatures employed are in the range 260–345 °C (500–655 °F), while the hydrogen pressures are about 500–1000 psi [8].

The reaction generally takes place in the vapor phase but, depending on the application, may be a mixed-phase reaction. Generally, it is more economical to hydrotreat high-sulfur feedstocks prior to catalytic cracking than to hydrotreat the products from catalytic cracking. The advantages are that (i) sulfur is removed from the catalytic cracking feedstock, and corrosion is reduced in the cracking unit, (ii) carbon formation during cracking is reduced so that higher conversions result, and (iii) the cracking quality of the gas oil fraction is improved.

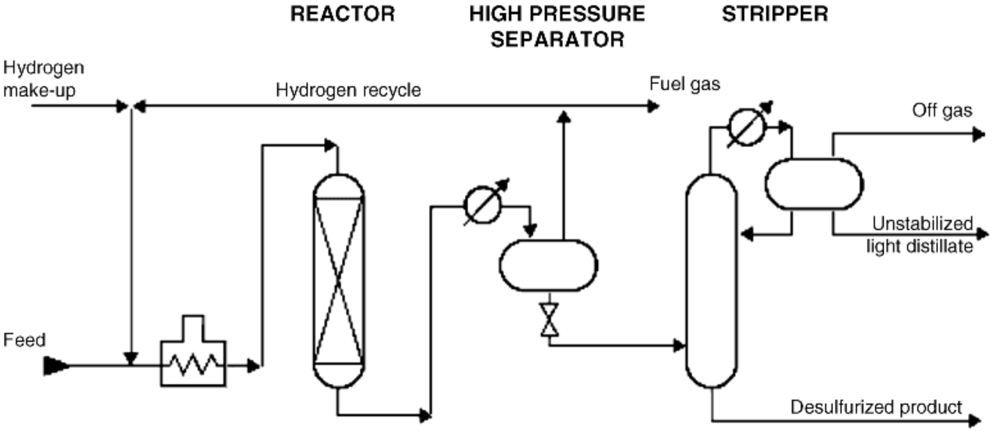

**Figure 1.2** A distillate hydrotreater for hydrodesulfurization. Source: US Department of Labor, OSHA Technical Manual, Section IV, Chapter 2: Petroleum Refining Processes. http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html.

Hydrotreating processes differ depending upon the feedstock available and catalysts used. Hydrotreating can be used to improve the burning characteristics of distillates such as kerosene. Hydrotreatment of a kerosene fraction can convert aromatics into naphthenes, which are cleaner-burning compounds. Lube-oil hydrotreating uses catalytic treatment of the oil with hydrogen to improve product quality. The objectives in mild lube hydrotreating include saturation of olefins and improvements in color, odor, and acid nature of the oil. Mild lubricating hydrotreating also may be used following solvent processing. Operating temperatures are usually below 315 °C (600 °F) and operating pressures below 800 psi. Severe lube hydrotreating, at temperatures in the 315–400 °C (600–750 °F) range and hydrogen pressures up to 3000 psi, is capable of saturating aromatic rings, along with sulfur and nitrogen removal, to impart specific properties not achieved at mild conditions.

Hydrotreating also can be employed to improve the quality of pyrolysis gasoline (*pygas*), a by-product from the manufacture of ethylene. Traditionally, the outlet for pygas has been motor gasoline blending, a suitable route in view of its high octane number. However, only small portions can be blended untreated owing to the unacceptable odor, color, and gum-forming tendencies of this material. The quality of pygas, which is high in di-olefin content, can be satisfactorily improved by hydrotreating, whereby conversion of di-olefins into mono-olefins provides an acceptable product for motor gas blending.

### 1.2.2
### Hydrocracking Processes

Hydrocracking (Figure 1.3) is similar to catalytic cracking, with hydrogenation superimposed and with the reactions taking place either simultaneously or

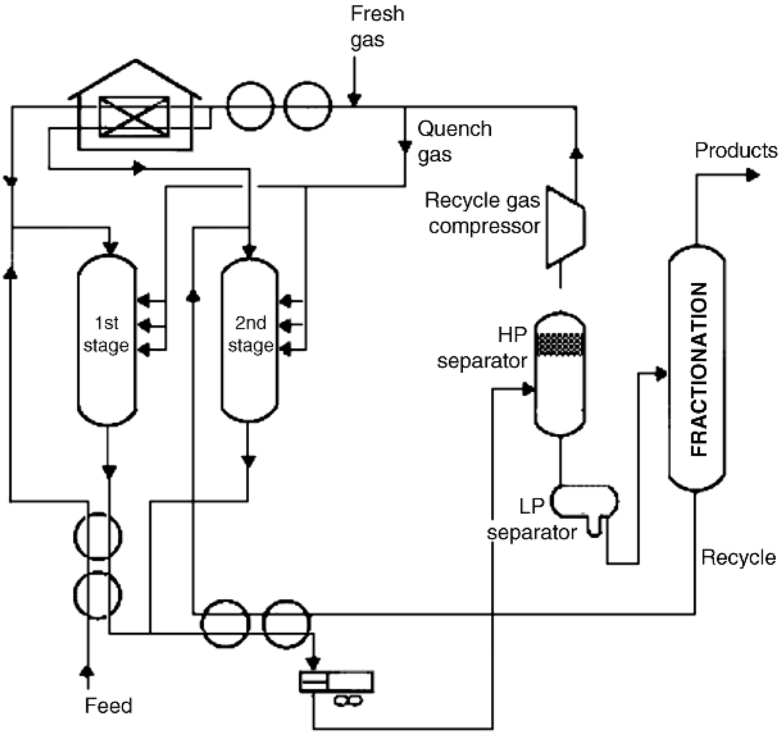

**Figure 1.3** A single-stage or two-stage (optional) hydrocracking unit. Source: US Department of Labor, OSHA Technical Manual, Section IV, Chapter 2: Petroleum Refining Processes. http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html.

sequentially [2–6]. Hydrocracking was initially used to upgrade low-value distillate feedstocks, such as cycle oils (high aromatic products from a catalytic cracker, which usually are not recycled to extinction for economic reasons), thermal and coker gas oils, and heavy-cracked and straight-run naphtha. These feedstocks are difficult to process by either catalytic cracking or reforming, since they are characterized usually by a high polycyclic aromatic content and/or by high concentrations of the two principal catalyst poisons – sulfur and nitrogen compounds.

Hydrocracking employs high pressure, high temperature, and a catalyst. Hydrocracking is used for feedstocks that are difficult to process by either catalytic cracking or reforming, since these feedstocks are characterized usually by high polycyclic aromatic content and/or high concentrations of the two principal catalyst poisons, sulfur and nitrogen compounds. The hydrocracking process largely depends on the nature of the feedstock and the relative rates of the two competing reactions, hydrogenation and cracking. Heavy aromatic feedstock is converted into lighter products under a wide range of very high pressures (1000–2000 psi) and fairly high temperatures (400–815 °C; 750–1500 °F), in the presence of hydrogen and special catalysts. When the feedstock has a high paraffinic content, the primary function of hydrogen is to prevent the formation of polycyclic aromatic compounds. Another important role of hydrogen in the hydrocracking process is to reduce tar formation and prevent buildup of coke on the catalyst. Hydrogenation also serves to convert sulfur and nitrogen compounds present in the feedstock into hydrogen sulfide and ammonia, respectively.

Typically, hydrocracking is a process with options: single stage hydrocracking or two-stage hydrocracking. In the first stage of the process (Figure 1.3), preheated feedstock is mixed with recycled hydrogen and sent to the first-stage reactor, where catalysts convert sulfur and nitrogen compounds into hydrogen sulfide and ammonia. Limited hydrocracking also occurs. After the hydrocarbon leaves the first stage, it is cooled and liquefied and run through a hydrocarbon separator. The hydrogen is recycled to the feedstock. The liquid is charged to a fractionator. Depending on the products desired (gasoline components, jet fuel, and gas oil), the fractionator is run to cut out some portion of the first stage reactor out-turn. Kerosene-range material can be taken as a separate side-draw product or included in the fractionator bottoms with the gas oil. The fractionator bottoms are again mixed with a hydrogen stream and charged to the second stage. Since this material has already been subjected to some hydrogenation, cracking, and reforming in the first stage, the operations of the second stage are more severe (higher temperatures and pressures). Like the outturn of the first stage, the second stage product is separated from the hydrogen and charged to the fractionator.

More often than not, especially with the influx of heavy feedstocks into refineries, hydrocracking is a two-stage process combining catalytic cracking and hydrogenation, wherein heavier feedstocks are cracked in the presence of hydrogen to produce more desirable products. Hydrocracking also produces relatively large amounts of iso-butane for alkylation feedstock and the process also performs isomerization for pour-point control and smoke-point control, both of which are important in high-quality jet fuel.

### 1.2.3
### Slurry Hydrocracking

In terms of slurry hydrocracking processes, metals that have been screened as potential slurry catalysts and include transition metal-based catalysts derived from vanadium, tungsten, chromium, and iron. Homogeneous catalysts based hydrocracking technology has been developed for upgrading of heavy crude and tar sand bitumen [6,9]. In this process the hydrocracking catalyst is homogeneously dispersed as a colloid with particles similar in size to that of asphaltene molecule, which results in high conversion of asphaltene constituents [10,11].

### 1.2.4
### Process Comparison

A comparison of hydrocracking with hydrotreating is useful in assessing the parts played by these two processes in refinery operations. Hydrotreating of distillates may be defined simply as the removal of nitrogen-, sulfur-, and oxygen-containing compounds by selective hydrogenation. The hydrotreating catalysts are usually cobalt plus molybdenum or nickel plus molybdenum (in the sulfide) form impregnated on an alumina base. The hydrotreating process conditions (1000–2000 psi hydrogen and approximately 370 °C, (700 °F)) are such that appreciable hydrogenation of aromatics will not occur. The desulfurization reactions are usually accompanied by small amounts of hydrogenation and hydrocracking.

Hydrocracking is an extremely versatile process that can be utilized in many different ways such as conversion of the high-boiling aromatic streams that are produced by catalytic cracking or by coking processes. To take full advantage of hydrocracking the process must be integrated in the refinery with other process units (Figure 1.1).

## 1.3
## Refining Heavy Feedstocks

Over the past three decades, crude oils available to refineries have generally decreased in API (American Petroleum Institute) gravity [3,6,7]. There is, nevertheless, a major focus in refineries on the ways in which heavy feedstocks (such as heavy oil and tar sand bitumen) can be converted into low-boiling high-value products [2–7,12–18]. Simultaneously, the changing crude oil properties are reflected in changes such as an increase in asphaltene constituents, an increase in sulfur, metal, and nitrogen contents. Pretreatment processes for removing such constituents or at least negating their effect in thermal process would also play an important role.

The limitations of processing these heavy feedstocks depend to a large extent on the amount of higher molecular weight constituents (i.e., asphaltene constituents and resin constituents) that contain the majority of the heteroatom-containing compounds, which are responsible for high yields of thermal and catalytic coke [6]. Be that as it may, the essential step required of a modern refinery is the upgrading of heavy feedstocks, particularly atmospheric and vacuum residua.

Upgrading feedstocks such as heavy oils and residua began with the introduction of hydrodesulfurization processes [8,19]. In the early days, the goal was desulfurization but, in later years, the processes were adapted to a 10–30% partial conversion operation, intended to achieve desulfurization and obtain low-boiling fractions simultaneously, by increasing severity in operating conditions. However, as refineries have evolved and feedstocks have changed, refining heavy feedstocks has become a major issue in modern refinery practice and several process configurations have evolved to accommodate the heavy feedstocks [2,6,7,12].

For example, hydrodesulfurization of light (low-boiling) distillate (naphtha or kerosene) is one of the more common catalytic hydrodesulfurization processes since it is usually used as a pretreatment of such feedstocks prior to deep hydrodesulfurization or prior to catalytic reforming. A similar concept of pretreating residua prior to hydrocracking to improve the quality of the products is also practiced [6,7]. Hydrodesulfurization of such feedstocks, which is required because sulfur compounds poison the precious-metal catalysts used in the hydrocracking process, can be achieved under *relatively* mild conditions. If the feedstock arises from a cracking operation (such as cracked residua), hydro-pretreatment will be accompanied by some degree of saturation resulting in increased hydrogen consumption.

Finally, there is not one single heavy feedstock upgrading solution that will fit all refineries. Market conditions, existing refinery configuration, and available crude prices all can have a significant effect on the final configuration. Furthermore, a proper evaluation, however, is not a simple undertaking for an existing refinery. Evaluation starts with an accurate understanding of the market for the various products along with corresponding product values at various levels of supply. The next step is to select a set of crude oils that adequately cover the range of crude oils that may be expected to be processed. It is also important to consider new unit capital costs as well as incremental capital costs for revamp opportunities along with the incremental utility, support, and infrastructure costs. The costs, although estimated at the start, can be better assessed once the options have been defined, leading to the development of the optimal configuration for refining the incoming feedstocks.

## 1.4
## Hydrogen Production

Hydrogen is generated in a refinery by the catalytic reforming process, but there may not always be the need to have a catalytic reformer as part of the refinery sequence. Nevertheless, assuming that a catalytic reformer is part of the refinery sequence, the hydrogen production from the reformer usually falls well below the amount required for hydroprocessing purposes. Consequently, an *external* source of hydrogen is necessary to meet the daily hydrogen requirements of any process where the heavier feedstocks are involved, which is accompanied by various energy changes and economic changes to the refinery balance sheet [20].

Thus, hydrogen production as a by-product is not always adequate to the needs of the refinery and other processes are necessary [6,7,21]. Thus, hydrogen production by steam reforming or by partial oxidation of residua has also been used, particularly where heavy oil is available. Steam reforming is the dominant method for hydrogen production and is usually combined with pressure-swing adsorption (PSA) to purify the hydrogen to greater than 99% v/v. However, the process parameters need to be carefully defined in order to optimize capital cost. An unnecessarily stringent specification in the hydrogen purity may cause undesired and unnecessary capital cost – an example is the residual concentration of nitrogen that should not be less than 100 ppm.

The most common, and perhaps the best, feedstocks for steam reforming are low boiling saturated hydrocarbons that have a low sulfur content, including natural gas, refinery gas, liquefied petroleum gas (LPG), and low-boiling naphtha.

*Natural gas* is the most common feedstock for hydrogen production since it meets all the requirements for steam–methane reformer feedstock. Natural gas typically contains more than 90% methane and ethane with only a small percentage of propane and higher boiling hydrocarbons [6,22]. Natural gas may (or most likely will) contain traces of carbon dioxide with some nitrogen and other impurities. Purification of natural gas, before reforming, is usually relatively straightforward. Traces of sulfur must be removed to avoid poisoning the reformer catalyst; zinc oxide treatment in combination with hydrogenation is usually adequate.

However, one of the key variables in operating the steam–methane reforming unit is maintaining the proper steam to carbon ratio, which can be difficult when natural gas containing various hydrocarbons [6,22] is used as the feedstock and if the feedstock is typically a mixture of refinery fuel gas and natural gas, the composition is not constant. If the steam to carbon ratio is too low, carbon will deposit on the catalyst, lowering the activity of the catalyst. In some cases, the catalyst can be completely destroyed, and the unit will need to be shut down to change the catalyst, thereby causing a disruption in the hydrogen supply. On the other hand, if the steam to carbon ratio is run too high, this wastes energy, increases steam consumption, and could also affect throughput.

Light *refinery gas*, containing a substantial amount of hydrogen, can be an attractive steam reformer feedstock since it is produced as a by-product. Processing of refinery gas will depend on its composition, particularly the levels of olefins and of propane and heavier hydrocarbons. Olefins, which can cause problems by forming coke in the reformer, are converted into saturated compounds in the hydrogenation unit. Higher boiling hydrocarbons in refinery gas can also form coke, either on the primary reformer catalyst or in the preheater. If there is more than a small percentage of $C_3$ and higher compounds, a promoted reformer catalyst should be considered, to avoid carbon deposits.

Refinery gas from different sources varies in suitability as hydrogen plant feed. Catalytic reformer off-gas, for example, is saturated, very low in sulfur, and often has high hydrogen content. The process gases from a coking unit or from a fluid catalytic cracking unit are much less desirable because of the content of unsaturated constituents. In addition to olefins, these gases contain substantial amounts of sulfur that must be removed before the gas is used as feedstock. These gases are also generally unsuitable for direct hydrogen recovery, since the hydrogen content is usually too low. Hydrotreater off-gas lies in the middle of the range. It is saturated, so it is readily used as hydrogen plant feed. The content of hydrogen and heavier hydrocarbons depends to a large extent on the upstream pressure. Sulfur removal will generally be required.

The gasification of petroleum residua, petroleum coke, and other feedstocks such as biomass [6,7,23,24] to produce hydrogen and/or power may become an attractive option for refiners. The premise that the gasification section of a refinery will be the *garbage can* for deasphalter residues, high-sulfur coke, as well as other refinery wastes is worthy of consideration. Other processes such as ammonia dissociation, steam–methanol interaction, or electrolysis are also available for hydrogen production, but economic factors and feedstock availability assist in the choice between processing alternatives.

Hydrogen is produced for use in other parts of the refinery as well as for energy and it is often produced from process by-products that may not be of any use elsewhere. Such by-products might be the highly aromatic, heteroatom, and metal containing reject from a deasphalting unit or from a mild hydrocracking process. However attractive this may seem, there will be the need to incorporate a gas cleaning operation to remove any environmentally objectionable components from the hydrogen gas.

When the hydrogen content of the refinery gas is greater than 50% v/v, the gas should first be considered for hydrogen recovery, using a membrane or pressure swing adsorption unit. The tail gas or reject gas that will still contain a substantial amount of hydrogen can then be used as steam reformer feedstock. Generally, the feedstock purification process uses three different refinery gas streams to produce hydrogen. First, high-pressure hydrocracker purge gas is purified in a membrane unit that produces hydrogen at medium pressure and is combined with medium pressure off-gas that is first purified in a pressure swing adsorption unit. Finally, low-pressure off-gas is compressed, mixed with reject gases from the membrane and pressure swing adsorption units, and used as steam reformer feed.

Various processes are available to purify the hydrogen stream but since the product streams are available as a wide variety of composition, flows, and pressures, the best method of purification will vary. And there are several factors that must also be taken into consideration in the selection of a purification method. These are: (i) hydrogen recovery, (ii) product purity, (iii) pressure profile, (iv) reliability, and (v) cost, an equally important parameter not considered here since the emphasis is on the technical aspects of the purification process.

## 1.5
## Hydrogen Management

In general, considerable variation exists from one refinery to another in the balance between hydrogen produced and hydrogen consumed in the refining operations. However, what is more pertinent to the present chapter is the amounts of hydrogen that are required for hydroprocessing operations, whether these be hydrocracking or the somewhat milder hydrotreating processes. For effective hydroprocessing, a substantial hydrogen partial pressure must be maintained in the reactor and, in order to meet this requirement, an excess of hydrogen above that actually consumed by the process must be fed to the reactor. Part of the hydrogen requirement is met by recycling a stream of hydrogen-rich gas. However, the need still remains to generate hydrogen as makeup material to accommodate the process consumption of 500–3000 scf/bbl depending upon whether the heavy feedstock is being subjected to a predominantly hydrotreating (hydrodesulfurization) or to a predominantly hydrocracking process.

Many existing refinery hydrogen plants use a conventional process, which produces a medium-purity (94–97% v/v) hydrogen product by removing the carbon dioxide in an absorption system and methanation of any remaining carbon oxides. Since the 1980s, most hydrogen plants have been built with pressure swing adsorption (PSA) technology to recover and purify the hydrogen to purities above 99.9%. Since many refinery hydrogen plants utilize refinery off gas feeds containing hydrogen, the actual maximum hydrogen capacity that can be synthesized via steam reforming is not certain since the hydrogen content of the off-gas can change due to operational changes in the hydrotreaters.

Hydrogen management has become a priority in current refinery operations and when planning to produce lower sulfur gasoline and diesel fuels [25–28]. Along with increased hydrogen consumption for deeper hydrotreating, additional hydrogen is needed for processing heavier and higher sulfur crude slates. In many refineries, hydroprocessing capacity and the associated hydrogen network is limiting refinery throughput and operating margins. Furthermore, higher hydrogen purities within the refinery network are becoming more important to boost hydrotreater capacity, achieve product value improvements, and lengthen catalyst life cycles.

Improved hydrogen utilization and expanded or new sources for refinery hydrogen and hydrogen purity optimization are now required to meet the needs of the future transportation fuel market and the drive towards higher refinery profitability. Many refineries developing hydrogen management programs fit into the two general categories of either a catalytic reformer supplied network or an on-purpose hydrogen supply.

Multiple hydrotreating units compete for hydrogen – either by selectively reducing throughput, managing intermediate tankage logistics, or running the catalytic reformer sub-optimally just to satisfy downstream hydrogen requirements. Part of the operating year still runs in hydrogen surplus, and the network may be operated with relatively low hydrogen utilization (consumption/production) at 70–80%. Catalytic reformer off gas hydrogen supply may swing from 75% to 85% hydrogen purity. Hydrogen purity upgrade can be achieved through some hydrotreaters by absorbing heavy hydrocarbons. But without supplemental hydrogen purification, critical control of hydrogen partial pressure in hydroprocessing reactors is difficult, which can affect catalyst life, charge rates, and/or gasoline yields.

More complex refineries, especially those with hydrocracking units, also have on-purpose hydrogen production, typically with a steam–methane reformer that utilizes refinery off gas and supplemental natural gas as feedstock. The steam methane reformer plant provides the swing hydrogen requirements at higher purities (92% to more than 99% hydrogen) and serves a hydrogen network configured with several purity and pressure levels. Multiple purities and existing purification units allow for more optimized hydroprocessing operation by controlling hydrogen partial pressure for maximum benefit. Typical hydrogen utilization is 85–95%.

Over the past four decades, the refining industry has been challenged by changing feedstocks and product slate. In the near future, hydroprocessing options (especially for heavy feedstocks) will become increasingly flexible with improved technologies and improved catalysts. The increasing focus to reduce sulfur content in fuels will assure that the role of *desulfurization* in the refinery increases in importance [29]. Currently, the process of choice is the hydrotreater, in which hydrogen is added to the fuel to remove the sulfur from the fuel.

Because of the increased attention for fuel desulfurization various new process-concepts are being developed with various claims of efficiency and effectiveness. The major developments in three main routes to desulfurization will be (i) advanced hydrotreating (new catalysts, catalytic distillation, processing at mild conditions), (ii) reactive adsorption (type of adsorbent used, process design), and (iii) oxidative desulfurization (catalyst, process design).

However, residuum hydrotreating requires considerably different catalysts and process flows, depending on the specific operation so that efficient hydroconversion through uniform distribution of liquid, hydrogen-rich gas and catalyst across the reactor is assured. In addition to an increase in *guard bed* use [6,7] the industry will see an increase in automated demetallization of fixed-bed systems as well as more units that operate as ebullating-bed hydrocrackers.

For heavy oil upgrading, hydrotreating technology and hydrocracking technology will be the processes of choice. For cleaner transportation fuel production, the main task is the desulfurization of gasoline and diesel. With the advent of various techniques, such as adsorption and biodesulfurization, the future development will be still centralized on hydrodesulfurization techniques.

In fact, hydrocracking will continue to be an indispensable processing technology to modern petroleum refining and petrochemical industry due to its flexibility to feedstocks and product scheme, and high quality products. In particular, high quality naphtha, jet fuel, diesel, and lube base oil can be produced through this technology. The hydrocracker provides a better balance of gasoline and distillates, improves gasoline yield, octane quality, and can supplement the fluid catalytic cracker to upgrade heavy feedstocks. In the hydrocracker, light fuel oil is converted into lighter products under a high hydrogen pressure and over a hot catalyst bed – the main products are naphtha, jet fuel, and diesel oil.

In summary, the modern refinery faces the challenge of meeting an increasing demand for cleaner transportation fuels, as specifications continue to tighten around the world and markets decline for high-sulfur fuel oil. Innovative ideas and solutions to reduce refinery costs must always be considered, including: (i) optimization of the hydrogen management network, (ii) multiple feedstock options for hydrogen production, (iii) optimization of plant capacity, and last but certainly not least (iv) use of hydrogen recovery technologies to maximize hydrogen availability and minimize capital investment.

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