# HYDROPROCESSING
## FOR CLEAN ENERGY

Design, Operation, and Optimization

**FRANK (XIN X.) ZHU • RICHARD HOEHN**
**VASANT THAKKAR • EDWIN YUH**

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# PREFACE

It all started during a conversation between Frank Zhu and Dick Hoehn over a beer while watching the big ships wind their way through the Bosphorus Strait during a trip to Istanbul for a customer meeting in 2009. The conversation centered on how to pass on some of the things that we have learned over the years, and in doing so, pay homage to those who were willing to share their knowledge with us along the way. We decided that a book would be a good medium to do this, and thus the seed was planted.

We eventually settled on a topic currently relevant to refiners: clean energy with a focus on the production of ultra-low-sulfur diesel (ULSD) in particular. The selection of this topic came from realizing that a paradox exists in the world: people want to enjoy life fueled with a sufficient and affordable energy supply and, at the same time, live in a clean environment. There is no magic formula for achieving this, but with a knowledge of fundamentals and appropriate application of technology, the goal can be realized.

ULSD is an important part of the clean energy mix. It is made by hydroprocessing of certain fractions of petroleum crude oil. It is used in cars, trucks, trains, boats, buses, heavy machinery, and off-road vehicles. The bad news is that without adequate processing to produce clean diesel fuel and upgraded engine technology, diesel engines emit sulfur dioxide and particulates. The impact of fuel sulfur on air quality is widely understood and known to be significant.

There are challenges in producing ULSD in an economical and reliable manner. Over the years, a great deal of effort has been poured into developing the catalysts and process technology to accomplish this. It is intended that this book will be a resource for hydroprocessing technology as it relates to hydroprocessing in general and ULSD

production in particular and that it will be a useful reference for plant managers, hydroprocessing unit engineers, operators, and entry-level design engineers.

We believe that there is currently no book available to provide relevant knowledge and tools for the process design and operation of facilities to produce ULSD, particularly considering the fact that these guidelines and methods have evolved over time to address the issues with the efficient production of ULSD. To this end, we decided that the book should cover four themes: fundamentals, design, assessment, and troubleshooting. That was the reason why the current team of authors was formed to create this book. The four themes correspond with each individual author's experience and expertise. An R&D specialist, Vasant, has an extensive background in the fundamentals of hydroprocessing catalysis (Chapters 3 and 4); Dick has many years of experience in the field of engineering design and development of hydroprocessing technology (Chapters 5–7); Edwin, a technical service specialist, brings a wealth of knowledge about operations and troubleshooting (Chapters 19 and 20); and Frank has both academic and practical background in process energy efficiency, process integration, and assessment methods (all other 13 chapters). The four authors represent a sum total of over 100 years of experience in the field of hydroprocessing.

The purpose of this book is to bridge the gap between hydroprocessing technology developers and the engineers who design and operate the processes. To accomplish this, 6 parts with 20 chapters in total are provided in this book. Part 1 provides an overview of the refining processes including the feeds and products together with their specifications, in particular, the fundamental aspects for hydroprocessing are discussed in detail. Part 2, mainly discusses on process design aspects for both diesel hydrotreating and hydrocracking processes. The focus of Part 3 is on process and heat integration methods for achieving high energy efficiency in design. In Part 4, the basics and operation assessment for major process equipment are discussed. In contrast, Part 5 focuses on process system optimization for achieving higher energy efficiency and economic margin. Last but not least, Part 6 deals with operation, in which operation guidelines are provided and troubleshooting cases are discussed.

Clearly, it was no small effort to write this book; but it was the desire to provide practical methods for helping people understand the issues involved in improving operations and designing for better energy efficiency and lower capital cost, which motivated us. In this endeavor, we owe an enormous debt of gratitude to many of our colleagues at UOP and Honeywell for their generous support in this effort. First of all, we would like to mention Geoff Miller, former vice president of UOP and now vice president of Honeywell, who has provided encouragement in the beginning of this journey for writing this book. We are very grateful to many colleagues for constructive suggestions and comments on the materials contain in this book. We would especially like to thank the following people for their valuable comments and suggestions: Bettina Marie Patena for Chapters 5 through 7, Zhanping (Ping) Xu for Chapter 10, Darren Le Geyt for Chapter 11, Bruce Lieberthal for Chapters 12 and 13, and Phil Daly for Chapter 14. Our sincere gratitude also goes to Charles Griswold, Mark James, and Rich Rossi for their constructive comments. Jane Shao produced beautiful drawings for many figures in the book. The contributions to this book from people

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*June 1, 2016*

# PART 1

# FUNDAMENTALS

# 1

# OVERVIEW OF THIS BOOK

## 1.1 ENERGY SUSTAINABILITY

There is a paradox in this world: people want to enjoy life fueled with sufficient and affordable energy supply. At the same time, people wish to live in a clean environment. This paradox defines the objective of clean energy: provide affordable energy with minimum climate impact. This is a huge challenge technically, economically, geographically, and politically. There is no silver bullet for solving this paradox and the practical path forward is to determine a good mix of different kinds of energy sources. The proportions of this mix depend on the availability of these energy sources and costs of converting them to useful forms in geographic regions.

Energy demand has been increasing significantly over recent years due to the fact that people in emerging regions wish to improve their living standard and enjoy the benefit that energy can bring. Therefore, in the short and middle term, there is more oil and natural gas production to satisfy increased energy demand. To reduce the climate impact, sulfur content for the fossil fuels must be reduced – in particular, ultra-low-sulfur diesel (ULSD) is the focus in the present time. As far as energy efficiency is concerned, cars and trucks have become more fuel efficient and will continue to improve mileage per gallon. Furthermore, electrical and hybrid vehicles will improve energy efficiency even further. On the renewable energy side, the percentage of renewable energy, such as ethanol for gasoline and biodiesel blended into diesel fuel, will gradually increase over time through governmental regulation. Further technology development will make renewable energy such as wind, solar, and biofuels more cost-effective and hence these energy sources will become a sustainable part of the energy mix. These trends will coexist to achieve a balance between

increased energy demand and a cleaner environment, and at the same time, less dependence on foreign oil imports. In the long term, the goal is to increase the proportion of alternative energy in the energy mix to reduce gradually the demand for fossil fuels.

In summary, clean energy is the pathway for meeting the increased energy demand with a sustainable environment and the best future for clean energy is to capitalize on all the options: renewable energy, fossil fuels, increased efficiency, and reduced consumption. When these multiple trends and driving forces work together, the transformation becomes more economical and reliable. Technology developments in clean energy will join forces with regulations and market dynamics in the coming decades and beyond.

## 1.2    ULSD – IMPORTANT PART OF THE ENERGY MIX

ULSD is an important part of clean energy mix. Diesel fuel is made from hydroprocessing of certain fractions of petroleum crude. It is used in cars, trucks, trains, boats, buses, heavy machinery, and off-road vehicles. The bad news is that most diesel engines emit nitrogen oxides that can form ground-level ozone and contribute to acid rain. Diesel engines are also a source of fine particle air pollution. The impact of sulfur on particulate emissions is widely understood and known to be significant. In the European Auto Oil program, detailed study of lower effect on particulate matter (PM) was studied. This study suggests significant benefit from sulfur reductions for heavy-duty trucks. Reductions in fuel sulfur will also provide particulate emission reductions in all engines.

Testing performed on heavy-duty vehicles using the Japanese diesel 13 mode cycle have shown significant PM emission reductions that can be achieved with both catalyst and noncatalyst equipped vehicles. The testing showed that PM emissions from a noncatalyst equipped truck running on 400 ppm sulfur fuel were about double the emissions when operating on 2 ppm fuel (Worldwide Fuel Charter, Sept. 2013).

When sulfur is oxidized during combustion, it forms $SO_2$, which is the primary sulfur compound emitted from the engine. Some of the $SO_2$ is further oxidized – in the engine, exhaust, catalyst, or atmosphere to sulfate ($SO_4$). The sulfate and nearby water molecules often coalesce to form aerosols or engulf nearby carbon to form heavier particulates that have a significant influence on both fine and total PM. Without oxidation catalyst systems, the conversion rate from sulfur to sulfate is very low, typically around 1%, so the historical sulfate contribution to engine-out PM has been negligible. However, oxidation catalysts dramatically increase the conversion rate to as much as 100%, depending on catalyst efficiency. Therefore, for modern vehicle systems, most of which include oxidation catalysts, a large proportion of the engine-out $SO_2$ will be oxidized to $SO_4$, increasing the amount of PM emitted from the vehicle. Thus, fuel sulfur will have a significant impact on fine particulate emissions in direct proportion to the amount of sulfur in the fuel.

In the past, diesel fuel contained higher quantities of sulfur. European emission standards and preferential taxation have forced oil refineries to dramatically reduce the level of sulfur in diesel fuels. Automotive diesel fuel is covered in the European Union by standard EN 590, and the sulfur content has dramatically reduced during the last 20 years. In the 1990s, specifications allowed a content of 2000 ppm maximum of

sulfur. Germany introduced 10 ppm sulfur limit for diesel from January 2003. Other European Union countries and Japan introduced diesel fuel with 10 ppm to the market from the year 2008.

In the United States, the acceptable level of sulfur in the highway diesel was first reduced from 2000 to 500 ppm by the Clean Air Act (CAA) amendments in the 1990s, then to 350, 50, and 15 ppm in the years 2000, 2005, and 2006, respectively. The major changeover process began in June 2006, when the EPA enacted a mandate requiring 80% of the highway diesel fuel produced or imported in order to meet the 15 ppm standard. The new ULSD fuel went on sale at most stations nationwide in mid-October 2006 with the goal of a gradual phase out of 500 ppm diesel.

In 2004, the US EPA also issued the clean air-nonroad-Tier 4 final rule, which mandated that starting in 2007, fuel sulfur levels in nonroad diesel fuel should be reduced from 3000 to 500 ppm. This includes fuels used in locomotive and marine applications, with the exception of marine residual fuel used by very large engines on ocean-going vessels. In 2010, fuel sulfur levels in most nonroad diesel fuel were reduced to 15 ppm, although exemptions for small refiners allowed for some 500 ppm diesel to remain in the system until 2014. After 1 December 2014, all highway, nonroad, locomotive, and marine diesel fuel produced and imported has been ULSD.

The allowable sulfur content for ULSD (15 ppm) is much lower than the previous US on-highway standard for low-sulfur diesel (LSD, 500 ppm), which allows advanced emission control systems to be fitted that would otherwise be poisoned by these compounds. EPA, the California Air Resources Board, engine manufacturers, and others have completed tests and demonstration programs showing that using the advanced emissions control devices enabled by the use of ULSD fuel reduces emissions of hydrocarbons and oxides of nitrogen (precursors of ozone), as well as particular matter to near-zero levels. According to EPA estimates, with the implementation of the new fuel standards for diesel, nitrogen oxide emissions will be reduced by 2.6 million tons each year and soot or particulate matter will be reduced by 110,000 tons a year. EPA studies conclude that ozone and particulate matter cause a range of health problems, including those related to breathing, with children and the elderly those most at risk, and therefore estimates that there are significant health benefits associated with this program.

ULSD fuel will work in concert with a new generation of diesel engines to enable the new generation of diesel vehicles to meet the same strict emission standards as gasoline-powered vehicles. The new engines will utilize an emissions-reducing device called a particulate filter. The process is similar to a self-cleaning oven's cycle: a filter traps the tiny particles of soot in the exhaust fumes. The filter uses a sensor that measures back pressure and indicates the force required to push the exhaust gases out of the engine and through to the tailpipes. As the soot particles in the particulate filter accumulate, the back pressure in the exhaust system increases. When the pressure builds to a certain point, the sensor tells the engine management computer to inject more fuel into the engine. This causes heat to build up in the front of the filter, which burns up the accumulated soot particles. The entire cycle occurs within a few minutes and is undetectable by the vehicle's driver.

Diesel-powered engines and vehicles for 2007 and later model year vehicles are designed to operate only with ULSD fuel. Improper fuel use will reduce the efficiency and durability of engines, permanently damage many advanced emissions control

systems, reduce fuel economy, and possibly prevent the vehicles from running at all. Manufacturer warranties are likely to be voided by improper fuel use. In addition, burning LSD fuel in 2006 and later model year diesel-powered cars, trucks, and buses is illegal and punishable with civil penalties.

The specifications proposed for clean diesel by Worldwide Fuel Charter (WWFC), which reflects the view of the automobile/engine manufactures concerning the fuel qualities for engines in use and for those yet to be developed, require increased cetane index, significant reduction of polynuclear aromatics (PNA), and lower T95 distillation temperature (i.e., the temperature at which 95% of a sample vaporizes) in addition to ultra-low sulfur levels. Automotive manufactures have concluded that substantial reductions in both gasoline and diesel fuel sulfur levels to quasi sulfur-free levels are essential to enable future vehicle technologies to meet the stringent vehicle emissions control requirements and reduce fuel consumption.

As a summary, to meet emission standards, engine manufactures will be required to produce new engines with advanced emission control technologies similar to those already expected for on-road (highway) heavy trucks and buses. Refiners will be producing and supplying ULSD for both highway and nonhighway diesel vehicles and equipment. Although there are still challenges to overcome, the benefits are clear: ULSD and the new emissions-reducing technology that it facilitates will help make the air cleaner and healthier for everyone.

In parallel, alternative technology such as electrical and hybrid-electric cars as well as biofuels for transportation is sought to address climate change issues and seek less dependence on fossil oil. The main driver for use of electrical and hybrid-electric cars is higher energy efficiency and lower greenhouse emissions; but electrical and hybrid-electric models are more expensive than conventional ones. On the other hand, biodiesel, made mainly from recycled cooking oil, soybean oil, other plant oils, and animal fats, has started to be used as blending stock for diesel. Biodiesel can be blended and used in many different concentrations. The most common are B100 (pure biodiesel), B20 (20% biodiesel, 80% petroleum diesel), B5 (5% biodiesel, 95% petroleum diesel), and B2 (2% biodiesel, 98% petroleum diesel). B20 is the most common biodiesel blend in the United States. B20 is popular because it represents a good balance of cost, emissions, cold-weather performance, materials compatibility, and ability to act as a solvent. Most biodiesel users purchase B20 or lower blends from their normal fuel distributors or from biodiesel marketers. However, not all diesel engine manufacturers cover biodiesel use in their warranties. Users should always consult their vehicle and engine warranty statements before using biodiesel.

There are two challenges to overcome in the use of biodiesel. One is the availability of feedstock and the other is the cost. Government subsidies for biofuels are currently being used to encourage expansion of production capacity. Although the social, economic, and regulatory issues associated with expanded production of biodiesel are outside the scope of this book, it is crucial that future commercialization efforts focus on sustainable and cost-effective methods of producing feedstock. Current and future producers are targeting sustainable production scenarios that, in addition to minimizing impact on land-use change and food and water resources, provide an energy alternative that is economically competitive with current petroleum-based fuels. Future growth will require a coordinated effort between feedstock producers, refiners, and industry regulators to ensure environmental impacts are minimized.

If done responsibly, increasing biofuel usage in the transportation sector can significantly reduce greenhouse-gas emissions as well as diversify energy sources, enhance energy security, and stimulate the rural agricultural economy.

## 1.3 TECHNICAL CHALLENGES FOR MAKING ULSD

ULSD is mainly produced from hydrocracking and diesel hydrotreating processes with crude oil as the raw feed in the refinery. Technical solutions for ULSD production can be summarized as follows (Stanislaus et al., 2010):

- Use of highly active catalysts
- Increase of operating severity (e.g., increased temperature, increase in hydrogen pressure, lower LHSV)
- Increase catalyst volume (by using additional reactor, dense loading, etc.)
- Removal of $H_2S$ from recycle gas
- Improve feed distribution in the reactor by using high-efficiency vapor/liquid distribution trays
- Use of easier feeds; reduce feedstock end boiling point
- Use of two-stage reaction system design for hydrocrackers

A combination of the above options may be necessary to achieve the target sulfur level cost-effectively. Selection of the most appropriate option or a combination of those is specific for each refinery depending on its configuration, existing process design, feedstock quality, product slate, hydrogen availability, and so on.

Clearly, there are many design parameters to consider during process design. As an example, consider the design choice for the use of one or two reaction stages in a hydrocracking unit. In single-stage hydrocrackers, all catalysts are contained in a single stage (in one or more series or parallel reactors). A single catalyst type might be employed or a stacked-bed arrangement of two different catalysts might be used. In single-stage hydrocracking, all catalysts are exposed to the high levels of $H_2S$ and $NH_3$ that are generated during removal of organic sulfur and nitrogen from the feed. Ammonia inhibits the hydrocracking catalyst activity, requiring higher operating temperatures to achieve target conversion, but this generally results in somewhat better liquid yields than would be the case if no ammonia were present. There is no interstage product separation in single-stage or series-flow operation.

However, two-stage hydrocrackers employ interstage separation that removes the $H_2S$ and $NH_3$ produced in the first stage. As a consequence, the second-stage hydrocracking catalyst is exposed to lower levels of these gases, especially $NH_3$. Some two-stage hydrocracker designs do result in very high $H_2S$ levels in the second stage. Frequently, unconverted product is separated and recycled back to either the pretreat or the cracking reactors.

Understanding of these fundamentals will be paramount and the related design considerations will be provided in details in this book. Apart from discussions of fundamental aspects of design, the book also provides explanation on how to design

hydrocracking and distillate hydrotreating units by applying applicable theory and design considerations in order to obtain a practical and economic design with the least capital cost and energy use possible. During operation, the primary goal is to achieve safe, reliable, and economic production. Achieving the operation objectives is another focus of discussions in this book.

## 1.4   WHAT IS THE BOOK WRITTEN FOR

The purpose of this book is to bridge the gap between hydroprocessing technology developers and the engineers who design and operate the processes. To accomplish this, 6 parts with 20 chapters in total are provided in this book. The first part provides an overview of the refining processes including the feeds and products together with their specifications, while the second part mainly discusses process design aspects for both diesel hydrotreating and hydrocracking processes. Part 3 focuses on process and heat integration methods for achieving high energy efficiency in design. With Part 4, the basics and operation assessment for major process equipment are discussed. In contrast, Part 5 focuses on process system optimization for achieving higher energy efficiency and economic margin. Last but not least, in Part 6, operation guidelines are provided and troubleshooting cases are discussed.

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# 2

# REFINERY FEEDS, PRODUCTS, AND PROCESSES

## 2.1   INTRODUCTION

Crude oils are feedstock for producing transportation fuels and petrochemical products. Many different kinds of crude oils are available in the market place with different properties and product yields and hence price. The crude price is largely based on its density (or °API gravity), sulfur content, and metals content. For example, light crude oils command a higher price as they contain a larger portion of gasoline, jet fuel, and diesel, which can be sold at higher prices and also requires less processing. Sulfur also impacts crude price. Low-sulfur crude oils command higher prices as they require less hydroprocessing.

The method to determine the properties of crude oils is called crude characterization, which provides the basis for design of new processes, or upgrading existing processes, or predicting how the refinery will need to operate to make the desired products with the required product quality. First, crude characterization can help a refiner to know if the process technology in the refinery can handle a certain crude feed in order to make desirable products with acceptable quality. Second, it provides insights into the compatibility of different crude oils being mixed together. Third, it sets the basis for developing operational guidelines for achieving predicted yields.

The ASTM (American Society for Testing Materials) methods for crude characterization are the most well known, which will be discussed in detail here. At the same time, major refining processes will be briefly explained.

## 2.2   ASTM STANDARD FOR CRUDE CHARACTERIZATION

Because crude oils are a mixture of many different chemical compounds, they cannot be evaluated based on chemical analysis alone. In order to characterize any crude oil and refining products, the petroleum industry has developed a number of shorthand methods for describing hydrocarbon compounds by the number of carbon atoms and unsaturated bonds in the molecule and using distillation temperatures and other easily obtained properties to specify crude and products.

In characterization of certain crude, the test methods, known as ASTM methods, are conducted in laboratory. Through distillation, crude is then cut into several products so that product yields and properties can then be predicted. Thus, crude characterization is about crude distillation, product fractions, and properties. This information can be used for simulation of the process streams in question. There are three types of ASTM crude characterization methods. The first one is the simplest using single stage of distillation, which include D-86 and D-1160. The second one is called TBP (true boiling point) distillation based on multiple theoretical stages, and D-2892 is an example of the TBP distillation. The third one is SD (simulated distillation) based on gas chromatography, which is the most consistent method. D-2287 and D-3710 are the examples of gas chromatography. The distillation data from these three methods can be intercorrelated. These ASTM methods are explained as follows.

### 2.2.1   ASTM D-86 Distillation

The D-86 distillation method was developed for characterization of the product fraction of the crude that can be obtained via atmospheric distillation. It can be used for characterizing crude oil and petroleum fractions with IBPs (initial boiling points) slightly above room temperature up to final boiling point above 750 °F.

D-86 is the most common refinery distillation because it is easy and quick to obtain and does not require expensive equipment. The products from atmospheric distillation include naphtha, kerosene, diesel, and atmospheric gas oil. D-86 distillation indicates the distillation temperature that corresponds to the volume percent vaporized for each product.

In determining D-86 distillation, the sample feed is put into a device whose dimensions are defined by the test specification and the sample is heated. As the sample gets hotter, more of the sample vaporizes. The vaporized material is collected and the temperature corresponding to a certain volume percent of the original sample vaporized (5%, 10%, … , 95%) is recorded.

It must be pointed out that D-86 is not a true distillation because there is only one stage. Consequently, the D-86 tends to have a much higher IBP temperature than the actual one due to entrainment as molecular interactions hold lighter molecules in the mixture. At the tail end of the D-86 distillation, due to entrainment, the heavier molecules can flash off readily, resulting in a lower EP (end-point) than the actual distillation. Therefore, D-86 has a higher IBP and a lower EP than the actual atmospheric distillation in a refinery. However, the deviations in the front and tail ends in

D-86 distillation can be overcome by TBP distillation, which is discussed below. It is important to know that the D-86 distillation can be correlated with TBP distillation.

## 2.2.2 ASTM D-1160 Distillation

This test is similar to D-86 using single theoretical stage but performed at vacuum conditions. It is used for determining the distillation of VGO (vacuum gas oil) and heavier materials. The reason for vacuum distillation comes from the fact that temperatures above 700–780 °F would be required for heavier oils to vaporize at the atmospheric pressure. Under these temperatures, the oil would begin to thermally crack into lighter components. Imposing a vacuum enables the heavy oils to vaporize before reaching the cracking temperature. Thus, there is a limit that is closely monitored and controlled in operation for the charge heater outlet temperature before an atmospheric distillation column. The heavy gas oil has to be recovered in a vacuum distillation column.

## 2.2.3 ASTM D-2892 Distillation

Instead of using flash (or single stage of distillation) in D-86, D-2892 distillation is obtained via a higher level of separation, that is, 14–18 theoretical stages. Thus, TBP distillation reasonably represents the actual atmospheric distillation. This fraction has a final boiling point below 750 °F. The following example for heavy naphtha (Table 2.1) is used to show how the shortcomings in the D-86 flash distillation, that is, the higher IBP and lower EP, can be overcome by TBP distillation.

## 2.2.4 ASTM D-2287 Distillation

This ASTM method also includes gas chromatography, which is regarded as most consistent method to describe the boiling range of a hydrocarbon fraction unanimously. This method can be applied to any hydrocarbon fractions with a final boiling point of 1000 °F or less under atmospheric pressure. This method is also limited to hydrocarbon fractions having an initial boiling point of 100 °F.

## 2.2.5 ASTM D-3710 Distillation

This method is used to determine the boiling points of gasolines below final boiling point of 500 °F at atmospheric pressure. It is also based on gas chromatography.

**TABLE 2.1. Use of TBP to Overcome the Shortcomings of D-86 (Sample Heavy Naphtha)**

| Unit: °F | IBP | 50% | EP |
|---|---|---|---|
| TBP | 160 | 250 | 400 |
| D-86 | 210 | 260 | 340 |

## 2.3 IMPORTANT TERMINOLOGIES IN CRUDE CHARACTERIZATION

### 2.3.1 TBP Cut

TBP cut defines a specific segment of the TBP distillation curve and it is usually a reference to breaking up crude. A TBP curve is indicative of the true nature of the hydrocarbons; it represents all of the material in a certain boiling range from the crude assay. For example, a 200–400 °F cut contains all components within this boiling range, but no 190 °F or 410 °F boiling range material.

TBP cut information is provided in the crude assay, often called nominal TBP cut, as it represents the fractions (or cuts) obtainable using the TBP distillation method based on infinite number of distillation trays; thus, it refers to theoretical yields. However, commercial distillation columns cannot achieve TBP cuts due to the limited number of column trays. As a result, some light material will be present in the heavier cut and some heavier material in the lighter cut. Thus, it is necessary to adjust TBP cuts provided in a crude assay to obtain a realistic product fractions, distillations cuts, and properties from commercial distillation columns.

### 2.3.2 Adjusted TBP Cut

In order to have a realistic estimate of the amount of material that can be obtained for a given cut, we compensate for the slumped material by making the boiling range of a corresponding TBP cut a little larger. Typical levels of slumping in the crude unit are 1% naphtha to kerosene, 3% kerosene to diesel, and 6% diesel to VGO.

For example, to compensate for the 1% of naphtha slumping, we make the naphtha cut 1% larger. This could increase the selected assay TBP end point by a few degrees.

### 2.3.3 Crude Assay

When a crude oil is offered for sale, a report of the physical and chemical properties for the crude and products is prepared and the report is known as "crude assay" in the industry. Crude assays are prepared from a laboratory fractionation column, and product fractions drawn from the laboratory fractionation are similar to those fractions to be drawn from the crude distillation unit in the refinery. Basically, a crude assay provides crude characterization and it is about various product fractions in TBP cuts and their properties as well as impurities such as sulfur, nitrogen, and metals.

### 2.3.4 Commercial Yields Versus Theoretical Yields

It is common that commercial yields from a refiner cannot match the theoretic yields obtained from TBP distillation in a crude assay because commercial distillation is not perfect with lighter materials slumping into heavier cuts. Typically, there are 6–10 fractionation theoretical stages between two adjacent cuts in a commercial crude distillation column in comparison with very large number of fractionation stages assumed in the TBP distillation. Not only are the product yields different but also the product properties can vary. A useful tool to verify the information in a crude assay is called crude oil breakup.

A crude breakup is performed to predict the potential gap or overlaps in product yields between crude assay and operation based on actual process conditions including flash zone temperature and pressure. The predicted product yields and properties can be used to compare with that claimed in crude assay and more importantly as guidelines for refinery operations, for example, determining distillation cuts and predicting their properties.

## 2.4 REFINING PROCESSES

Crude assay and crude breakup information can indicate what potential products are available in a crude oil, but it is up to refining processes to produce them. There are many processes involved in a modern oil refinery and only the major ones are briefly explained as follows.

### 2.4.1 Atmospheric Distillation

This is the first process where the crude oil enters the refinery. Under near atmospheric pressure, the crude oil is heated to vaporize most of the hydrocarbons boiling in diesel and lighter range. Diesel and kerosene are withdrawn as sidecuts from the atmospheric column and naphtha and lighter materials are produced as overhead products. The above materials are sent downstream for further processing, while the bottom product of the atmospheric distillation column is sent to the vacuum distillation to recover the heavy gas oil.

### 2.4.2 Vacuum Distillation

Heavy crude oil components have high boiling temperatures and cannot be boiled at atmospheric pressure. These components must be further fractionated under vacuum. The vacuum condition lowers the boiling temperature of the material and thereby allows distillation of the heavier fractions without use of excessive temperatures that would lead to thermal decomposition. Steam ejectors are commonly employed to create the vacuum conditions required.

### 2.4.3 Fluid Catalytic Cracking

Some of heavy gas oil or atmospheric residue fractions are sent to a fluid catalytic cracking (FCC) where the feed reacts with catalyst under high temperatures and is converted to lighter materials. The catalyst is then separated and regenerated, while the reaction products are fractionated into several products by distillation. The main product of FCC is gasoline and this is the reason why FCC has been the most widely used refinery conversion technique for around 60 years. FCC units also produce a highly aromatic distillate product called light cycle oil (LCO).

### 2.4.4 Catalytic Reforming

Reforming is a catalytic process that converts low-octane naphtha to high-octane product, which is called reformate with an octane number of 96 or above. Reformate

is blended into gasoline to increase the octane number. The feed is passed over a platinum catalyst where the predominant reaction is the removal of hydrogen from naphthenes and the conversion of naphthenes to aromatics. The process also produces high purity hydrogen that can be used in hydrotreating processes.

### 2.4.5 Alkylation

In the alkylation process, isobutane, a low-molecular-weight material, is chemically combined with olefins, such as propylene and butylene in the presence of a catalyst such as hydrofluoric acid or sulfuric acid. The resulting product, called alkylate, is a branched chain hydrocarbon, which has a much higher octane number compared to a straight-chained material of the same carbon number. Similar to reformate, alkylate is blended into gasoline to increase the octane number, thus reduce knocking.

### 2.4.6 Isomerization

Light straight run (LSR) naphtha, mainly pentane–hexane fraction, is characterized by low octane, typically 60–70 RON. In the isomerization process, the octane numbers of the LSR numbers can be improved significantly up to 90 via converting normal paraffins to their isomers in the presence of catalysts containing platinum on various bases including alumina, molecular sieve, and metal oxide. The resulting product is isomerate, which is blended into gasoline pool.

### 2.4.7 Hydrocracking

This is a catalytic, high-pressure process that converts a wide range of hydrocarbons to lighter, more valuable products such as low-sulfur gasoline, jet fuel, and diesel. By catalytically adding hydrogen under very high pressure, the process increases the ratio of hydrogen to hydrocarbon in the feed and produces low-boiling materials, thus improving the product quality. It also removes contaminants such as sulfurs and nitrogen. Hydrocracking is especially adapted to the processing of low-value stocks, such as vacuum gas oils, and is most often used to produce high-quality distillate range products. FCC, which can process the same feed, is primarily geared toward naphtha production.

### 2.4.8 Hydrotreating

It is the most widely used treating process in today's refineries. This process uses the catalytic addition of hydrogen to remove sulfur compounds from naphtha and distillates (light and heavy gas oils). Removal of sulfur is essential for meeting product specifications for gasoline, jet fuel, diesel, and heavy burner fuel as well as for protecting the catalyst in subsequent processes (such as catalytic reforming). In addition to removing sulfur, it can eliminate other undesirable impurities (e.g., nitrogen and oxygen) and saturate olefins.

### 2.4.9 Residue Desulfurizing

With the increasing need for products produced from heavier and higher boiling components (the "bottom of the barrel"), desulfurization is used to process the residues

from atmospheric and vacuum column distillation and the desulfurized residues can be used as a blending component of low-sulfur fuel oils. Residue desulfurizing unit can also be used to improve the quality of residue feedstock to a Residue FCC (RFCC) process.

### 2.4.10 Coking

The residual bottoms from the crude unit contribute lighter fractions (naphtha and gas oils) via a thermal cracking process called "coking," in which the feed is heated to high temperatures and routed to a drum where the material is allowed to remain for sufficient time for thermal cracking to take place. The lighter portions leave the drum and are recovered as liquid products. The heavier portions remain in the drum and eventually turn into coke, a nonvolatile carbonaceous material. Depending on the amount of sulfur, metals, and aromatic content of the coke, it may be used for boiler fuel or further processed into anodes for aluminum production. Since the recovered liquid products were produced through a thermal process, their quality will not meet current fuel standards, as the sulfur and nitrogen contents are usually high. In addition, they tend to have high olefin contents, making them slightly unstable for storage or blending with other materials. As a result, these products generally must be hydrotreated or upgraded further to produce suitable product blending components.

### 2.4.11 Blending

After the products are made from the above process units and other sources, they are blended to make final products meeting desirable specifications, which are discussed as follows.

## 2.5 PRODUCTS AND PROPERTIES

Although there are a large variety of products that can be produced, most refineries are designed to make liquefied petroleum gas (LPG), gasoline, jet fuel, diesel, heavy fuel oil, and feedstocks for petrochemical processes. All products must meet desirable specifications in the local markets. Making desirable products dictate refinery technology selection and process designs while optimizing product yields for high economic margin directs refinery operation.

### 2.5.1 LPG

LPG is a mixture of propane (C3) and butane (C4) and can be used for heating fuel as well as a refrigeration working fluid. Over half the propane produced goes to petrochemical processes as feed for olefins production and other chemical manufacturing. Some LPG range material is used in the alkylation process to produce a high-octane gasoline blending component.

Normal butane ($n$-C4) is frequently used as gasoline blending stock to regulate its vapor pressure due to its lower vapor pressure than isobutene ($i$-C4). $n$-C4 has Reid vapor pressure (RVP) of 52 psi compared with 71 psi RVP of $i$-C4. Generally, the

lower the RVP of a gasoline blend, the more it costs. For example, in winter you can blend butane, which is relatively plentiful and cheap, with gasoline to promote better startup in cold weather. But butane with a high RVP cannot be used in summer as it would immediately boil off.

### 2.5.2  Gasoline

About 90% of the total gasoline produced in the United States is used as automobile fuel. Thus, demand of motor fuel has been the major driving force for oil refining processes. For most refineries in the United States, most crude oils contain only about 30% of gasoline range components. To make more gasoline, other components are converted into gasoline blending stock. As the result, around 50% or more of the crude oil is converted into gasoline. Most service stations provide three grades based on octane number that is designed to meet the requirements of the specific engine installed.

*2.5.2.1  Gasoline Cut*  The standard distillation range for automobile gasoline is between 10% boiling point at 122 °F and end point of 437 °F. Typically, heavy naphtha and lighter materials are produced from the crude column overhead and then are routed to a gasoline stabilizer to remove butane and lighter materials. These lighter materials are sent to the saturate gas concentration unit where LPG is recovered out of refinery fuel gas. The pentane and heavier naphtha range materials go to a naphtha hydrotreater for making low-sulfur gasoline. Treated light naphtha consisting of primarily C5 and some C6 hydrocarbons can either be blended directly into gasoline or processed in an isomerization process to increase its octane. The heptane and heavier hydrocarbons usually have an octane lower than that required by current engine technology; thus, they are treated further by catalytic reforming to yield a high-octane gasoline blending component.

*2.5.2.2  Gasoline Specifications*  Three properties can be used to describe the main features of gasoline: octane number, ease of startup, and RVP.

Octane number is the most important specification of motor gasoline and it delivers smooth burning in the engine without knocking. The octane number is an expression of the antiknocking performance of the engine using two reference fuels as the basis, namely normal *n*-heptane, defined to have an octane number of 0, and *iso*-octane, defined to have an octane number of 100. A gasoline with an octane number of 90 means the engine performance is equivalent to a mixture of 90 vol% of iso-octane and 10% *n*-heptane. In the past, the gasoline octane was increased by including olefins, aromatics, and alkyl lead components. Under current regulations, lead addition to gasoline is not permitted due to the health risk while many countries set limits on gasoline aromatics in general, benzene in particular, as well as olefin (alkene) content as these two components generate volatile organic compounds (VOCs) causing ground-level ozone pollution.

Second, the engine must start easily in cold weather. The easy startup is affected by the amount of light components in the gasoline, which is measured as the percentage that is distilled at 158 °F or lower. Obviously, a fuel requires more of this percentage in cold climate for the car engine to start quickly.

Third, the engine must not have vapor lock at high temperatures, which is measured by the vapor specification, namely RVP. RVP is defined as the vapor pressure of the gasoline at 100 °F in lb/in.$^2$ absolute. The RVP limit is a function of ambient temperature. A lower RVP is required in warm climate compared to cold one.

Altitude has significant effects on gasoline properties. The main effect is the octane requirement, approximately with 5 RON (research octane number) less for a 5000 ft increase in elevation. In general, same model of engines could vary by 7–12 RON to suit different altitudes according to climatic conditions.

*2.5.2.3  Gasoline Production*   Automobile gasoline is blended to meet the demand and local conditions. Blending components for making gasoline include straight run naphtha, catalytic reformate, FCC gasoline, hydrocracked gasoline, alkylates, isomerate, and *n*-butane. Proper blending is essential to achieve the proper antiknock properties, ease of startup, low vapor lock potential, and low engine deposits, which are the main characteristics that a good gasoline product must have.

LSR naphtha consists of C5-190 °F (TBP), but the final cut-point can vary from 180 °F to 200 °F (a swing cut), depending on economic conditions or local requirements. As LSR naphtha cannot be upgraded in octane in a catalytic reformer, it is processed separately from heavy naphtha. In some refineries, it is sent to isomerization units for upgrading its octane.

Heavy straight run (HSR) naphtha, the fraction of 190–370 °F, usually goes to a catalytic reformer to make high-octane reformate. Thus, a catalytic reformer is operated to give satisfactory antiknock properties within an RON of 90–100.

Historically, FCC naphtha had been blended directly into gasoline due to its inherently high octane. However, FCC naphtha contains high sulfur and it has to be hydrotreated for gasoline blending due to the gasoline sulfur limits required in regulations. Naphtha derived from hydrocracking units is usually rather low in octane and may need further upgrading via catalytic reforming if the amount available would adversely affect the overall octane rating of the gasoline pool. Alkylate is the product from the reaction between isobutene, propylene, and butylene to make a sulfur-free and high-octane gasoline blending component.

Normal butane is also used as the gasoline blending stock to adjust the RVP of the gasoline. The gasoline RVP is a compromise between a high RVP for easy startup and a low RVP for preventing vapor lock. Gasoline RVP is also subject to regulations in many regions to minimize hydrocarbon vapor emissions.

### 2.5.3  Jet Fuel

There are two types of jet fuels, namely naphtha and kerosene. Naphtha jet fuel, also called aviation gasoline, is made mainly for military jets. It is similar to automotive gasoline but has a narrower distillation range of 122 °F at 10% and 338 °F TBP end point. Commercial jet fuel (simply called as jet fuel in the following discussions) is in kerosene boiling range, with 401 °F at 10% and a 572 °F end point. Kerosene includes hydrocarbons boiling in the C9–C16 range; therefore, the cut can be as wide as 300–570 °F on a D-86 basis. The front end of the kerosene is limited by the kerosene flash, which is set at 100 °F.

Typically, SR (straight run) kerosene and hydrotreated or hydrocracked kerosene are blended into commercial jet fuel. Most jet fuel is SR stock and it is treated using the Merox process from which the mercaptans in the feed are converted to disulfides. Stocks containing olefins are not acceptable because they have poor thermal stability and will polymerize, forming gums that can harm jet engines. Stocks containing high quantities of straight-chain paraffins are also restricted due to unacceptable cold flow properties (i.e., freeze point) causing plugging at low temperatures.

**2.5.3.1   *Jet Fuel Specifications***   Unlike the spark ignition engines in cars, jet engines rely on continuous burn in a combustion chamber. Jet fuel needs to be mostly paraffinic as benzene and other aromatics exhibit undesirable combustion characteristics, and olefins present a gum stability risk. Thus, the main specifications for jet fuel include flash point, smoke point, freezing point, aromatics content, olefin content, and sulfur content.

*Smoke Point*   The smoke point describes the combustion effects on mechanical integrity. It is defined as the maximum height, in millimeters, of a smokeless flame when the fuel sample is burned in a lamp of a specified design. The smoke point is related to the hydrocarbon type comprising the fuel. The more aromatic the jet fuel, the smokier the flame. The smoke point specification limits the blending percentage of cracked products that are high in aromatics. The smoke point is quantitatively related to the potential radiant heat transfer from the combustion products of the fuel. Because radiant heat transfer exerts a strong influence on the metal temperature of combustor liners and other hot parts of jet engines, the smoke point provides the basis to derive the relationship between the life of the mechanical components and the fuel characteristics.

*Aromatics*   Aromatics in jet fuel increase with boiling range; therefore, a lighter jet fuel will have less aromatics. Some crudes are too high in aromatic content to be acceptable for jet fuel and must be cut back with other paraffinic crudes. Typical kerosene aromatics content is in the range of 20–25%.

*Flash Point*   The flash point is an indication of the maximum temperature for fuel handling and storage without serious fire hazard. This specification provides the basis for determining the regulations and insurance requirements for jet fuel shipment, storage, and handling precautions.

In order to obtain acceptable flash point, a stripper with steam stripping is used on the kerosene sidecut from the crude column, specifically to strip out lighter molecules in order to meet the flash specification for the kerosene.

*Freeze Point*   Freeze point is defined based on the temperature at which waxy crystals are formed as the jet fuel is cooled. Freeze point is related to the composition of the jet fuel. Higher paraffin content results in a poor freeze point because waxy crystals start to form at a high temperature. Cyclics, especially aromatics, improve freeze point. Unfortunately, as the freeze point gets better due to higher aromatics, the smoke point gets worse; therefore, there is always a trade-off between these two properties.

The freeze point specification must be sufficiently low to preclude interference with flow of fuel through filter screens to the engines at low temperatures experienced

at high altitude. The fuel temperature in an aircraft tank decreases at a rate proportional to the duration of flight. Long duration flights would require lower freeze point than short duration flights. Hydrocracking is used to isomerize the paraffins and reduce the freeze point. Hydrocracking also produces jet fuel with a very low smoke point and is therefore a premium jet fuel blending component.

### 2.5.4 Diesel

The diesel cut is normally in the TBP range of 480–650 °F crude cut. The diesel cut typically contains C14–C22 hydrocarbons. This range can be as wide as C10–C22 if kerosene is included in diesel fuel. In the case of kerosene blended into the diesel, the diesel pour point improves and that is particularly relevant in very cold climates (e.g., Alaska, Canada, Russia) where a low pour point is critical. At the same time, the diesel IBP can be below 350 °F, but the IBP will largely be set by the flash point specification, which for a typical diesel fuel is around 125 °F. Flash point is adjusted by using a reboiled or steam stripped sidecut stripper at the crude column to strip out lighter molecules in order to meet the flash point specification.

Sulfur is a major issue for diesel produced according to current standards. To meet current standards, most diesel fuel must be hydrotreated. Achieving the required sulfur levels requires ability to remove sulfur from different hydrocarbon species, some of which are easily amenable to treatment and others are more difficult. The most difficult sulfur species is dimethyl-dibenzo-thiophene, which boils at 646 °F. This molecule is sterically hindered because the two methyl groups prevent hydrogen from getting at the sulfur in hydrotreating.

***2.5.4.1 Diesel Specifications*** Cetane number, flash point, pour point, cloud point, and sulfur content are the most important properties of diesel fuels. Typical diesel specifications are shown in Table 2.2. The fuel volatility requirements depend on engine design and applications. For automotive diesel fuel with fluctuating speeds and loads, the more volatile fuels have advantages. For railroads, ships, and power stations, the heavier fuels are more economic due to their high heat of combustion.

*Cetane Number* It is the ignition performance indicator, which is similar to the octane number for gasoline. For diesel fuels, the reference fuel is cetane (*n*-hexadecane) with a cetane number of 100 and $\alpha$-methylnaphthalene with a cetane number of 0. Cetane number is better with paraffins than with olefins or aromatics. Acceptable cetane numbers are 40 and higher at 90 is preferred for very cold climate. Hydrocracked diesel typically has a high cetane number and is a good diesel

TABLE 2.2. Typical Diesel Specification

|  | US | EURO IV Property |
|---|---|---|
| Cetane number (Engine test) | 40 | 51 |
| Sulfur (wt-ppm) | 15 | 10 |
| Flash (°C) | 52 | 52–60 |
| Pour and cloud points | Seasonal by location | |

blending component. Thermally cracked diesel, on the other hand, is particularly low in cetane and requires upgrading by hydrotreating before being blended into the diesel pool.

*Cloud Point*  It indicates the suitability of the fuel for low temperature operations and it is a guide to the temperature at which it may clog filters and restrict flow as paraffinic fuel consists of precipitate as wax.

*Pour Point*  It is another low temperature performance indicator, which defines the lowest temperature at which the fuel can be pumped. This temperature (pour point) often occurs about 8 °F below the cloud point.

*Sulfur Content*  Sulfur has strong negative impact on the environment and there have been continuous efforts from legislation to production to reduce sulfur content in diesel. Before 2007, standard highway-use diesel fuel sold in the United States contained an average of 500 ppm (parts per million) sulfur. After 2010, nonroad diesel contained 10–15 ppm. In Europe, Germany introduced 10 ppm sulfur limit for diesel from January 2003. Other European Union countries and Japan introduced diesel fuel with 10 ppm to the market from the year 2008.

## 2.6  BIOFUEL

For completeness, biofuel is also briefly described and the following discussion is largely based on Wikipedia (https://en.wikipedia.org/wiki/Biofuel).

Biofuels can be derived directly from plants, or indirectly from agricultural, commercial, domestic, and/or industrial wastes. Renewable biofuels generally involve contemporary carbon fixation, such as those that occur in plants or microalgae through the process of photosynthesis. Other renewable biofuels are made through the use or conversion of biomass (referring to recently living organisms, most often referring to plants or plant-derived materials). This biomass can be converted into convenient energy containing substances in three different ways: thermal conversion, chemical conversion, and biochemical conversion. This biomass conversion can result in fuel in solid, liquid, or gas form. This new biomass can also be used directly for biofuels.

There are two major biofuels currently produced as transportation fuels, namely bioethanol for gasoline addition and biodiesel for diesel additive.

### 2.6.1  Bioethanol

Bioethanol is an alcohol made by fermentation, mostly from carbohydrates produced in sugar or starch crops such as corn, sugarcane, or sweet sorghum. Cellulosic biomass, derived from nonfood sources, such as trees and grasses, is also being developed as a feedstock for ethanol production. Ethanol can be used as a fuel for vehicles in its pure form, but it is usually used as a gasoline additive to increase octane and improve vehicle emissions. Bioethanol is widely used in the United States and Brazil. Current plant design does not provide for converting the lignin portion of plant raw materials to fuel components by fermentation.

### 2.6.2    Biodiesel

Biodiesel can be produced from oils or fats either using transesterification or hydrotreatment. Biodiesel is used as a diesel additive to reduce levels of particulates, carbon monoxide, and hydrocarbons from diesel-powered vehicles.

### 2.6.3    Blending of Biofuel

In 2010, worldwide biofuel production reached 105 billion liters (28 billion gallons), up 17% from 2009 and biofuels provided 2.7% of the world's fuels for road transport, a contribution largely made up of ethanol and biodiesel (Wikipedia, Biofuel cite note 2). Global ethanol fuel production reached 86 billion liters (23 billion gallons) in 2010, with the United States and Brazil as the world's top producers, accounting together for 90% of global production. The world's largest biodiesel producer is the European Union, accounting for 53% of all biodiesel production in 2010. As of 2011, mandates for blending biofuels exist in 31 countries at the national level and in 29 states or provinces (Wikipedia, Biofuel cite note 3).

The International Energy Agency has a goal for biofuels to meet more than a quarter of the world demand for transportation fuels by 2050 to reduce dependence on petroleum and coal (Wikipedia, Biofuel cite note 4). There are various social, economic, environmental, and technical issues relating to biofuel production and use, which have been debated in the popular media and scientific journals. These include the effect of moderating oil prices, the "food versus fuel" issue, poverty reduction potential, carbon emissions levels, sustainable biofuel production, deforestation and soil erosion, loss of biodiversity, impact on water resources, rural social exclusion and injustice, shantytown migration, rural unskilled unemployment, and nitrous oxide ($NO_2$) emissions.

# 3

# DIESEL HYDROTREATING PROCESS

## 3.1 WHY DIESEL HYDROTREATING?

Diesel hydrotreating (DHT) or catalytic hydrogen treating is mainly to reduce undesirable species from straight-run diesel fraction by selectively reacting these species with hydrogen in a reactor at elevated temperatures and at moderate pressures. These objectionable materials include, but are not solely limited to, sulfur, nitrogen, olefins, and aromatics. Many of the product quality specifications are driven by environmental regulations that have become more stringent over recent time.

In the early 1900s, diesel fuel standards were first developed to ensure that diesel engine owners could buy a fuel that was compatible with the requirements of their engines. To achieve this, these early standards controlled primarily the distillation and boiling ranges, volatility, its cold flow properties, and its cetane number. Currently, these diesel standards are embodied in standards such as American Society for Testing Materials (ASTM) D975 and its equivalents under European (EN 590) and Japanese normalization organizations. In the United States, as in many other jurisdictions, several basic grades of diesel fuel are in use:

- No. 1 Diesel Fuel – A special-purpose, light distillate fuel for automotive diesel engines requiring higher volatility than that provided by Grade Low Sulfur No. 2-D
- No. 2 Diesel Fuel – A general-purpose, middle distillate fuel for automotive diesel engines, which is also suitable for use in nonautomotive applications, especially in conditions of frequently varying speed and load.

The D975 standard defines two ultra-low-sulfur diesel (ULSD) standards: Grade No. 2-D S15 (regular ULSD) and Grade No. 1-D S15 (a higher volatility fuel with a lower gelling temperature than regular ULSD). As the sulfur level in diesel is reduced, the inherent lubricity of the diesel is also reduced. So for this reason, the ASTM D975 standard also imposes lubricity requirement.

Since the 1980s, diesel fuel specifications have increasingly been tightened to meet environmental objectives, in addition to ensuring compatibility with diesel engines. The most stringent current specifications, those promulgated by the California Air Resources Board (CARB), limits sulfur, aromatics, polycyclic aromatic hydrocarbons (PAHs), and several other fuel impurities. As air quality problems persist, there is continued pressure to further reduce emissions from diesel engines, and hence to further tighten diesel specifications. By 2010, on-road diesel fuel sulfur levels was reduced to 15 parts per million (ppm) (in the United States) or even 10 ppm [in the European Union (EU)]. Recently proposed regulations will extend these specifications to virtually all diesel fuel used in engines.

In some jurisdictions, aromatics and PAH content in diesel fuel, which is strongly correlated with soot production, are also under pressure. CARB and the EU will have limits at 10% and 14%, respectively, while the US federal specifications limit aromatics to 35%.

Significant reductions in oxides of nitrogen ($NO_x$) and particulate matter (PM) will be required in almost all classes of diesel engines, and, in most cases, requiring significant changes in powertrain technology. The proposed rules may require electronic engine controls and exhaust after treatment system such as exhaust gas recirculation (EGR) and diesel particulate filter (DPF). Selective catalytic reduction (SCR) is frequently employed to reduce $NO_x$ emissions.

With the advent of ultra-low-sulfur fuel regulations ushering in the first decade of the twenty-first century, however, it was required for hydrotreating (HDT) research and development to deliver quantum improvements in catalyst performance and process technology. This was accomplished in the form of so-called Type II supported transition metal sulfide (TMS) catalysts, unsupported/bulk TMS catalysts, improved bed grading catalysts and stacking strategies, advanced catalyst loading techniques, improved trickle-flow reactor internals designs, and more effective catalyst activation methodologies.

Key changes in diesel quality across various regions of the world sulfur and aromatic/cetane are summarized in Worldwide Refinery Process Review (2012) as shown in Table 3.1.

**TABLE 3.1. Worldwide Diesel Fuel Specification**

| Region | Sulfur (ppm) | Aromatics (vol%) |
| --- | --- | --- |
| The United States | 10–15 | 35 |
| Canada | 15 | 30 |
| Latin America | 2000 to as low as 10–50 in some area | NA |
| Western Europe | 10 | 10 |
| Central/Eastern Europe | 50 | NA |
| Middle East/Africa | 50–5000 | NA |
| Asia Pacific | 10–350 | 10–35 |

ULSD was developed to enable the use of improved pollution control devices that reduce diesel emissions more effectively since these devices can be damaged by sulfur. ULSD is also safe to use with older diesels.

## 3.2  BASIC PROCESS FLOWSHEETING

Due to ULSD legislation, distillate HDT has become a key process in the refining industry. Rate limiting parameters that had previously been overlooked, such as aromatic inhibition, may need to be considered for the production of ULSD (<10 wppm S). As hydrodesulfurization (HDS) and hydroaromatics (HDA) saturation reactions occur in parallel in a shared environment, they compete for the necessary resources, namely hydrogen and catalyst sites. For this reason, the effectiveness factors for HDS and HDA decrease in the presence of increased aromatics concentrations. Furthermore, the data indicate that the presence of polyaromatics has a more significant impact on the slower HDS reactions (sterically hindered dibenzothiophenes, DBTs).

In order to successfully produce ULSD, essentially all of the organo-sulfur species must be removed including the substituted DBTs and other refractory sulfur species. The mechanisms and kinetics for deep desulfurization are more complicated than the simple first-order reactions that hold for the less refractory sulfur species, for example, thiols, sulfides, and disulfides. These more refractory sulfur species remain present at 500 and 50 ppm levels of sulfur. It is therefore critical to have a thorough understanding of desulfurization chemistry in order to successfully accomplish the deep desulfurization required.

Multiple reactions occur in parallel on the HDT catalyst surface including HDS, hydrodenitrogenation (HDN), and aromatic saturation/hydrogenation (HDA). In the development of the kinetic model, the key parameters influencing the HDS rate need careful investigation.

In modeling HDS, the sulfur species are generically characterized as "easy" or "difficult" sulfurs. The sulfur species are grouped based on the relative difficulty of sulfur extraction from the compound. In general, "easy" sulfur species (boiling range <610 °F) experience little steric hindrance and are converted quickly. Conversion of the "difficult" sulfur species (boiling range >610 °F) is much slower than it is with the "easy" sulfurs due to steric hindrance and more complex reaction pathways. Several species have been identified as being particularly difficult to convert in HDS, mostly substituted DBTs. The HDS chemistry for easy sulfur is reasonably represented by an irreversible first-order reaction. It is widely accepted that there are two primary desulfurization paths for difficult sulfur species: direct desulfurization (also known as sulfur extraction) and hydrogenation (also known as saturation). Direct desulfurization follows the same chemistry as the easy sulfur.

There are many ways to achieve sulfur removal of the more difficult molecules. Some of the options include the following:

- Use of more active catalyst
- Operating at higher temperature
- Reduction of feed endpoint
- Higher purity hydrogen

- Adding additional reactor volume
- H$_2$S removal from the recycle/treat gas
- Improving the feed distribution to the trickle-bed (conventional) reactor.

It is therefore goal of the refineries to find the most effective combination of these options to most economically produce ULSD in their plants. Depending on the needs of the refinery, some of these alternatives may be economically viable to consider either individually or in combination. Most of the HDS reactions are considered to be irreversible, while aromatic saturation is a reversible reaction that is controlled by equilibrium.

Typical HDT units designed have trickle-bed reactors. Reactors are operated with large quantities of hydrogen circulating over the catalyst bed, up to 10 times the quantity of hydrogen consumed by the chemical reaction. The vapor and liquid are mixed and passed through a distributor; as a result, they are in equilibrium as they enter the catalyst bed. As the reaction occurs at the catalyst surface between the dissolved hydrogen and the reactive species in the feed, hydrogen is depleted from the liquid and must be replenished from the vapor phase. Insufficient replacement of the hydrogen can lead to accelerated deactivation of the catalyst and reduced performance.

Figures 3.1 and 3.2 show basic DHT schemes used in the industry.

Diesel feed with recycle gas is introduced to the multibed reactor after exchanging heat with reactor effluent. Reactor feed is further heated in the charge heater to achieve reactor inlet temperature.

HDS and HDA reactions are exothermic; thus, reactor interbed quench is required to manage temperature and performance. The amount of quench and the number of beds depend on the aromatic and olefin content of feed. Presence of the cracked stocks, for example, fluid catalytic cracking (FCC) light cycle oil (LCO) and light coker gas oil (LCGO) require more quench and more beds to manage heat release.
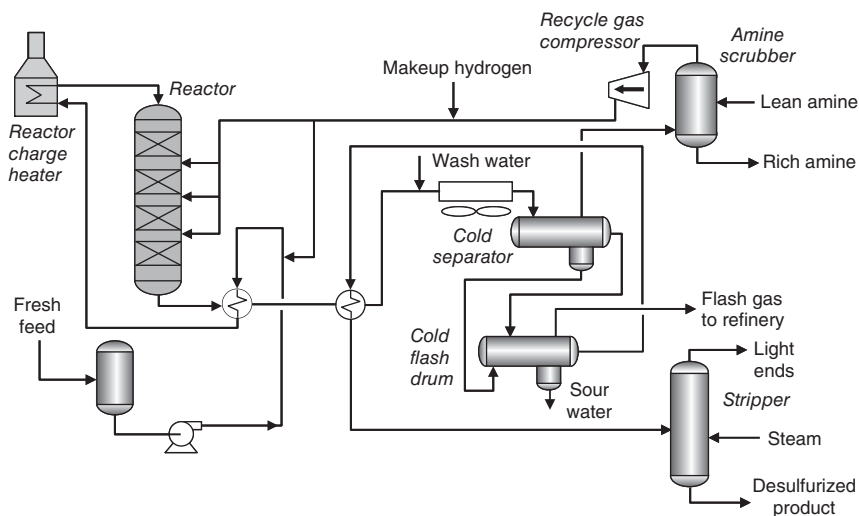


**FIGURE 3.1.** Diesel hydrotreating cold separator flow scheme.
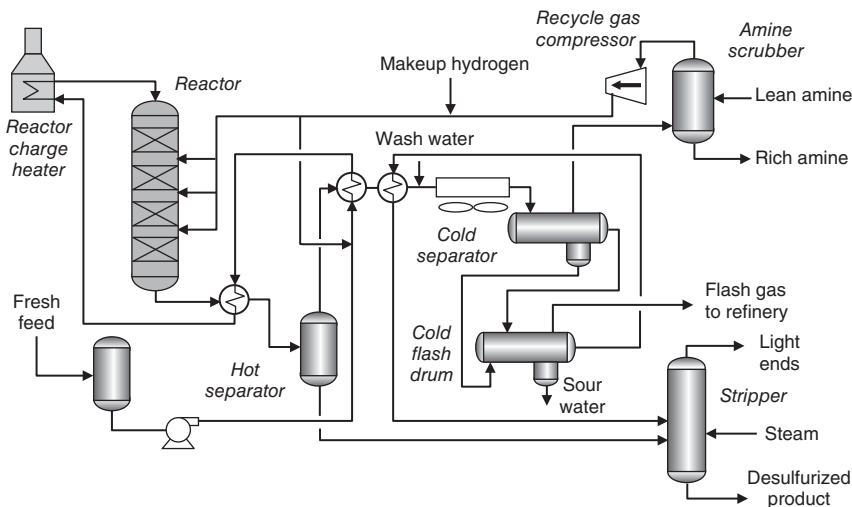
**FIGURE 3.2.** Diesel hydrotreating hot separator flow scheme.

Reactor effluent heats the combined feed and flows to a hot, high-pressure separator (HHPS) in some cases or to cold high-pressure separator (CHPS) separating vapor and liquid. Depending upon the flow scheme used, there may be different heat exchanger network possible for heat recovery.

Wash water is injected upstream of the product's condenser to remove ammonium hydrosulfide, which can foul heat exchanger tubes and cause plugging. HHPS liquid combines with heated CHPS liquid and flows to the product stripper.

Vapor from the CHPS contacts with amine in a scrubber for $H_2S$ removal and flows to the recycle compressor suction drum. Makeup hydrogen is compressed and combines with recycle gas in the suction drum. The compressor suction drum can purge some recycle gas to improve recycle gas hydrogen purity. The quantity depends on the reactor's hydrogen-partial-pressure requirements and makeup hydrogen purity available.

In the product stripper, superheated steam feeds the tower's bottom and helps remove $H_2S$. Stripper overhead vapors condense and flow to the stripper accumulator. Accumulator vapor and liquid, known as wild naphtha, are processed in offsite facilities.

Stripped ULSD product supplies heat to the feed stream and then flows to drying facilities, which can be a coalescer-salt dryer or vacuum drying system.

Design is optimized for reactor space velocity, hydrogen treat gas quantity, hydrogen partial pressure, and reactor temperature for a given cycle length and treating severity.

Revamps are more challenging for existing equipment, and reactor loop piping will limit the hydrogen partial pressure due to hydraulic limitations. A higher treat gas rate can increase the hydrogen partial pressure; this is usually limited due to an associated increase in the reactor loop pressure drop and the corresponding maximum operating pressure of system components. Use of higher purity makeup gas can also help by reducing the quantity of light hydrocarbon gases in the recycle gas loop.

Lower-purity makeup hydrogen requires higher hydrogen circulation rates to maintain a target hydrogen partial pressure; it may even require a purge stream from the cold separator. If makeup hydrogen purity is too low, there is no combination of recycle rate and purge that will achieve the target reactor outlet partial pressure.

Catalyst cycle lengths of 24–36 months are typical for new designs. This is because, at some point, factors other than catalyst activity (such as reactor pressure drop) will limit the cycle. For a fixed space velocity, cycle length increases with a higher hydrogen partial pressure.

## 3.3 FEEDS

Feeds for DHT unit typically have a nominal distillation range of 300–700 °F. These feeds in the refinery are referred to as various names such as diesel, gas oil, or atmospheric gas oil (AGO). Generally speaking, streams derived from crude oil distillation are also referred to as straight run. DHT feed can also come from other process units such as FCC (LCO), Coker (LCGO), thermal cracker such as visbreaking unit (light visbroken gas oil), or low-pressure mild hydrocracking unit. Diesel range material can be produced in a synthetic fuel upgrading unit, such as those operating in Canada or Venezuela.

DHT feed distillation front end is limited by diesel flash point, typically 55–60 °C. Front end can be adjusted posthydrotreating by stripper operation. Back end of the distillation is limited by cold flow properties such as pour point, cold flow filtering point (CFPP), or cloud in addition to 95% distillation point (T95). Typical T95 is around 360 °C. Typical properties of some of the feed stream are shown in Table 3.2.

Challenges associated with gas oil produced in upstream processing unit are given, in order of importance:

- FCC gas oil (LCO): It has a high S content and low cetane number and may be hydrotreated after blending (e.g., ~30%) with straight-run gas oil, but the high aromaticity makes it difficult to improve the cetane number of the LCO (6–15 points only depending on conditions).
- Steam cracking diesel fuels: These have a very high content of aromatics especially dealkylated polyaromatics.
- Coker gas oil: These have high olefin content and higher aromatics. Coking unit uses additive that contain silicone to control foaming. These silicone compounds decompose and distribute in coker products. These compounds typically

**TABLE 3.2. Typical Properties of Feed Examples**

| Source | $S$ (ppm) | Aromatics (vol%) | Cetane | Cloud Point |
|---|---|---|---|---|
| GO Str. run | $3$–$20 \times 10^3$ | 20–40 | 42–54 | −10 to +5 |
| GO pyrolysis | $>20 \times 10^3$ | 30–60 | 28–45 | −4 to −8 |
| LCO FCC | $14 \times 10^3$ | 60–85 | 18–27 | −10 |

decompose upon encountering a hot surface (i.e., catalyst) and deposit there. Over time, this leads to catalyst deactivation. Silicone needs to be handled to avoid premature deactivation of catalyst.

The typical aromatics content of most diesel fuels is more in the 30–35% range, and although there are no particular specifications for the total aromatics content, this content drops across the HDT unit to produce ULSD. Since aromatics have low cetane number, lower aromatics feeds are desirable, particularly when attempting production of EURO diesel (EN 590), which requires a cetane number of 51.

Johnson et al. (2007) have compared various diesel range hydrocarbon composition, saturates (paraffin, naphthene, and olefins), and aromatic distribution as shown in Figure 3.3. Aromatics are identified as single- and multiring aromatics. As discussed, LCO is usually rich in aromatics and contains multiring aromatics. LCGO contains aromatics but relatively lower amount compared to LCO but has significantly higher amounts of saturates. Light gas oil (LGO) is typically composed of saturates and single-ring aromatics with relatively small quantities of 2- and 3-ring aromatics.

The relative difficulty of processing distillate range feed streams for deep HDS and/or HDA is highly dependent on their aromaticity and multiring aromatic content.

A typical commercial HDT unit processes blends of distillate streams from various sources to manage processing difficulty while achieving target sulfur and cetane number.

Distillate feed streams can also have cold flow property limitations. Cold flow characteristics are not improved by process in a distillate HDT unit but may get worst depending upon the degree of saturation. Cold flow is typically controlled by feed
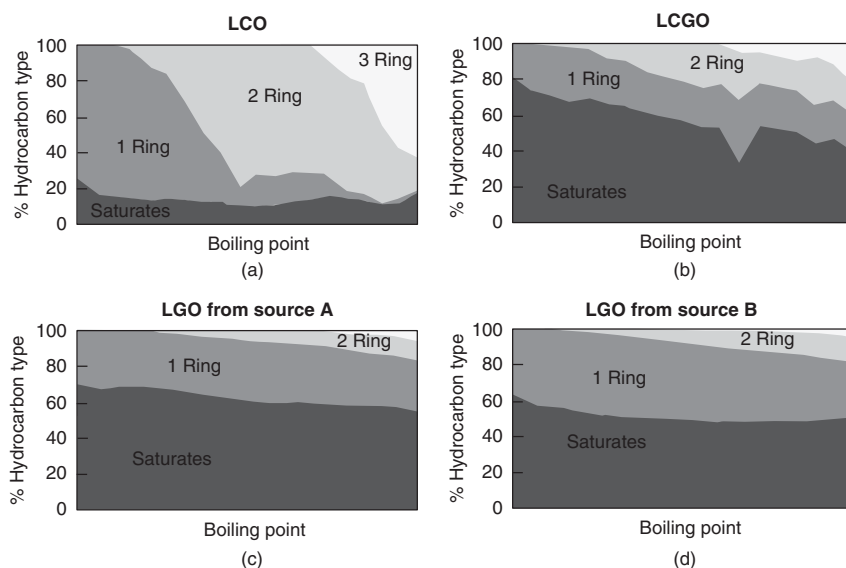


**FIGURE 3.3.** Saturates (paraffin, naphthene, and olefins) and aromatic distribution.

distillation unless dewaxing catalyst is utilized. Dewaxing catalysts generally fall into two categories – those that dewax the feed by cracking straight-chain paraffins and those that isomerize straight-chain paraffins to isoparaffins. The second type of catalyst is generally preferred because it retains most of the distillate range paraffins, while the first type will crack some of the paraffins to lighter products, thus reducing distillate yields.

## 3.4  PRODUCTS

Diesel fuel has become important transportation fuel in the last 20 years. Diesel is used for from consumer goods moved cross-country, to the generation of electric power, to increased efficiency on the nation's farms. Thus, diesel fuel plays a vital role in the nation's economy and standard of living. The major uses of diesel fuel are as follows:

- On-road for transportation
- Off-road (mainly mining, construction, and logging)
- Military transportation
- Farming
- Electric power generation
- Rail transportation
- Marine shipping.

### 3.4.1  Sulfur Specificatio

Reducing sulfur in diesel has been the focus of many countries, starting with the European Union and the United States. US Highway Diesel Program requires 15 ppm sulfur specification, known as ULSD; ULSD was phased-in for highway diesel fuel from 2006 to 2010. Off-road diesel was phased-in to use of ULSD (15 ppm) fuel from 2007 to 2014. Before EPA began regulated sulfur in diesel, diesel fuel could have contained as much as 5000 ppm of sulfur. The EU introduced regulations requiring 10 ppm sulfur in on-road in 2005, and the United States EPA began regulating diesel fuel sulfur levels in 1993. Beginning in 2006, EPA began to phase-in more stringent regulations to lower the amount of sulfur to 15 ppm in 2006. After 2010, all highway diesel fuel supplied to the market has been ULSD and all highway diesel vehicles are required to use ULSD. After 2014, all nonroad, locomotive, and marine (NRLM) diesel fuel must be ULSD, and all NRLM engines and equipment must use this fuel. More recently, China and India have announced regulations aimed at reducing the sulfur content of diesel fuel in use to 10 ppm by not later than 2021.

ASTM D975 specification is intended permissible limits of significant fuel properties used for specifying the wide variety of commercially available diesel fuel oils. Limiting values of significant properties are prescribed for seven grades of diesel fuel oils. Transportation diesel typically used is Grade 1 and/or 2 diesel. ULSD is identified as Grade No. 1-D S15, comprises the class of very low sulfur, volatile fuel oils from kerosene to the intermediate middle distillates. Fuels within this grade are
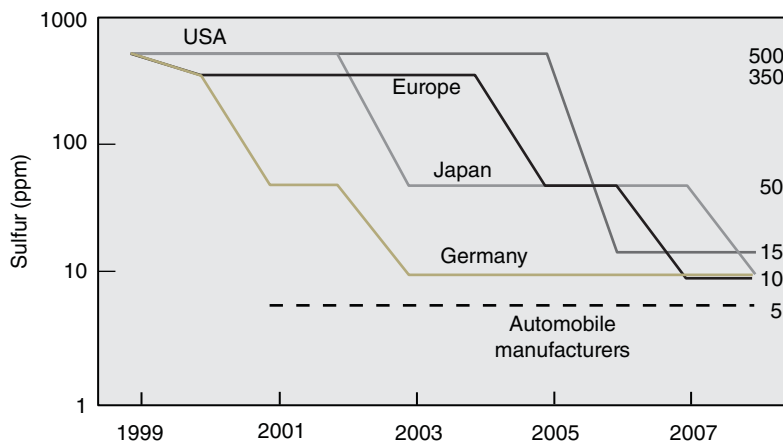
**FIGURE 3.4.** Trends of sulfur specification change over time.

applicable for use in (1) high-speed diesel engines and diesel engine applications that require ultra-low-sulfur fuels, (2) applications necessitating frequent and relatively wide variations in loads and speeds, and (3) applications where abnormally low operating temperatures are encountered.

ASTM Grade No. 2-D S15 includes the class of very low sulfur, middle distillate gas oils of lower volatility than Grade No. 1-D S15. These fuels are applicable for use in (1) high-speed diesel engines and diesel engine applications that require ultra-low-sulfur fuels, (2) applications necessitating relatively high loads and uniform speeds, or (3) diesel engines not requiring fuels having higher volatility or other properties specified in Grade No. 1-D S15.

Ackelson et al. (2007) have discussed how diesel sulfur specifications have changed around the world over time. In general, sulfur specifications are converging to lower sulfur over time as shown in Figure 3.4.

### 3.4.2 Diesel Fuel Properties

Diesel fuel needs to enable a number of engine performance characteristics that are generally recognized as important. Their relative importance depends on engine type and duty cycle (truck, passenger car, stationary generator, marine vessel, etc.). Examples of the performance criteria include starting ease, sufficient power, low noise, good fuel economy, good lubricity for low wear, low temperature operability (cold flow), long filter life (stability), and low emissions. Although engine design has the greatest impact on most of these characteristics, fuel quality impacts the designer's ability to attain the required performance.

In order to achieve the performance characteristics noted above, product from ULSD operation needs to meet certain specifications. Various properties and their relevance in meeting performance of diesel engine are given here. It is important to note that diesel in various parts of the world has its own specifications typically related to powertrain requirement environmental regulations and climate conditions, to name a few. The United States typically follows ASTM D975 specification for Grade 1 and Grade 2 Diesel. The European region uses EN 590. There also is the Worldwide

Fuel Charter (2013), which represents an attempt to harmonize diesel specification worldwide in Categories 1–5. For a variety of reasons, other organizations may establish additional requirements, for example:

- State governments may want to reduce emissions beyond the limits established by the country. One example is the regulations established in California. CARB established additional requirements for vehicular diesel fuel that became effective in 1993.
- Pipeline companies that transport diesel fuel have limits for density and pour point, properties that D975 does not limit.
- Some purchasers such as the military may have unique requirement, for example, U.S. Department of Defense (DOD) formerly purchased fuels meeting military specifications that often included special requirements in addition to the D975 requirements. Now the DOD buys commercial fuel when possible.

The following section describes several key properties discussed by Bacha et al. (1998) in a technical review of diesel fuel. Diesel fuel properties and their significance in emission and/or engine performance are discussed as follows.

*Sulfur* content of diesel fuel affects PM emissions because some of the sulfur in the fuel is converted to sulfate particles in the exhaust. The fraction converted to PM varies from engine to engine design, but reducing sulfur decreases PM. For this reason, the EPA limits the sulfur content of on-road diesel fuel. Also sulfur in diesel fuel is converted to $SO_2$ which can be converted to sulfuric acid consequently; a reduction in sulfur also reduces production of acid rain. ULSD fuel enables the use of advanced emission control devices (after treatment systems) further lowering harmful exhaust emissions.

*Cetane number* is measure of the ignition quality of diesel fuel based on ignition delay in an engine (readiness to spontaneously combust under the temperature and pressure conditions in the combustion chamber of the engine). It relates to the starting and warm-up characteristics of the fuel. Increasing the cetane number improves fuel combustion characteristics and reduces $NO_x$ and PM emissions. The higher the cetane number, the shorter the ignition delay and the better the ignition quality, important for ease of ignition, better starting in cold temperature, reduced engine noise, and to control legislated emissions. Cetane number is measured by ASTM D613.

*Cetane Index (CI)* is an approximation of cetane number based on an empirical relationship with density and volatility parameters. CI can be calculated by ASTM D976 or D4737.

*Density:* Changes in fuel density affect the energy content of the fuel brought into the engine at a given injector setting. European studies have indicated that reducing fuel density tends to decrease $NO_x$ emissions.

*Aromatics:* Reduction of diesel fuel reduces $NO_x$ and PM10 in some engines. Recent European studies indicate that polynuclear aromatics content is key to the reduction and that the concentration of single-ring aromatics is not a significant factor.

*Flash point* is diesel property usually specified that is not directly related to engine performance. It is, however, of importance for safety precautions involved in fuel handling and storage and is normally specified to meet insurance and fire regulations.

*Volatility:* T95 is the temperature at which 95% of a particular diesel fuel distills in a standardized distillation test (ASTM D86). Reducing T95 decreases $NO_x$ emissions slightly but increases hydrocarbon and CO emissions. PM10 emissions are unaffected.

*Viscosity* is primarily related to molecular weight and not so much to hydrocarbon class. For a given carbon number, naphthenes generally have slightly higher viscosity compared to paraffins or aromatics. Normal paraffins have excellent cetane numbers but very poor cold flow properties and low volumetric heating values. Aromatics have very good cold flow properties and volumetric heating values but very low cetane numbers. Isoparaffins and naphthenes are intermediate, with values of these properties between those of normal paraffins and aromatics.

The diesel fuel injection is controlled volumetrically or by timing of the solenoid valve. Variations in fuel density (and viscosity) result in variations in engine power and, consequently, in engine emissions and fuel consumption. The European Programme on Emissions, Fuels and Engine Technologies (EPEFE) found that fuel density also influences injection timing of mechanically controlled injection equipment, which also affects emissions and fuel consumption. Therefore, in order to optimize engine performance and tailpipe emissions, both minimum and maximum density limits must be defined in a fairly narrow range.

Fueling and injection timing are also dependent on fuel viscosity. High viscosity can reduce fuel flow rates, resulting in inadequate fueling. A very high viscosity may actually result in pump distortion. Low viscosity, on the other hand, will increase leakage from the pumping elements, and in worst cases (low viscosity, high temperature) can result in total leakage. As viscosity is impacted by ambient temperature, it is important to minimize the range between minimum and maximum viscosity limits to allow optimization of engine performance.

*Cold flow:* Diesel fuel can have a high content (up to 20%) of paraffinic hydrocarbons that have a limited solubility in the fuel and, if cooled sufficiently, will come out of solution as wax, causing filters to plug. Adequate cold flow performance, therefore, is one of the most fundamental quality criteria for diesel fuels. The cold flow characteristics are primarily dictated by fuel distillation range, mainly the back-end volatility and hydrocarbon composition, that is, paraffins, naphthenes, and aromatics content (Worldwide Fuel Charter, 2013).

The diesel fuel cold flow performance can be specified by cloud point (CP), by CFPP (with maximum delta between CFPP and CP), or by low temperature flow test (LTFT) (in the United States and Canada).

- If CP (only) or LTFT is used, the maximum allowed temperature should be set no higher than the lowest expected ambient temperature.
- If CFPP is used to predict cold flow, the maximum allowed CFPP temperature should be set equal to, or lower than, the lowest expected ambient temperature. In this case, the CP should be no more than 10 °C above the CFPP specified.

Diesel cold flow properties must be specified according to the seasonal and climatic needs in the region where the fuel is to be used. The low-temperature properties of diesel fuels are therefore defined by the following specific tests:

*Cloud Point*, CP (ISO 3015, ASTM D2500): The temperature at which the heaviest paraffins start to precipitate and form wax crystals; the fuel becomes "cloudy."

*Cold Filter Plugging Point*, CFPP (EN116): The lowest temperature at which the fuel can pass through the filter in a standardized filtration test. The CFPP test was developed from vehicle operability data and demonstrates an acceptable correlation for fuels and vehicles in the market. For North American fuels, however, CFPP is not a good predictor of cold flow operability. Diesel fuel CFPP can be improved by addition of cold flow additives.

*Low Temperature Flow Test*, LTFT (ASTM D4539): The LTFT was developed to predict how diesel fuels in the United States and Canada will perform at low temperatures in the diesel vehicles available in these markets. LTFT is a slow cooling test and therefore more severe than CFPP. Similar to CFPP, LTFT temperature can be improved by addition of cold flow additives.

*Foam:* Diesel fuel has a tendency to generate foam during tank filling, which slows the process and risks an overflow. Antifoaming agents are sometimes added to diesel fuel, often as a component of a multifunctional additive package, to help speed up or to allow more complete filling of vehicle tanks. Silicon surfactant additives are effective in suppressing the foaming tendency of diesel fuels, the choice of silicon and cosolvent depending on the characteristics of the fuel to be treated. It is important that the additive chosen should not pose any problems for the long-term durability of the emission posttreatment control systems.

*Carbon residue* gives a measure of the carbon depositing tendencies of a fuel oil when heated in a bulb under prescribed conditions. While not directly correlating with engine deposits, this property is considered an approximation.

*Electrical conductivity* of fuels is an important consideration in the safe handling characteristics of any fuel. The risk associated with explosions due to static electrical discharge depends on the amount of hydrocarbon and oxygen in the vapor space and the energy and duration of a static discharge. There are many factors that can contribute to the high risk of explosion. For ULSD fuels in particular, electrical conductivity can likely be very low before the addition of static dissipater additive (SDA). The intent of this requirement is to reduce the risk of electrostatic ignitions while filling tank trucks, barges, ship compartments, and rail cars, where flammable vapors from the past cargo can be present. Generally, it does not apply at the retail level where flammable vapors are usually absent.

*Lubricity:* As diesel fuel refined to remove the polluting sulfur (ULSD), it is inadvertently stripped of its lubricating properties. This important lubrication property is critical for engine component as it prevents wear in the fuel delivery system. Specifically, it lubricates pumps, high-pressure pumps, and injectors. Traditional low-sulfur diesel fuel typically contained enough lubricating ability to suffice the needs of these vital components. ULSD fuel, on the other hand, is considered to be very "dry" and incapable of lubricating. As a result, engine components are at risk of premature and even catastrophic failure when ULSD fuel is introduced to the system. As a result, all oil companies producing ULSD fuel must replace the lost lubricity with additives. All ULSD fuel purchased at retail fuel stations should be adequately treated with additives to replace this lost lubricity. In addition, many additives can offer added benefits such as cetane improver, antigel agents, and water separators (demulsifiers).

Diesel fuel and other fluids are tested for lubricating ability using a device called a "high frequency reciprocating rig" or HFRR. The HFRR is currently the internationally accepted, standardized method to evaluate fluids for lubricating ability. It uses a ball bearing that reciprocates or moves back and forth on a metal surface at a very high frequency for a duration of 90 min. The machine does this while the ball bearing and metal surface are immersed in the test fluid. At the end of the test, the ball bearing is examined with a microscope and the "wear scar" on the ball bearing is measured in microns. The larger the wear scar, the poorer the lubricating ability of the fluid. The ASTM standard for diesel fuel requires diesel fuel to produce a wear scar of no greater than 520 μm. The Engine Manufacturers Association prefers a standard of a wear scar no greater than 460 μm, typical of the pre-ULSD fuels. Most experts agree that a 520 μm standard is adequate, but also that the lower the wear scar, the better.

*Corrosion:* A severe and rapid corrosion has been observed in systems storing and dispensing ULSD since 2007. In addition, the corrosion is coating the majority of metallic equipment in both the wetted and unwetted portions of ULSD underground storage tanks (USTs). This phenomenon was investigated by the industrial group project (Clean Diesel Fuel Alliance, 2012).

Their conclusion was that corrosion in systems storing and dispensing ULSD is likely due to the production of acetic acid throughout USTs. The acetic acid is believed to be produced by Acetobacter feeding on low levels of ethanol contamination. The presence of Acetobacter in the tank samples suggested that ethanol was being converted into acetic acid. Dispersed into the humid vapor space by the higher vapor pressure and by disturbances during fuel deliveries, acetic acid is deposited throughout the system. The source of ethanol is unknown; however, diesel fuel is often delivered in the same trucks as ethanol-blended gasoline. Also, ULSD USTs that have been converted from a gasoline tank could have manifolded ventilation systems with gasoline tanks. Thus, Clean Diesel Fuel Alliance (2012) suggests that it is possible that there be some cross-contamination of ethanol into ULSD. This results in a cycle of wetting and drying of the equipment concentrating the acetic acid on the metallic equipment and corroding it quite severely and rapidly.

The studies have also noted that corrosion was not much of a problem in tanks that were on a regular biocide treatment program to kill tank microbes. In the past, the sulfur acted as a natural biocide, but with the development of ULSD, the sulfur is now almost gone. Since there's nothing now to prevent bacterial growth, the use of biocides to treat the fuel is recommended to prevent microbial growth that normally would occur otherwise.

Storage and thermal stability of normally produced diesel fuel has adequate stability to withstand normal storage and use without the formation of troublesome amounts of insoluble degradation products.. Fuels that are to be stored for prolonged periods or used in complex applications should be selected to avoid formation of sediments or gums, which can overload filters or plug injectors. The stability properties of middle distillates are highly dependent on the crude oil sources, severity of processing, use of additives, and whether additional refinery treatment has been carried out.

**TABLE 3.3.  Diesel Properties and Effect on Performance**

| Property | Effect of Property on Performance | Time Frame of Effect |
|---|---|---|
| Flash point | Safety in handling and use – not directly related to engine performance | — |
| Water and sediment | Affects fuel filters and injectors | Long term |
| Volatility | Affects ease of starting and smoke | Immediate |
| Viscosity | Affects fuel spray atomization and fuel system lubrication | Immediate and long term |
| Ash | Can damage fuel injection system and cause combustion chamber deposits | Long term |
| Sulfur | Affects particulate emissions, cylinder wear, and deposits | Particulates: Immediate Wear: Long term |
| Copper strip corrosion | Indicates potential for corrosive attack on metal parts | Long term |
| Cetane number | Measure of ignition quality – affects cold starting, combustion, and emissions | Immediate |
| Cloud point and pour point | Allow low temperature operability | Immediate |
| Carbon residue | Measures coking tendency of fuel, may relate to engine deposits | Long term |
| Heating value (energy content) | Affects fuel economy | Immediate |
| Density | Affects heating value | Immediate |
| Stability | Indicates potential to form insolubles during use and/or in storage | Long term |
| Lubricity | Affects fuel pump and injector wear | Long term (typically) |
| Water separability | Affects ability to produce dry fuel | — |

Available fuel additives can improve the suitability of marginal fuels for long-term storage and thermal stability, but can be unsuccessful for fuels with markedly poor stability properties.

The relationship between diesel properties and effects on performance as summarized by Bacha et al. (1998) is presented in Table 3.3.

## 3.5   REACTION MECHANISMS

ULSD regulations require very low sulfur (i.e., <15 ppm sulfur). North America has implemented ULSD since 2006 and regulations requiring <10 ppm sulfur are in effect in Europe since 2009. In order to comply with these regulations, essentially all of the organo-sulfur species need to be removed including the substituted DBTs and other

refractory sulfur species. The mechanisms and kinetics for deep desulfurization are more complicated than the simple first-order reactions that hold for the less refractory sulfur species, for example, thiols, sulfides, and disulfides, due to the treatment of sterically hindered sulfur species. These sulfur species remain present at 500 and 50 ppm levels of sulfur and in some cases are left untouched. For this reason, some sources have suggested that it may be as difficult to reduce the sulfur levels from 50 to 10 ppm as it was to change from 500 to 50 ppm (Jones and Kokayeff, 2004, 2005).

Multiple reactions occur in parallel on the HDT catalyst surface. Companies and academia have investigated distillate HDT reaction mechanism and kinetic in great detail as ULSD became important.

In general, the following reactions occur in parallel depending upon feed composition:

- Sulfur removal, also referred to as desulfurization or HDS, in which the organic sulfur compounds are converted into hydrogen sulfide.
- Nitrogen removal, also referred to as denitrogenation or HDN, in which the organic nitrogen compounds are converted into ammonia.
- Metals (organometallics) removal, also referred to as hydrodemetallization (HDM), in which the organometallics are converted into the respective metal sulfides.
- Oxygen removal, also referred to as hydrodeoxygenation, in which the organic oxygen compounds are converted into water.
- Olefin saturation, in which organic compounds containing double bonds are converted to their saturated homologues. Olefins are not found in petroleum but are formed when processed in thermal or catalytic units. In general, olefins are unstable and thus must be protected from contact with oxygen prior to HDT to prevent the formation of polymer gums. That is especially true of feedstocks derived from thermal cracking operations such as coking and ethylene manufacturing. Typical olefin saturation reactions are rapid and exothermic, so heat release occurs near the inlet of bed.
- Aromatic saturation, also referred to as hydrodearomatization (HDA), in which some of the aromatic compounds are converted into naphthenes.

### 3.5.1   Hydrodesulfurization

Sulfur removal occurs via the conversion to $H_2S$ of the organic sulfur compounds present in the feedstock. Sulfur is found throughout the boiling range of petroleum fractions in the form of many different organic sulfur compounds. Following are six sulfur types: mercaptans, sulfides, disulfides, thiophenes, benzothiophenes, and DBTs. Typical reactions for each kind of sulfur compounds are shown in Table 3.4.

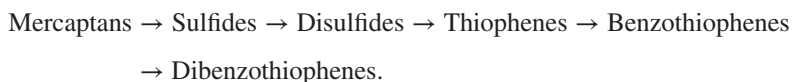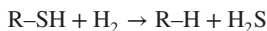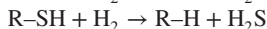Kokayeff et al. (2015) rank six sulfur types on the basis of ease of removal; easiest to hardest to remove as

Mercaptans → Sulfides → Disulfides → Thiophenes → Benzothiophenes

→ Dibenzothiophenes.

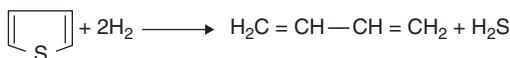**TABLE 3.4. Typical Reactions for Each Kind of Sulfur Compound**

Mercaptans      $R–SH + H_2 \rightarrow R–H + H_2S$

Sulfides      $R–SH + H_2 \rightarrow R–H + H_2S$

Disulfides      $R_1–S–S–R_2 + 3H_2 \rightarrow R_1–H + R_2–H + 2H_2S$

Thiophene      Step (1)



$+ 2H_2 \longrightarrow H_2C = CH—CH = CH_2 + H_2S$

Step (2)

$H_2C = CH–CH = CH_2 + 2H_2 \rightarrow H_3C–CH_2–CH_2–CH_3$
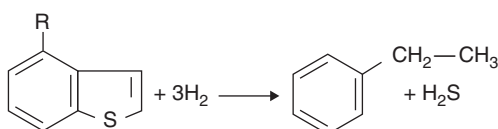
Benzothiophenes



$+ 3H_2 \longrightarrow$ ... $CH_2—CH_3$ ... $+ H_2S$
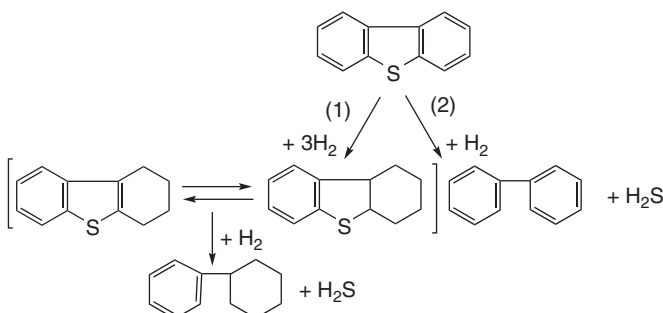
Dibenzothiophenes



In HDS, the sulfur species are generically characterized as "easy" or "difficult" sulfurs. In general, Jones and Kokayeff (2004) defined "easy" sulfur species (present in diesel typically boiling at <610 °F) experience little steric hindrance and are converted quickly. Conversion of the "difficult" sulfur species (boiling range >610 °F) is much slower than the "easy" sulfurs due to steric hindrance and more complex reaction pathways. Several species have been identified as being particularly difficult to convert in HDS, mostly substituted DBTs. In order to illustrate the difference in kinetics 4,6-dimethyldibenzothiophene (4,6-DMDBT), 4-ethyl,6-methyl dibenzothiophene, and C3-DBT-A have been used as representatives of the "difficult" sulfurs. Although the specific structure of C3-DBT-A has not been identified, it has been established that it is a C3-substituted DBT.

The HDS chemistry for easy sulfur is reasonably represented by an irreversible first-order reaction with hydrogen inhibited by $H_2S$ that competes for catalyst sites. It is widely accepted that there are two primary desulfurization paths for difficult sulfur species.

(1) Direct desulfurization (also known as sulfur extraction or hydrogenolysis) and hydrogenation (also known as saturation). Direct desulfurization follows the same chemistry as the easy sulfur.

(2) Catalyst sites are not readily accessible to difficult sulfur species such as for substituted DBTs due to the rigidity of the fused aromatic rings and steric hindrance. As a result, the second prevalent reaction route includes a reversible hydrogenation reaction preceding the sulfur extraction. The saturation of one of the aromatic rings increases the flexibility of the molecule causing the sulfur to be more accessible for desulfurization. Desulfurization of difficult sulfur species is known to be inhibited by both $H_2S$ and organo-nitrogen.

### 3.5.2 Aromatic Saturation

Aromatic saturation is an important reaction in distillate HDT. The aromatic content of the feedstock varies widely depending on the source of the material; however, in all cases, the aromatic compounds undergo saturation during HDT. As aromatics can be single, di and polyaromatics, for modeling purposes Jones and Kokayeff (2004, 2005) have considered mechanism as series of reversible reactions as shown in equation (3.1):

$$A + H_2 \longleftrightarrow B + H_2 \longleftrightarrow C + H_2 \longleftrightarrow D, \qquad (3.1)$$
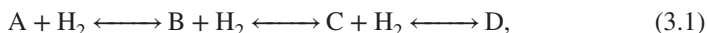
where A, B, and C represent poly (tri+), di-, and monoaromatic compounds, respectively, and D represents cyclic compounds (saturated aromatics). When producing ULSD, hydrogen consumption increases far beyond the stoichiometric requirement for desulfurization alone due to additional aromatics saturation that takes place. Although hydrogenation is limited by the thermal equilibrium at high temperatures, the rate of aromatic saturation is much faster than HDS reactions for difficult sulfurs and also varies with the number of fused rings.

Significant disagreement exists in the literature regarding inhibition of the HDS reaction by polycyclic aromatic compounds; there is also disagreement regarding the significance and magnitude of aromatics inhibition among those who confirm that it exists. Inhibition of 4,6-DMDBT desulfurization by the addition of naphthalene was observed in studies. The conversion of 4,6-DMDBT over a CoMo catalyst decreased with increasing naphthalene concentrations present. Analyses of desulfurization product distribution results in the presence of naphthalene suggest that inhibition is stronger for the hydrogenation route than for the direct extraction pathway.

Further complicating the determination of aromatic inhibition is the variation observed in the degree of inhibition depending on the number of fused rings. Studies investigating desulfurization of DBTs in the presence of di- and tricyclic aromatic compounds indicate no inhibition in the presence of methylnaphthalene (2-ring aromatic); however, a significant decrease in HDS activity was observed in the presence of phenanthrene (3-ring aromatic). The adsorption constant increases as the number of fused rings increases. In literature review, authors have suggested that the adsorption constant may increase by as much as an order of magnitude when the number of fused rings is increased from 3 to 4.7.

The conclusions regarding the influence of aromatic compounds on the rate of HDS in the literature vary even among those reviewing HDS on a broad scale. The conflicting conclusions about the influence of aromatics, coupled with the organo-nitrogen inhibition, cause the mechanism by which aromatics influence HDS questionable. Although there is a lack of agreement in the literature as to the