

AN INTRODUCTION TO PETROLEUM REFINING AND THE PRODUCTION OF ULTRA LOW SULFUR GASOLINE AND DIESEL FUEL

Prepared for:



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1. INTRODUCTION

This tutorial addresses the basic principles of petroleum refining, as they relate to the production of ultra-low-sulfur fuels (ULSF), in particular gasoline (ULSG) and diesel fuel (ULSD).¹ This is the first work product of a comprehensive analysis of the economics of ULSG and ULSD production and supply in Brazil, China, India, and Mexico, being conducted by HART Energy and MathPro Inc. for the International Council on Clean Transportation (ICCT).

The purpose of the tutorial is to (1) provide context and an organizing framework for the overall analysis, (2) identify the technical factors that determine the refining cost of ULSG and ULSD production, and (3) facilitate interpretation of the results of the analysis. The tutorial addresses:

- ◆ Fundamentals of the petroleum refining industry
- ◆ Crude oil and its properties
- ◆ Classes of refinery processes and refinery configurations
- ◆ Properties of the refinery-produced streams (“blendstocks”) that make up gasoline and diesel fuel
- ◆ Refinery processing options for producing ULSG and ULSD

The tutorial is written for readers having an interest in ULSG and ULSD production but having no familiarity with refining operations in general and sulfur control in particular.

¹ For purposes of this tutorial, we define ULSF as fuel with sulfur content < 30 parts per million (ppm).

2. PETROLEUM REFINING AT A GLANCE

Petroleum refining is a unique and critical link in the petroleum supply chain, from the wellhead to the pump. The other links add value to petroleum mainly by moving and storing it (e.g., lifting crude oil to the surface; moving crude oil from oil fields to storage facilities and then to refineries; moving refined products from refinery to terminals and end-use locations, etc.). Refining adds value by converting crude oil (which in itself has little end-use value) into a range of refined products, including transportation fuels. The primary economic objective in refining is to maximize the value added in converting crude oil into finished products.

Petroleum refineries are large, capital-intensive manufacturing facilities with extremely complex processing schemes. They convert crude oils and other input streams into dozens of refined (co-)products, including:

- ◆ Liquefied petroleum gases (LPG)
- ◆ Gasoline
- ◆ Jet fuel
- ◆ Kerosene
(for lighting and heating)
- ◆ Diesel fuel
- ◆ Petrochemical feedstocks
- ◆ Lubricating oils and waxes
- ◆ Home heating oil
- ◆ Fuel oil (for power generation, marine fuel, industrial and district heating)
- ◆ Asphalt (for paving and roofing uses).

Of these, the transportation fuels have the highest value; fuel oils and asphalt the lowest value.

Many refined products, such as gasoline, are produced in multiple grades, to meet different specifications and standards (e.g., octane levels, sulfur content).

More than 660 refineries, in 116 countries, are currently in operation, producing more than 85 million barrels of refined products per day. Each refinery has a unique physical configuration, as well as unique operating characteristics and economics. A refinery's configuration and performance characteristics are determined primarily by the refinery's location, vintage, availability of funds for capital investment, available crude oils, product demand (from local and/or export markets), product quality requirements, environmental regulations and standards, and market specifications and requirements for refined products.

Most refineries in North America are configured to maximize gasoline production, at the expense of the other refined products. Elsewhere, most of the existing refining capacity and virtually all new capacity is configured to maximize distillate (diesel and jet fuel) production and, in some areas, petrochemical feedstock production, because these products are enjoying the fastest demand growth in most regions of the world.

3. CRUDE OIL AT A GLANCE

Refineries exist to convert crude oil into finished petroleum products. Hence, to understand the fundamentals of petroleum refining, one must begin with crude oil.

3.1 The Chemical Constituents of Crude Oil

Hundreds of different crude oils (usually identified by geographic origin) are processed, in greater or lesser volumes, in the world's refineries.

Each crude oil is unique and is a complex mixture of thousands of compounds. Most of the compounds in crude oil are hydrocarbons (organic compounds composed of carbon and hydrogen atoms). Other compounds in crude oil contain not only carbon and hydrogen, but also small (but important) amounts of other ("hetero"-) elements – most notably sulfur, as well as nitrogen and certain metals (e.g., nickel, vanadium, etc.). The compounds that make up crude oil range from the smallest and simplest hydrocarbon molecule – CH_4 (methane) – to large, complex molecules containing up to 50 or more carbon atoms (as well hydrogen and hetero-elements).

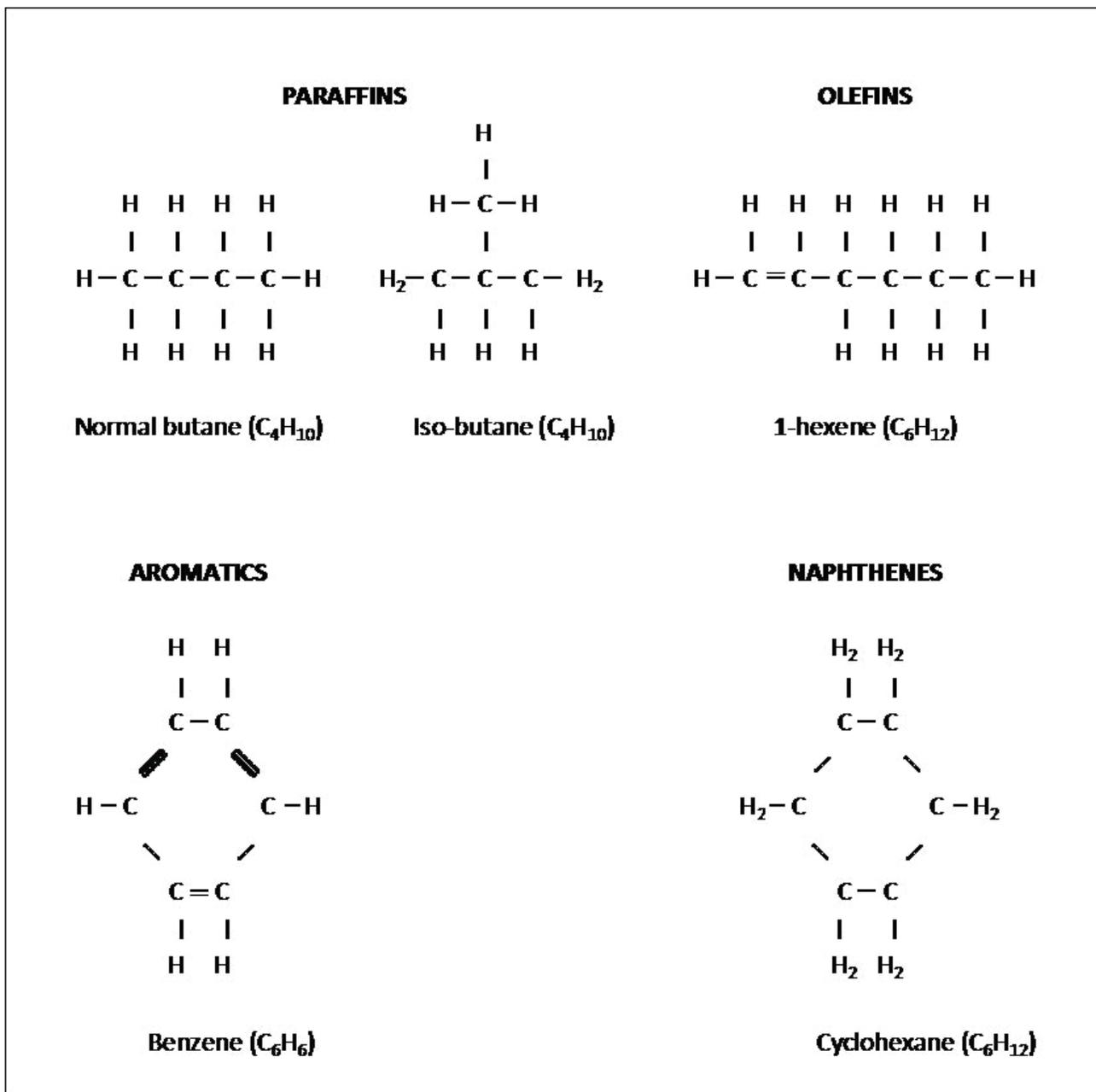
The physical and chemical properties of any given hydrocarbon species, or molecule, depends not only on the number of carbon atoms in the molecule but also the nature of the chemical bonds between them. Carbon atoms readily bond with one another (and with hydrogen and hetero-atoms) in various ways – single bonds, double bonds, and triple bonds – to form different classes of hydrocarbons, as illustrated in **Exhibit 1** on the following page.

Paraffins, *aromatics*, and *naphthenes* are natural constituents of crude oil, and are produced in various refining operations as well. *Olefins* usually are not present in crude oil; they are produced in certain refining operations that are dedicated mainly to gasoline production. As Exhibit 1 indicates, aromatic compounds have higher carbon-to-hydrogen (C/H) ratios than naphthenes, which in turn have higher C/H ratios than paraffins.

The heavier (more dense) the crude oil, the higher its C/H ratio. Due to the chemistry of oil refining, the higher the C/H ratio of a crude oil, the more intense and costly the refinery processing required to produce given volumes of gasoline and distillate fuels. Thus, the chemical composition of a crude oil and its various boiling range fractions influence refinery investment requirements and refinery energy use, the two largest components of total refining cost.

The proportions of the various hydrocarbon classes, their carbon number distribution, and the concentration of hetero-elements in a given crude oil determine the yields and qualities of the refined products that a refinery can produce from that crude, and hence the economic value of the crude. Different crude oils require different refinery facilities and operations to maximize the value of the product slates that they yield.

Exhibit 1: Important Classes of Hydrocarbon Compounds in Crude Oil



3.2 Characterizing Crude Oils

Assessing the refining value of a crude oil requires a full description of the crude oil and its components, involving scores of properties. However, two properties are especially useful for quickly classifying and comparing crude oils: *API gravity* (a measure of *density*) and *sulfur* content.

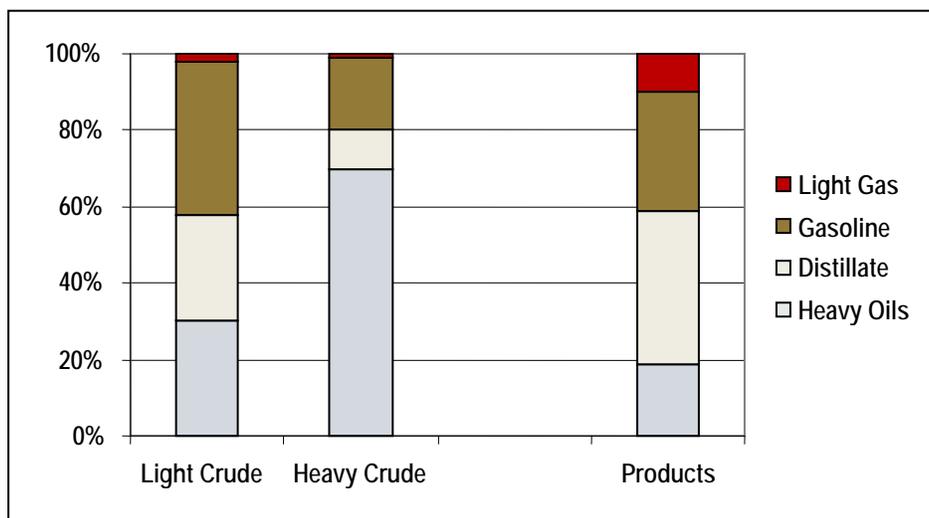
3.2.1 API Gravity (Density)

The *density* of a crude oil indicates how light or heavy it is, as a whole. Lighter crudes contain higher proportions of small molecules, which the refinery can process into gasoline, jet fuel, and diesel (for which demand is growing). Heavier crudes contain higher proportions of large molecules, which the refinery can either (1) use in heavy industrial fuels, asphalt, and other heavy products (for which the markets are less dynamic and in some cases shrinking) or (2) process into smaller molecules that can go into the transportation fuels products.

In the refining industry, the density of an oil is usually expressed in terms of *API gravity*, a parameter whose units are degrees ($^{\circ}$ *API*) – e.g., 35 $^{\circ}$ *API*. *API gravity* varies inversely with density (i.e., the lighter the material, the higher its *API gravity*). By definition, water has *API gravity* of 10 $^{\circ}$.

Exhibit 2 indicates the quality of a typical *light* crude (35 $^{\circ}$ *API*) and a typical *heavy* crude (25 $^{\circ}$ *API*), in terms of their natural yields of light gases, gasoline components, distillate (mainly jet fuel and diesel) components, and heavy oils. The exhibit also shows the average demand profile for these product categories in the developed countries.

Exhibit 2: Typical Natural Yields of Light and Heavy Crude Oils



Source: Hart Energy Consulting (2010)

The natural yields of the heavy oils from both the light and the heavy crudes exceed the demand for heavy refined products, and the natural yield of heavy oil from the heavy crude is more than twice that of the light crude. These general characteristics of crude oils imply that (1) refineries must be capable of converting at least some, and perhaps most, of the heavy oil into light products, and (2) the heavier the crude, the more of this conversion capacity is required to produce any given product slate.

3.2.2 Sulfur Content

Of all the hetero-elements in crude oil, sulfur has the most important effects on refining.

- ◆ Sufficiently high sulfur levels in refinery streams can (1) deactivate (“poison”) the catalysts that promote desired chemical reactions in certain refining processes, (2) cause corrosion in refinery equipment, and (3) lead to air emissions of sulfur compounds, which are undesirable and may be subject to stringent regulatory controls.
- ◆ Sulfur in vehicle fuels leads to undesirable vehicle emissions of sulfur compounds and interferes with vehicle emission control systems that are directed at regulated emissions such as volatile organic compounds, nitrogen oxides, and particulates.

Consequently, refineries must have the capability to remove sulfur from crude oil and refinery streams to the extent needed to mitigate these unwanted effects. The higher the sulfur content of the crude, the greater the required degree of sulfur control and the higher the associated cost.

The sulfur content of crude oil and refinery streams is usually expressed in weight percent (wt%) or parts per million by weight (ppmw). In the refining industry, crude oil is called *sweet* (low sulfur) if its sulfur level is less than a threshold value (e.g., 0.5 wt% (5,000 ppmw)) and *sour* (high sulfur) if its sulfur level is above a higher threshold. Most sour crudes have sulfur levels in the range of 1.0–2.0 wt%, but some have sulfur levels > 4 wt%.

Within any given crude oil, sulfur concentration tends to increase progressively with increasing carbon number. Thus, crude fractions in the fuel oil and asphalt boiling range have higher sulfur content than those in the jet and diesel boiling range, which in turn have higher sulfur content than those in the gasoline boiling range. Similarly, the heavier components in, say, the gasoline boiling range have higher sulfur content than the lighter components in that boiling range.

3.2.3 Classifying Crude Oils by API Gravity and Sulfur Content

Exhibit 3 shows a widely-used scheme for classifying crude oils on the basis of their API gravity and sulfur content. Each crude class is defined by a range of API gravity and a range of sulfur content; the names of the categories indicate these ranges in qualitative terms.

Exhibit 4 lists some important crude oils in the world oil trade and indicates the API gravity/sulfur classification for each of these crudes.

Exhibit 3: Crude Oil Classes

Crude Oil Class	Property Range	
	Gravity (°API)	Sulfur (wt.%)
Light Sweet	35-60	0-0.5
Light Sour	35-60	> 0.5
Medium Medium Sour	26-35	0-1.1
Medium Sour	26-35	> 1.1
Heavy Sweet	10-26	0-1.1
Heavy Sour	10-26	> 1.1

Exhibit 4: °API Gravity and Sulfur Levels of Some Important Crude Oils

Crude Oil	Country of Origin	Crude Oil Class	Properties	
			Gravity (°API)	Sulfur (wt.%)
Brent	U.K.	Light Sweet	40.0	0.5
West Texas Intermediate	U.S.A.		39.8	0.3
Arabian Extra Lt. Export	Saudi Arabia	Light Sour	38.1	1.1
Daqing	China	Medium Medium Sour	33.0	0.1
Forcados Export	Nigeria		29.5	0.2
Arabian Light Export	Saudi Arabia	Medium Sour	34.0	1.9
Kuwait Export Blend	Kuwait		30.9	2.5
Marlim Export	Brazil	Heavy Sweet	20.1	0.7
Cano Limon	Colombia		25.2	0.9
Oriente Export	Ecuador	Heavy Sour	25.0	1.4
Maya Heavy Export	Mexico		21.3	3.4

3.3 Crude Oil Quality and Refining Economics

3.3.1 Average Crude Oil Quality is Trending Down

The average API gravity and sulfur content of aggregate refinery crude slates varies by region; some regions process lighter, sweeter crude slates than others. However, over time, the average quality of the global crude slate has been declining gradually. Average API gravity has been decreasing, but slowly. Average sulfur content has been increasing more rapidly, a trend likely to continue for the foreseeable future.

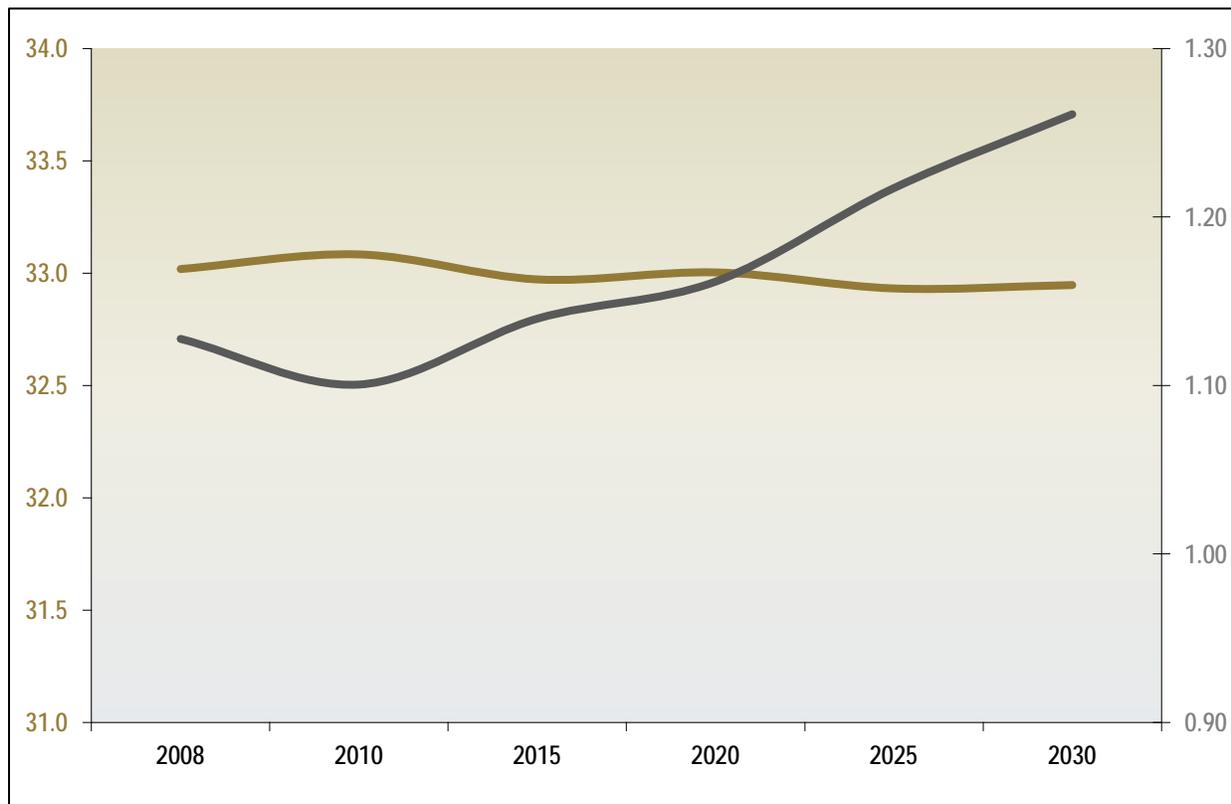
Illustrating this trend, **Exhibit 5** shows estimated crude quality, in terms of API gravity and sulfur content, in various regions of the world for 2008 (actual) and 2030 (projected), and **Exhibit 6** shows projected time profiles of average API gravity and sulfur content for the period 2008 to 2030.

Exhibit 5: Average Regional and Global Crude Oil Quality:
2008 (Actual) and 2030 (Projected)

Region	2008 (Actual)		2030 (Projected)	
	Gravity (°API)	Sulfur (wt%)	Gravity (°API)	Sulfur (wt%)
North America	31.2	1.21	28.7	1.66
Latin America	25.1	1.59	23.5	1.57
Europe	37.1	0.37	37.4	0.38
Commonwealth of Independent States	32.5	1.09	35.1	0.97
Asia-Pacific	35.4	0.16	35.7	0.16
Middle East	34.0	1.75	33.9	1.84
Africa	36.5	0.31	37.1	0.26
World Average	33.0	1.1	32.9	1.3

Source: Hart Energy Consulting analysis (2010)

Exhibit 6: Global Crude Oil Quality Trends (2008-2030)
 (—) °API, (—) Sulfur [wt%]



Source: Hart Energy Consulting analysis (2010)

These trends reflect the changing relationship between the average qualities of world crude oil reserves and annual crude oil production. On average, total world *reserves* of crude oil are of lower API gravity and higher sulfur content than is current world *production*. The large reserves in the Middle East (predominately medium sour), South America (predominately heavy sour), and Canada (predominately heavy sour) are contributing increasing shares of global crude oil supply. Crude oil produced in Europe and Asia is, on average, of high API gravity and low sulfur content, but it constitutes a decreasing share of global crude oil supply.

3.3.2 Crude Oil Quality Influences Crude Oil Pricing

The popular press often refers to “the price of crude oil,” as though all crude oils were priced the same. In fact, they are not. The higher the crude quality, the higher the market price relative to the prevailing average price for all crude oil. In other words, light sweet crudes carry a price premium relative to medium and heavy sour crudes.

Light sweet crudes have higher refining value than heavier, more sour crudes, because (1) light crudes have higher natural yields of the components that go into the more valuable light products, and (2) sweet crudes contain less sulfur. Hence, light sweet crudes require less energy to process

and call for lower capital investment to meet given product demand and quality standards than heavier, more sour crudes.

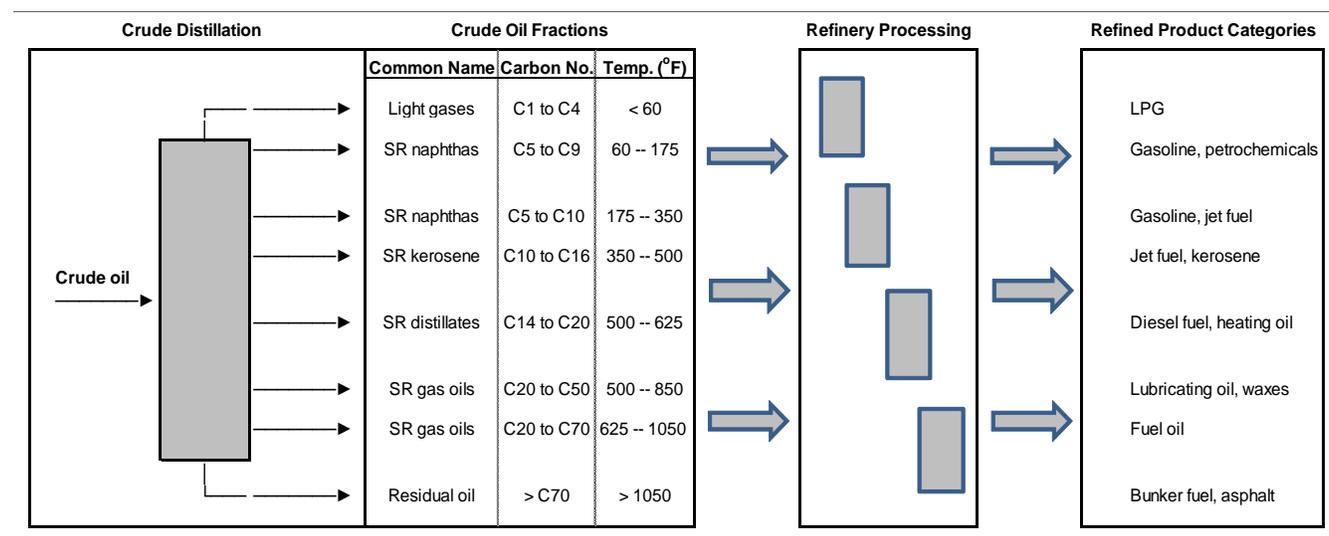
Refiners therefore face a key economic choice in meeting product demand and quality standards. They can either pay a price premium for higher quality crudes to capture their economic benefits or incur higher investment in refinery capital stock and higher refining costs to take advantage of the relatively lower prices of lower quality crudes.

Light sweet/heavy sour price differentials fluctuate over time and vary from place to place, due to the interplay of many technical and economic factors. These factors include crude quality differentials, crude supply/demand balances, local product markets and product specifications, and local refining capacity and upgrading capabilities. However, in general, the light sweet/heavy sour price differential tends to (1) increase (in absolute terms) with increasing world oil price level and (2) range from about 15% to 25% of the average price of light sweet crude.

Several aspects of refining operations suggested by Exhibit 7 merit comment. Refineries produce dozens of refined products (ranging from the very light, such as LPG, to the very heavy, such as residual fuel oil). They do so not only because of market demand for the various products, but also because the properties of crude oil and the capabilities of refining facilities impose constraints on the volumes of any one product that a refinery can produce. Refineries can – and do – change the operations of their refineries to respond to the continual changes in crude oil and product markets, but only within physical limits defined by the performance characteristics of their refineries and the properties of the crude oils they process. Finally, the complexity of refinery operations is such that they can be fully understood and optimized, in an economic sense, only through the use of refinery-wide mathematical models. Mathematical models of refinery operations are the only reliable means of generating achievable (i.e., feasible) and economic (i.e., optimal) responses to changes in market environment and to the introduction of new (usually more stringent) product specifications.

Exhibit 8 is a simpler schematic representation of a petroleum refinery, more useful for purposes of this tutorial. This exhibit illustrates, in schematic form, the separation of crude oil into specific boiling range (carbon number) fractions in the crude distillation process, shows standard industry names for these crude fractions, and indicates the subsequent refinery processing of these streams to produce a standard slate of finished refined products.²

Exhibit 8: Schematic View of Crude Oil Distillation and Downstream Processing



The balance of this section (1) describes the standard classification scheme for refineries based on the combinations of refining processes that they employ (Section 4.1) and then (1) briefly describes the most important types of processes by which refineries transform crude oil into finished products (Section 4.2).

² The designation SR in Exhibit 7 stands for “straight run”, a refining term meaning that the designated stream comes straight from the crude distillation unit, without further processing.

4.1 Classifying Refineries by Configuration and Complexity

Each refinery’s configuration and operating characteristics are unique. They are determined primarily by the refinery’s location, vintage, preferred crude oil slate, market requirements for refined products, and quality specifications (e.g., sulfur content) for refined products.

In this context, the term *configuration* denotes the specific set of refining process units in a given refinery, the size (throughput capacity) of the various units, their salient technical characteristics, and the flow patterns that connect these units.

Although no two refineries have identical configurations, they can be classified into groups of comparable refineries, defined by refinery *complexity*.

In this context, the term *complexity* has two meanings. One is its non-technical meaning: intricate, complicated, consisting of many connected parts. The other is a term of art in the refining industry: a numerical score that denotes, for a given refinery, the extent, capability, and capital intensity of the refining processes downstream of the crude distillation unit (which, by definition, has complexity of 1.0). The higher a refinery’s complexity, the greater the refinery’s capital investment intensity and the greater the refinery’s ability to add value to crude oil by

- (1) Converting more of the heavy crude fractions into lighter, high-value products and
- (2) Producing light products to more stringent quality specifications (e.g., ultra-low sulfur fuels).

Broadly speaking, all refineries belong to one of four classes, defined by process configuration and refinery complexity, as shown in **Exhibit 9**.

Exhibit 9: Refinery Classification Scheme

Configuration	Complexity	
	Ranking	Range
Topping	Low	< 2
Hydroskimming	Moderate	2 -- 6
Conversion	High	6 -- 12
Deep Conversion	Very high	> 12

◆ *Topping* refineries have only *crude distillation* and basic *support operations*. They have no capability to alter the natural yield pattern of the crude oils that they process; they simply separate crude oil into light gas and refinery fuel, naphtha (gasoline boiling range), distillates (kerosene, jet fuel, diesel and heating oils), and residual or heavy fuel oil. A portion of the naphtha material may be suitable for very low octane gasoline in some cases.

Topping refineries have no facilities for controlling product sulfur levels and hence cannot produce ULSF.

- ◆ *Hydroskimming* refineries include not only crude distillation and support services but also *catalytic reforming*, *various hydrotreating units*, and *product blending*. These processes enable (1) upgrading naphtha to gasoline and (2) controlling the sulfur content of refined products. Catalytic reforming upgrades straight run naphtha to meet gasoline octane specification and produces by-product hydrogen for the hydrotreating units. Hydrotreating units remove sulfur from the light products (including gasoline and diesel fuel) to meet product specifications and/or to allow for processing higher-sulfur crudes.

Hydroskimming refineries, commonplace in regions with low gasoline demand, have no capability to alter the natural yield patterns of the crudes they process.

- ◆ *Conversion* (or *cracking*) refineries include not only all of the processes present in hydroskimming refineries but also, and most importantly, *catalytic cracking* and/or *hydrocracking*. These two conversion processes transform heavy crude oil fractions (primarily *gas oils*), which have high natural yields in most crude oils, into light refinery streams that go to gasoline, jet fuel, diesel fuel, and petrochemical feedstocks.

Conversion refineries have the capability to improve the natural yield patterns of the crudes they process as needed to meet market demands for light products, but they still (unavoidably) produce some heavy, low-value products, such as residual fuel and asphalt.

- ◆ *Deep Conversion* (or *coking*) refineries are, as the name implies, a special class of conversion refineries. They include not only catalytic cracking and/or hydrocracking to convert gas oil fractions, but also *coking*. Coking units “destroy” the heaviest and least valuable crude oil fraction (*residual oil*) by converting it into lighter streams that serve as additional feed to other conversion processes (e.g., catalytic cracking) and to upgrading processes (e.g., catalytic reforming) that produce the more valuable light products.

Deep conversion refineries with sufficient coking capacity destroy essentially all of the residual oil in their crude slates, converting them into light products.

Almost all U.S. refineries are either *conversion* or *deep conversion* refineries, as are the newer refineries in Asia, the Middle East, South America, and other areas experiencing rapid growth in demand for light products. By contrast, most refining capacity in Europe and Japan is in hydroskimming and conversion refineries.

Exhibit 10 summarizes the salient features of the different refinery classes and indicates their characteristic product yield patterns at constant crude oil quality.³

In the U.S. and in many other countries, including Brazil, China, India, and Mexico, conversion and deep conversion refineries constitute more than 95% of total crude running capacity, and essentially 100% of crude running capacity in refineries with > 50 K Bbl/day of crude distillation

³ Actual refinery yield patterns can vary significantly from these patterns, depending on the specific crude slate and the specific performance characteristics of the refinery’s process units.

capacity. All new refineries being built in these countries are either conversion or deep conversion refineries. Consequently, the discussion in the next section (Section 5) applies specifically to these two refinery types.

Exhibit 10: Refinery Classes and Characteristic Yield Patterns

Refinery Category	Characteristic Processes	Product Yield Profile (vol%)		Comments
		Gasoline	Diesel & Jet	
Topping	Crude distillation	31	30	<ul style="list-style-type: none"> ◆ Product sulfur levels same as crude fraction sulfur levels ◆ Product yields and quality determined solely by crude properties ◆ Gasoline has low octane
Hydroskimming	Crude distillation Reforming Hydrotreating	28	30	<ul style="list-style-type: none"> ◆ Product sulfur levels controllable by hydrotreating ◆ Some capability to improve product yields and quality ◆ Gasoline octane improved by reforming
Conversion	Crude distillation FCC and/or hydrotreating Reforming Alkylation & other upgrading Hydrotreating	44	32	<ul style="list-style-type: none"> ◆ Product sulfur levels controllable by hydrotreating ◆ Substantial capability for yield and quality improvement
Deep Conversion	Crude distillation Coking FCC and/or hydrotreating Reforming Alkylation & other upgrading Hydrotreating	47	42	<ul style="list-style-type: none"> ◆ Product sulfur levels controllable by hydrotreating ◆ Maximum yields of high-value refined products ◆ Maximum capability for quality improvement ◆ Essentially all residual oil "destroyed"

Notes:

(1) Gasoline and distillate fuel yields are nominal estimates, based on processing an average quality crude oil

Source: Hart Energy Consulting

4.2 Classes of Refining Processes

The physical and chemical transformations that crude oil undergoes in a refinery take place in numerous distinct processes, each carried out in a discrete facility, or process unit. Large modern refineries comprise as many as fifty distinct processes, operating in close interaction. However, for tutorial purposes, these processes can be thought of in terms of a few broad classes, shown in **Exhibit 11**.

Exhibit 11: Important Classes of Refining Processes

Class	Function	Examples
Crude Distillation	<ul style="list-style-type: none"> ◆ Separate crude oil charge into boiling range fractions for further processing 	<ul style="list-style-type: none"> ◆ Atmospheric distillation ◆ Vacuum distillation
Conversion ("Cracking")	<ul style="list-style-type: none"> ◆ Break down ("crack") heavy crude fractions into lighter refinery streams for further processing or blending 	<ul style="list-style-type: none"> ◆ Fluid catalytic cracking (FCC) ◆ Hydrocracking
Upgrading	<ul style="list-style-type: none"> ◆ Rearrange molecular structures to improve the properties (e.g., octane) and value of gasoline and diesel components 	<ul style="list-style-type: none"> ◆ Catalytic reforming ◆ Alkylation, Isomerization
Treating	<ul style="list-style-type: none"> ◆ Remove hetero-atom impurities (e.g., sulfur) from refinery streams and blendstocks ◆ Remove aromatics compounds from refinery streams 	<ul style="list-style-type: none"> ◆ FCC feed hydrotreating ◆ Reformer feed hydrotreating ◆ Gasoline and distillate hydrotreating ◆ Benzene saturation
Separation	<ul style="list-style-type: none"> ◆ Separate, by physical or chemical means, constituents of refinery streams for quality control or for further processing 	<ul style="list-style-type: none"> ◆ Fractionation (numerous) ◆ Aromatics extraction
Blending	<ul style="list-style-type: none"> ◆ Combine blendstocks to produce finished products that meet product specifications and environmental standards 	<ul style="list-style-type: none"> ◆ Gasoline blending ◆ Jet and diesel blending
Utilities	<ul style="list-style-type: none"> ◆ Refinery fuel, power, and steam supply; sulfur recovery; oil movements; crude and product storage; emissions control; etc. 	<ul style="list-style-type: none"> ◆ Power generation ◆ Sulfur recovery

These categories are discussed briefly below.

4.2.1 Crude Distillation

Crude oil distillation is the front end of every refinery, regardless of size or overall configuration. It has a unique function that affects all the refining processes downstream of it.

Crude distillation separates raw crude oil feed (usually a mixture of crude oils) into a number of intermediate refinery streams (known as "crude fractions" or "cuts"), characterized by their boiling ranges (a measure of their *volatility*, or propensity to evaporate). Each fraction leaving the crude distillation unit (1) is defined by a unique boiling point range (e.g., 180°–250° F, 250°–350° F, etc.) and (2) is made up of hundreds or thousands of distinct hydrocarbon compounds, all of which have boiling points within the cut range. These fractions include (in order of increasing boiling range) light gases, naphthas, distillates, gas oils and residual oil (as shown in Exhibit 7). Each goes to a different refinery process for further processing.

The *naphthas* are gasoline boiling range materials; they usually are sent to upgrading units (for octane improvement, sulfur control, etc.) and then to gasoline blending. The *distillates*, including

kerosene, usually undergo further treatment and then are blended to jet fuel, diesel and home heating oil. The *gas oils* go to conversion units, where they are broken down into lighter (gasoline, distillate) streams. Finally, the *residual oil* (or *bottoms*) is routed to other conversion units or blended to heavy industrial fuel and/or asphalt. The bottoms have relatively little economic value – indeed lower value than the crude oil from which they come. Most modern refineries convert, or upgrade, the low-value heavy ends into more valuable light products (gasoline, jet fuel, diesel fuel, etc.).

Because all crude oil charged to the refinery goes through crude distillation, refinery capacity is typically expressed in terms of crude oil distillation throughput capacity.

4.2.2 Conversion (Cracking) Processes

Conversion processes carry out chemical reactions that fracture (“crack”) large, high-boiling hydrocarbon molecules (of low economic value) into smaller, lighter molecules suitable, after further processing, for blending to gasoline, jet fuel, diesel fuel, petrochemical feedstocks, and other high-value light products. Conversion units form the essential core of modern refining operations because they (1) enable the refinery to achieve high yields of transportation fuels and other valuable light products, (2) provide operating flexibility for maintaining light product output in the face of normal fluctuations in crude oil quality, and (3) permit the economic use of heavy, sour crude oils.

The conversion processes of primary interest are *fluid catalytic cracking (FCC)*, *hydrocracking*, and *coking*.⁴

Exhibit 12 provides a brief comparison of some salient properties of these three processes.

The **C/H Ratio Adjustment** item in Exhibit 12 requires some explanation. As noted previously, the heavier (more dense) the crude oil, the higher its C/H ratio. Similarly, within any given crude oil, the heavier the boiling range fraction, the higher its C/H ratio. The same phenomenon applies to refined products: the heavier the product, the higher its C/H ratio. Consequently, refining operations must, in the aggregate, reduce the C/H ratio of the crude oil and intermediate streams that they process. Much (but not all) of this burden falls on the conversion processes.

Broadly speaking, reducing the C/H ratio can be accomplished in one of two ways: either by rejecting excess carbon (in the form of petroleum coke) or by adding hydrogen. FCC and coking follow the former path; hydrocracking follows the latter path.

Fluid Catalytic Cracking

FCC is the single most important refining process downstream of crude distillation, in terms of both industry-wide throughput capacity and its overall effect on refining economics and operations. The

⁴ *Visbreaking*, another conversion process, is similar in function to coking. *Visbreaking* is used primarily in Europe.

process operates at high temperature and low pressure and employs a catalyst⁵ to convert heavy gas oil from crude distillation (and other heavy streams as well) to light gases, petrochemical feedstocks, gasoline blendstock (*FCC naphtha*), and diesel fuel blendstock (*light cycle oil*).

Exhibit 12: Salient Features of Primary Conversion Processes

Features	FCC	Hydro-cracking	Coking
Primary Feeds			
SR Distillate	♦	♦	
SR Gas Oil	♦	♦	
SR Residual Oil			♦
Coker Gas Oil	♦		
FCC Slurry Oil		♦	♦
Process Type			
Catalytic	♦	♦	
Thermal			♦
C/H Ratio Adjustment			
Carbon rejection	♦		♦
Hydrogen addition		♦	
Primary Functions			
Increase light product yield	♦	♦	♦
Produce additional FCC feed			♦
Remove hetero-atoms (including sulfur)		♦	
Sulfur Content of Cracked Products	Moderate to High	< 100 ppm	Very High

FCC offers (1) high yields of gasoline and distillate material (in the range of 60–75 vol% on FCC feed), (2) high reliability and low operating costs, and (3) operating flexibility to adapt to changes in crude oil quality and refined product requirements. In a large, transportation fuels oriented refinery, the FCC unit accounts for more than 40% of the total refinery output of gasoline and distillate fuels (e.g., diesel). The ratio of gasoline to distillate (G/D) in the FCC output depends on

⁵ A catalyst is a material (usually a metal or metal oxide) that promotes or accelerates a specific chemical reaction, without itself participating in the reaction.

FCC operating conditions and catalyst. In U.S. refineries, the G/D ratio is higher in the summer than in the winter, reflecting changes in the fuel demand pattern. Elsewhere, the G/D ratio tends to be lower than in the U.S., again in response to local demand patterns.

FCC also produces significant volumes quantities of light gases (C1 to C4), including olefins. Light olefins are highly reactive chemicals that are valuable either as petrochemical feedstocks or as feedstocks to the refinery's upgrading processes (which produce high-octane, low-sulfur gasoline blendstocks). With suitable catalyst selection, FCC units can be designed to maximize production of gasoline blendstock (FCC naphtha), distillate blendstock (light cycle oil), or petrochemical feedstocks.

Sulfur is a "poison" to FCC catalysts; that is, contact with sulfur reduces the effectiveness of FCC catalysts. To alleviate this problem, many refineries have desulfurization units in front of the FCC that remove much of the sulfur from the FCC feed. Even with such units in place, the refinery streams produced by the FCC unit still contain some of the sulfur that was present in the FCC feed. Indeed, untreated FCC products (FCC naphtha and light cycle oil) are the primary sources of sulfur in gasoline and diesel fuel.

Un-reacted FCC feed (called *slurry oil*) has various dispositions in the refinery, including feed to the coking unit (in refineries that have both FCC and coking units).

Hydrocracking

Hydrocracking, like FCC, converts distillates and gas oils from crude distillation (as well as other heavy refinery streams), primarily to gasoline and distillates. Hydrocracking is a catalytic process that operates at moderate temperature and high pressure. It applies externally-generated hydrogen to crack distillate and heavy gas oil feeds into light gases, petrochemical feedstocks, and gasoline and diesel fuel blendstocks.

Like FCC, hydrocracking offers high yields of light products and extensive operating flexibility. Product yields from hydrocracking depend on how the unit is designed and operated. At one operating extreme, a hydrocracker can convert essentially all of its feed to gasoline blendstocks, with yields ≈ 100 vol% on feed. Alternatively, a hydrocracker can produce jet fuel and diesel fuel, with combined yields of 85% to 90 vol%, along with small volumes of gasoline material.

Hydrocracking has a notable advantage over FCC; the hydrogen input to the hydrocracker not only leads to cracking reactions but also to other reactions that remove hetero-atoms – especially sulfur – from the hydrocracked streams. These "hydrotreating" reactions yield hydrocracked streams with very low sulfur content and other improved properties.

Consequently, hydrocracked streams are especially useful blendstocks for ULSF production. Hydrocracked streams are not only near sulfur-free but also low in aromatics content. Aromatics are hydrocarbons having ring-shaped molecules (Exhibit 1). Aromatics in the distillate boiling range have poor engine performance (i.e., low cetane number) and poor emission characteristics in diesel fuel. The chemical reactions in hydrocracking break open the aromatic rings, and thereby

produce premium distillate blendstocks with outstanding performance and emissions characteristics. Consequently, hydrocrackers in refineries with FCC and/or coking units often receive as feed the high-aromatics-content, high-sulfur distillate streams from these units.

Hydrocracking is more effective in converting heavy gas oils and producing low-sulfur products than either FCC or coking, but hydrocrackers are more expensive to build and operate, in large part because of their very high hydrogen consumption.

Coking

Coking is a thermal, non-catalytic conversion process that cracks residual oil, the heaviest residue from crude distillation, into a range of lighter intermediates for further processing. Coking is the refining industry's primary (but not sole) means of converting residual oil – the “bottom of the crude barrel” – into valuable lighter products.

The cracked products from coking comprise light gases (including light olefins), low quality naphtha (*coker naphtha*) and distillate streams (*coker distillate*) which must be further processed, and large volumes of *coker gas oil* and of *petroleum coke* ($\approx 25\text{--}30$ wt% on feed).

The coker gas oil is used primarily as additional FCC feed. However, coker gas oil contains high levels of sulfur and other contaminants, which make it a less valuable FCC feed than straight run gas oils.

Depending on the crude oil, the petroleum coke produced in the coker can be sold for various end uses, used as fuel in refinery or external power plants, or simply buried.

4.2.3 Upgrading Processes

Upgrading processes carry out chemical reactions that combine or re-structure molecules in low-value streams to produce higher-value streams, primarily high-octane, low sulfur gasoline blendstock. The upgrading processes of primary interest all employ catalysts, involve small hydrocarbon molecules, and apply to gasoline production.

The most important of the many upgrading processes are *catalytic reforming*, *alkylation*, *isomerization*, *polymerization*, and *etherification*.

Exhibit 13 provides a brief summary of some of the salient properties of these processes.

These processes are discussed briefly below, in roughly decreasing order of installed capacity and importance to gasoline production.

Catalytic Reforming

Catalytic reforming (or, simply, “reforming”) is the most widely used upgrading process, particularly in U.S. refineries. Reforming units process various naphtha streams (primarily, but not

exclusively, straight run naphthas from crude distillation).⁶ Reformers carry out a number of catalytic reactions on these naphtha streams that significantly increase the octane of these streams (in some instances by as much as 50 octane numbers). The reformer output (called *reformate*) is premium, high-octane gasoline blendstock. Reformate accounts for about 25% of the U.S. gasoline pool.

Exhibit 13: Salient Features of Primary Upgrading Processes

	Reforming	Alkylation	Isomerization	Polymerization	Etherification
Primary Feeds					
SR Naphtha (med. and hvy.)	◆				
SR Naphtha (light)			◆		
Natural Gasoline			◆		
Iso-butane		◆			
C3 Olefin		◆		◆	
C4 Olefins		◆		◆	◆
Methanol / Ethanol					◆
Primary Products					
Gasoline Blendstock	Reformate	Alkylate	Isomerase	Poly Gasoline	MTBE
Other	Hydrogen				
Primary Functions					
Improve refinery yield of gasoline	◆	◆		◆	◆
Add octane to the gasoline pool	◆◆◆	◆◆	◆	◆	◆◆◆
Control gasoline pool octane	◆				
Produce refinery hydrogen	◆				

The primary chemical reactions in reforming produce aromatic compounds (hydrocarbons with ring-shaped molecules, as shown in Exhibit 1). Aromatics in the gasoline boiling range have very high octane and other characteristics that are desirable for gasoline production.

⁶ SR naphthas and other naphtha streams are in the gasoline boiling range (≈ 60°–400° F).

Catalytic reforming is a core refining process. It is both the primary refinery source of incremental octane for gasoline and the primary means of regulating the octane of the gasoline pool. Reforming can produce reformates with octanes > 100 RON.⁷ Reforming is the only refining process in which product octane is subject to control by manipulation of operating conditions. Minor adjustments in operating conditions allow reformers to operate at different “severities”, to produce reformat octanes anywhere in the range of 85 to 100 RON.

Reformers have another important refinery function. Aromatics compounds have a higher C/H ratio than the hydrocarbon compounds from which they produced in reforming. Consequently, reformers produce hydrogen as a co-product. Reformer-produced hydrogen supplies about 45% of the hydrogen consumed in U.S. refineries.

The high concentration of aromatic compounds in reformat is the main source of reformat octane. These aromatics compounds are also valuable as petrochemical feedstocks. Hence, many refineries located near petrochemical centers have processes to extract some of these aromatics for sale as petrochemical feedstock.

Aromatics, especially benzene, are deemed to be toxic compounds, which has led to external pressures to generate incremental octane from sources having lower aromatic content.

Alkylation

Alkylation combines light olefins (primarily C4s, and some C3) with iso-butane (see Exhibit 1) to produce a high-octane (\approx 90–94 RON) gasoline blendstock (*alkylate*). The light olefins and most or all of the iso-butane come from the refinery FCC unit.⁸ Hence, alkylation units are found only in refineries having FCC units. The U.S. has the most FCC capacity of any country and, consequently, the most alkylation capacity.

Due to the nature of the alkylation process, alkylate contains no aromatics and no sulfur, making it a premium gasoline blendstock.

Virtually all alkylation units use a strong liquid acid catalyst – either hydrofluoric acid (HF) or sulphuric acid (H₂SO₄), depending on the process. Both processes require careful operation because of the possible environmental and public health hazards posed by the acids. Concern with HF units centers mainly on possible release of highly toxic HF vapour. Concern with H₂SO₄ units centers more on the handling, storage, and transportation of large volumes of the concentrated strong acid.

Isomerization

Isomerization rearranges the low-octane C5 and C6 *normal*-paraffin molecules (Exhibit 1) in light SR naphtha to produce the corresponding, higher-octane C5 and C6 *iso*-paraffins, thereby

⁷ Research Octane Number (**RON**) and Motor Octane Number (**MON**) are the two standard measures of gasoline octane. The octane specifications of gasoline grades are usually specified as averages of RON and MON (designated (R+M)/2 at the pump).

⁸ Some refineries located near natural gas production sites obtain additional iso-butane from natural gas liquids plants.

significantly increasing the octane of the resulting naphtha stream (*isomerase*) and making it a valuable gasoline blendstock.

As an additional process benefit, isomerization produces a product containing essentially no sulfur and no benzene. Hence, some refineries recently have added isomerization capacity as a means of meeting stringent new benzene standards on their gasoline output.

Polymerization

Polymerization combines two or three light olefin molecules (C3 or C4) to produce a high- octane, olefinic gasoline blendstock (*poly gasoline*) component.

Polymerization is a relatively inexpensive process. But it is not widely used, because poly gasoline is a relatively undesirable gasoline blendstock. It is highly olefinic, and olefins are unstable in gasoline (they tend form gum in storage).

Etherification

Etherification combines C4 and/or C5 olefins produced by FCC plants with a purchased alcohol (methanol or ethanol) to produce an *ether* (a class of oxygen-containing organic compounds).

Ethers are premium gasoline blendstocks, with very high octane and other desirable blending properties.

The most common etherification process combines methanol with iso-butene (a C4 olefin) to produce methyl tertiary butyl ether (*MTBE*). Other ethers in commercial use (though only in small volumes) include ethyl tertiary butyl ether (ETBE) (made from ethanol and iso-butene) and tertiary amyl methyl ether (TAME) (made from methanol and iso-amylene (a C5 olefin)). Ethers are produced in both refinery-based units (which tend to be small) and in dedicated merchant plants (which tend to be much larger).

By federal law, MTBE has been phased out of the U.S. gasoline pool (as of 2006), in response to public concerns over reported leaks of MTBE into groundwater. The phase-out has led U.S. refiners to shut down their etherification units. However, U.S. merchant plants continue to produce some MTBE, for export to markets in Europe, Mexico, and elsewhere. In these regions, use of ethers (mainly MTBE and ETBE) as gasoline blendstocks is continuing and growing. In 2010, Mexico consumed about 43 K Bbl/day of MTBE, and China consumed about 49 K Bbl/day.

4.2.4 Treating (Hydrotreating) Processes

Treating processes carry out chemical reactions that remove hetero-atoms (e.g., sulfur, nitrogen, heavy metals) and/or certain specific compounds from crude oil fractions and refinery streams, for various purposes. The most important purposes are (1) meeting refined product specifications (e.g.; sulfur in gasoline and diesel fuel, benzene in gasoline, etc.) and (2) protecting the catalysts in many refining processes from deactivation ("poisoning") resulting from prolonged contact with

hetero-atoms.⁹ By far the most widely-used of the various treating technologies is catalytic hydrogenation, or *hydrotreating*.

Hydrotreaters remove hetero-atoms by reacting the refinery streams containing the hetero-atom(s) with hydrogen in the presence of a catalyst. The hydrogen combines with the hetero-atom(s) to form non-hydrocarbon molecules that are easily separated from refinery streams.¹⁰

Hydrotreating has many forms and degrees of severity; as a result, it goes by many names in the refining industry and in the literature. Hydrotreating focused on sulfur removal is often referred to as *hydro-desulfurization*; hydrotreating focused on nitrogen removal is called *hydro-denitrification*; and so on. Hydrotreating conducted at high severity (i.e., high temperature, pressure, and hydrogen concentration) often involves some incidental hydrocracking as well. Deep hydrotreating of this kind is called *hydro-refining*. Hydrotreating conducted at low severity is used to modify certain characteristics of specialty refined products (e.g., various lubricating oil properties) to meet specifications. Mild hydrotreating is often called *hydro-finishing*.

Most refineries that produce light products have many hydrotreating units. They operate on many different crude oil fractions, intermediate refinery streams, feedstocks, and blendstocks, ranging from light naphthas to heavy residue, and serve many purposes. For example,

- ◆ All catalytic reformers have *naphtha hydrotreaters* that reduce the sulfur content of reformer feed to < 1 ppm, to protect the reformer catalyst. Some reformers also have post-hydrotreaters (*benzene saturation units*) to remove benzene from the reformat.
- ◆ Many FCC units, especially in refineries running sour crude slates or producing low-sulfur gasoline and diesel fuel, have *FCC feed hydrotreaters*. These hydrotreaters reduce the FCC's emissions of sulfur oxides, protect the FCC catalyst from poisoning by nitrogen and metals, improve cracking yields, and reduce the sulfur content of the FCC products (including those going to gasoline and diesel blending).

Almost all FCC units in refineries producing low-sulfur gasoline have post-hydrotreaters (FCC *naphtha hydrotreaters*) to remove most of the sulfur in the *FCC naphtha*, an important gasoline blendstock that the FCC produces.

- ◆ *Distillate hydrotreaters* remove sulfur from individual distillate fuel blendstocks or mixtures of these blendstocks, as well as other refinery streams, to meet final sulfur specifications on the finished products (and, in some cases, aromatics and cetane number specifications as well).

4.2.5 Separation Processes

Virtually all refinery streams are mixtures of hydrocarbon compounds. *Separation* processes use differences in the physical and chemical properties of these compounds to separate one refinery stream into two or more new ones.

⁹ Some catalysts cannot tolerate sulfur concentrations in excess of 1 ppm.

¹⁰ For example, hydrogen reacts with sulfur to produce hydrogen sulfide, a light, readily-separated gas.

Distillation, or fractionation, the most common separation process, uses differences in boiling point temperatures to effect separations into relatively lighter (lower boiling) and relatively heavier (higher boiling) mixtures. Distillation employs well-established technology and is doubtless the most widely used refining process; distillation units (*fractionators*) are ubiquitous in refineries.

Distillation units require significant inputs of thermal energy, to boil the more volatile components of the mixture being separated. Consequently, a refinery's distillation units, including crude distillation (Section 4.1.1), collectively account for a significant fraction of the refinery's total energy use,

Extraction, another common separation process, uses differences in the relative solubilities of different compounds in a liquid solvent to remove specific compounds from hydrocarbon mixtures. The most common refining application of extraction is *aromatics extraction*, which selectively removes certain aromatics compounds (see Exhibit 1) from the highly aromatic reformat stream produced in catalytic reforming (Section 4.1.3). The extracted aromatics (benzene, toluene, and xylenes) are primary petrochemical feedstocks.

4.2.6 Utilities and Support Operations

Refineries encompass many additional process units of varying complexity and purpose. Some produce specialty products (waxes, lubricants, asphalt, etc.); others control emissions to air and water; and still others provide support to the mainline processes discussed above.

The primary support facilities include

- ◆ Hydrogen production and recovery,
- ◆ Sulfur recovery (from desulfurization processes)
- ◆ Light gas handling and separation,
- ◆ Wastewater treatment
- ◆ Oil movement and storage
- ◆ Electricity and steam generation

Hydrocrackers and hydrotreaters require substantial inputs of hydrogen. As noted above, some of the refinery hydrogen requirement (about 45% of the total in U.S. refineries) is met by by-product hydrogen produced in the reformer. The rest of the hydrogen requirement is met by on-purpose hydrogen production units in the refinery or (in some locales) by purchases of hydrogen from near-by merchant hydrogen plants. These units produce hydrogen from natural gas. Because on-purpose hydrogen is expensive, regardless of its source, most refineries also have facilities for recovering and recycling the spent hydrogen in hydrocracking and hydrotreating effluent streams.

Refinery processes use fuel and steam to heat and/or boil process streams and to provide the energy needed to drive chemical reactions, and they use electricity for running pumps and compressors. Some refineries purchase fuel (natural gas), electricity, and/or steam; others

generate some or all of their utilities on-site. On-site generation involves traditional steam boilers and power generation facilities, or co-generation. Co-generation is the integrated production of electricity and steam, at very high thermal efficiency, using either purchased natural gas or refinery-produced light gas as fuel.

4.2.7 Product Blending

Product blending, the operation at the back end of every refinery, regardless of size or overall configuration, blends refinery streams in various proportions to produce finished refined products whose properties meet all applicable industry and government standards, at minimum cost. The various standards pertain to physical properties (e.g., density, volatility, boiling range); chemical properties (e.g., sulfur content, aromatics content, etc.), and performance characteristics (e.g., octane number, smoke point).

Production of each finished product requires multi-component blending because (1) refineries produce no single blend component in sufficient volume to meet demand for any of the primary blended products such as gasoline, jet fuel, and diesel fuel, (2) many blend components have properties that satisfy some but not all of the relevant standards for the refined product into which they must be blended, and (3) cost minimization dictates that refined products be blended to meet, rather than exceed, specifications to the extent possible. Typically, gasoline is a mixture of ≈ 6 – 10 blendstocks; diesel fuel is a mixture of ≈ 4 – 6 blendstocks.

Gasoline blending is the most complex and highly automated blending operation. In modern refineries, automated systems meter and mix blendstocks and additives. On-line analyzers (supplemented by laboratory analyses of blend samples) continuously monitor blend properties. Computer control and mathematical models establish blend recipes that produce the required product volumes and meet all blend specifications, at minimum production cost. Blending of other products usually involves less automation and mathematical analysis.

5. FUNDAMENTALS OF ULSF PRODUCTION

This section addresses four topics bearing on the production of ULSG and ULSD in conversion and deep conversion refineries.

1. Key properties – especially sulfur content – of the refinery streams and blendstocks that are blended to produce gasoline and diesel fuel
2. The refining processes needed for producing ULSG and ULSD
3. Routes for upgrading existing refineries to meet ULSG and ULSD standards
4. Refining costs associated with meeting ULSF standards

5.1 Key Properties of Gasoline and Diesel Blendstocks

5.1.1 Gasoline Blendstocks

Individual refineries produce one to four gasoline grades (distinguished by their octane, sulfur content, and other physical properties). Typically, each grade is a blend of six to ten blendstocks (refinery-produced or purchased). All of the grades are blended from the same set of blendstocks, but with different recipes.

Exhibit 14 lists the most common gasoline blendstocks and indicates typical ranges for the more important blending properties of each blendstock, including sulfur content.

Exhibit 14: Typical Volume Shares and Properties of Standard Gasoline Blendstocks

Source	Blendstock	Typical Share (Vol%)	Typical Properties						
			Octane		Sulfur (ppm)	RVP (psi)	Aromatics (vol%)	Benzene (vol%)	Olefins (vol%)
			RON	MON					
Crude Distillation	Str. Run Naphtha	5 - 10	71	70	≈ 120	12	-	-	-
Upgrading Units	Isomerase	0 - 10	82	80	1	13	-	-	-
	Alkylate	5 - 10	94	92	< 10	3	-	-	-
	Reformate	20 -30	97	88	< 4	5	60	5	-
Conversion Units	FCC Naphtha	30 - 35	92	80	500 - 1500	5	25	1	30
	Coker Naphtha	0 - 5	88	80	≈ 500	19	0.5	0.5	50
	Hydrocracked Naphtha	5 - 15	78	76	< 4	11	2	2	-
Purchases	Natural Gas Liquids	0 - 5	73	71	≈ 150	13	3	1	1
	MTBE	0 - 15	118	102	< 5	8	-	-	-
	Ethanol	0 - 10	123	103	< 5	18	-	-	-

Exhibit 14 shows ranges for many of the blendstock properties because specific property values depend on the properties of the crude oil and (for some blendstocks, notably reformat and FCC naphtha) the processing severity in the units that produce them. For example, as a rough rule of thumb, the sulfur content of FCC naphtha is about 1/10 that of the crude oil from which it is produced. Thus, a crude oil containing 2 wt% sulfur (20,000 ppm) would yield an FCC naphtha with sulfur content ≈ 0.2 wt% (2000 ppm).

The indicated properties are for “raw” streams – that is, for streams that have not been further processed to improve their properties. In particular, the indicated sulfur contents reflect no hydrotreating downstream of the units that produced the streams.

Due to its high sulfur content and high volume share in the gasoline pool, FCC naphtha is the primary source of sulfur in gasoline, contributing up to 90% of the sulfur in gasoline, prior to processing for sulfur control. Coker naphtha and straight run naphtha contribute most of the remaining sulfur.

Consequently, ULSG production requires severe desulfurization (primarily via hydrotreating) of FCC naphtha. In deep conversion refineries, it requires desulfurization of coker naphtha as well. For the most stringent sulfur standards, ULSG production also requires desulfurization of straight run naphtha and natural gas liquids.

5.1.2 Diesel Blendstocks

Individual refineries produce one or two diesel grades (distinguished by their sulfur content, primarily, as well as by cetane number, density, and other physical properties). Typically, each grade is a blend of three to five refinery-produced blendstocks (plus, in some locales, purchased bio-diesel and (in a few instances) Fischer-Tropsch diesel). As with gasoline, all of the diesel grades are blended from the same set of blendstocks, but with different recipes.

Exhibit 15 lists the most common diesel blendstocks and indicates typical ranges for the more important blending properties of each blendstock.

Exhibit 15: Typical Volume Shares and Properties of Standard Diesel Blendstocks

Source	Blendstock	Typical Share (Vol%)	Typical Properties			
			Sulfur (ppm)	Cetane Number	Aromatics (vol%)	Specific Gravity
Crude Distillation	Str. Run Kerosene	25 - 33	≈ 3000	45	19	0.82
	Str. Run Distillate	31 - 35	≈ 7000	53	21	0.85
Conversion Units	FCC Light Cycle Oil	15 - 21	≈ 12500	22	80	0.93
	Coker Distillate	8 - 10	≈ 32000	33	40	0.89
	Hydrocracked Distillate	7 - 15	≈ 100	45	20	0.86

This exhibit does not show ranges for the blendstock properties, but (as with gasoline blendstocks) the values of these properties depend on the properties of the crude oil slate.

As before, the indicated properties are for “raw” streams – that is, for streams that have not been further processed to improve their properties. In particular, the indicated sulfur contents reflect no hydrotreating downstream of the units that produced the streams.

FCC light cycle oil is the largest single contributor to the sulfur content of the diesel pool, prior to processing for sulfur control. Coker distillate (in deep conversion refineries) and straight run distillates account for the remaining sulfur.

ULSD production requires severe desulfurization (primarily via hydrotreating) of all of the refinery-produced diesel blendstocks.

5.1.3 The Special Role of the Conversion Units

Exhibits 14 and 15 indicate that

- ◆ The upgrading processes, by virtue of their process technology and catalyst requirements, produce ultra-low sulfur gasoline blendstocks.
- ◆ The conversion processes – FCC, hydrocracking, and coking – produce blendstocks for both gasoline and diesel. In many refineries, the FCC unit, in particular, is the largest single contributor to both the gasoline pool and the diesel pool.
- ◆ FCC and coking are primary sources of sulfur in the gasoline pool and the diesel pool (and particularly the gasoline pool).

Consequently, the primary task in producing ULSG and ULSD is controlling the sulfur content of the gasoline and diesel blendstocks produced by the conversion processes (although the straight run kerosene and distillate streams also require desulfurization).

5.2 Refining Processes Involved in Meeting ULSG and ULSD Standards

Using advanced versions of a few well-established refining processes, refineries can produce ULSG and ULSD with sulfur content as low as < 5 ppm at the refinery gate.¹¹

Many of the elements of current sulfur control technology were developed in direct response to the stringent ULSG and ULSD standards adopted in the U.S., Canada, Western Europe, and Japan and elsewhere in the last decade. By now, the economics, performance, and reliability of stringent sulfur control technology are well understood.

Exhibit 16 shows the primary refining processes that contribute to meeting ULSF standards.

¹¹ In addition, pipeline technology and operating procedures are available for delivering these fuels to their end-use sites with sulfur content < 10 ppm.

Exhibit 16: Refining Processes for Producing ULSF

Process	Process Type	Primary Purpose	Reduces Sulfur In....	
			Gasoline	Diesel
Hydrocracking	Conversion	Yield Improvement	✓	✓
FCC Feed Hydrotreating	Treating	Yield Improvement	✓	✓
FCC Naphtha Hydrotreating	Treating	Sulfur Control	✓	
Other Naphtha Hydrotreating	Treating	Sulfur Control	✓	
Distillate Hydrotreating	Treating	Sulfur Control		✓

Exhibit 16 shows these processes in two categories.

- ◆ **Sulfur Control:** The sole purpose of these processes is to achieve the sulfur control needed to meet prevailing ULSF standards. In virtually all instances, these processes are *required* for ULSF production, and in most instances, they are sufficient for that purpose.

Investments in these processes are “stay-in-business” investments. They do not yield an economic return on the investment; they simply enable the refinery to meet the prevailing standards on sulfur and thereby remain in business.

- ◆ **Yield Improvement:** The primary purpose of these processes is to increase the refinery yield of light products by converting heavy crude fractions to lighter streams. Hydrocracking increases refinery yields of light products directly; FCC feed hydrotreating serves the same purpose indirectly, by improving FCC operations (Section 4.2). These processes *contribute to* meeting ULSF standards, but are not required for doing so. In general, these processes alone are not sufficient for producing ULSF.

Investments in these processes are primarily “profitability” investments. They are made to improve product realizations and overall refining economics sufficiently to yield a satisfactory return on the investment. These investments provide ancillary benefits, including some bearing on sulfur control, but these benefits are seldom sufficient in themselves to economically justify investment in these processes.

ULSF production also requires adequate capacity for hydrogen production, refinery energy supply, sulfur recovery, oil movement and storage.

Both kinds of refinery capacity investment (as well as others) come into play in (1) the design and construction of new, “grass-roots” refineries and (2) the expansion of existing refineries to increase crude running capacity and product out-turns, as well as meet new regulatory standards. However, in most instances, only Sulfur Control investments come into play when a refinery is upgraded to meet new regulatory standards without any concurrent increase in product demand.

5.3 Refinery Upgrading to Meet More Stringent Sulfur Standards

In broad terms, there are three routes for upgrading an existing refinery to produce ULSF or to produce ULSF to a new, more stringent standard.

- ◆ *Add* new, “grass-roots” process units for sulfur control – most likely FCC naphtha hydrotreating for ULSG and distillate hydrotreating for ULSD and (less likely) FCC naphtha hydrotreating);
- ◆ *Expand* the throughput capacity of existing process units for sulfur control; and
- ◆ *Retrofit* existing process units to enable more stringent sulfur control.¹²

In some cases, the most practical or economic route to producing ULSF may be some combination of these three routes.¹³ Each route requires upgrading or added capacity for hydrogen production and recovery, refinery energy supply, sulfur recovery, oil movement and storage, and other support facilities, as well as new catalysts, new operating procedures, etc.

Because each refinery is unique, each is likely to have a unique upgrading path.

5.3.1 ULSG Production

As Exhibit 15 suggests, reducing the sulfur content of gasoline calls for desulfurizing (in order of priority) FCC naphtha, coker distillate (in deep conversion refineries), and straight run naphtha.

- ◆ **FCC naphtha**, the main contributor to gasoline sulfur, can be desulfurized to < 10 ppm sulfur in a suitably configured *FCC naphtha hydrotreater*. These units can be designed or upgraded to achieve > 97% reduction in the sulfur content of FCC naphtha and can produce FCC naphtha with sulfur content as low as 10 ppm. In conversion refineries, this step alone can suffice to meet gasoline sulfur standards as low as 10 ppm.
- ◆ **Coker naphtha**, produced in deep conversion refineries, is usually desulfurized either in the FCC naphtha hydrotreater (for direct blending to gasoline) or in the naphtha hydrotreater, (for use as reformer feed).
- ◆ **Straight run naphtha**, from the crude distillation unit, is desulfurized in the isomerization unit (an upgrading process, discussed in Section 4.1.3), if the refinery already has one. Otherwise, and if necessary, straight run naphtha can be desulfurized in a dedicated (new) hydrotreater.

One other approach, though rare, deserves mention. A few large U.S. refineries have FCC feed hydrotreaters that operate at exceptionally high severity (almost verging on hydrocracking). These units accomplish such a high degree of FCC feed desulfurization that the FCC naphtha needs no

¹² Retrofitting usually involves some combination of (1) providing additional reactor volume, (2) increasing the concentration of hydrogen, (3) improving liquid/vapor contacting in the reactor, and (4) switching to a more effective catalyst.

¹³ This set of upgrading routes does not include changing the refinery crude oil slate. Switching to lower-sulfur crudes is seldom economic and seldom feasible without additional investments to conform the refinery’s processing capability to the new crude oil yield pattern. Similarly, it does not include construction of new refineries expressly to produce ULSF, as opposed to satisfying increasing domestic and export demand.

further desulfurization (i.e., no FCC naphtha hydrotreating) in order for the refinery's gasoline pool to meet a very stringent sulfur standard.

5.3.2 ULSD Production

As Exhibit 16 suggests, reducing the sulfur content of diesel calls for desulfurizing all of the primary diesel fuel blendstocks: straight run kerosene and diesel, light cycle oil, coker distillate (in deep conversion refineries), and hydrocracked distillate (in refineries with hydrocrackers).

The usual practice is to blend all of these streams and then desulfurize them in a single distillate hydrotreater. Meeting a new, more stringent diesel sulfur standard involves replacing, expanding, and/or retrofitting an existing distillate hydrotreater, depending on the specific capabilities of that unit and the sulfur standard to be met.

Severe FCC hydrotreating, of the type discussed above, can substantially reduce the sulfur content of FCC-produced light cycle oil, but not nearly enough to obviate the need for additional distillate hydrotreating capability to meet more stringent diesel sulfur standards.

5.4 Economics of Meeting ULSF Standards

5.4.1 Investment Requirements

The capital investment required to meet a given ULSF standard depends not only on the upgrading path of choice but also on local economic factors, such as refinery ownership, labor costs, construction lead times, currency exchange rate, tax rates, etc.

These factors make it difficult to generalize on the investment requirements for ULSF production.

5.4.2 Refining Cost

The primary components of the additional per-gallon refining cost associated with meeting a new, more stringent gasoline or diesel sulfur standard are:

- ◆ Capital charge associated with the investment in new or upgraded process capacity and support facilities
- ◆ Cost of additional hydrogen supply

Hydrogen consumption in the various processes involved in sulfur control depends on the refinery crude slate and the operating severity in the various processes. **Exhibit 17** shows *approximate* levels of hydrogen consumption in the processes of interest.

Exhibit 17: Approximate Hydrogen Consumption in Processes for Producing ULSF¹⁴

Process	Process Type	Primary Purpose	Approximate H ₂ Consumption (Scf/Bbl)
Hydrocracking	Conversion	Yield Improvement	1200 - 2500
FCC Feed Hydrotreating	Treating	Yield Improvement	800 - 2000
FCC Naphtha Hydrotreating	Treating	Sulfur Control	50 - 200
Other Naphtha Hydrotreating	Treating	Sulfur Control	25 - 100
Distillate Hydrotreating	Treating	Sulfur Control	250 - 1000

◆ **Cost of replacing lost product yield**

Hydrotreating processes always incur some yield loss, as a result of unwanted (but unavoidable) side reactions that convert hydrotreater feed material into light gases. The yield loss is small, usually on the order of ≈ 1 vol%), but increases with increasing hydrotreating severity.

◆ **Cost of replacing lost gasoline octane**

FCC naphtha contains a high concentration of olefin compounds (Exhibit 1). Olefins react readily with hydrogen to form paraffins – a reaction known as *olefin saturation*, a side reaction to the desired desulfurization. The paraffins in general have lower octane than the olefins, so that olefin saturation, to the extent that it occurs, reduces the octane of the FCC naphtha. FCC naphtha hydrotreating catalysts are designed to limit olefin saturation, but they do not eliminate it altogether. Consequently, FCC naphtha hydrotreating results in a loss of $\approx 1\frac{1}{2}$ octane numbers. The lost octane must be made up by increased output of upgrading units, primarily reforming, with attendant operating costs.

The first three of the above cost categories apply to both ULSG and ULSD; the last clearly applies only to ULSG.

Finally, the refining cost of meeting a new, more stringent ULSF standard is a function of the new sulfur standard and the prior sulfur standard. For example, the cost of meeting a 10 ppm sulfur standard is higher if the current standard is 500 ppm than if it is 50 ppm.

5.4.3 Energy Use and CO₂ Emissions

Reducing the sulfur content of a refinery stream or a finished product (i.e., gasoline, diesel fuel, residual fuel) requires the expenditure of some refinery energy and, consequently, leads to some increase in refinery emissions of CO₂. Refinery energy must be expended to (1) produce the additional hydrogen required for the necessary desulfurization, (2) increase refinery and process

¹⁴ Hydrogen use is measured in *Standard Cubic Feet (Scf)* per barrel (Bbl) of hydrocarbon throughput. In terms of energy content, approximately 20,000 Scf of hydrogen is equivalent to 1 Bbl of fuel oil.

throughput as needed to replace the product yield losses incurred in desulfurization, and (3) increase the severity of reforming and other upgrading operations as needed to replace the octane losses incurred in desulfurization. The required increment of refinery energy comes from burning additional natural gas (purchased) and, to a lesser extent, additional *still gas* (a mixture of light gas streams that are by-products of various refining processes). The combustion of the additional hydrocarbons leads to additional refinery emissions of CO₂. (In addition, hydrogen plants produce CO₂ as a by-product.)

As with refining costs, the magnitudes of the additional energy consumption and CO₂ emissions associated with meeting a new, more stringent ULSF standard are functions of the new sulfur standard and the prior sulfur standard. For example, the additional energy requirements and CO₂ emissions associated with meeting a 10 ppm sulfur standard are higher if the current standard is 500 ppm than if it is 50 ppm.

The recent history of U.S. refinery energy use provides a rough indication of the magnitude of the additional energy use associated with production of low-sulfur fuels. On a per-barrel basis, aggregate U.S. refinery energy use decreased by about 10% in the twenty-year period ending in 2005. The downward trend in energy use per barrel of crude reversed in 2006, and by 2010 energy use per barrel of crude had increased by about 5% from its 2006 level. This reversal probably was the result of compliance with new federal gasoline sulfur (Tier 2) and diesel fuel sulfur (ULSD) standards that took effect in 2006 in most parts of the country.

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