Chapter 8

RECENT ADVANCES IN HYDROCRACKING

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1. INTRODUCTION

Hydrocracking is a versatile catalytic refining process that upgrades petroleum feedstocks by adding hydrogen, removing impurities and cracking to a desired boiling range. Hydrocracking requires the conversion of a variety of types of molecules and is characterized by the fact that the products are of significantly lower molecular weight than the feed. Hydrocracking feeds can range from heavy vacuum gas oils and coker gas oils to atmospheric gas oils. Products usually range from heavy diesel to light naphtha. Hydrocrackers are designed for and run at a variety of conditions depending on many factors such as type of feed, desired cycle length, expected product slate but in general they will operate at the following range of conditions: LHSV - 0.5-2.0 hr^{-1}, H_2 circulation - 5,000-10,000 SCFB (850-1,700 NM^3/M^3), H_{2PP} 1,500-2,000 psia (103-138 bars) and SOR temperatures ranging between 675 and 725 °F (357-385 °C). Hydrocracking is particularly well suited to generating products that meet or exceed all of the present tough environmental regulations.

2. HISTORY

While the first commercial installation of a unit employing the type of technology in use today was started up in Chevron's Richmond, California refinery in 1960, hydrocracking is one of the oldest hydrocarbon conversion processes. Its origin is the work done by Sabatier and Senderens, who in 1897 published the discovery that unsaturated hydrocarbons could be hydrogenated in the vapor phase over a nickel catalyst.[1] In 1904, Ipatieff extended the range of feasible hydrogenation reactions by the introduction of elevated hydrogen pressures.[2] At the time, the progress of the automobile industry was expected to entail a considerable increase in the consumption of gasoline. This led to the experimental work by Bergius,[3] started in 1910 in Hanover, Germany. He sought to produce gasoline by cracking heavy oils and oil residues as well as converting coal to liquid fuels. He realized that to remedy the inferior quality of the unsaturated gasoline so produced, the hydrogen removed mostly in the form of methane during the cracking operation has to be replaced by addition of new hydrogen. Thus, formation of coke was avoided and the gasoline produced was of a rather saturated character. Bergius also noted that the sulfur contained in the oils was eliminated for the most part as H_2S. Ferric oxide was used in the Bergius process to remove the sulfur. Actually, the ferric oxide and sulfides formed in the process acted as catalysts, though the activity was poor. Actual hydrocracking technology for coal conversion was developed in Germany as early as 1915 designed to secure a supply of liquid fuels derived from domestic deposits of coal. The first plant for hydrogenation of brown coal was put on stream in Leuna Germany in 1927,[4] applying what may be considered the first commercial hydrocracking process. Conversion of coal to liquid fuels was a catalytic process operating at high pressures, 3000 - 10,000 psig (207-690 bar) and high temperatures, 700 - 1000 ^oF (371-538 ^oC).

The large scale industrial development of hydrogenation in Europe, particularly in Germany, was due entirely to military considerations. Germany used hydrogenation extensively during World War II to produce gasoline: 3.5 million tons were produced in 1944.[5] The emergent availability of Middle Eastern crude after World War II removed the incentive to convert coal to liquid fuels, so continuing the development of hydrocracking technology became less important.

Even though hydrogenation has been of interest to the petroleum industry for many years, little commercial use of hydrogen-consuming processes has been made because of the lack of low-cost hydrogen. That changed in the early 1950s with the advent of catalytic reforming, which made available by-product hydrogen. That brought up an extensive and increased interest in processes that will utilize this hydrogen to upgrade petroleum stocks.

Another factor was that in the mid-1950's the automobile industry started manufacturing high-performance cars with high-compression ratio engines, which required high-octane gasoline. Thus catalytic cracking expanded rapidly and generated, in addition to gasoline, large quantities of refractory cycle stock that was difficult to convert to gasoline and lighter products. This need to convert refractory stock to gasoline was filled by hydrocracking. Furthermore, the switch of railroads from steam to diesel engines after World War II and the introduction of commercial jet aircraft in the late 1950s increased the demand for diesel fuel and jet fuel. The flexibility of the newly developed hydrocracking processes made possible the production of such fuels from heavier feedstocks.[6]

The early hydrocrackers used amorphous silica alumina catalysts. The rapid growth of hydrocracking in the 1960s was accompanied by the development of new, zeolite based hydrocracking catalysts. They showed a significant improvement in certain performance characteristics as compared with amorphous catalysts: higher activity, better ammonia tolerance and higher gasoline selectivity. While hydrocracking was used in the United States primarily in the production of high-octane gasoline, it grew in other parts of the world, starting in the 1970s primarily for the production of middle distillates. The amorphous catalysts remained the catalysts of choice for this application, though some 'flexible' catalysts were developed that made it possible to maximize the yield of different products by using the same catalyst but changing the operating conditions. As of the beginning of 2002, there were more than 150 hydrocrackers operating in the world with a total capacity in excess of 3,800,000 B/D (500,000 MT/D).[7]

3. FLOW SCHEMES

Various licensors have slightly different names for their hydrocracking units flow schemes, but in general, they can be grouped into major two categories: single stage and two stage. Table 1 shows the general evolution of flows schemes, generally driven by improvements in catalysts.[8]

Table 1. Evolution of Hydrocracking Units Flow Schemes

Date	Process Scheme	Reason
Early 60's	Separate Hydrotreating	Low activity amorphous catalyst
Mid 60's	Two Stage Hydrocracking	Advent of zeolitic catalysts More economical scheme
Late 60's	Single Stage	More efficient design & cost
70's and 80's	Once through, partial conversion	Upgraded unconverted oil for FCC or ethylene plant feed, lube oil base stock

3.1 Single Stage Once-Through Hydrocracking

Figure 1 shows a schematic of a single stage, once through hydrocracking unit, which is the simplest configuration for a hydrocracker. It is a variation of the single stage hydrocracking with recycle configuration (described in 3.2). The feed mixes with hydrogen and goes to the reactor. The effluent goes to fractionation, with the unconverted material being taken out of the unit as unconverted material. This type of unit is the lowest cost hydrocracking unit, can process heavy, high boiling feed stocks and produces high value unconverted material which becomes feed stock for FCC units, ethylene plants or lube oil units. In general, the conversion of the feed stock to products is 60-70 vol%, but can range as high as 90 vol%.

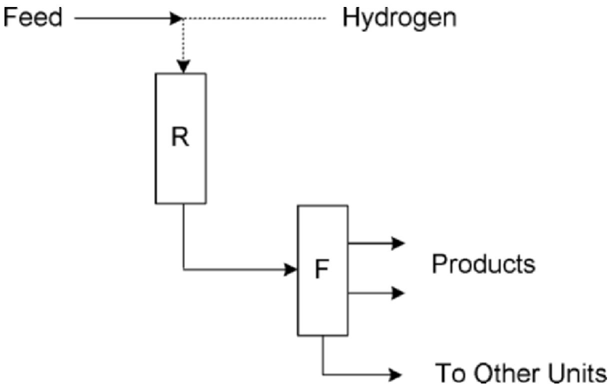


Figure 1. Single Stage Once Through Hydrocracking Unit. R = Reactor(s), F = Fractionation

3.2 Single Stage with Recycle Hydrocracking

The most widely found hydrocracking unit is the single stage with recycle in which the unconverted feed is sent back to the reactor section for further conversion. Figure 2 depicts this type unit. It is the most cost-effective design for 100% (or near 100%) conversion and is especially used to maximize diesel product.

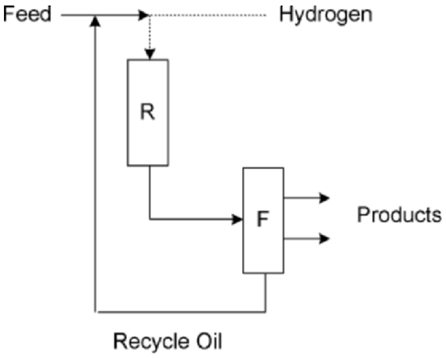


Figure 2. Single Stage Hydrocracking unit with Recycle. R = Reactor(s), F = Fractionation

A more detailed flow diagram (than those shown in either Figures 1 & 2) of the reactor section in a single stage hydrocracker is shown in Figure 3. The fresh feed is passed downward through the catalyst in presence of hydrogen, after being preheated to reaction temperature by passing it through heat exchangers and a heater. The effluent from the reactors goes through a series of separators where hydrogen is recovered and, together with make up hydrogen, is recycled to the reactors.

The liquid product is sent to fractionation where the final products are separated from unconverted oil. In once-through units, the unconverted oil leaves the unit, as previously described. In units designed to operate with recycle, the unconverted oil combines with the fresh feed (Figure 3). As described in the next section, the reaction section fulfills two functions: pre-treating and cracking. In most units, these functions occur in separate reactors, though both can occur in one reactor when using amorphous catalysts

When using a pre-treat & cracking catalyst configuration, the first catalyst (a hydrotreating catalyst) converts organic sulfur and nitrogen from hetero compounds in the feedstock to hydrogen sulfide and ammonia, respectively. The deleterious effect of H_2S and NH_3 on hydrocracking catalysts is considerably less than that of the corresponding organic hetero compounds. The hydrotreating catalyst also facilitates the hydrogenation of aromatics. In the single stage, two reactor configuration, the products from the first reactor are passed over a hydrocracking catalyst in the second reactor where most of the hydrocracking takes place. The conversion occurs in the presence of NH_3, H_2S, and small amounts of unconverted amounts of hetero compounds. The hydrotreating catalyst in the first reactor is designed to convert the hetero compounds in the feed stock. Typically, such catalysts comprise sulfided molybdenum and nickel on an alumina support. The reactor operates at temperatures varying from 570 to 800 °F (300-425 °C) and hydrogen partial pressures between 1,250 and 2,500 psig (85-170 bar). Under these conditions, in addition to heteroatom elimination, significant hydrogenation occurs and some cracking also takes place. The cracking reactor operates at the same hydrogen pressures but at temperatures varying from 570 to as high as 840 °F (300 - 450 °C) for amorphous hydrocracking catalysts and up to 440 °C (825 °F) for zeolite containing catalysts.

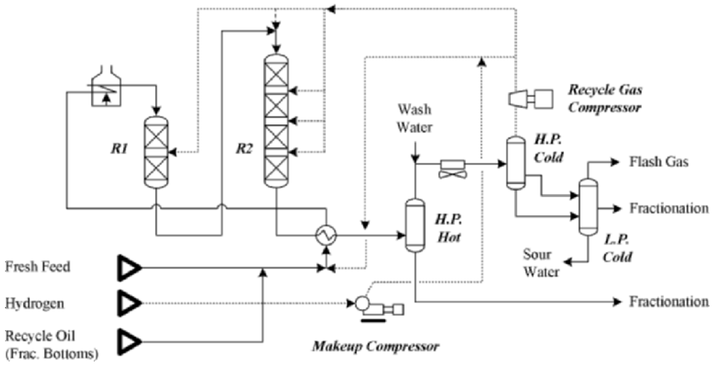


Figure 3. Typical Flow Diagram of Reactor Section of Single Stage Hydrocracker (or first stage of a two stage hydrocracker)

3.3 Two Stage Recycle Hydrocracking

The two stage hydrocracking process configuration is also widely used, especially for large throughput units. In two stage units, the hydrotreating and some cracking takes place in the first stage. The effluent from the first stage is separated and fractionated, with the unconverted oil going to the second stage. The unconverted oil from the second stage reaction section goes back to the common fractionator. A simplified schematic of a two stage hydrocracker is shown in Figure 4. The catalysts in the first stage are the same types as those used in the single stage configuration. The catalyst in the second stage is operating in near absence of ammonia, and depending on the particular design, in the absence or presence of hydrogen sulfide. The near absence of NH_3 and H_2S allows the use of either noble metal or base metal sulfide hydrocracking catalysts.

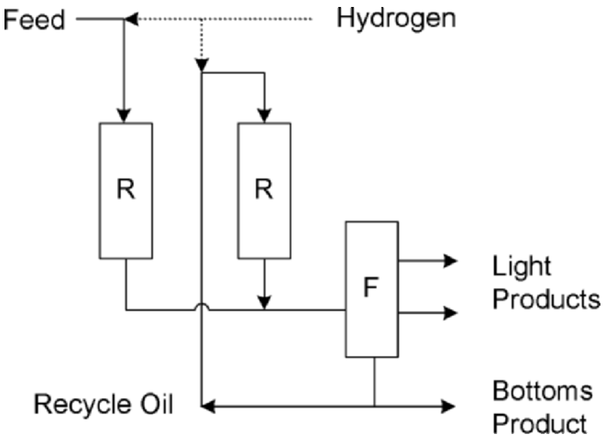


Figure 4. Two Stage Hydrocracking. R = Reactor(s), F = Fractionation

3.4 Separate Hydrotreat Two Stage Hydrocracking

A variation of the typical two stage hydrocracking with common hydrogen circulation loop is the separate hydrotreat hydrocracking shown in Figure 5 in which each stage has a separate hydrogen circulation loop, allowing for operation of the second stage in the near absence of hydrogen sulfide (and ammonia).

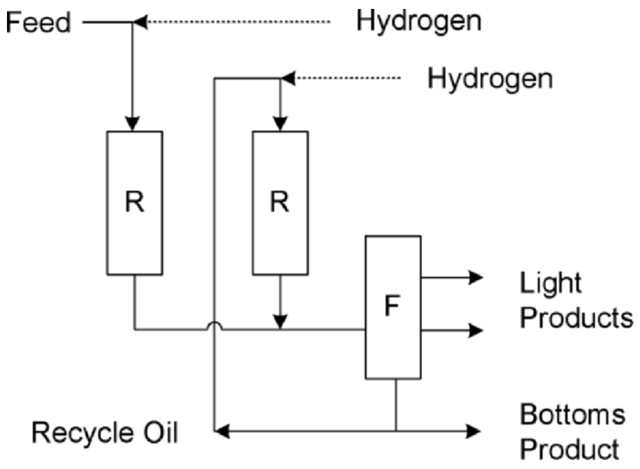


Figure 5. Separate Hydrotreat Two Stage Hydrocracking. R = Reactor(s), F = Fractionation

4. CHEMISTRY

Hydrocracking converts the heavy feed stock to lower molecular weights products, removes sulfur and nitrogen and saturates olefins and aromatics. The organic sulfur is transformed into H_2S, the nitrogen is transformed into NH_3 and the oxygen compounds (not always present) are transformed into H_2O. The reactions in hydrocracking can be classified in two categories: desirable and undesirable. Desirable are the treating, saturation and cracking reactions. Undesirable reactions are contaminant poisoning as well as coking of the catalyst. There are two types of reactions taking place in hydrocracking units: treating (also called pre-treating) and cracking (also called hydrocracking). The cracking reactions require bi-functional catalyst, which possess a dual function of cracking and hydrogenation.

4.1 Treating Reactions

The treating reactions that will take place (if the respective contaminants are present) are the following: sulfur removal, nitrogen removal, organo-metallic compound removal, olefin saturation, oxygen removal and halides removal. The first three types of compounds are always present though in varying amounts depending on the source of feed stock. The others are not always present. In general, the treating reactions proceed in the following descending order of ease: (organo) metals removal, olefin saturation, sulfur removal, nitrogen removal, oxygen removal and halide removal. Some aromatic saturation also occurs in the pre-treating section. Hydrogen is consumed in all treating reactions. In general, the desulfurization reaction consumes 100-150 SCFB/wt% change (17-25 NM^3/M^3/wt% change) and the denitrogenation reaction consumes 200-350 SCFB/wt% change (34-59 NM^3/M^3/wt% change). Typically, the heat released in pretreating is about 0.02 °F/SCFB H_2 consumed (0.002 °C/NM^3/M^3 H_2).

The postulated mechanism for the desulfurization reaction is shown in Figure 6: first, the sulfur is removed followed by the saturation of the intermediate olefin compound. In the example below the thiophene is converted to butene as an intermediate which is then saturated into butane.

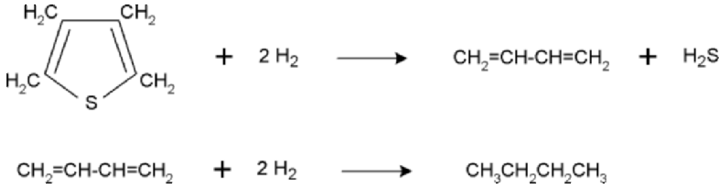


Figure 6. Postulated Mechanism for Hydrodesulfurization

Listed below in Figure 7 are several desulfurization reactions arranged in increasing order of difficulty.

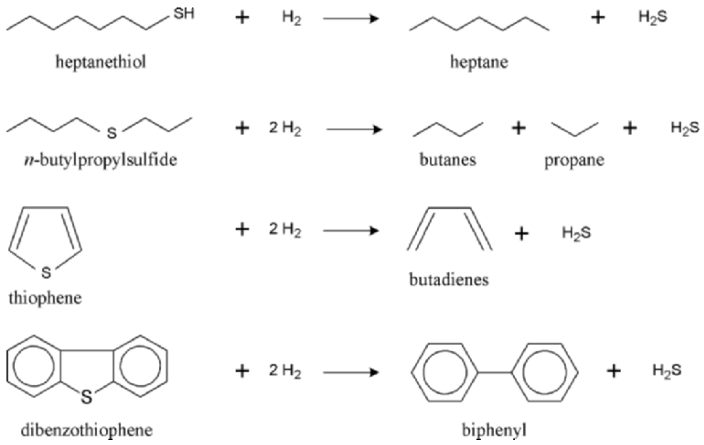


Figure 7. Typical Desulfurization Reactions

The denitrogenation reaction proceeds through a different path. In the postulated mechanism for hydrodenitrogenation the aromatic hydrogenation occurs first, followed by hydrogenolysis and, finally denitrogenation. This is shown in Figure 8. Figure 9 shows a few typical examples of denitrogenation reactions.

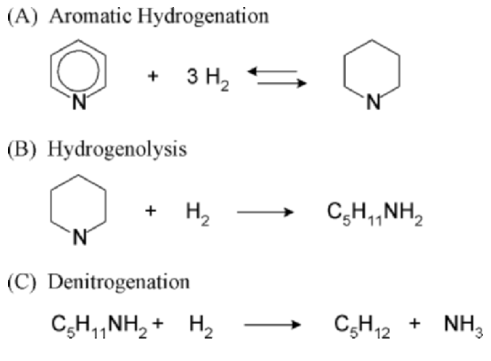


Figure 8. Postulated mechanism for Hydrodenitrogenation

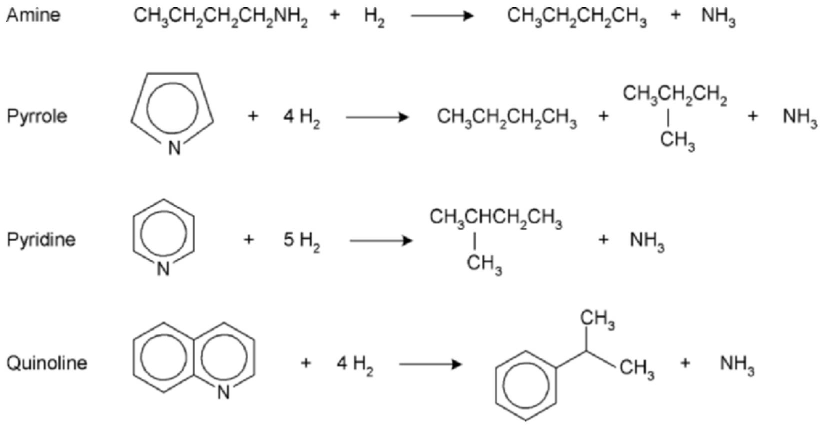


Figure 9. Typical Denitrogenation Reactions

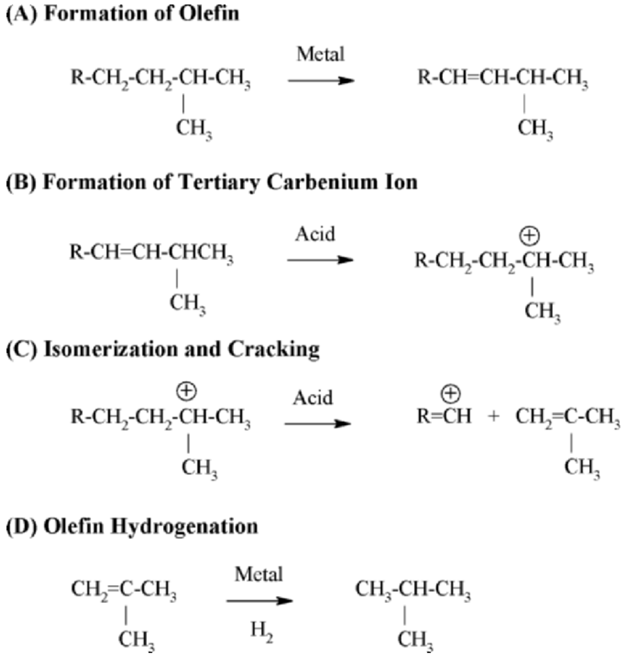
4.2 Cracking Reactions

Hydrocracking reactions proceed through a bifunctional mechanism. A bifunctional mechanism is one that requires two distinct types of catalytic sites to catalyze separate steps in the reaction sequence. These two functions are the acid function, which provide for the cracking and isomerization and the metal function, which provide for the olefin formation and hydrogenation. The cracking reaction requires heat while the hydrogenation reaction generates heat. Overall, there is heat release in hydrocracking, and just like in treating, it is a function of the hydrogen consumption (the higher the consumption, the more important the exotherm). Generally, the hydrogen consumption in hydrocracking (including the pretreating section) is 1200-2400 SCFB/wt% change (200-420 NM^3/M^3/wt% change) resulting in a typical heat release of 50-100 BTU/SCF H_2 (2.1-4.2 $Kcal/M^3$ H_2) which translates into a temperature increase of about 0.065 °F/SCF H_2 consumed

(0.006 °C/NM^3/M^3 H_2). This includes the heat release generated in the treating section.

In general, the hydrocracking reaction starts with the generation of an olefin or cycleolefin on a metal site on the catalyst. Next, an acid site adds a proton to the olefin or cycloolefin to produce a carbenium ion. The carbenium ion cracks to a smaller carbenium ion and a smaller olefin. These products are the primary hydrocracking products. These primary products can react further to produce still smaller secondary hydrocracking products. The reaction sequence can be terminated at primary products by abstracting a proton from the carbenium ion to form an olefin at an acid site and by saturating the olefin at a metal site. Figure 10 illustrates the specific steps involved in the hydrocracking of paraffins. The reaction begins with the generation of an olefin and the conversion of the olefin to a carbenium ion. The carbenium ion typically isomerizes to form a more stable tertiary carbenium ion. Next, the cracking reaction occurs at a bond that is β to the carbenium ion charge. The β position is the second bond from the ionic charge. Carbenium ions can react with olefins to transfer charge form one fragment to the other. In this way, charge can be transferred from a smaller hydrocarbon fragment to a larger fragment that can better accommodate the charge. Finally, olefin hydrogenation completes the mechanism. The hydrocracking mechanism is selective for cracking of higher carbon number paraffins. This selectivity is due in part to a more favorable equilibrium for the formation of higher carbon number olefins. In addition, large paraffins adsorb more strongly. The carbenium ion intermediate causes extensive isomerization of the products, especially to α methyl isomers, because tertiary carbenium ions are more stable. Finally, the production of C_1 to C_3 is low because the production of these light gases involves the unfavorable formation of primary and secondary carbenium ions. Other molecular species such as alkyl naphthenes, alkyl aromatics and so on react via similar mechanisms eg via the carbenium ion mechanism.

In summary, hydrocracking occurs as the result of a bifunctional mechanism that involves olefin dehydrogenation-hydrogenation reactions on a metal site, carbenium ion formation on an acid site, and isomerization and cracking of the carbenium ion. The hydrocracking reactions tend to favor conversion of large molecules because the equilibrium for olefin formation is more favorable for large molecules and because the relative strength of adsorption is greater for large molecules. In hydrocracking, the products are highly isomerized, C_1 and C_3 formation is low, and single rings are relatively stable.


(A) Formation of Olefin

(B) Formation of Tertiary Carbenium Ion

(C) Isomerization and Cracking

(D) Olefin Hydrogenation

Figure 10. Postulated Hydrocracking Mechanism of n-Paraffins

In addition to treating and hydrocracking several other important reactions take place in hydrocrackers. These are aromatic saturation, polynuclear aromatics (PNA) formation and coke formation. Some aromatic saturation occurs in the treating section and some in the cracking section. Aromatic saturation is the only reaction in hydrocracking which is equilibrium limited at the higher temperatures reached by hydrocrackers toward the end of the catalyst cycle life. Because of this equilibrium limitation, complete aromatic saturation is not possible toward the end of the catalyst cycle when reactor temperature has to be increased to make up for the loss in catalyst activity resulting from coke formation and deposition. Figure 11 shows the thermodynamics of the major reactions taking place in a hydrocracker. Of course, the principles of thermodynamics provide the means to determine which reactions are possible. In general, the thermodynamic equilibrium for hydrocracking is favorable. Cracking reactions, desulfurization and denitrogenation are favored at the typical hydrocracker operating conditions. The initial step in the hydrocracking of paraffins or naphthenes is the generation of an olefin or cycloolefin. This step is unfavorable under the high hydrogen partial pressure used in hydrocracking. The dehydrogenation of the smaller alkanes is most unfavorable. Nevertheless, the concentration of olefins and cycloolefins is sufficiently high, and the conversion of these intermediates to carbenium ions is sufficiently fast so that the overall hydrocracking rate is not limited by the equilibrium olefin levels.

Reaction	**Equilibrium**	**Heat of Reaction**
Olefin Formation	**Unfavorable But Not Limiting**	**Endothermic**
Aromatic Saturation	**Unfavorable At High Temperature**	**Exothermic**
Cracking	**Favorable**	**Endothermic**
HDS	**Favorable**	**Exothermic**
HDN	**Favorable**	**Exothermic**

Figure 11. Thermodynamics of Major Reactions in Hydrocracking

Polynuclear aromatics (PNA), sometimes called polycyclic aromatics (PCA) or polyaromatic hydrocarbons (PAH) are compounds containing at least two benzene rings in the molecule. Normally, the feed to a hydrocracker can contain PNA with up to seven benzene rings in the molecule. PNA formation is an important, though undesirable, reaction that occurs in hydrocrackers. Figure 12 shows the competing pathways for conversion of multiring aromatics. One pathway starts with metal-catalyzed ring saturation and continues with acid-catalyzed cracking reactions. The other pathway begins with an acid-catalyzed condensation reaction to form a large aromatic-ring compound. This molecule may undergo subsequent condensation reactions to form a large PNA.

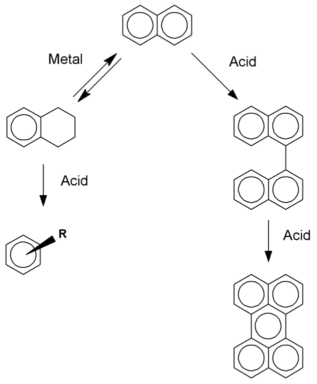


Figure 12. Possible Pathways for Multiring Aromatics

When a hydrocracker is operated with recycle of the unconverted feed, PNA with more than seven benzene rings are created. These are called HPNA (heavy polynuclear aromatics). The consequences of PNA formation are shown in Figure 13. The HPNA produced on the catalyst may exit the reactor and cause downstream fouling; or they may deposit on the catalyst and form coke, which deactivates the catalyst. Their presence results in plugging of equipment. For mitigation a stream of 5 to as much as 10% of unconverted material might have to be taken out of the hydrocracker, resulting in much lower than expected conversion of the feed.

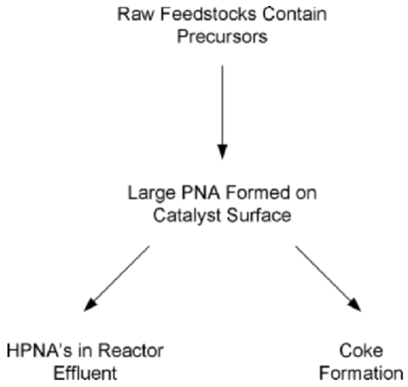


Figure 13. HPNA Formation

5. CATALYSTS

Hydrocracking catalysts are dual function catalysts. For the cracking reaction to occur (as well as some of the other reactions taking place in hydrocracking, such as hydroisomerization and dehydrocyclization), both metallic sites and acidic sites must be present on the catalyst surface. Hydrocracking catalysts have a cracking function and hydrogenation function. The cracking function is provided by an acidic support, whereas the hydrogenation function is provided by metals.

The acidic support consists of amorphous oxides (e.g., silica-alumina, a crystalline zeolite (mostly modified Y zeolite) plus binder (e.g., alumina), or a mixture of crystalline zeolite and amorphous oxides. Cracking and isomerization reactions take place on the acidic support. The metals providing the hydrogenation function can be noble metals (palladium, platinum), or nonnoble (or base) metal sulfides from group VIA (molybdenum, tungsten) and group VIIIA (cobalt, nickel). These metals catalyze the hydrogenation of the feedstock, making it more reactive for cracking and heteroatom removal, as well as reducing the coking rate. They also initiate the cracking by forming a reactive olefin intermediate via dehydrogenation.

The ratio between the catalyst's cracking function and hydrogenation function can be adjusted in order to optimize activity and selectivity. Activity and selectivity are but two of the four key performance criteria by which hydrocracking catalysts are measured:

- Initial activity, which is measured by the temperature required to obtain desired product at the start of the run
- Stability, which is measured by the rate of increase of temperature required to maintain conversion
- Product selectivity, which is a measure of the ability of a catalyst to produce the desired product slate
- Product quality, which is a measure of the ability of the process to produce products with the desired use specifications, such as pour point, smoke point, or cetane number.

For a hydrocracking catalyst to be effective, it is important that there be a rapid molecular transfer between the acid sites and hydrogenation sites in order to avoid undesirable secondary reactions. Rapid molecular transfer can be achieved by having the hydrogenation sites located in the proximity of the cracking (acid) sites.

5.1 Acid Function of the Catalyst

A solid oxide support material supplies the acid function of the hydrocracking catalyst. Amorphous silica-alumina provides the cracking function of amorphous catalysts and serves as support for the hydrogenation metals. Amorphous silica-alumina catalysts are commonly used in distillate producing hydrocracking catalysts. Amorphous silica-alumina also plays a catalytic role in low-zeolite hydrocracking catalysts. In high-zeolite hydrocracking catalysts it acts primarily a support for metals and as binder. Zeolites, particularly Y zeolite, are commonly used in high activity distillate catalysts and in naphtha catalysts. Other acidic support components such as acid-treated clays, pillared clays, layered silicates, acid metal phosphates and other solid acids have been tried in the past, however, present day hydrocracking catalysts do not contain any of these materials.

Amorphous mixed metal oxide supports are acidic because of the difference in charge between adjacent cations in the oxide structure. The advantages of amorphous silica-alumina for hydrocracking are that it has large pores, which permit access of bulky feed stock molecules to the acidic sites, and moderate activity, which makes the metal-acid balance needed for distillate selectivity easier to obtain. Figure 14 is an illustration of silica-alumina acid sites. The substitution of an Al_3^+ cation for a Si_4^+ cation leaves a net negative charge on the framework that can be balanced by an acidic proton. The removal of water from this Bronsted acid site creates a Lewis acid site. A Bronsted acid site on a catalyst is an acid site where the acidic entity is an ionizable hydrogen. A Lewis acid site on a catalyst is an acid site where the acidic entity is a positive ion such as Al_3^+ rather than an ionizable hydrogen. Although plausible hydrocracking mechanisms can be written for both Bronsted or Lewis sites, Bronsted acidity is believed to be more desirable because Lewis acid sites may catalyze coke formation.

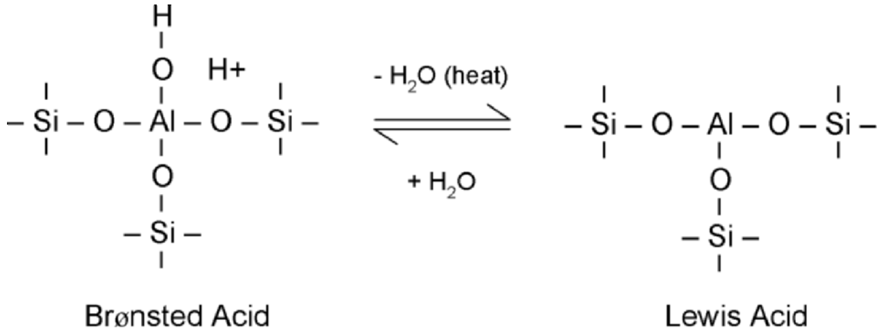


Figure 14. Silica-Alumina Acid Sites

Zeolites are crystalline aluminosilicates composed of Al_2O_3 and SiO_2 tetrahedral units that form a negatively charged microporous framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion-exchange and reversible dehydration. Mobile cations, which are not part of the framework but are part of the zeolites, are readily exchanged. If the mobile cations are exchanged with NH_4^+, followed by calcination to remove NH_3, a Bronsted acid site is formed. The zeolite used in hydrocracking, Y zeolite, is synthetic. It has a structure nearly identical to the naturally found zeolite faujasite. The Y zeolite has both a relatively large free aperture, which controls access of reactants to acid sites, and a three-dimensional pore structure, which allows diffusion of the reactants in and products out with minimal interference. Both Bronsted and Lewis acids are possible in zeolites. The number of acid sites and the strength of the acid sites may be varied. These sites are highly uniform, but each zeolite may have more than one type of site. The following factors influence the number and strength of acid sites in zeolites: the types of cations occupying the ion exchange sites, thermal treatments that the sample has received, and the ratio of silica to alumina of the framework. For example, Y zeolite can be dealuminated by a variety of methods, including thermal and hydrothermal treatments. Dealumination decreases the total numbre of acid sites because each proton is associated with a framework aluminum. However, dealumination also increases the strength of the acid sites to a certain point. As a result, the total acidity of the zeolite, which is a product of the number of sites and strength per site, peaks at an intermediate extent of dealumination. Clearly, the acid site concentration and strength of zeolites affect the final hydrocracking catalyst properties. The principal advantage of zeolites for hydrocracking is their high acidity.

5.2 Metal Function of the Catalyst

A metal, a metal oxide, a metal sulfide, or a combination of these compounds may supply the metal function of the catalyst. The key requirement for the metal function is that it must activate hydrogen and catalyze dehydrogenation and hydrogenation reactions. In addition, metal-catalyzed hydrogenolysis (carbon-carbon breaking) is undesirable because the distribution of the hydrogenolysis products is less desirable relative to hydrocracking.

The most commonly used metal function for hydrocracking catalysts is a combination of Group VIA (Mo,W) and Group VIIIA (Co,Ni) metal sulfides. The major advantage of this combination of metal sulfides is that it is sulfur tolerant; however, it has only moderate activity compared to Pd or Pt. The combination of Group VIA and Group VIIIA metal sulfides has been extensively characterized because of its importance to hydrocracking. Although Group VIIIA metal sulfides have some hydrogenation activity, these sulfides alone are much less active than the Group VIA metal sulfides and are considered to be promoters. The Group VIIIA metal promoter interacts synergistically with the Group VIA metal sulfide to produce a substantial increase in activity.

Because the Group VIA and Group VIIIA metals are most conveniently prepared as oxides, a sulfiding step is necessary. That will be discussed in Section 7 (Catalyst Loading and Activation).

6. CATALYST MANUFACTURING

Hydrocracking catalysts can be manufactured by a variety of methods. The method chosen usually represents a balance between manufacturing cost and the degree to which the desired chemical and physical properties are achieved. Although there is a relationship between catalyst formulation, preparation procedure, and catalyst properties, the details of that relationship are not always well understood due to the complex nature of the catalyst systems. The chemical composition of the catalyst plays a decisive role in its performance; the physical and mechanical properties also play a major role.

The preparation of hydrocracking catalysts involves several steps:

- Precipitation
- Filtration (decantation, centrifugation)
- Washing
- Drying
- Forming
- Calcination
- Impregnation

Other steps, such as kneading or mulling, grinding, and sieving, may also be required. Depending on the preparation method used, some of these steps may be eliminated, whereas other steps may be added. For example, kneading or comulling of the wet solid precursors is used in some processes instead of precipitation. When the metal precursors are precipitated or comulled together with the support precursors, the impregnation step can be eliminated. Described below are the steps that are an integral part of any hydrocracking catalyst manufacturing process

6.1 Precipitation

Precipitation involves the mixing of solutions or suspension of materials, resulting in the formation of a precipitate, which may be crystalline or amorphous. Mulling or kneading of wet solid materials usually leads to the formation of a paste that is subsequently formed and dried. The mulled or kneaded product is submitted to thermal treatment in order to obtain a more intimate contact between components and better homogeneity by thermal diffusion and solid state reactions. Precipitation or mulling is often used to prepare the support for the catalyst and the metal component is subsequently added by impregnation.

The support determines the mechanical properties of the catalyst, such as attrition resistance, hardness, and crushing strength. High surface area and proper pore size distribution is generally required. The pore size distribution and other physical properties of a catalyst support prepared by precipitation are also affected by the precipitation and the aging conditions of the precipitate as well as by subsequent drying, forming and calcining.

6.2 Forming

The final shape and size of catalyst particles is determined in the forming step. Catalysts and catalyst supports are formed into several possible shapes such as spheres, cylindrical extrudates or shaped forms such as trilobes or quadrilobes. Spherical catalyst support catalyst is obtained by ‘oil dropping’ whereby precipitation occurs upon the pouring of a liquid into a second immiscible liquid. Spherical bead catalyst are obtained by this process which is shown in Figure 15.

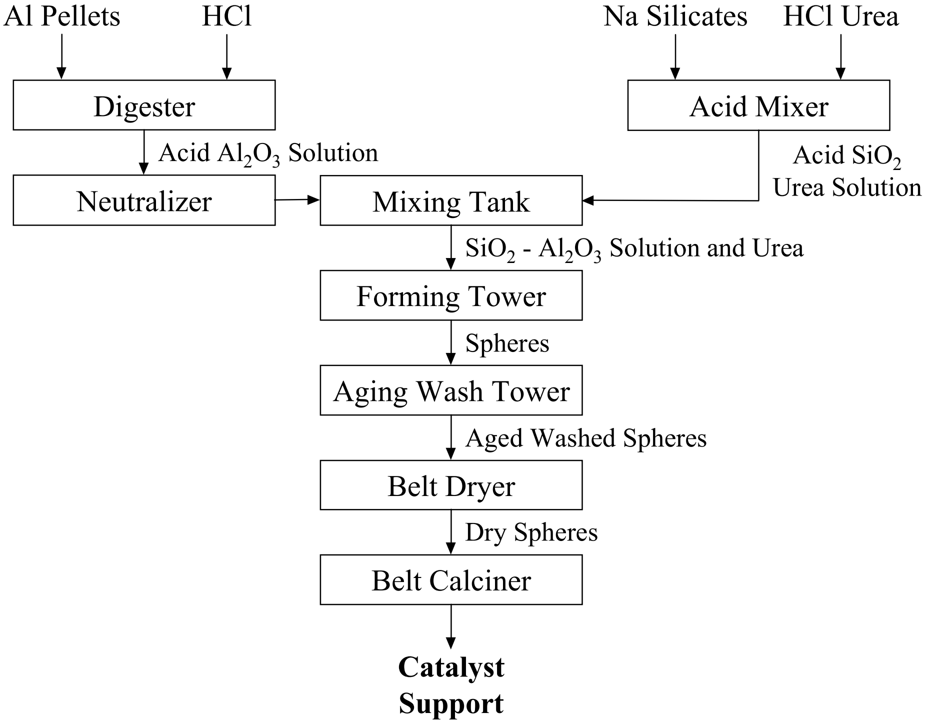


Figure 15. Spherical Catalyst Support Manufacturing

Generally, because of cost considerations, the majority of catalysts are formed in shapes other than spheres. Only amorphous silica-alumina catalysts are formed as spheres.

Extrudates are obtained by extruding a thick paste through a die with perforations. Peptizing agents are usually included in the paste. The spaghetti-like extrudate is usually dried and then broken into short pieces. The typical length to diameter ratio of the extrudates varies between 2 and 4. The extrudate is then dried and/or calcined. The water content of the paste submitted to extrusion is critical because it determines the density, pore size distribution, and mechanical strength of the product. The water content of the paste is usually kept close to the minimum at which extrusion is still possible. Figure 16 shows a typical extrudate support manufacturing.

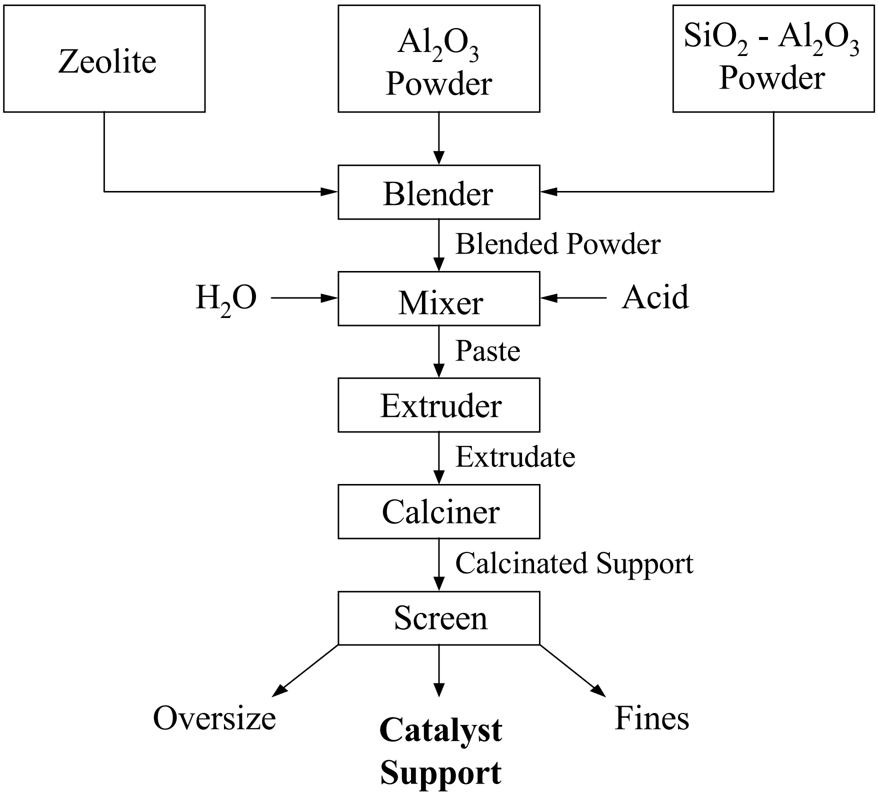


Figure 16. Extrudate Catalyst Support Manufacturing

The form of extrudates may vary. The simplest form is cylindrical, but other forms such as trilobes, twisted trilobes, or quadrilobes, are also found commercially. Catalysts with multilobal cross-sections have a higher surface-to-volume ratio than simple cylindrical extrudates. When used in a fixed bed, these shaped catalyst particles help reduce diffusional resistance, create a more open bed, and reduce pressure drop. Figure 17 depicts several shapes of commercial catalysts used in hydrocracking.

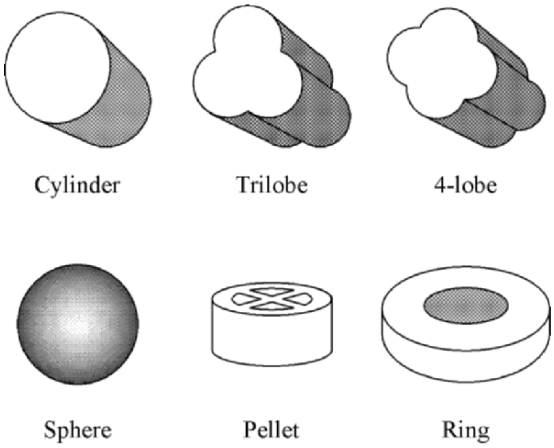


Figure 17. Commercial Catalyst Shapes

6.3 Drying and Calcining

Thermal treatment is generally applied before or after impregnation of the formed catalyst. For catalysts prepared by precipitation or comulling of all the components (including the metal components), only drying may be required prior to forming, with subsequent calcination of the formed product. Thermal treatment of the catalyst or support eliminates water and other volatile matter. The drying and calcination conditions are of critical importance in determining the physical as well as catalytic properties of the product. Surface area, pore size distribution, stability, attrition resistance, crushing strength, as well as the catalytic activity are affected by the drying and calcination conditions.

6.4 Impregnation

Impregnation is used to incorporate a metal component into a preformed catalyst support. Several impregnation methods may be used for catalyst preparation: a) impregnation by immersion (dipping), b) impregnation by incipient wetness, and c) diffusional impregnation. In the first method, which is the most commonly used, the calcined support is immersed in an excess of solution containing the metal compound. The solution fills the pores and is also adsorbed on the support surface. The excess volume is drained off. Impregnation to incipient wetness is carried out by tumbling or spraying the activated support with a volume of solution having the proper concentration of metal compound, and equal to or slightly less than the pore volume of the support. The impregnated support is dried and calcined. Because metal oxides are formed in the process, The calcination step is also called oxidation. In diffusional impregnation the support is saturated with water or with acid solution, and immersed into the acqueous solution containing the metal compound. That compound subsequently diffuses into the pores of the support through the aqueous phase. Figure 18 shows an example of catalyst finishing (impregnation).

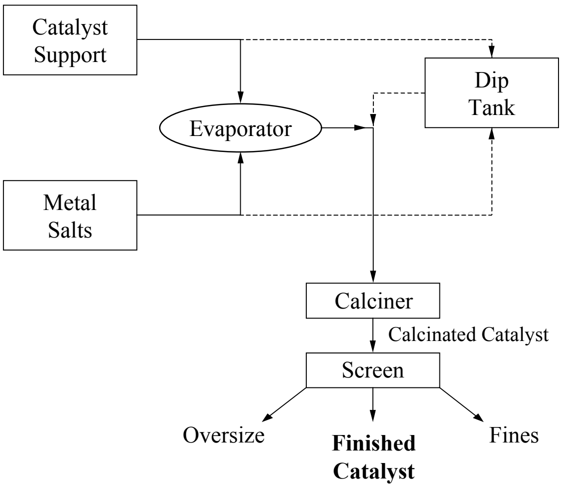


Figure 18. Example of Catalyst Finishing

7. CATALYST LOADING AND ACTIVATION

7.1 Catalyst Loading

There are two methods of catalyst loading sock loading and dense loading. Sock loading is done by pouring catalyst into a hopper mounted on top of the reactor and then allowing it to flow through a sock into the reactor. Dense loading or dense bed packing is done with the help of a mechanical device. The dense loading method was introduced in mid 1970's. Catalyst loaded by sock loading will have a higher void fraction than catalyst that was dense loaded. Dense bed packing and the resulting higher pressure drop provides a more even distribution of liquid in a trickle flow which is the flow regime for most hydrocracker applications. If diffusion limitations are negligible, dense loading is desirable in order to maximize the reaction rate per unit reactor volume. This is often the case in hydrocracking reactors. The other advantage of dense loading is that it orients the catalyst particles in a horizontal and uniform manner. This improves the vapor/liquid distribution through the catalyst beds. Catalyst particle orientation is important especially for cylindrically shaped extruded catalyst in vapor/liquid reactant systems. When the catalyst particles are oriented in a horizontal position in the catalyst bed, liquid maldistribution or channeling is eliminated. This maldistribution tends to occur when the catalyst loading is done by the sock loading method, which generally causes the extrudates to be oriented in a downward slant toward the reactor walls increasing bed voids and creating liquid maldistribution. Of all the factors influencing catalyst utilization, catalyst loading has generally proven to be the most important factor. Except for the hydrocrackers that have reactor pressure drop limitations mainly due to operation at higher than design throughputs, the great majority of units worldwide are dense loaded.

7.2 Catalyst Activation

Hydrocracking catalysts have to be activated in order to be catalytically active. Several names are used for that purpose, such as sulfiding, presulfiding, presulfurizing in addition to activation. The metals on the greatest majority of catalysts are in an oxide form at the completion of the manufacturing process. The noble metal catalysts are activated by hydrogen reduction of the finished catalyst, in which the metal is also in an oxide form. Calcination in air prior to reduction is necessary to avoid metal sintering. The presence of water vapors is generally avoided, also to prevent metal sintering. By using an excess of hydrogen, the water formed during reduction can be swept away. The activation of noble metal catalysts by hydrogen reduction occurs at 570-750 ^{0}F (300-400 ^{0}C).

The nonnoble (base metal) catalysts are activated by transforming the catalytically inactive metal oxides into active metal sulfides (thus the name sulfiding, etc). This is accomplished mainly in situ though some refiners have started to do the activation outside the unit (ex situ). It is likely more and more refiners will opt to receive the catalyst at the refinery site in presulfided state to accelerate the start up of the unit. In situ sulfiding can be accomplished either in vapor or liquid phase. In vapor phase sulfiding, the activation of the catalyst is accomplished by injecting a chemical which decomposes easily to H_2S, such as di-methyl-di-sulphide (DMDS) or di-methyl-sulfide (DMS); use of H_2S was fairly common until a few years ago, but now it is only rarely used because of environmental and safety concerns. Liquid phase sulfiding can be accomplished with or without spiked feedstocks. In the latter case, the feedstock is generally a gas oil type material that contains sulfur compounds in ranges from a few thousand to twenty thousand ppm. The H_2S necessary for the activation of the catalyst is generated by the decomposition of the sulfur compounds. This method is in very little use today, but it was 'state of the art' in the 1960's and early 1970's. The preferred sulfiding procedure in the industry is liquid phase with a spiking agent (generally DMDS or DMS). It results in important savings of time when compared to either vapor phase or liquid phase without spiking agents. Another advantage of liquid phase over gas phase sulfiding is that by having all the catalyst particles wet from the very beginning there is very little chance of catalyst bed channelling which can occur if the catalyst particles are allowed to dry out. The in-situ sulfiding occurs at temperatures between 450 and 600 ^{0}F (230-315 ^{0}C) regardless of the method used. Some catalyst manufacturers recommend the sulfiding be conducted at full operating pressure while others prefer it be done at pressures lower than the normal operating pressure. Ammonia injection is practiced during the sulfiding of high activity (high zeolite content) catalysts to prevent premature catalyst deactivation.

In the case of ex-situ presulfurization of catalyst, sulfur compounds are loaded onto the catalyst. The activation occurs when the catalyst, which has been loaded in the reactor, is heated up in the presence of hydrogen. The activation can be conducted either in vapor or liquid phase. Generally, activation of ex-situ presulfurized catalyst is accomplished faster than if the sulfiding is done in situ, however there is the additional expense due to the need for the ex-situ presulfurization step.

The economics vary from refiner to refiner, however ex-situ presulfurization is rarely used for hydrocracking catalysts.

8. CATALYST DEACTIVATION AND REGENERATION

Catalyst deactivation is the gradual loss of the catalyst's ability to convert the feed into useful products. Catalyst activity is a measure of the relative rate of feedstock conversion. In practical terms it is the temperature required obtaining a fixed conversion. As the run progresses, the catalyst loses activity. Catalyst will lose activity in several ways described below.

8.1 Coke Deposition

Coke deposition is a byproduct of the cracking reactions. The laydown of coke on a catalyst is a time-temperature phenomenon in that the longer the exposure and/or the higher the temperature the catalyst is subjected to, the more severe the deactivating effect. It begins with adsorption of high-molecular weight, low hydrogen/carbon ratio ring compounds; it proceeds with further loss of hydrogen content, and ends with varying degrees of hardness of coke. This coke can cover active sites and/or prevent access to these sites by physical blockage of the entrance to the pores leading to the sites. Coke is not a permanent poison. Catalyst, which has been deactivated by coke deposition, can be, relatively easily, restored to near original condition by regeneration.

8.2 Reversible Poisoning

Catalyst poisoning is primarily the result of strong chemisorption of impurities on active sites. This type of poisoning is reversible - that is, when the deactivating agent is removed, the deactivating effect is gradually reversed. In some cases, raising the catalyst temperature can compensate for the deactivating effect. But, raising temperatures will, however, increase the rate of coke deposition. One example of a reversible poison is carbon monoxide, which can impair the hydrogenation reactions by preferential adsorption on active sites. Another example is H_2S, which in moderate to high concentrations can reduce the desulfurization, rate constant. In this case, the removal of H_2S from the recycle gas system solves the problem.

8.3 Agglomeration of the Hydrogenation Component

Another reversible form of catalyst deactivation is the agglomeration of the hydrogenation component of the catalyst. It can be caused by poor catalyst activation conditions in which a combination of high water partial pressure and high temperature may exist for a prolonged period.

Regeneration can restore the catalyst to near original condition.

8.4 Metals Deposition

Deposition of metals is not reversible, even with catalyst regeneration. The metals may come into the system via additives, such as silicon compounds used in coke drums to reduce foaming, or feedstock contaminants such as Pb, Fe, As, P, Na, Ca, Mg, or as organometallic compounds in the feed primarily containing Ni and V. The deposition of Ni and V takes place at the pore entrances or near the outer surface of the catalyst, creating a ‘rind’ layer - effectively choking off access to the interior part of the catalyst, where most of the surface area resides. Metals deposition can damage the acid sites, the metal sites, or both.

8.5 Catalyst Support Sintering

This is another reason for loss of catalyst activity and it also is irreversible. This is also a result of high temperatures and particularly in connection with high water partial pressures. In this case the catalyst support material can lose surface area from a collapse of pores, or from an increase in the diameter of pores, with the pore volume remaining approximately constant.

8.6 Catalyst Regeneration

A coked catalyst is usually regenerated by combustion in a stream of diluted oxygen or air, although steam or steam-air mixtures have also been used in the past. Upon combustion, coke is converted to CO_2 and H_2O. In the absence of excess oxygen, CO may also form. Except for the noble metal catalysts, hydrocracking catalysts contain sulfur, as the metals are in a sulfide form. In the regeneration process, the sulfur will be emitted as SO_2. In general, sulfur oxide emission starts at lower temperature than CO_2 emission. Regeneration of commercial catalysts can be done in-situ or ex-situ. The majority of commercial catalysts regeneration is performed ex-situ because of environmental considerations as well as because it results in a better performing catalyst. There are several companies that perform ex-situ regeneration by using different equipment for burning off the coke. One company uses a continuous rotolouver, which is a cylindrical drum rotating slowly on a horizontal axis and enclosing a series of overlapping louvers. The spent catalyst passes slowly through the rotolouver, where it encounters a countercurrent of hot air. Another company uses a porous moving belt as a regenerator. The catalyst is moved with the stainless steel belt through a stationary tunnel furnace vessel where the regeneration takes place. A third company regenerator uses ebullated bed technology to perform the catalyst regeneration. Regardless of the process, the spent catalyst is submitted to de-oiling prior to regeneration. This is to eliminate as much hydrocarbon as possible as well as to remove as much sulfur as possible to prevent formation of sulfates which could deposit on the catalyst and not be removed during regeneration. Sulfates are deleterious to catalyst performance.

9. DESIGN AND OPERATION OF HYDROCRACKING REACTORS

9.1 Design and Construction of Hydrocracking Reactors

Hydrocracking reactors are downflow, fixed-bed catalytic reactors, generally operating in trickle flow regime. Because hydrocracking occurs at high pressure and relatively high temperature and in the presence of hydrogen and hydrogen sulfide the reactors are vessels with thick wall constructed from special materials. The reactors are usually cylindrical vessels fabricated from $2^1/_4$ Cr - 1 Mo or 3 Cr - 1 Mo material with stabilized austenitic stainless steel weld overlay or liner, for added corrosion protection. More specialized materials, in which a small amount of Vanadium is added to the $2^1/_4$ Cr - 1Mo or 3 Cr - 1 Mo reactor base metal to increase its strength characteristics, started being used by some fabricators in the last 3 - 5 years. A typical drawing of a hydrocracking reactor is shown in Figure 19.

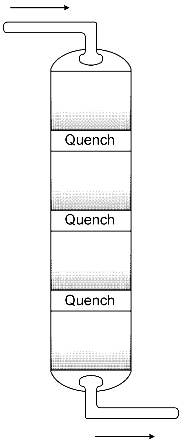


Figure 19 . Typical Hydrocracking Reactor

The size of the hydrocracking reactors varies widely depending on the design conditions and is dependent on the desired mass velocity and acceptable pressure drops. Commercially, reactors with inside diameters of up to 16 ft (4.9 m) have been fabricated. Depending on the design pressure and inside diameter, the thickness of the reactor walls can be as much as 1 ft (30 cm). Since heat release is a common feature for all hydrocrackers, reactor temperature control has to be exercised. As shown schematically in Figure 8.1, a hydrocracking reactor will contain several separate catalyst beds. The number of catalytic beds in a reactor and their respective lengths are determined from the temperature rise profile. The maximum acceptable temperature rise per bed defines the length of the catalyst bed. The acceptable temperature maximum, in turn, depends on the operating mode of the hydrocracker. For example, operations designed to maximize naphtha have a different maximum from those designed the production of middle distillate. A typical reactor operated to maximize naphtha yields will have five or six beds. A typical reactor operated to produce middle distillate will have three or four beds. Commercial catalyst beds can reach lengths up to 20 ft (6 m). A typical pretreating reactor will have two or three beds if the feed is straight run material, and up to five beds if the feed contains appreciable amounts of cracked material. Cold hydrogen gas, introduced in the quench zones, is used for reactor temperature control. The quench zones separating successive catalyst beds have the following functions: (a) to cool the partially reacted fluids with hydrogen quench gas; (b) to assure a uniform temperature distribution the fluids entering the next catalyst bed; and (c) to mix efficiently and disperse evenly the fluids over the top of the next catalyst bed. Since hydrocracking is an exothermic process, the fluids exiting one catalyst bed have to be cooled prior to entering the next catalyst bed, in order to avoid overheating and to provide a safe and stable operation. This is accomplished by thorough mixing with cool hydrogen. Furthermore, the temperature distribution in the cooled fluids entering the next catalyst bed has to be uniform in order to minimize the radial temperature gradients in successive catalyst beds. Unbalanced temperatures in a catalyst bed may result in different reaction rates in the same bed. This can lead to different deactivation rates of the catalyst, and, in worse cases, to temperature excursions. In addition to a uniform temperature distribution, it is also important to achieve a good mass flow distribution. The effective vapor/liquid mixing and uniform distribution of fluids over the top of the catalyst bed, accomplished in the quench zone, reestablishes an even mass flow distribution through the bed. There is a multitude of companies providing vapor/liquid distribution devices, from process licensors, to catalyst manufacturers and, engineering contractors. Most distribution devices perform well, provided they are properly installed. Another important parameter is liquid flux (lbs/hr/sq ft of crossectional area). While gas mass flux has practically no influence on liquid distribution, liquid mass flux is determinant in avoiding maldistribution in the catalyst bed. Operation at a liquid mass flux of more than 2,000 lbs/hr/sq ft is recommended; operation at liquid fluxes lower than 1,500 lbs/hr/sq ft is strongly discouraged. Furthermore, it should be noticed that if the liquid mass flux is below the recommended limit, increasing the gas mass flux will have very little effect, if any, on the liquid distribution (eg it will not improve it).

9.2 Hydrocracking Reactor Operation

During operation, the hydrocracking catalyst gradually loses some of its activity. In order to maintain the conversion of feedstock to products constant, the average bed temperature is gradually increased. The temperature increase in many cases is very small, less than 2 °F/month (1 ^{O}C/month). When the average bed temperature reaches a value close to the designed maximum, the catalyst has to be replaced or reactivated. Because the required temperature increase per unit time is relatively small, the reactor can be operated with the same catalyst for several years before replacement of the deactivated catalyst becomes necessary. Similar changes take place in the pretreating reactor.

Kinetics is the study of the rates of reaction. The rates of reaction determine the key properties of a hydrocracking catalyst: initial activity, selectivity, stability and product quality. The temperature required to obtain the desired product at the start of the run measures the initial activity. In general, the catalyst activity is a measure of the relative rate of feedstock conversion. In hydrocracking, activity is defined as the temperature required obtaining fixed conversion under certain process conditions. Hydrocracking conversion is usually defined in terms of change of endpoint:

$$\% \text{ Conversion} = ((EP^{+}_{\text{feed}} - EP^{+}_{\text{product}})/EP^{+}_{\text{feed}})\text{x}100$$

where EP^{+} indicates the fraction of material in the feed or product boiling above the desired endpoint.

Catalyst selectivity is a measure of the rate of formation of a desired product relative to the rate of conversion of the feed (or formation of other products). Hydrocracking selectivity is expressed as the yield of desired product at a specific conversion. Yield is determined by the rate of formation of the desired product relative to the feed rate. At 100% conversion, catalyst yield equals catalyst selectivity. Hydrocracking selectivity is affected by operating conditions. In general, more severe operating conditions cause higher selectivity for secondary products.

Catalyst stability is a measure of change of reaction rate over time. Hydrocrackers are typically operated in the constant conversion mode, with temperature adjustments made to maintain the desired conversion. Hydrocracking activity stability is defined as the temperature change required maintaining constant conversion. Changes in product yield over time on-stream occur when using zeolitic catalysts. Hydrocracking yield stability is defined as the yield change with time at constant conversion and is usually expressed as a function of temperature change.

The product quality is a measure of the ability of the process to yield products with the desired use specification such as pour point, smoke point or octane. Table 8.2 shows some of the important product quality measurements and the chemical basis for these measurements.

Table 2. Chemical Basis for Product Quality

Quality Measurement	Chemical Basis
High Smoke Point	Low Concentration of Aromatics
Low Pour Point	Low Concentration of n-Paraffins
Low Freeze Point	Low Concentration of n-Paraffins
Low Cloud Point	Low Concentration of n-Paraffins
Low CFPP	Low Concentration of n-Paraffins
High Octane	High Raio of i/n Paraffins
	High Concentration of Aromatics
	High Concentration of Naphthenes

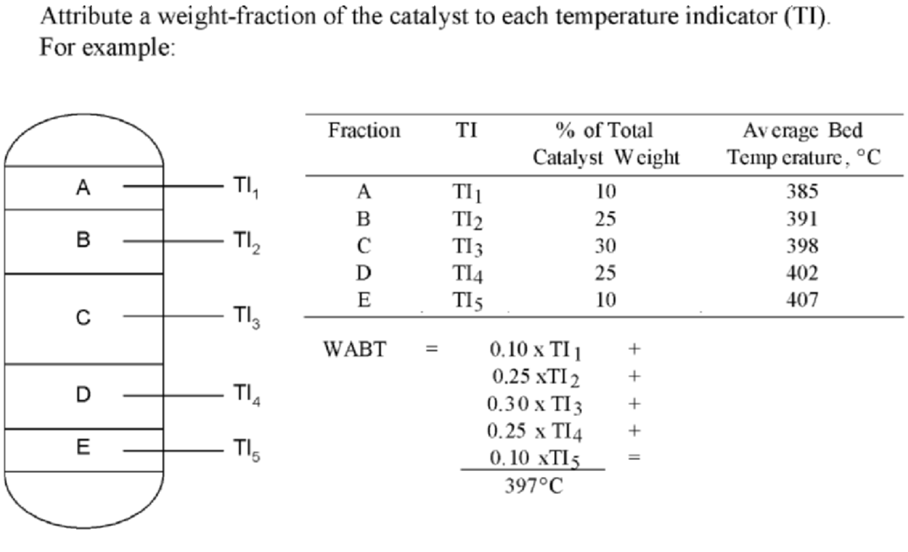
10. HYDROCRACKING PROCESS VARIABLES

The proper operation of the unit will depend on the careful selection and control of the processing conditions. By careful monitoring of these process variables the unit can operate to its full potential.

10.1 Catalyst Temperature

The amount of conversion which takes place in the reactors is going to be determined by several variables; the type of feedstock, the amount of time the feed is in the presence of catalyst, the partial pressure of hydrogen in the catalyst bed, and, most important, the temperature of the catalyst and reactants. The obvious generalization about temperature is that the higher the temperature, the faster the rate of reaction and therefore, the higher the conversion. Since hydrocracking is exothermic, overall, the temperature increases as the feed and recycle gas proceed through the catalyst beds. It is very important that the temperature increase (ΔT) be controlled carefully at all times. It is possible to generate more heat from the reactions than the flowing streams can remove from the reactors. If this happens, the temperature may increase very rapidly. This condition is called a temperature excursion or a temperature runaway. A temperature runaway is a very serious situation since extremely high temperatures can be generated within a short period of time. These high temperatures can cause damage to the catalyst and/or to the reactors. To avoid these situations temperature guidelines have to be observed. These guidelines are dependent on the type of feedstock, and the type of catalyst, and vary from catalyst supplier to catalyst supplier, but by and large, limit the temperature rise of catalyst beds loaded with noble metal catalyst to about 30 °F (17 °C). The temperature rise of catalyst beds loaded with high activity base metal catalysts (for naphtha production) is limited to about 40 °F (22 °C) and those loaded with low zeolite content catalyst (for middle distillate production) the temperature rise is limited to 50 °F (28 °C). Finally, maximum bed temperature rises of about 75 °F (42 °C) are recommended for amorphous catalysts. The same maximum bed temperature rise is also recommended for most pretreating reactors. To properly monitor the reactions as the reactants pass through the catalyst bed, it is not sufficient to just measure the temperature of the flowing stream at the inlet and outlet of each bed and/or the reactor. It is necessary to observe the temperature at the inlet, outlet, and radially throughout the catalyst bed. A temperature profile plot is a useful tool for evaluating performance of catalyst, effectiveness of quench, and reactor flow patterns. A temperature profile can be constructed by plotting the catalyst temperature versus distance into the catalyst bed (or more accurately versus weight percent of catalyst). The hydrocracking reactor should be operated with equal catalyst peak temperatures. In this manner the total catalyst volume is utilized during the entire cycle. The weight average bed temperature (WABT) is typically used to compare the catalyst activity. Figure 20 gives a general description of how the WABT is calculated for a reactor.

The rate of increase of the reactor WABT to maintain both hydrotreating and hydrocracking functions, in order to obtain the desire conversion level and product quality, is referred to as the deactivation rate. It is one of the key variables used to monitor the performance of the catalyst systems. The deactivation rate can be expressed in °F per barrel of feed processed per pound of catalyst (°C per m^3 of feed per kilogram of catalyst) or more simply stated as °F per day (°C per day). The decrease in catalyst activity for hydrotreating catalyst will show up in a decrease in its ability to maintain a constant nitrogen level in the hydrotreating catalyst effluent. For hydrocracking catalyst, a decrease in catalyst activity will generally show up in its ability to maintain a constant conversion to the desired product slate. To hold the same conversion level to the desired product slate the reactor WABT is gradually increased.



Attribute a weight-fraction of the catalyst to each temperature indicator (TI).
For example:

Fraction	TI	% of Total Catalyst Weight	Average Bed Temperature, °C
A	TI_1	10	385
B	TI_2	25	391
C	TI_3	30	398
D	TI_4	25	402
E	TI_5	10	407

$$\text{WABT} = 0.10 \times TI_1 + 0.25 \times TI_2 + 0.30 \times TI_3 + 0.25 \times TI_4 + 0.10 \times TI_5 = 397°\text{C}$$

Figure 20. Example Calculation of Weight Average Reactor Temperature (WABT)

10.2 Conversion

The term “conversion” is usually defined as:

Conversion, vol% = (Fresh Feed - ((Fractionator Bottoms)/Fresh Feed))*100

where:
FF = Fresh feed rate, BPD or m^3/hr
Frac Bottoms = Net fractionator bottoms product to storage, BPD or m^3/hr

Conversion is useful as a measure of the severity of the operation. It requires higher severity (meaning higher catalyst temperature) to go to higher conversion levels and higher severity to reduce the endpoint of the product at a constant conversion. Conversion is normally controlled by catalyst temperature.

10.3 Fresh Feed Quality

The quality of the raw oil charged to a Hydrocracker will affect the temperature required in the catalyst bed to reach the desired conversion, the amount of hydrogen consumed in the process, the length of time before the catalyst is deactivated, and the quality of products. The effect of the feedstock quality on the performance of the unit is important and should be well understood, especially with regard to contaminants that can greatly reduce the life of the catalyst.

10.3.1 Sulfur and Nitrogen Compounds

In general, increasing the amount of organic nitrogen and sulfur compounds contained in the feed results in an increase in severity of the operation. The sulfur content of the feed for a normal vacuum gas oil charge stock can vary up to as high as 2.5 to 3.0 wt. percent. The higher sulfur levels will cause a corresponding increase in the H_2S content of the recycle gas that will normally have little or no effect on catalyst activity.

The organic nitrogen compounds are converted to ammonia which, if allowed to build up in the recycle gas, competes with the hydrocarbon for the active catalyst sights. This results in a lower apparent activity of the catalyst as the ammonia concentration increases. Because of this, feedstocks with high organic nitrogen contents are more difficult to process and require higher catalyst temperatures

10.3.2 Hydrogen Content

The amount of unsaturated compounds (such as olefins and aromatics) contained in the feed will have an effect on the heat released during the reaction and on the total hydrogen consumption on the unit. In general, for a given boiling range feedstock, a reduction in API gravity (increase in specific gravity) indicates an increase in the amount of unsaturated compounds and, therefore, higher heats of reaction and higher hydrogen consumption. Large amounts of unsaturated hydrocarbons can also cause a heat balance problem if the unit has not been designed to process this type of feed.

10.3.3 Boiling Range

The typical charge stock to a Hydrocracker is a 700°F+ (370°C+) boiling range HVGO. Increasing the boiling range usually makes the feed more difficult to process which means higher catalyst temperatures and shorter catalyst life. This is especially true if the feed quality is allowed to decrease significantly due to entrainment of catalyst poisons in the feed. Higher endpoint feeds also usually have higher sulfur and nitrogen contents, which again make it more difficult to process.

10.3.4 Cracked Feed Components

Cracked feedstocks derived from catalytic cracking or thermal cracking can also be processed in a Hydrocracker. These cracked components tend to have higher contaminants such as sulfur, nitrogen, and particulates. They are also more refractory, with high aromatics content and polynuclear aromatic precursors. These compounds make cracked stocks harder to process to produce quality products.

10.3.5 Permanent Catalyst Poisons

Organo-metallic compounds contained in the feed will be decomposed and the metals will be retained on the catalyst, thus decreasing its activity. Since metals are normally not removable by oxidative regeneration, once metals have poisoned a catalyst, its activity cannot be restored. Therefore, metals content of the feedstock is a critical variable that must be carefully controlled. The particular metals which usually exist in vacuum gas oil type feeds are naturally occurring nickel, vanadium and arsenic as well as some metals which are introduced by upstream processing or contamination such as lead, sodium, silicon and phosphorous. Iron naphthenates are soluble in oil and will be a poison to the catalyst. Iron sulfide as corrosion product is normally not considered a poison to the catalyst and is usually omitted when referring to total metals.

The tolerance of the catalyst to metals is difficult to quantify and is somewhat dependent upon the type of catalyst being employed and the severity of the operation, i.e., the higher the severity, the lower will be the metals' tolerance since any impairment of activity will affect the ability to make the desired conversion. It is recommended to keep the total metals in the feedstock as low as possible and certainly not higher than 2 wt-ppm.

10.4 Fresh Feed Rate (LHSV)

The amount of catalyst loaded into the reactors is based upon the quantity and quality of design feedstock and the desired conversion level. The variable that is normally used to relate the amount of catalyst to the amount of feed is termed liquid hourly space velocity (LHSV). LHSV is the ratio of volumetric feed rate per hour to the catalyst volume. Hydrocrackers are normally designed for a LHSV that depends on the severity of the operation. Increasing the fresh feed rate with a constant catalyst volume increases the LHSV and a corresponding increase in catalyst temperature will be required to maintain a constant conversion. The increased catalyst temperature will lead to a faster rate of coke formation and, therefore, reduce the catalyst life. If the LHSV is run significantly higher than the design of the unit, the rate of catalyst deactivation may become unacceptable. Liquid Hourly Space Velocity (LHSV) can be defined as:

$$\text{LHSV (hr}^{-1}\text{)} = \frac{\text{Total Feed to Reactor Inlet}}{\text{Total Catalyst Volume}}$$

10.5 Liquid Recycle

Most Hydrocrackers are designed to recycle unconverted feed from the product fractionator bottoms back to the reactors. This stream is normally material distilled above the heaviest fractionator side cut product. For a distillate producing Hydrocracker, the recycle stream is normally a 600-700°F (315-370°C) heavy diesel plus material.

The liquid recycle rate is normally adjusted as a ratio with fresh feed. This variable is called combined feed ratio (CFR), and is defined as follows:

$$\text{CFR} = \frac{\text{Fresh Feed Rate} + \text{Liquid Recycle Rate}}{\text{Fresh Feed Rate}}$$

It can be seen that if the unit has no liquid recycle from the fractionator back to the reactors, the CFR is 1.0 and the unit is said to operate once-through, i.e., the fresh feed goes through the catalyst bed only once. If the amount of liquid recycle is equal to fresh feed, the CFR will be 2.0.

An important function of liquid recycle is to reduce the severity of the operation. Considering conversion per pass that is defined as follows can show this:

$$\text{Conversion per Pass} = \left(\frac{\text{Feed Rate} - \text{Frac Bottoms Rate to Storage}}{\text{Feed Rate} + \text{Liquid Recycle Rate}}\right) \times 100$$

If a unit were operating once-through (CFR = 1.0), and 100 percent of the feed were converted into products boiling below, i.e. 700°F (370°C), the conversion per pass is 100 percent since the feed only makes one pass through the catalyst. At the other extreme, if a unit is designed at a CFR of 2.0 and

100 percent of the feed converted into products, the conversion per pass is only 50 percent. In this way, it can be seen that as the CFR increases, the conversion per pass decreases. It is also seen that the catalyst temperature requirement is reduced as the CFR is increased (at a constant fresh feed conversion level). Therefore, reducing the CFR below the design value can lead to higher catalyst temperatures and shorter catalyst cycle life. Increasing the CFR above design can be helpful when operating at low fresh feed rates since it does not allow the total mass flow through the catalyst bed to reach such a low value that poor distribution patterns are established.

10.6 Hydrogen Partial Pressure

The reactor section operating pressure is controlled by the pressure that is maintained at the high pressure separator. This pressure, multiplied by the hydrogen purity of the recycle gas, determines the partial pressure of hydrogen at the separator. The hydrogen partial pressure required for the operation of the unit is chosen based on the type of feedstock to be processed and the amount of conversion desired.

The function of hydrogen is to promote the saturation of olefins and aromatics and saturate the cracked hydrocarbons. It is also necessary to prevent excessive condensation reactions from forming coke. For this reason, running the unit for extended periods of time at lower than design partial pressure of hydrogen will result in increased catalyst deactivation rate and shorter time between regeneration.

Hydrogen partial pressure has an impact on the saturation of aromatics. A decrease in system pressure or recycle gas purity has a sharp effect on the product aromatic content. This will be especially true for kerosene aromatic content, which will in turn affect the kerosene product smoke points.

A reduction in operating pressure below its design will have a negative effect on the activity of the catalyst and will accelerate catalyst deactivation due to increased coke formation.

Operating at higher than design pressure may not be possible. There will be a practical equipment limitation on most units that will not allow significantly higher pressure than design, such as the pressure rating of the heaters, exchangers, and vessels. The major control variable for hydrogen partial pressure is the recycle gas purity that should be monitored closely to assure it is always maintained above the minimum value. The hydrogen purity can be improved by increasing the hydrogen purity of the makeup hydrogen, venting gas off the high-pressure separator, or reducing the temperature at the high-pressure separator.

10.7 Recycle Gas Rate

In addition to maintaining a prescribed partial pressure of hydrogen in the reactor section, it is equally important to maintain the physical contact of the hydrogen with the catalyst and hydrocarbon so that the hydrogen is available at the sites where the reaction is taking place. This is accomplished by circulating the recycle gas throughout the reactor circuit continuously with the recycle gas compressor. The amount of gas that must be recycled is a design variable again set by the design severity of the operation. The standard measure of the amount of gas required is the ratio of the gas being recycled to the rate fresh feed is being charged to the catalyst.

As with hydrogen partial pressure, the recycle gas/feed ratio should be maintained at the design ratio. The actual calculation for the gas-to-oil ratio, can be defined as:

$$\text{Gas - To - Oil Ratio} = \frac{\text{Total Circulating Gas to Reactor, Nm}^3\text{/hr}}{\text{Total Feed to Reactor Inlet, m}^3\text{/hr}} = \text{Nm}^3\text{/m}^3 \text{ Feed}$$

As with hydrogen partial pressure, any reduction of the gas-to-oil ratio below the design minimum will have adverse effects on the catalyst life. During normal operations and through out the cycle length, there will be a gradual increase in the reactor section pressure drop. As the pressure drop increases, there will be a tendency for the gas-to-oil ratio to decrease. When the pressure drop through the system increases to the point where the minimum gas-to-oil ratio can not be kept, either the unit throughput will have to be decreased to bring the gas-to-oil ratio back above the minimum, or the unit shutdown for catalyst replacement.

Gas-to-oil ratio recommendations vary between licensors and/or catalyst vendors but in general the minimums recommended are as follows: (a) 4,000 SCFB (675 nm^3/m^3) for amorphous catalyst systems and 5,500 SCFB (925 nm^3/m^3) for zeolitic catalyst systems.

10.8 Makeup Hydrogen

The quality of the hydrogen-rich gas from the hydrogen plant is an important variable to the performance of Hydrocrackers since it can affect the hydrogen partial pressure and recycle gas/feed ratio and thereby influence the catalyst stability (deactivation rate). The following guidelines should be used in operating the hydrogen plant to produce acceptable feed gas to a Hydrocracker.

10.8.1 Hydrogen Purity

The purity of hydrogen in the makeup gas to a Hydrocracker will have a major influence on the hydrogen partial pressure and recycle gas/feed ratio. Therefore, the minimum purity on the makeup gas should be set to provide the minimum recycle gas purity allowed. If the hydrogen plant is unable for some reason to produce minimum hydrogen purity product, it may be possible to purge sufficient recycle gas off the high-pressure separator to maintain the recycle gas purity requirements.

10.8.2 Nitrogen and Methane Content

The total of the nitrogen and methane contained in the makeup gas is only harmful as a diluent, i.e., it will reduce the hydrogen partial pressure and as long as the minimum hydrogen purity is maintained, it will not affect the unit. However, it should be noted that excessive quantities of molecular nitrogen entering a hydrocracker in the makeup gas stream can cause a buildup of nitrogen in the recycle gas since the nitrogen is non-condensable. If this is the case, the nitrogen will have to be removed from the reactor circuit by a small, continuous purge of recycle gas off the high-pressure separator.

10.8.3 CO + CO_2 Content

The normal specification for CO plus CO_2 in the makeup gas stream to a Hydrocracker is in low two-digit mol-ppm maximum. Larger quantities can have a harmful effect on catalyst activity. CO is considered the worst impurity due to the fact that it has a limited solubility in both hydrocarbon and water and will, therefore, build up in the recycle gas. CO_2, on the other hand, is much more soluble and is readily removed from the system in the high-pressure separator liquids.

Both CO and CO_2 have similar effects on the Hydrocracking catalyst; they are converted on the active sites of the catalyst in the presence of hydrogen to methane and water. This methanation of CO and CO_2 competes with the normal hydrocarbon reactants for the catalyst. Therefore, if CO + CO_2 is allowed to build up, higher catalyst temperatures will be required. In an extreme case where a large quantity of CO or CO_2 would be introduced to the Hydrocracker in a short period of time, it is theoretically possible that a temperature excursion would result since the methanation reaction is highly exothermic.

It is recommended practice that if the CO + CO_2 content exceeds the maximum design limit, the catalyst temperature should not be increased to compensate for a resulting decrease in conversion. Catalyst temperature should be maintained at the same level or reduced until the problem causing the high CO + CO_2 is eliminated. In this way the catalyst will not be harmed by increased deactivation at a higher temperature and it will also eliminate the possibility of a temperature runaway due to methanation.

11. HYDROCRACKER LICENSORS AND CATALYST MANUFACTURERS

11.1 Licensors

Hydrocracking licensing started in 1960. Chevron, UOP, Unocal, Shell and Exxon were active from the beginning. Since that time, some 250 hydrocrackers have been licensed worldwide. As of the beginning of 2001, 154 hydrocrackers were in operation. Through the years, the licensing 'landscape' has changed. Currently, the active licensors are Chevron, EMAK (ExxonMobil-Akzo Nobel-Kellogg), IFP and UOP.

11.2 Catalyst Suppliers

Catalysts used in hydrocrackers are pretreating catalysts and cracking catalysts. Following is a list of the current major suppliers of pretreating catalysts: Advanced Refining Technology (in conjunction with Chevron), Albemarle, Criterion, Haldor Topsoe, Procatalyse (in connection with IFP) and UOP. The major cracking catalyst suppliers are: Albemarle, Chevron, Criterion & Zeolyst, Procatalyse (in connection with IFP and UOP).

12. REFERENCES

1. Sabatier, P., Senderens, J.B. Acad. Sci. Paris, **1897**, (124), 1358-1360.
2. Ipatieff, V.N. *Catalytic Reactions at High Pressures and Temperatures*, Macmillan (New York) 1936.
3. Bergius, F. Nobel Prize Lecture, Stockholm, Sweden, 1931
4. Borkin, J. *The Crime and Punishment of I.G. Farben*, Free Press (New York), 1978.
5. Radovic, L.R. in "Synthetic Fuels, Oil Shale, and Tar Sands," http://www.ems.psu.edu/
6. ~Radovic/Chapter10.pdf
7. Sullivan, R.F., Egan, C.J., Langolis, G.E., Seig, R.P. *J. Amer. Chem. Soc.*, **1961** (83) 1156.
8. "Worldwide Refineries, Capacities as of January 1, 2004," *Oil & Gas J.*, Dec. 22, 2003
9. Scherzer, J.; Gruia, A.J., Hydrocracking Science and Technology, Marcell Dekker, Inc.: New York, 1996