Chapter 8

Hydrotreating

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Hydrotreating or catalytic hydrogen treating removes objectionable materials from petroleum fractions by selectively reacting these materials with hydrogen in a reactor at relatively high temperatures at moderate pressures. These objectionable materials include, but are not solely limited to, sulfur, nitrogen, olefins, and aromatics. The lighter materials such as naphtha are generally treated for subsequent processing in catalytic reforming units, and the heavier distillates, ranging from jet fuel to heavy vacuum gas oils, are treated to meet strict product quality specifications or for use as feedstocks elsewhere in the refinery. Hydrotreating is also used for upgrading the quality of atmospheric resids by reducing their sulfur and organo-metallics level. Many of the product quality specifications are driven by environmental regulations that are becoming more stringent every year. Hydrotreaters are designed for and run at a variety of conditions depending on many factors such as type of feed, desired cycle length, expected quality of the products but in general they will operate at the following range of conditions: LHSV—0.2 to 8.0, \( \text{H}_2 \) circulation—300 to 4,000 SCFB (50–675 Nm\(^3\)/m\(^3\)), \( \text{H}_2\text{pp} \)—200–2,000 psia (14–138 bars) and SOR temperatures ranging between 550 and 700°F (290–370°C), with the lower limits representing minimum operating conditions for naphtha hydrotreating and the higher values showing operating conditions used for hydrotreating atmospheric resids. Until about 1980, hydrotreating was a licensed technology being offered by a fairly large number of companies. In the past 25 years, hydrotreating catalysts have become commodities and the process has been offered without licensing fees.

The common objectives and applications of hydrotreating are listed below:

- Naphtha (catalytic reformer feed pretreatment)—to remove sulfur, nitrogen, and metals that otherwise would poison downstream noble metal reforming catalysts
- Kerosene and diesel—to remove sulfur and to saturate olefins and some of the

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aromatics, resulting in improved properties of the streams (kerosene smoke point, diesel cetane number or diesel index) as well as storage stability

- Lube oil—to improve the viscosity index, color, and stability as well as storage stability
- FCC feed—to improve FCC yields, reduce catalyst usage and stack emissions
- Resids—to provide low sulfur fuel oils to effect conversion and/or pretreatment for further conversion downstream.

Brief history

Hydrotreating has its origin in the hydrogenation work done by Sabatier and Senderens, who in 1897 published their discovery that unsaturated hydrocarbons could be hydrogenated in the vapor phase over a nickel catalyst. In 1904, Ipatieff extended the range of feasible hydrogenation reactions by the introduction of elevated hydrogen pressures. 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, started in 1910 in Hanover, Germany who 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 H₂S. 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 very poor. The first plant for hydrogenation of brown coal was put on stream in Leuna Germany in 1927. The past 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. The first commercial hydorefining installation in the United States was at the Standard Oil Company of Louisiana in Baton Rouge in the 1930s. WWII plants were developed by Humble Oil and Refining Company and Shell Development Company, though there was considerably less dependence on hydrogenation as a source of gasoline. 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. As a result of the enormous growth of hydrotreating, as of the beginning of 2001, there were more than 1,600 hydrotreaters operating in the world with a total capacity in excess of 39,000,000 B/D (4,800,000 MT/D).