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

Hydroprocessing for Clean Energy: Design, Operation, and Optimization, First Edition.
Frank (Xin X.) Zhu, Richard Hoehn, Vasant Thakkar, and Edwin Yuh.

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, non-road, 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.

REFERENCES

Stanislaus A, Marafi A, Rana M (2010) Recent advances in the science and technology of ultra-low sulfur diesel (ULSD) production, *Catalysis Today*, **153** (1), 1–68.

5th Worldwide Fuel Charter (2013) *ACEA*, European Automobile Manufacturers Association, Brussels, Belgium.