

# PETROLEUM REFINING

## IN NONTECHNICAL LANGUAGE

Fourth Edition

William L. Leffler



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# PREFACE

*The secret of a good sermon is to have a good beginning and a good ending, then having the two as close together as possible.*

—George Burns

If you have somehow been charmed by the ads of my publisher or beguiled by the word-of-mouth ravings of a colleague about the inestimable merit of this book, you probably don't need an introduction to this subject. It's not likely you would have opened the cover if you didn't already have at least an uneasy feeling, and maybe a genuine need to know, about petroleum refining. In either event, you have come to the right place.

The layout of the material in this book is designed to satisfy three needs. It can be used as a reference book because there's a good table of contents in the front, a good index in the back, and a glossary of terms. The book has been used extensively as a text for courses on refinery processes. A combination of lectures, reading, and problem solving should be very reinforcing. Because most people do not have the luxury of listening to a lecturer like me, the layout is designed primarily for personal study. With that in mind, the dry material has been moistened with as much levity and practicality as I could render.

For personal study the following plan might work. Chapters 1 and 2 are pleasant precursors, but chapter 3 on crude oil is the most important part of the book. For what goes on inside a refinery, chapter 4 has a lot of mechanical detail that's not fundamentally important. Don't let it dismay you. The materials on vacuum flashing, cat cracking, alkylation, reforming, hydrocracking, and residue reduction are all important as lead-ins to gasoline and other product blending. Struggle through chapter 6 on chemistry.

The chapter on gasoline blending is the most fun (in a cerebral sort of way) because it deals with things familiar yet mysterious—car engines and octane numbers. For anyone in the business part of the business, the chapter on simple and complex refineries will wrap up all the processes into a nice economic package.

The other chapters are like *lagniappe*, a nearly forgotten tradition where a Cajun merchant gives a small gift of appreciation at the time of sale. The information in those chapters, which reflect just as much labor on my part as the rest of the book, is useful but nevertheless not vital to understanding petroleum refining. So plan to manage your attention span to work through at least the first 15 chapters.

Many thanks go to the people who have contributed to this and earlier editions of *Petroleum Refining in Nontechnical Language*. This fourth edition has had the advantageous insights and inputs of Mike Dossey, longtime refining executive. With his guidance, omissions and commissions of previous editions have been dealt with. Bob Awe and his authoritative views on lubricants helped me polish the new chapter on that subject to an acceptable patina. Robert Junge graciously filled me in on the nearly impenetrable turmoil in gasoline blending activities and the industry responses. Of course none of these could overcome my final say and massaging, and therefore I carry the ultimate responsibility for getting everything right. And as always, I benefited from my wife allowing me long hours of solitude while I ground away at research and prose.

Winter 2008

W.L.L.

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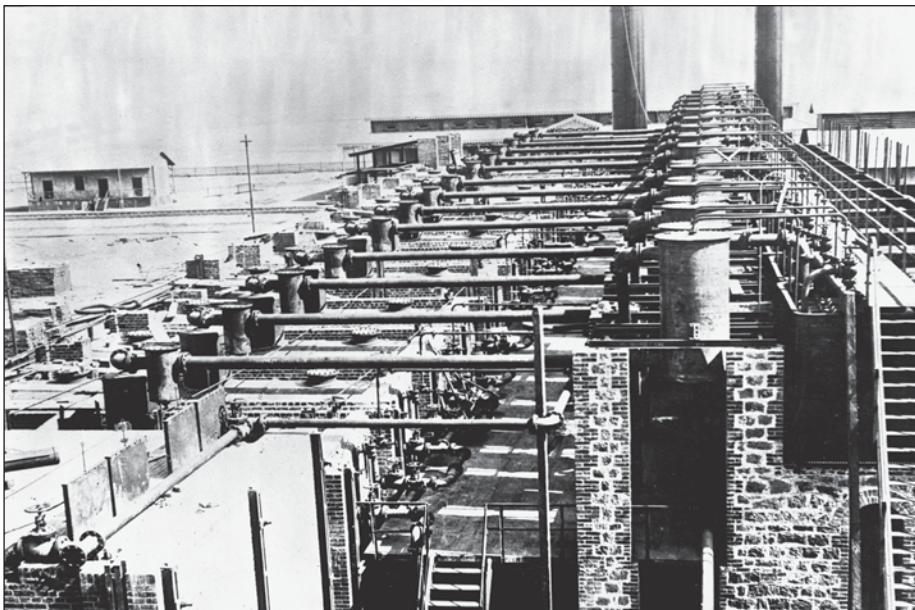
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# 1

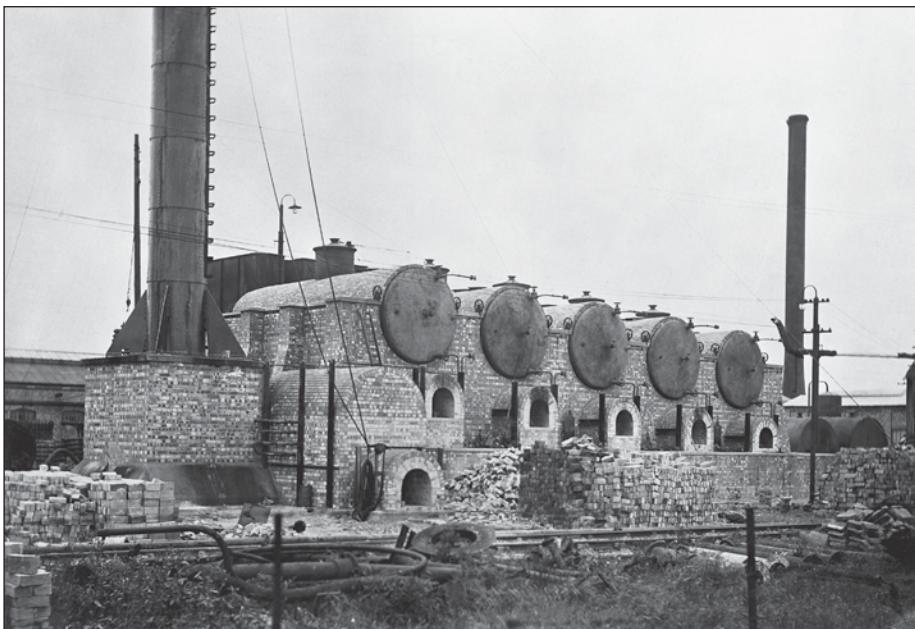
## THE EVOLUTION OF PETROLEUM REFINING

Until the advent of the gasoline engine in the late 19th century, people used petroleum products for what we now consider basic needs—lighting, heating, cooking, and lubricating. When Colonel Edwin Drake drilled the first well to a depth of 69 feet in 1859 in Titusville, Pennsylvania, and initiated the oil era, his investors were thrilled. They saw the opportunity to compete with whale oil in the illumination market by providing a similar product, kerosene. Gasoline and naphtha were mostly considered waste products, often allowed to “weather,” a euphemism for evaporating into the atmosphere, before the kerosene was recovered. Sometimes refiners just burned the light material in pits or dumped it into nearby streams to get rid of it. It did not take long for refiners to recognize that the heavier parts of the crude oil could be used as fuel oil for raising steam and heating buildings.

For 30 years after the discovery of crude oil, refining consisted of separating these various products by batch processing, tediously handling one tank of crude at a time. Batch processing operations consisted essentially of a tank where the oil was heated and vaporized and a condenser where the vapors were returned to the liquid state. Starting around 1900, refiners strung these tanks in series and used a so-called continuous batch process, still a capital- and energy-intensive way to do separation (figs. 1-1 and 1-2). Fractional distillation, using the trayed columns now used worldwide, did not come into widespread use, especially in the United States, for another two decades. This technique had been used for nearly a decade to distill alcohols. Translation to the refining industry came shortly after the Prohibition Act of 1920 as out-of-work technologists from the spirits industry brought their expertise and enthusiasm to refining research and development. The efficiency of separating crude oil into its constituents increased by 25%.



**Fig. 1-1.** Crude oil separation. The towers at Shell's Suez refinery, circa 1912, are of the continuous batch type, separating one fraction per column. *Courtesy Royal Dutch Shell.*



**Fig. 1-2.** Batch processing unit. Lube oils separation at the London and Thames Haven Refinery, circa 1922. *Courtesy Royal Dutch Shell.*

Early automobiles such as the famous Stanley brothers' Stanley Steamer were steam-driven, fueled by kerosene. By 1890 inventor-entrepreneurs with the venerable names Karl Benz, Henry Ford, Ransom Olds, and Dave Buick, among others, were marketing their automotive namesakes with internal combustion engines that needed a light fuel, gasoline. That changed the profile and purpose of refining.

By 1910, some 500,000 cars traveled U.S. roads, and the demand for gasoline exceeded even the formally disposed of volumes. Running more crude oil to satisfy the growing gasoline demand only created surpluses of the nongasoline fractions. Chemical engineers then realized they could convert some of the heavier parts of the crude oil by cooking it until it cracked into lighter fractions. Vladimir Shukov patented the thermal cracking process in Russia in 1891, but Amoco brought the first American cracker on stream in 1912 in Chicago. Their chief scientist William Burton took a victory lap for one of the most important breakthroughs in refining history, the cracker. The timing was fortuitous because electricity was devastating the illumination market for kerosene and the jet plane had not yet been invented.

The chemists of General Motors, led by Charles Kettering, discovered in 1921 that adding small amounts of lead compounds to gasoline significantly improved the octane number. Thereafter engine efficiency improved, but lead emissions polluted the environment until they were prohibited in the 1970s.

Catalysis was still an emerging science when Eugene Houdry introduced in 1936 the grandfather of all catalytic crackers—a fixed bed design that doubled the volume of quality gasoline made from heavy feedstocks, compared to thermal cracking. The first fluidized bed cat cracker followed at Esso's Baton Rouge refinery in 1942.

Meanwhile the auto industry continued to demand better quality gasoline, and in 1949 the first catalytic reformer started up at, of all places, the Old Dutch Refining Company in Muskegon, Michigan, improving the octane number of the naphtha already being blended into gasoline.

Hydroprocessing became increasingly important in the latter half of the 20th century. It includes hydrotreating to remove contaminants, a response to social demands to preserve the environment. Hydrocracking had its origin in concerns about the burgeoning supplies of middle distillates (home heating oil, diesel fuel, and kerosene) manufactured as refiners struggled to meet growing gasoline demands. A technology that could convert one into the other lent quick solution to the imbalance.

Finally, refiners solved the problem of coking in thermal crackers by delaying it until it could take place in a vessel where the coke could be

harvested—the coke drum in a delayed coker. As environmental regulations and growing crude runs pushed down the relative value of residual fuel, refiners built ever more cokers to eliminate the bottom of the barrel from their product offerings.

## Why the evolution is important

Most of the technological change in the last 20 years has been driven by environmental concern, causing refiners to tweak existing processes, especially with the introduction of new and improved catalysts. Responding to environmental mandates almost always costs money and undermines refining capabilities (otherwise the refiners would already have done it). Successions of improved and new designer catalysts have enabled most refiners to respond without the albatross of totally debilitating capital expenditure.

Holding aside the totally baffling chemistry of catalysis, this slow evolution should be especially good news to you. It is tough enough to understand the basic processes without having to worry about what is becoming obsolete before you have learned it. The basic five refining processes remain the same:

- **Separation.** Either by distillation or absorption; the molecules remain intact and no chemistry takes place.
- **Cracking.** Uses catalysts, with or without hydrogen, to break apart large molecules into smaller ones, as in cat cracking, hydrocracking, and coking.
- **Reshaping.** Changes the configuration of individual molecules, as in cat reforming and isomerization.
- **Combining.** Makes larger molecules from smaller molecules so they can be used in gasoline, as in alkylation and polymerization.
- **Treating.** Uses catalysts and hydrogen to chemically remove contaminants.

You will have to keep reminding yourself as you go through the first half of this book that only the first process, separation, has **no** chemistry associated with it—the molecules going in are the same as the molecules coming out. They just end up in different buckets.

The other four processes are all about chemical change. Some of them are substantial, as in cracking and alkylation. One or more kinds of molecules go in, and different molecules come out. Some processes have only minor change, as in treating, where contaminants like sulfur are removed, with only a few by-products generated in the process.

# 2

## FROM THE OIL PATCH TO THE REFINERY

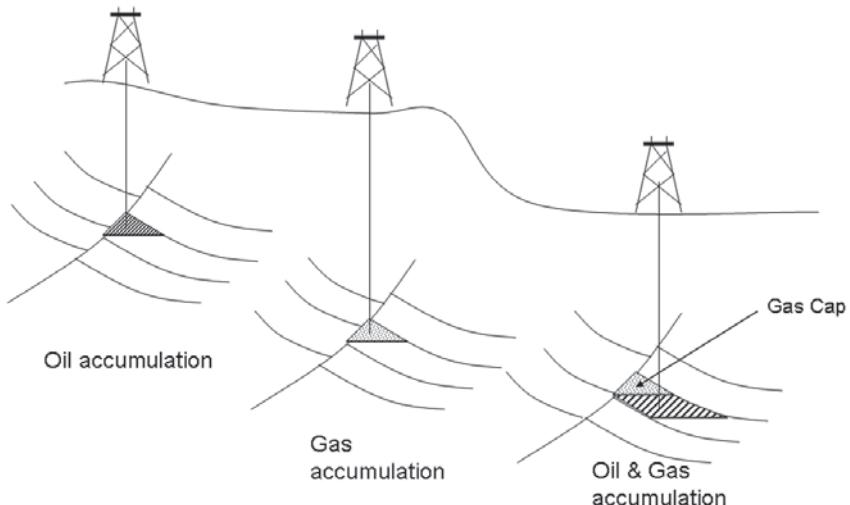
*Get your facts first, and then you can distort them as much as you please.*

—Mark Twain

It is a good idea to know something about the raw materials before thinking about how to transform them into finished, marketable products. Raw materials from the oil patch have colorful, but sometimes not too descriptive names. Some sound alike. After all, what is the difference between crude oil and condensate, or between gasoline, natural gasoline, natural gas liquids, and liquefied petroleum gas?

### Oil Patch Operations

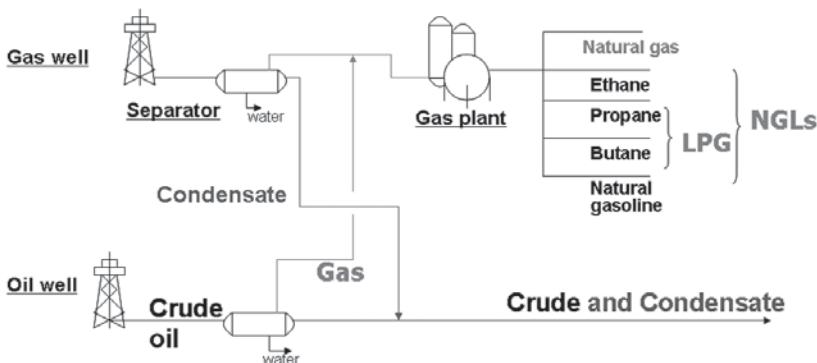
The simplistic crosscut of the oil patch in figure 2-1 shows what goes on at oil and gas producing fields. The underground accumulation of hydrocarbons can be in several forms. The well on the left has tapped a crude oil reservoir, the middle a gas reservoir, and the right an oil reservoir with a gas cap atop it. Life is not that simple, however.



**Fig. 2-1.** Oil and gas reservoirs

Almost every oil reservoir has some gas dissolved in the oil, sometimes substantial amounts. Likewise, almost every gas reservoir has some oil dissolved in it.

As an oil stream comes up from the reservoir and out through the wellhead, the pressure drops. As in figure 2-2, the oil and previously dissolved gas mixture goes into a vessel right at the well site called a *field separator*, sometimes referred to as a “wide spot in the line.” As the gas and liquid enter the larger space, the “beer bottle” effect happens. The pressure drops further and light gases that were dissolved in the crude oil vaporize and bubble out, just like the fizz in a beer when you pop the top. Natural gas is drawn off the top of the separator, and crude oil from the side. Almost every reservoir also has water vapor entrained in the oil and gas, and almost all of that separates in the field separator and is drawn off the bottom. The crude oil comes off from above the water. The natural gas coming from this well is called *associated gas*. Oil patch processing of this gas is not finished, however, but more explanation follows in a few lines.



**Fig. 2–2.** Processing hydrocarbons in the oil patch

The well at the top of figure 2–2 has tapped a gas reservoir. The production from this well is called *nonassociated gas* or *gas well gas*. In most cases, some oil is dissolved in the gas. When the gas from the wellhead goes through a field separator, the heaviest hydrocarbons drop out in the form of liquids called *condensate*, which are like a very light crude oil. Sometimes the gas production has almost no hydrocarbons heavier than butane, in which case it is referred to as *dry gas*.

The well at the right of figure 2–1 has tapped an oil formation that is topped by a gas cap, like that at Prudhoe Bay in Alaska. The gas cap may be untapped for decades to maintain the pressure needed to push the crude out of the reservoir up the well bore. Later when the oil is substantially evacuated, the gas can be harvested.

The distinction between associated and nonassociated gas is not important chemically, but only from a management point of view. Natural gas consumption varies with seasonal change or may have limited market access, especially if the well is in a remote location (then called *stranded gas*). Producers may have a ready market for the crude oil but not the gas. The penalty for shutting in the gas is huge because the oil would have to be shut in as well. Historically, in every part of the world, unmarketable gas was *flared*, or burned on site. Nowadays, in the case of stranded gas, it is more likely reinjected into the reservoir, saving it for later production and meanwhile enhancing the producability of the crude oil.

The basic constituent of natural gas is methane, but despite the fact that the natural gas has gone through a field separator, some hydrocarbons heavier than methane (but not as heavy as condensate) may still remain in the vapor stream. The natural gas may be processed in a gas processing plant, or simply gas plant (fig. 2–2), for the removal of these *natural gas liquids (NGLs)*.

## Gas Plants

The NGLs consist of *ethane*, *propane*, *butanes*, and *natural gasoline*. The first three are volatile and gaseous at room temperature. By itself natural gasoline is liquid at room temperature, but it can remain gaseous when mixed with enough natural gas. Sometimes the natural gasoline and the butanes content can be large enough, perhaps 10% or more, that during cold winter months they can condense (liquefy) in a natural gas transmission line. The buildup of the liquid in low spots in the line can reduce the capacity of the pipeline or, more seriously, droplets can damage the turbines that push the gas through the pipeline system. For that reason, some gas streams **must** be processed in gas plants to remove these components.

Besides these operational aspects of removing butane and natural gasoline, there is often an economic incentive to remove them, as well as the propane and the ethane, at the gas plant. These streams may be worth more in other markets than being sold as constituents of natural gas. Various gas plant designs can handle the removal of some or all the NGLs, which each have their own markets:

- **Ethane.** Goes to chemical plants as feedstocks for ethylene plants.
- **Propane.** Goes to the *liquefied petroleum gas (LPG)* market for heating, lighting, and cooking, or to chemical plants as feedstocks to ethylene plants.
- **Butanes.** Go to gasoline blenders or refiners as raw material, or to chemical plants as feedstocks. In some places, butanes are used together with propane as LPG.
- **Natural gasoline.** A low-octane gasolinelike material that you would not want to use by itself in your car. Goes to blenders or refiners for gasoline blending or to chemical plants as feedstocks.

## Transportation

Crude and condensate from the storage tanks at the well site can be moved to refining centers by combinations of trucks, rail cars, pipelines, and tankers. Often a number of crude oils with different qualities are admixed, especially in pipelines. Condensate may be included as well to achieve economies of scale. Both buyer and seller agree to price adjustments for

the composite. Some crudes are worth more than others, and condensate is generally worth more than crude oil.

Sometimes the natural gasoline and butane are also admixed into nearby crude oil pipelines for economies of transport. In this case, the crude oil coming into the refinery is called *diluted crude*. Otherwise the natural gasoline can be transported neat by rail car, truck, or pressure pipeline. Butane and propane move as liquids in pressurized rail cars, trucks, and high pressure pipelines. Ethane, being so volatile, moves only by high pressure pipeline.

## LNG

When natural gas is found in remote locations, far from adequate fuel markets, the producers face a dilemma. They must choose whether it is better not to produce the gas, to reinject it into the reservoir if crude oil or condensate accompanies it, or to transport it at high cost to a distant market.

Beyond about 1,500 to 2,000 miles or so, the cost of a pipeline gets prohibitive. A pipeline across the sea is generally out of the question, though pipelines under the Mediterranean turned out okay. The remaining alternative involves turning the natural gas into the liquid state and shipping it in ocean-going liquefied natural gas (LNG) tankers.

Gas liquefaction plants are capital intensive and energy hogs. LNG tankers are far more expensive than conventional tankers. Still, the cost of bringing the natural gas up from the reservoir to the liquefaction plant may be relatively inexpensive, making the venture viable.

When the LNG reaches the destination market, it goes through a receiving and regasification facility before it is introduced as a vapor into the local natural gas pipeline system.

## Exercises

1. What are the differences between LPG, NGLs, and LNG?
2. Give two good reasons to put natural gas through a gas plant.

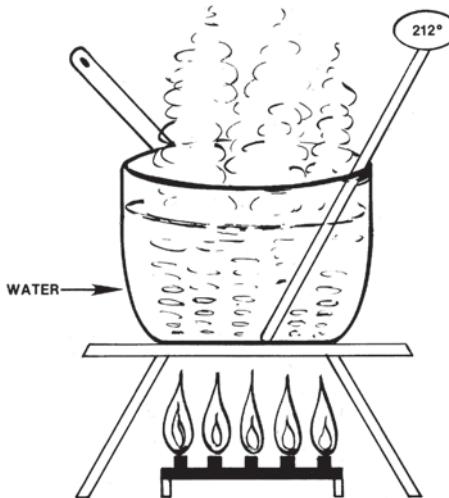
# 3 CRUDE OIL CHARACTERISTICS

*Let these describe the indescribable.*

—*Childe Harold's Pilgrimage*, Lord Byron

What is crude oil anyway? The best way to describe it is to start by saying what it is not and how it does not behave. It is not a single chemical compound; it is a mixture of different chemical compounds. The most important of its behavioral characteristics happens when it heats up. When you raise the temperature of crude oil to a temperature at which it starts to boil, and hold it at that temperature, some of it will vaporize, and some of it will not.

Contrast that with water to make a point. Take the pot of water in figure 3-1 and heat it to 212°F (Fahrenheit) and keep the heat on. What happens? The water starts to boil. (It vaporizes or *flashes*.) Eventually, if you keep the heat on, all the water will boil off.



**Fig. 3–1.** Boiling water

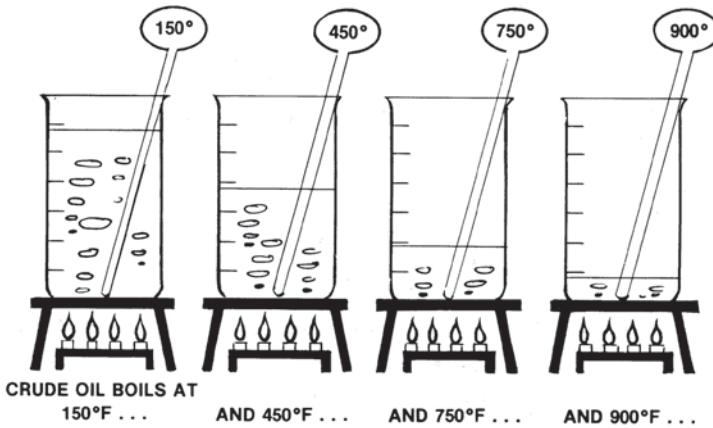
If you had a thermometer in the pot, you would notice that the temperature of the water just before the last bit boiled off would still be 212°F. That is because the chemical compound  $\text{H}_2\text{O}$  boils at 212°F. At atmospheric pressure, it boils at a temperature no higher, no lower.

## Crude Oil Composition

Now the discussion can return to crude oil. Unlike water, crude is not a single chemical compound but thousands, sometimes hundreds of thousands, of different compounds. Some are as simple as  $\text{CH}_4$  (methane); some are as complex as  $\text{C}_{35}\text{H}_{50}$ .  $\text{CH}_4$  and  $\text{C}_{35}\text{H}_{50}$  are the chemist's shorthand for individual types of chemical compounds. There is no need to get bogged down about that right now. (You can get bogged down with it in chapter 6.) They are all generally combinations of hydrogen and carbon atoms, called *hydrocarbons*. Each of these types of compounds has its own boiling temperature, and therein lies the most useful and used physical phenomenon in the petroleum industry.

## Distillation Curves

Take the same pot and fill it with a typical crude oil. Put the flame under it and heat it up. As the temperature reaches 150°F, the crude oil will start to boil, as in figure 3–2. Now keep enough flame under the pot to maintain the temperature at 150°F. After a while, the crude stops boiling.



**Fig. 3–2.** Boiling crude oil

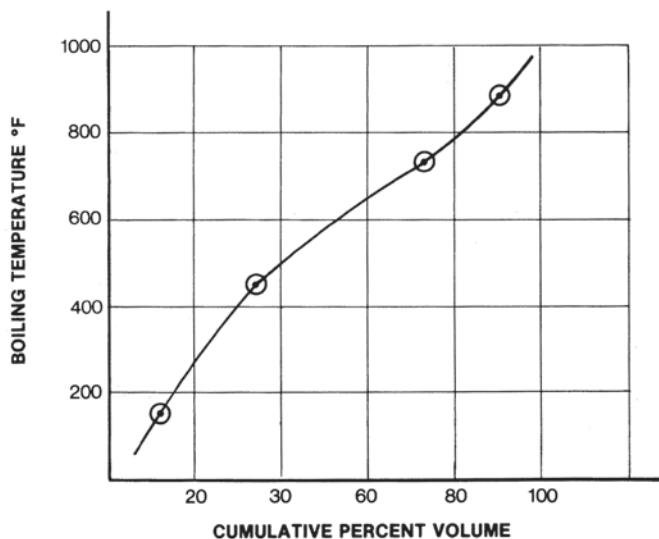
In step two, raise the flame and heat the crude to 450°F. Again the crude starts boiling, and after a while, it stops.

You could repeat the steps on and on, and more and more crude would boil off. What is happening? The compounds that individually boil below 150°F vaporized in the first step; the compounds that boil at temperatures between 150°F and 450°F vaporized in the second step; and so on.

What you are developing is called a *distillation curve*, a plot of temperature on one scale and the percent evaporated on the other, as in figure 3–3. Each type of crude oil has a unique distillation curve that helps characterize what kinds of hydrocarbons are in that crude. Generally the more carbon atoms in the compound, the higher the boiling temperature, as shown in the examples below (table 3–1):

**Table 3-1.** Boiling temperatures for selected hydrocarbons

Compound	Formula	Boiling Temperature	Weight (lb/gal)
Propane	C <sub>3</sub> H <sub>8</sub>	-44°F	4.2
Butane	C <sub>4</sub> H <sub>10</sub>	31°F	4.9
Decane	C <sub>10</sub> H <sub>22</sub>	345°F	6.1
Cetane	C <sub>16</sub> H <sub>34</sub>	549°F	6.5

**Fig. 3-3.** Crude oil distillation curve

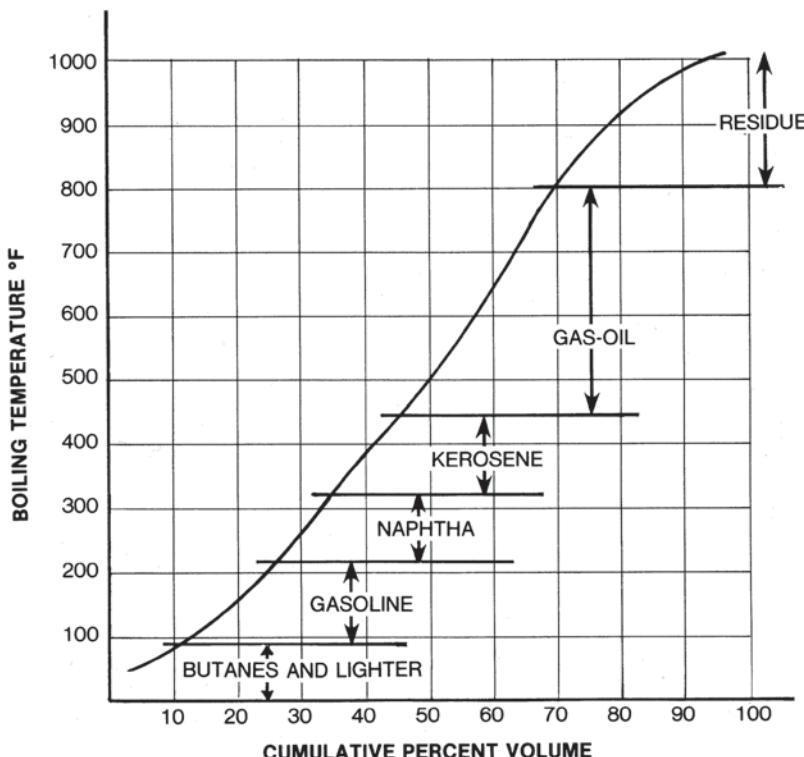
## Fractions

To further specify the character of crude oil, the refiners have found it useful to lump certain compounds into groups called *fractions*. Fractions or *cuts* are the generic names for all the compounds that boil between two given temperatures, called *cut points*. Commonly used cut points to describe the fractions in crude oil are:

**Table 3-2.** Typical crude oil cut points

Temperatures	Fraction
Less than 90°F	Butanes and lighter
90–220°F	Gasoline
220–315°F	Naphtha
315–450°F	Kerosene
450–800°F	Gas oil
800°F and higher	Residue

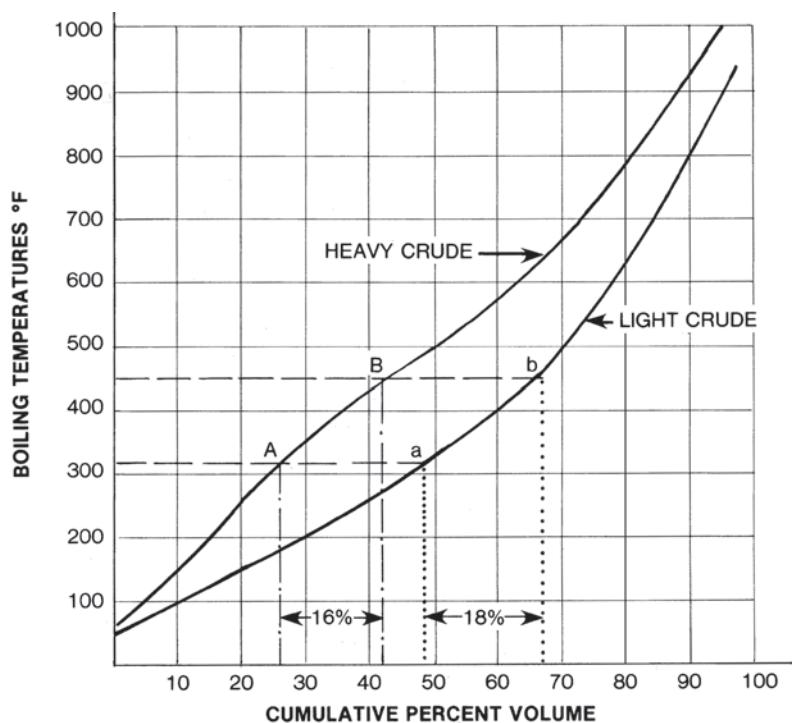
Later chapters will spend a lot of words discussing the characteristics of each of those fractions, but some are already apparent from their names. Figure 3-4 shows where the various cuts plot on a typical distillation curve.

**Fig. 3-4.** Crude oil distillation curve and its fractions

It is important to note that crude oil compositions vary widely. The light crudes tend to have more gasoline, naphtha, and kerosene; the heavy crudes tend to have more gas oil and residue. You might have noticed that phenomenon from the relationship between the weight of the compounds and the temperature at which they boil. Generally, the more carbon atoms in a compound, the heavier (more dense) the compound and the higher the boiling temperature. Conversely, the lower the carbon count, the lighter the compound and the lower the cut points.

## Cutting Crudes

To pull together all this information on distillation curves, follow this quick arithmetic manipulation. Take the curves for the two crudes in figure 3-5 and run through the steps to determine which crude has higher kerosene content (a bigger kerosene cut).



**Fig. 3-5.** Kerosene fraction in two types of crude

Kerosene has a boiling temperature range from 315°F to 450°F. Using figure 3–5, complete the following steps:

1. For the heavy crude (the curve that starts off higher because it has very little light stuff in it), start from the vertical axis at 315°F and intersect the distillation curve, going right to point A. Going down from point A hits 26% on the horizontal axis. That is the amount that will have boiled off before any kerosene boils off.
2. Now start at 450°F and intersect the same distillation curve, going right, at point B, which is 42% on the horizontal axis. That is the amount that has boiled off when kerosene stops boiling off.
3. Calculate the cumulative percent volume from the *initial boiling point* of the kerosene to the *end point*:  $42\% - 26\% = 16\%$ . The heavy crude contains 16% kerosene.
4. Now do the same procedure for the light crude and find that there is  $66.5\% - 48.5\% = 18\%$ .

Therefore the light crude has more kerosene in it than the heavy crude. If some refiners were in the business of trying to produce as much kerosene as possible, and they sometimes are, they might prefer to buy the lighter crude to the heavier, notwithstanding a dozen or more other considerations.

## Gravities

Gravities measure the weight of a compound, another important characteristic. Chemists always use a measure called *specific gravity*, which relates everything to something universally familiar, water.

The specific gravity of any liquid is equal to the weight of some volume of that compound divided by the weight of the same volume of water, all at standard pressures and temperatures.

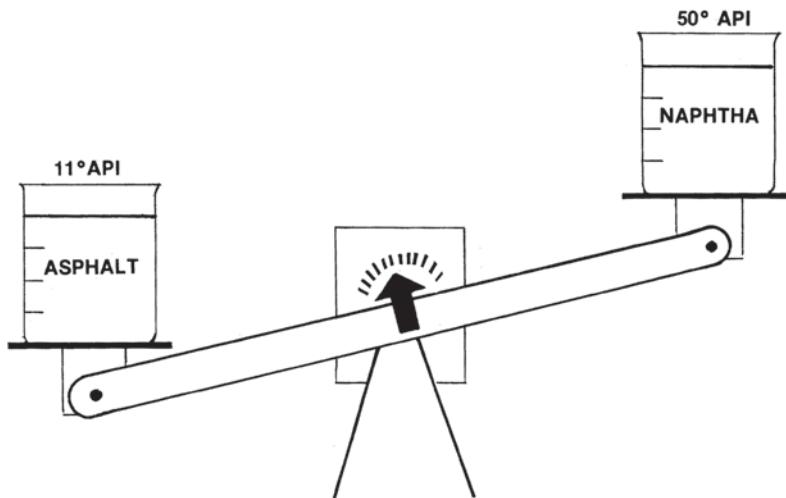
$$\text{Specific gravity} = \frac{\text{weight of the compound}}{\text{weight of water}}$$

The chemists' approach must have been too simple for the petroleum engineers because the popular measure of gravity in the oil industry is a diabolical measure called *API gravity*. The formula for API gravity, which is measured in degrees (but has nothing to do with temperature or angles), is:

$$^{\circ}\text{API} = \frac{141.5}{\text{specific gravity}} - 131.5$$

The origin of the 141.5 and 131.5 appears to be lost in the mists of history. Nevertheless, if you play with the formula a little bit, you will find the following relationships, which might be the mental hooks on which you can hang the concepts:

1. Water has a specific gravity of 1 and an API gravity of 10°.
2. The higher the API gravity, the lighter the compound, as shown in figure 3–6.
3. The reverse is true for specific gravity.



**Fig. 3–6.** The lower the API, the heavier the liquid

**Table 3–3.** Typical gravities

API Gravity	
Heavy Crude	18°
Light Crude	36°
Gasoline	60°
Asphalt	11°

Common knowledge says oil floats on water. The sheen you might have seen from a boat or a dock results from oil not dissolving in water and being at an API gravity above 10°. However, not all oil weighs that little. Industry lore has stories of barge operators who assumed that all oils are lighter than water. To their horror, as they filled their barge with asphalt, it sank before their eyes. After the fact they learned they were loading 9° API material.

## Sulfur Content

One more excursion on the subject of crude oil is appropriate at this point—a discussion of the sulfur content in crude oil. One of the annoying aspects nature endowed on crude oils is the differing amounts of sulfur content in various types of crude oil. To complicate this bequest, the sulfur is not in the form of elemental sulfur, a chemical all by itself, but is almost always a sulfur compound. It is chemically bonded to some of the more complicated hydrocarbon molecules so that it is not easily separated from the pure carbon compounds. That is, not until it is burned. Then it will form one of several smelly or otherwise environmentally objectionable sulfur/oxygen compounds. So sulfur removal before hydrocarbons ever get to the burner tip remains a big issue for refiners today and will be the subject of more words later on.

### Sulfur vs. Sulphur

*Sulfur or sulphur? Americans generally spell sulfur with an f, while the British use a ph. Both are acceptable, but the Yanks are unaccountably more frugal in this regard.*

The parlance in discussing crude oils of varying sulfur content is to categorize them into *sweet* crudes and *sour* crudes. This quaint designation of sweet and sour has more to do with taste than you might think. In the early days of Pennsylvania crude oil production, petroleum was primarily sought after to make kerosene as a substitute for the whale oil used as lamp oil for indoor lighting. If a kerosene fraction had too much sulfur, it would have an unacceptable smell when it burned. In addition, the sulfur would accelerate the rate at which silver would tarnish—clearly a bad thing to have in a home. Somewhere along the line, someone discovered that kerosene

with higher sulfur content had a more sour taste, while that with a low sulfur content had a more sweet taste. Over a time long enough for the designation to become permanent, tasting was the generally acceptable method for determining which crudes would make good lamp oil.

Today, sweet crudes typically have 0.5% sulfur content or less, sour 1.5% or more. The area in between is sometimes called *intermediate sweet* or *intermediate sour*, but the distinction is not clear. What may be sweet to some may be sour to others, now that refiners have no more tasters around.

### **Sweets and Sours**

*Typical sweet crudes include West Texas Intermediate (the popular traded crude on the New York Mercantile Exchange), most Louisiana, Oklahoma, and Nigerian crudes, and Brent North Sea (the crude traded on the International Petroleum Exchange).*

*Sour crudes include Alaska North Slope, Venezuelan, and West Texas Sour from fields like Yates and Wasson.*

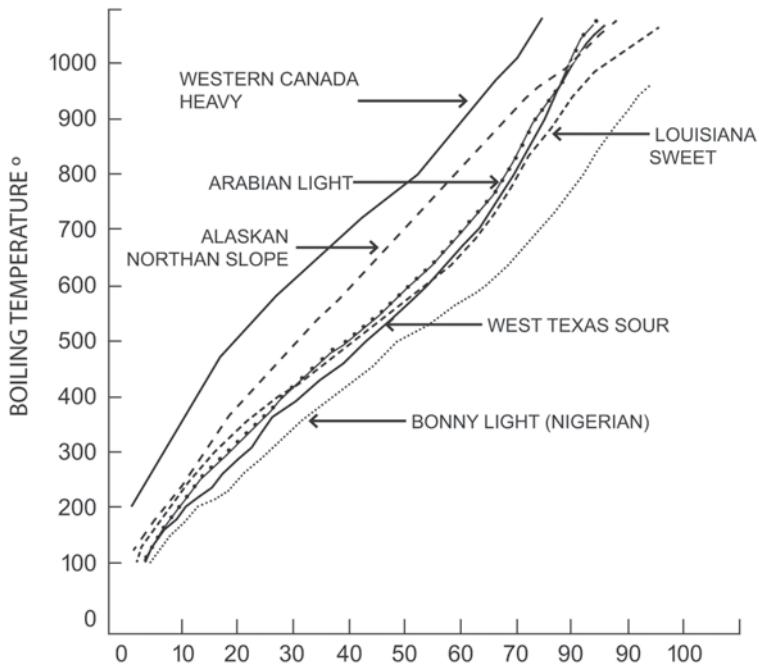
*Intermediate crudes include California Heavy, such as from the San Joaquin Valley, and many Middle East crudes.*

One other convention grew out of the Pennsylvania oil fields, according to oil patch lore. Oil was initially shipped to market by horse-drawn wagon or flatcar in used 46-, 48-, and 50-gallon wine, pickle, and other type barrels. Refiners insisted on allowing for spillage and leakage after producers hauled it over poorly constructed roads from the oil fields to the refineries. They paid producers on the basis of 42 gallons, which became the “oil barrel.”

Transportation in the United States was primarily by wagon, train, and eventually truck and pipeline. Measuring by volume made sense. In the rest of the world, particularly in Europe, the industry moved oil by seagoing vessels. That required calculating the weight of the cargo to assure the load would not exceed the displacement of the ship. (King Henry VIII found out the mechanics of displacement when he overloaded his flagship, the *Mary Rose*, with cannon and troops and watched with horror as it sank off Portsmouth Harbor as it set off to battle the French in 1545.) In Europe and Asia, weight, usually measured in *tonnes* (2,240 U.S. pounds) became the maritime standard by which oil was bought, sold, and transported. Curiously enough, gasoline at the retail pump has always been sold everywhere by volume, in gallons or liters, more because of the metering devices than anything else.

## Review

Figure 3-7 shows the distillation curves for five different crudes; three U.S. and two non-U.S. Some have more light fractions, some have more heavy. All have different prices, so refiners will have different incentives to process them as each emphasizes different cuts.



**Fig. 3-7.** Distillation curves for some crudes

## Exercises

- 1 a. Draw the distillation curve for the following crude oils (on the same graph).

	% Volume	
	Oklahoma Sweet	California Heavy
Lighter than 113°F	5.1	—
113 to 220	9.2	—
220 to 260	4.0	—
260 to 315	5.7	4.2
315 to 390	9.3	5.1
390 to 450	5.4	4.8
450 to 500	5.8	8.5
500 to 550	4.7	7.9
550 to 650	10.8	8.1
650 to 750	8.6	14.8
750 to 900	13.5	15.1
900 to 1000	5.9	13.4
over 1,000	12.0	18.1

- b. How much naphtha (220°F–315°F) is there in each crude?
2. Suppose you had a beaker of asphalt (11°API) and a beaker of naphtha (50°API), both equal volumes. If you mixed them together, what would be the resulting API gravity? (The answer is **not** 30.5°API.)

# 4 DISTILLING

*Why should we rise, because 'tis light?*

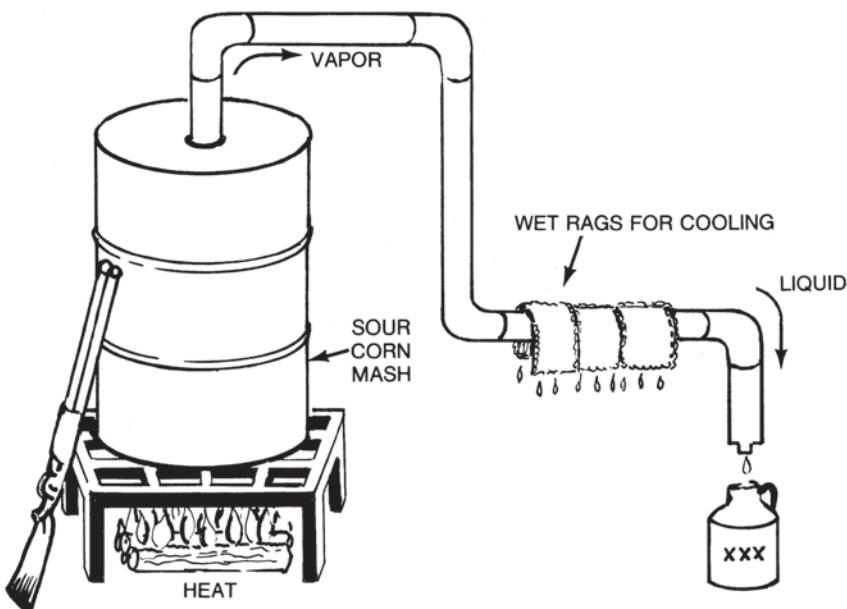
—“Break of Day,” John Donne

A casual passerby of a refinery can make an easy mistake by referring to the many tall columns inside as “cracking towers.” In fact, most of them are distilling columns of one sort or another. Cracking towers, which are usually shorter and squatter, will be covered in a later chapter.

Distilling units are the clever invention of process engineers who exploit the important characteristic discussed in the last chapter, the distillation curve. The mechanism they use is not too complicated but, for that matter, not all that interesting. However, in the quest for completeness and familiarity, you can cover the rudiments here.

## The Simple Still

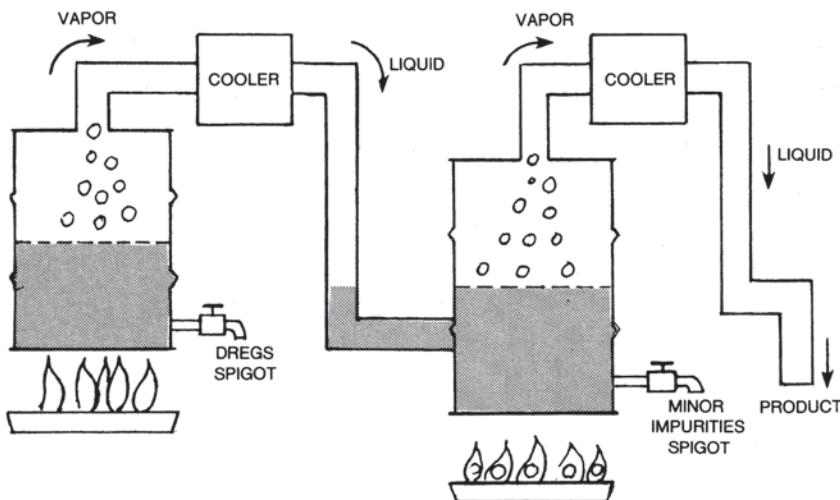
For years Kentucky moonshiners used the simple still in figure 4-1 to separate the white lightning from the dregs. After the sour mash fermented, i.e., a portion of it had slowly undergone a chemical change to alcohol, they heated it to the boiling range of the alcohol. The white lightning vaporized. As a vapor, it was less dense (lighter) than liquid, and gravity moved it up, out of the liquid, and then through the condenser, where it cooled and turned back to liquid. What was left in the still was discarded. What went overhead was bottled. A process engineer would call this a simple *batch process distillation*.



**Fig. 4-1.** The moonshiner's still

If the moonshiners wanted to sell a better-than-average product, one that might have given them some return customers, they might have run the product through a second batch still much like the first. There they could have separated the best part of the liquor from some of the nonalcoholic impurities that inevitably flowed along with the alcohol in the first still. Some impurities might have gone overhead because of the inadequacy of the temperature controls. Sometimes the moonshiners wanted to be sure they got all they could, so they set the temperature a little high on the first batch.

Such a two-step operation could be made into the continuous operation shown in figure 4-2. In fact, many early oil distilling operations looked like that, as apparent from the images in chapter 1 (figs. 1-1 and 1-2).

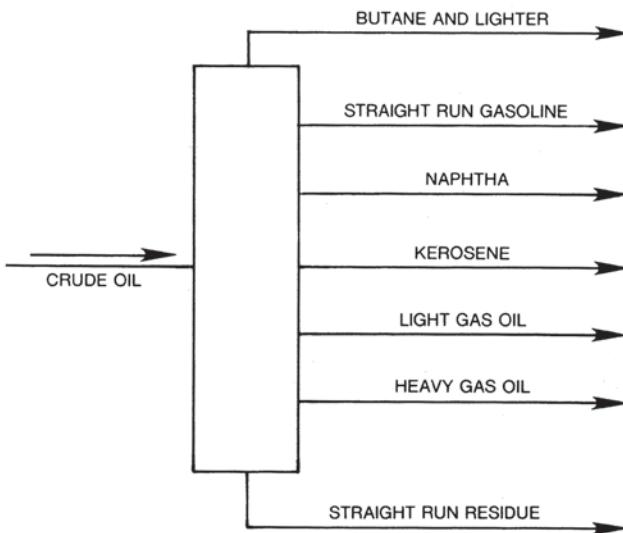


**Fig. 4-2.** Two stage batch still

## The Distilling Column

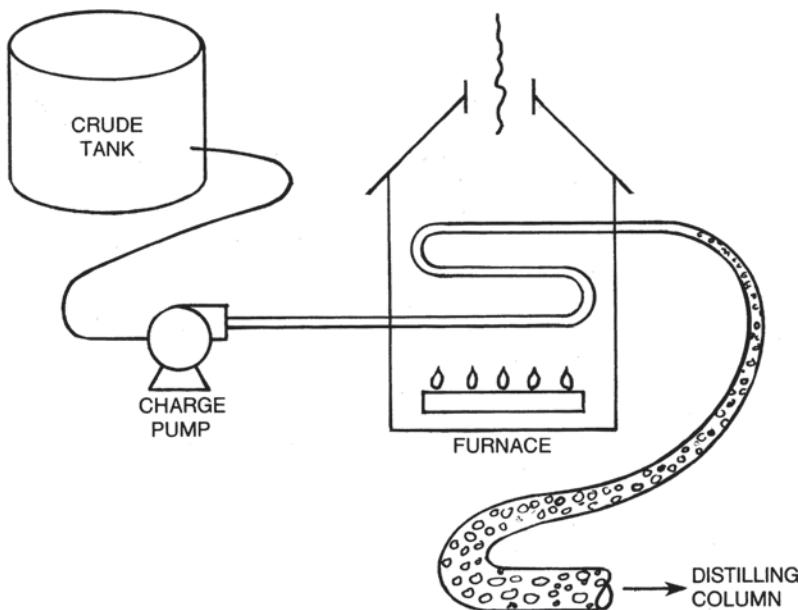
The preceding batch distilling operation is clearly not suited for handling a couple of hundred thousand barrels per day of crude oil with five or six different components being separated. A *distilling column*, one that does *fractional distillation*, can do it on a continuous basis with much less labor, facilities, and energy consumption.

Figure 4-3 shows from afar what happens at a crude distilling column. Crude goes in, and the products go out: gases (butane and lighter), gasoline, naphtha, kerosene, light gas oil, heavy gas oil, and residue.



**Fig. 4-3.** Distilling schematic

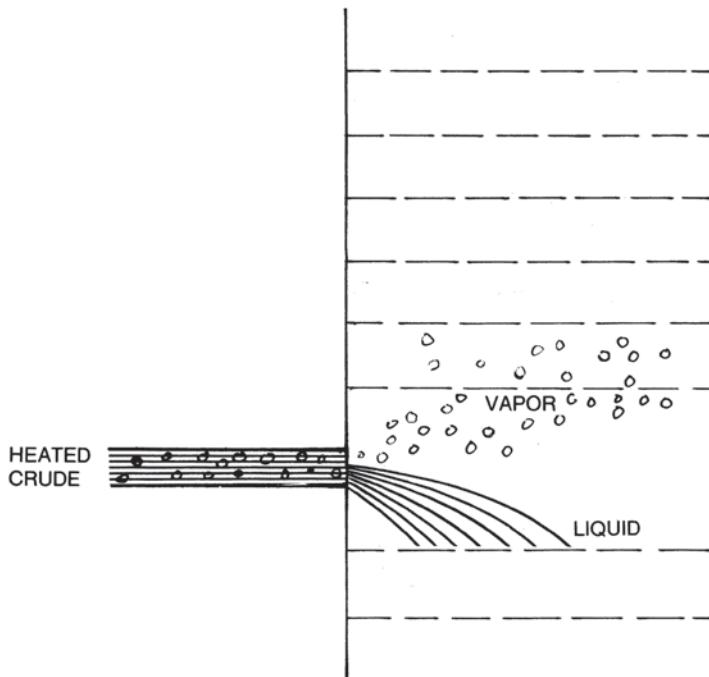
What goes on in and about the distilling column is more complicated. The first piece of equipment important to the operation, the *charge pump*, moves the crude from the storage tank through the system (see fig. 4-4). The crude is first pumped through a furnace where it is heated to a temperature of around 750°F. From the knowledge developed in the last chapter, you can see that more than one-half of the crude oil changes to the vapor form as the furnace heats it to this temperature. This combination of liquid and vapor is then introduced to the distilling column.



**Fig. 4-4.** Crude oil feed to the distilling column

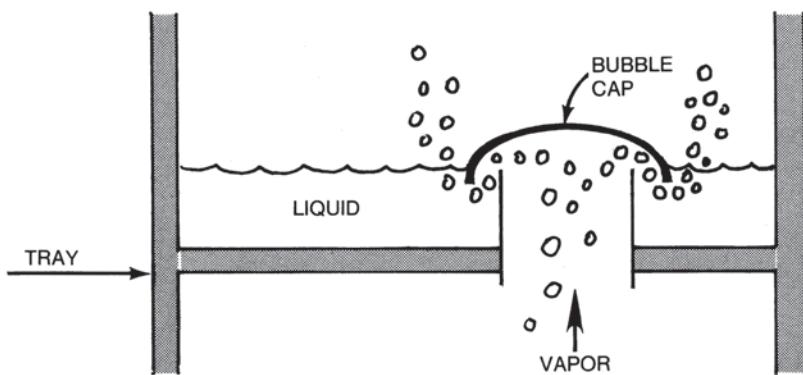
The innards of a distilling column come in many variations. The first example used here is the simplest and easiest to describe. More elaborate designs come later.

Inside the distilling column is a set of *trays*, one to two feet apart, with perforations in them. The perforations permit the vapors to rise through the column and the liquids to fall. When the crude liquid/vapor charge hits the inside of the distilling column, the simple law of gravity causes the denser (heavier) liquid to drop toward the column bottom. The less dense (lighter) vapors start moving through the trays toward the top, as figure 4-5 shows.



**Fig. 4-5.** Crude oil entering the distilling column

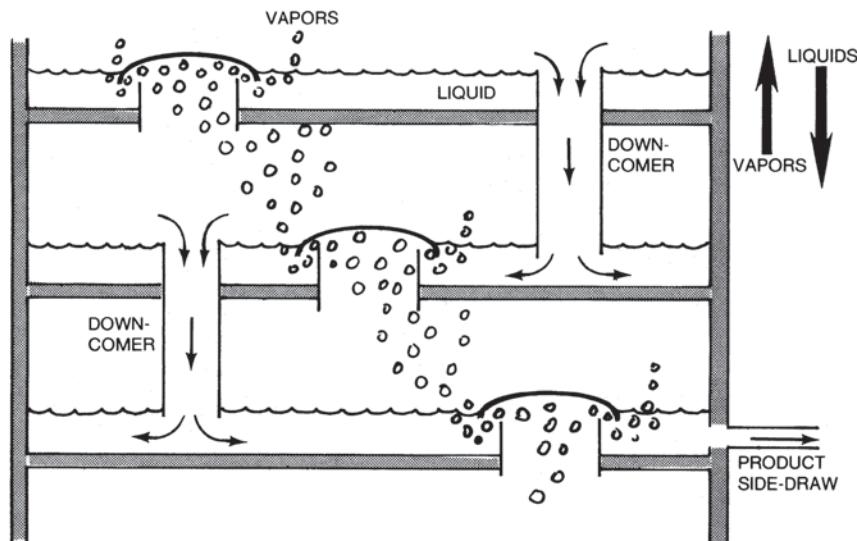
There are lots of tray configurations, but in the most illustrative, the perforations are fitted with a device called *bubble caps* (fig. 4-6). Their purpose is to force the vapor coming up through the trays to bubble through the liquid standing several inches deep on that tray. This bubbling is the essence of the distilling operation: the hot vapor (starting out at 750°F) bubbles through the liquid. Heat transfers from the vapor to the liquid during the bubbling. As the vapor bubbles cool a little, some of the hydrocarbons in them will change from the vapor to the liquid state. The temperature of the vapor drops, and the lower temperature of the liquid causes any heavier compounds that remain in the vapor to condense (liquefy) as they climb the tower.



**Fig. 4-6.** Bubble cap on a distilling tray

After passing through the liquid and shedding some of the heavier hydrocarbons, the vapor continues to move up to the next tray where the same process takes place.

Meanwhile, the amount of liquid on each tray is growing as some of the hydrocarbons from the vapor are stripped out. Figure 4-7 shows a device called a *downcomer*, installed to permit excess liquid to overflow to the next lower tray.



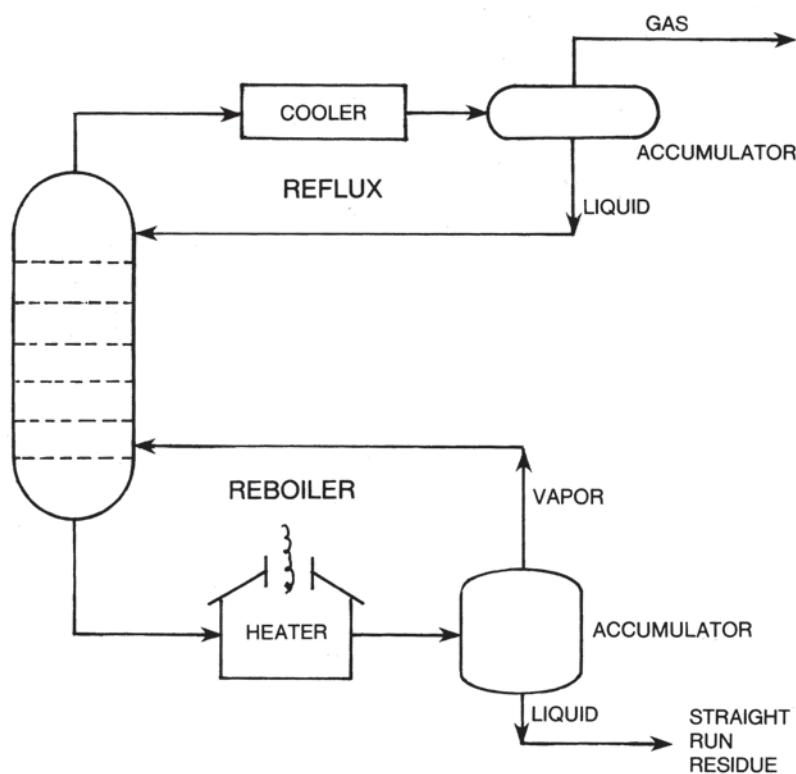
**Fig. 4-7.** Downcomers and sidedraws

At several levels on the column, the *sidedraws* shown in figure 4-7 take the liquid off—the lighter products from the upper parts of the column, the heavier liquids from the parts closer to the bottom.

Some molecules actually make several round trips: up a couple trays as vapor, finally condensing, then down a few trays via the downcomer as a liquid. It is this vapor/liquid mutual scrubbing that separates the cuts. Once through will not do it.

## Reflux and Reboil

Several things go on outside the distilling column that facilitate the operation. To assure that some of the heavies do not get out the top of the column, usually some of the vapor will be run through a cooler. Whatever is condensed is reintroduced to a lower tray. Whatever is still vapor is sent off as product. The process is a form of *refluxing* (fig. 4-8).



**Fig. 4-8.** Reboil and reflux

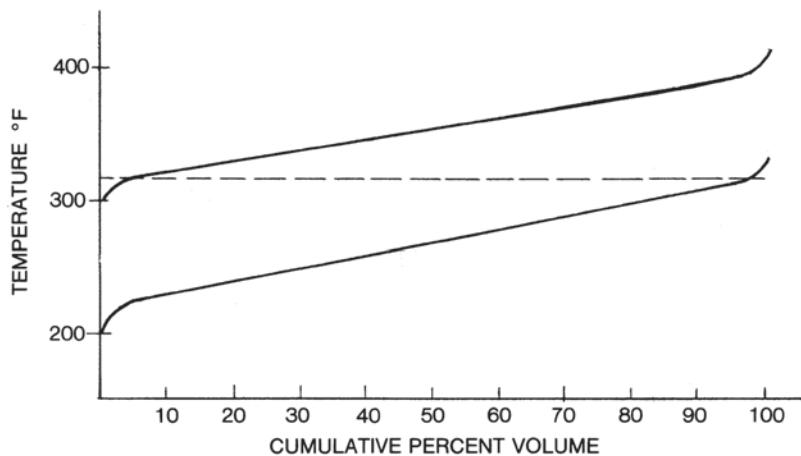
Conversely, some lighter hydrocarbon could be entrained on the bottom of the column where the liquid part of the heated crude oil ended up. So the bottom stream may be circulated through a heater to drive off any lighter hydrocarbons for reintroduction at some higher level in the distilling column as a vapor. This is called *reboiling*.

Reboilers are often used effectively in the middle of the column as well, driving off the lighter hydrocarbons, facilitating good, sharp separations. The reboiler also has the advantage of giving heat input to help push lighter molecules up the column.

## Cut Points

For analyzing and controlling distilling operations, the key parameters are *cut points*, the temperatures at which the various distilling products are separated. The temperature at which a product (or *cut* or *fraction*) begins to boil is called the *initial boiling point (IBP)*. The temperature at which it is 100% vaporized is the *end point (EP)*. So every cut has two cut points, the IBP and the EP.

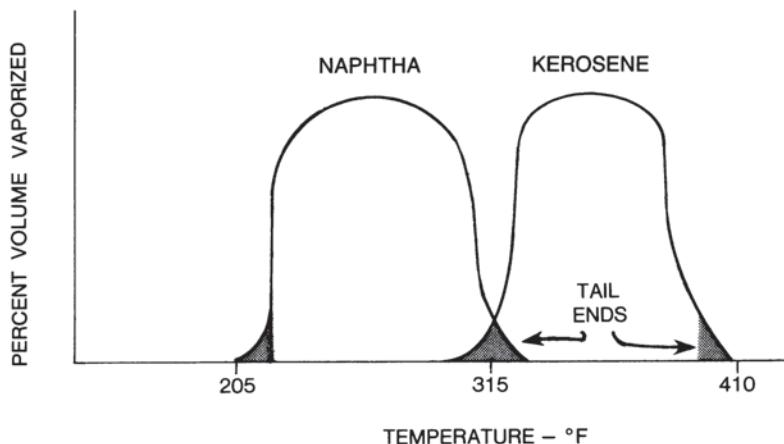
The diagram in figure 4–9 makes it readily apparent that the EP of naphtha is the IBP of kerosene. At a cut point, the EP and IBP of the two adjacent cuts are the same, at least nominally. But that depends on how good a separation job the distilling column does. The IBP of the kerosene could be higher than the EP of the naphtha. You may have wondered, looking at the mechanics of trays and bubble caps, how well the process works. In fact, the operation is a little sloppy, resulting in what is referred to as, pardon the expression, *tail ends*.



**Fig. 4-9.** Overlapping distillation curves

For instance, in a laboratory analysis of the naphtha and kerosene, the two distillation curves would look like the curves in figure 4-9. Looking closely, the end point of naphtha is about 325°F; the true IBP of the kerosene is about 305°F.

A better way of visualizing the tail ends is in figure 4-10, which plots temperature—this time not against cumulative percent vaporized but against percent being vaporized at that temperature (the first derivative of the diagram in figure 4-9, if you know calculus).



**Fig. 4-10.** Tail ends in distillation curves

Almost all refining operations generate the phenomenon of tail ends. It is so common, everyone takes it for granted. However, to simplify analysis, most people make an accommodation. Refiners usually mean *effective cut* points when they talk about distillation. These represent the compromise temperature at which the cuts can be considered effectively cleanly cut. Typically 1% might evaporate lower than the IBP and higher than the EP. In the petrochemicals business, producers deal with single chemicals and delicate chemical reactions. Variations like this cannot be tolerated, but most end uses of petroleum are more accommodating. When you see *cut point* in the rest of this book, it will implicitly mean *effective cut point*.

## Setting Cut Points

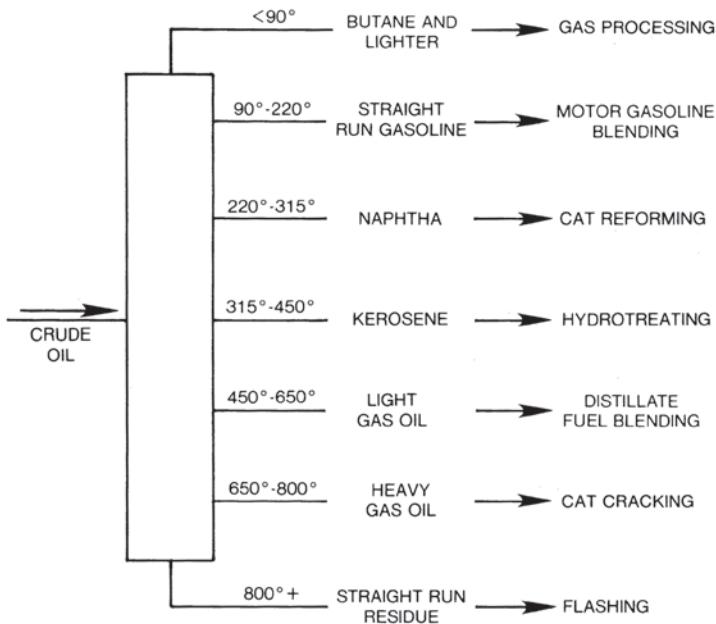
You might have taken the cut points referred to in the last chapter and in the discussions so far in this one as an immutable given for naphtha, kerosene, etc. (even considering the little discussion of the difference between cut points and effective cut points). There is some latitude in setting the cut points on a distilling column. Changing the cut point between naphtha and kerosene has several implications. If the cut point were changed from 315°F to 325°F, several things would happen. First, the *volumes* coming out of the distilling column would change—more naphtha, less kerosene. That is because the fraction between 315°F and 325°F now comes out of the naphtha spigot instead of the kerosene spigot.

At the same time the *gravities* of both naphtha and kerosene get heavier. How can that be? The cut moving out of kerosene into naphtha is heavier than the average naphtha gravity. It is also lighter than the average kerosene gravity. So both cuts get heavier. That might remind you of the comment of the cynical coach who just lost a player to a rival. “I figure the quality of both teams just improved.”

Some of the other properties also change, but gravity is the only one that has been discussed so far. When the operations downstream of the distilling unit are discussed in later chapters, you will appreciate the important implications of changing cut points on the distilling unit.

The listing shown in figure 4–11 of the destinations of all the distilling unit cuts will help set up future chapters. The light ends from the top of the column (the overhead) go to the gas plant for separation. The straight run gasoline goes to motor gasoline blending or perhaps isomerization. Naphtha goes to the cat reformer for upgrading to a better quality gasoline blending stock. Kerosene goes to a hydrotreater for cleanup. Light gas oil goes to

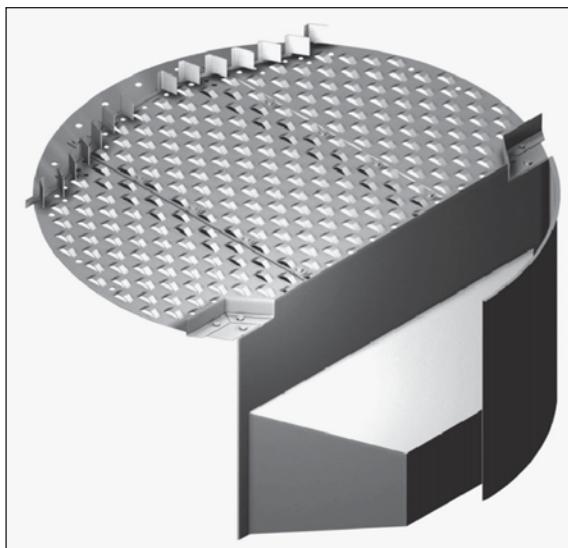
distillate fuel oil blending. Heavy gas oil goes to the cat cracker as feed. And straight run residue is used for heavy fuel oil or is fed to the flasher.



**Fig. 4-11.** Distilling crude and product disposition

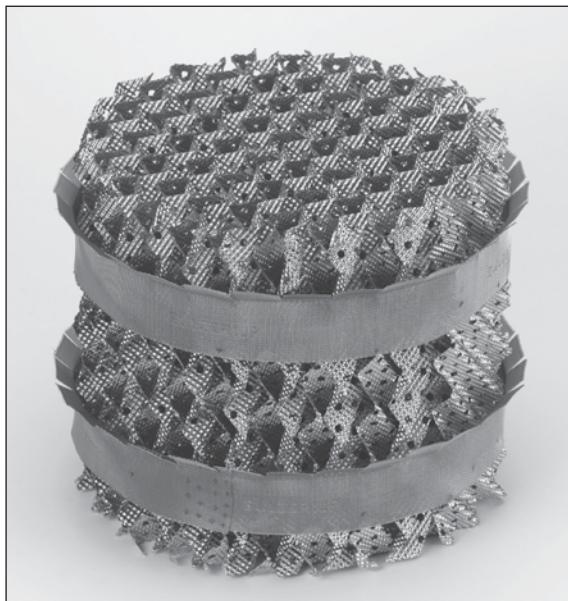
## Variations

The internals of any fractionator can have a variety of designs besides the bubble caps, many tailored to the type of feed expected and the required sharpness of the cutpoints. For example, the valves in the trays in figure 4-12 do not have a bubble cap but still allow the liquid/vapor scrubbing action as the vapors rise. Other devices help assure that the bubbling action does not create froth, which could soon clog up the scrubbing action. Some columns are designed to make only tops and bottoms and no side draws. Instead of trays, the column can be filled with packing, sort of perforated corrugated metal (fig. 4-13). The extensive surface area of the packing acts as a receptor to allow condensing and contact with the rising vapors. Petrochemicals plants are more likely to have *packed columns* than trayed columns because of their efficiency. They are more likely to become fouled, however, which limits their attractiveness in refineries.



**Fig. 4-12.** Alternate distilling internals.

*Courtesy of Sulzer Chemtech*



**Fig. 4-13.** Packing for a packed column.

*Courtesy of Sulzer Chemtech*

## Desalting

As crude oil comes into the refinery tankage, it generally contains oilfield trash—not the people, but sand, minerals, and salts plus iron oxides that have flaked off pipelines or tanker walls. All of these will foul the distilling unit.

Much of the trash settles out in the crude oil tanks, ending up in the tank bottom as *bottom sediment and water* (BS&W). The salt is mostly in tiny droplets of water dispersed throughout the crude oil. Much of this water will not drop out with just settling, so desalting is carried out by adding fresh water to the crude. In many cases, the water will dissolve almost all the salt and will then drop to the bottom of the tank. In other, more stubborn situations, the mixture is passed through a high voltage electric field, 12,000 to 35,000 volts. That causes the tiny, salt-laden water droplets to coalesce, i.e., draw together into larger globs, and then settle out.

## Review

The distilling unit, the first large unit that crude oil meets in the refinery, acts as a post office clerk, sending different parts to appropriate places. Distilling units or fractionators operate on two main principles, gravity and temperature. Liquids fall and vapors rise; as they rise they cool, and some of them condense back to liquids. To control the rate at which they condense, the distilling columns have trays perforated with devices that allow vapors to rise and condense. External sources of heat transfer, reflux, and reboil units, aid in the purification of the streams that come out of a distilling unit.

## Exercises

1. Fill in the blanks below with nomenclature from the following list:

tail ends	downcomer	overhead
IBP	EP	cooler
furnace	straight run gasoline	continuous
crude oil	fractionator	
Batch	bubble cap	
increases	decreases	

- a. After moonshine comes out the top of a still, it *must* be run through a \_\_\_\_\_ before it can be bottled.
- b. \_\_\_\_\_ processing is not very practical in a modern refinery. Today all crude distillation is a \_\_\_\_\_ operation.
- c. Tail ends occur because the \_\_\_\_\_ of one cut overlaps the \_\_\_\_\_ of another.
- d. As vapor moves up the distilling column, its temperature \_\_\_\_\_.
- e. Lowering the end point of a distilling column cut \_\_\_\_\_ the volume of that cut and \_\_\_\_\_ the API gravity.
2. The refinery operations manager is told he must produce 33 M B/D of furnace oil this winter. He is also told he will be supplied with 200 M B/D of crude—30 M B/D of Louisiana crude and 170 M B/D of West Texas. The distillation curves for those crudes are given below. Also he must maximize jet fuel. That is, he must squeeze as much kerosene out of the crude as possible. He knows that the boiling range for kerosene is 300°F to 525°F, so he will have to set the cut points on his distilling units at these two temperatures.

Finally in order to meet the specifications for the 33 M B/D of furnace oil, 20 M B/D of straight run light gas oil (SRLGO) will have to be cut from the crude on the distilling units and provided to the furnace oil blending operation.

*Problem:* At what temperatures will the operations manager have to cut SRLGO to make 20 M B/D?\*

*Distillation Data:*

	<b>West Texas % Volume</b>	<b>Louisiana % Volume</b>
IBP-113°F	15	20
113-260	12	18
260-315	18	15
315-500	10	15
500-750	20	12
750-1,000	10	10
over 1,000	15	10

*Hints:* Calculate a composite crude oil distillation curve. The kerosene EP is the SRLGO IBP. So calculate the SRLGO EP that gives 20 M B/D.

\*Save the answer to this problem. Problems in subsequent chapters will build on this exercise.

# 5

## VACUUM FLASHING

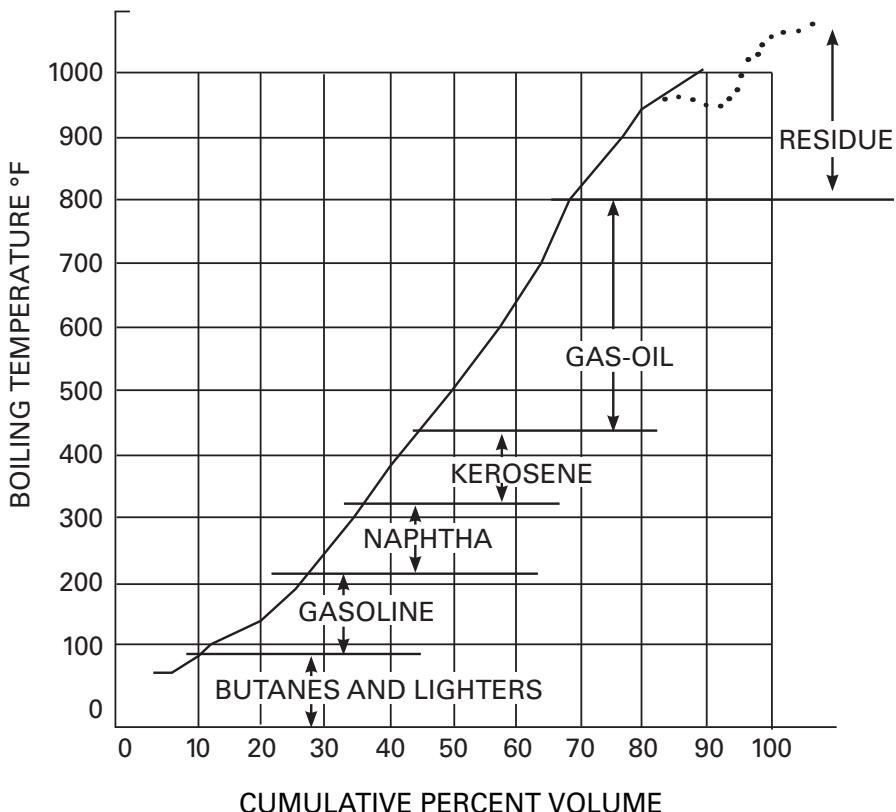
*A vacuum is repugnant to reason.*

—*Principles of Philosophy*, Rene Descartes

The discussions so far about distillation curves and distilling columns have treated the shape of the curves at temperatures around and above 900°F somewhat vaguely, but on purpose. There is a phenomenon that happens at these temperatures called *cracking*. Refiners use cracking extensively, but in controlled ways. In the distillation process, all the uncontrolled symptoms of cracking could occur. To avoid them, refiners developed vacuum flashing.

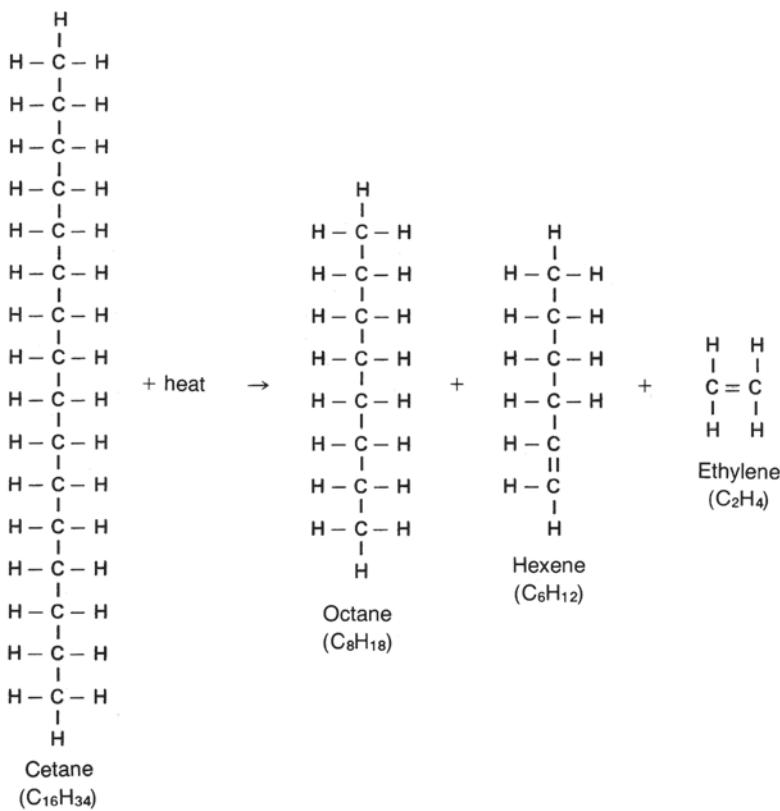
### The Cracking Phenomenon

Suppose a technician were going to develop a crude distillation curve in the laboratory. Technicians do that all the time to prepare *assays* for use by refiners to help assess the suitability of crudes. The technician would heat the crude oil; note and record the temperature; capture the vapor and condense (liquefy) it; and record and cumulate the volume of the liquids. If the technician permitted the temperature of the crude to rise to about 900°F, a sudden change in the shape of the distillation curve would take place. As the temperature went from 900°F to 1,000°F, the cumulative volume recovered would exceed 100%—and crude would still be boiling in the pot (fig. 5-1).



**Fig. 5–1.** Distillation curve anatomy

This might exaggerate what anyone can easily observe with the naked eye, but it makes the point. As the complicated hydrocarbon molecules that have not yet vaporized at 900°F are heated to higher temperatures, the energy transfer via the heat is enough to cause the molecules to crack into two or more smaller molecules. For example, in figure 5–2 a molecule of  $C_{16}H_{34}$  may crack into three pieces:  $C_8H_{18}$ ,  $C_6H_{12}$ , and  $C_2H_4$ . (A fuller discussion of the chemical reaction of cracking will be covered in the chapter on cat cracking.) But if you look carefully, the numbers of carbon and hydrogen atoms on the left side of the arrow are the same as on the right side. No matter has been created or destroyed. The atoms are just rearranged into different compounds.

**Fig. 5–2.** Molecule cracking

If you recall the discussion on boiling points, it starts to become apparent why the shape of the distillation curve behaves so strangely at this point. The smaller molecules boil at much lower temperatures than the large ones. As cracking creates them, they leap out of the crude oil. But that tells only half the story. Why does more volume get created so that the distillation curve exceeds 100%? In simplest terms, the small molecules take up more room than the larger ones.

Again, recall the discussion on hydrocarbon properties and specific gravities. The compound C<sub>16</sub>H<sub>34</sub> weighs 7.2 lb/gal, and C<sub>8</sub>H<sub>18</sub>, C<sub>6</sub>H<sub>12</sub>, and C<sub>2</sub>H<sub>4</sub>, the other compounds in fig. 5–2, weigh 5.9, 5.6, and 3.1, respectively. Take a gallon of C<sub>16</sub>H<sub>34</sub> and suppose you could crack it completely into these three compounds. (It never happens that way; combinations of different compounds turn up too.) The chemistry of it says that there would be 50%

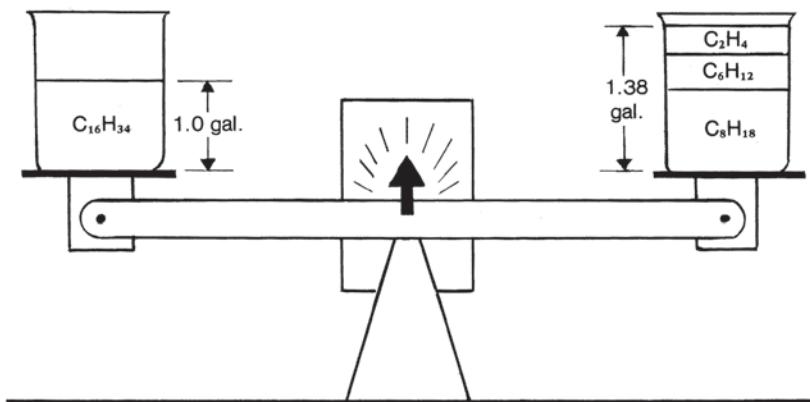
$C_8H_{18}$ , 38%  $C_6H_{12}$ , and 12%  $C_2H_4$ . But the percentages are **by weight, not by volume**. To make the calculation easy, start with 7.2 pounds of  $C_{16}H_{34}$  and calculate the change as follows:

$$\text{cracking } 100\% \text{ of } C_{16}H_{34} = 7.2 \text{ lb} \div 7.2 \text{ lb/gal} = 1.00 \text{ gal}$$

results in

50% yield of $C_8H_{18}$	= $3.6 \text{ lb} \div 5.9 \text{ lb/gal} = 0.61 \text{ gal}$
38% yield of $C_6H_{12}$	= $2.7 \text{ lb} \div 5.6 \text{ lb/gal} = 0.48 \text{ gal}$
<u>12% yield of <math>C_2H_4</math></u>	= <u><math>0.9 \text{ lb} \div 3.1 \text{ lb/gal} = 0.29 \text{ gal}</math></u>
100%	<u><math>7.2 \text{ lb}</math></u>

So, 7.2 lb of  $C_{16}H_{34}$  take up 1 gal, but 7.2 lb of the components take up 1.38 gal (fig. 5-3). You can think of it this way: in the larger  $C_{16}H_{34}$  molecule, the atoms are held together by atomic attraction. In the three smaller atoms those atomic forces have partially dissipated into three subsets. So the smaller ones collectively take up more space per pound.



**Fig. 5-3.**  $C_{16}H_{34}$  and its cracked counterparts

Cracking is a lucrative process only when it is controlled. The distilling unit is not designed to control it, so refiners avoid it by not raising the temperatures too high in the distilling process. The heaviest cut points on the distilling column are around 750°F. There are, nonetheless, lots of hydrocarbons that need to be separated from the straight run residue and the technique used is vacuum flashing.

## Effects of Low Pressure

Suppose you are at a rowdy party and you yell across the room for someone to toss you a beer. They pull a long neck out of the cooler and lob it to you. When you pop the top off, you have a classic but messy reaction right out of a college physical chemistry book: foam bubbles out, all over your hand and the floor.

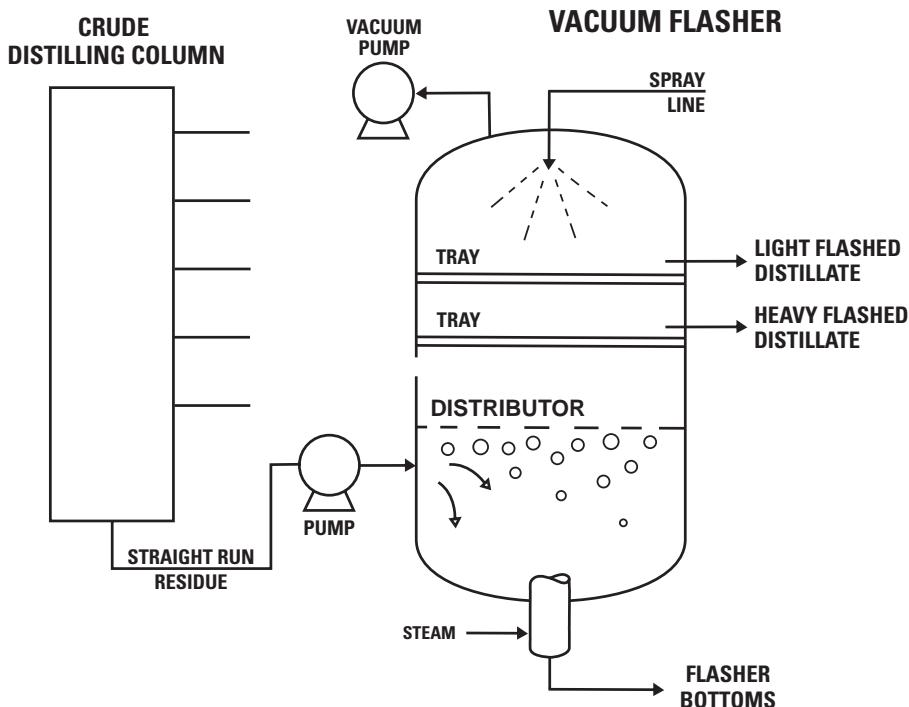
What happened? As you opened the bottle, you reduced the pressure on the contents. Immediately the carbon dioxide that had been dissolved in the liquid started to vaporize—rapidly, since you agitated it when you caught the bottle. Some of the liquid comes out with the CO<sub>2</sub> as well in the form of foam.

No temperature change has taken place; just lower pressure causes the gases to escape by “boiling off.” The point is the lower the pressure, the lower the boiling temperature.

## Vacuum Flashing

Apply the pressure/boiling relationship to the crude oil cracking problem. The straight run residue will crack if the temperature goes too high, but straight run residue needs to be separated into more cuts. The solution is to do the distillation at reduced pressure.

In the vacuum flasher shown in figure 5-4, straight run residue from the distilling unit transfers to the flasher. (It may go through a heater furnace first.) The flasher is a large diameter vessel, too squat to be called a column, but that is more or less what it is. The straight run residue enters the flasher, where the pressure has been lowered well below atmospheric pressure. The lighter portions of the straight run residue vaporize, but at that temperature, no cracking will take place.



**Fig. 5–4.** Vacuum flashing

Various gadgets inside the flasher facilitate separating and capturing the offtake streams. As the mixed stream of vapor and liquid enters the flasher, almost all the liquid falls to the bottom. Some of the liquid forms droplets—not quite gaseous, but carried along with the vaporized part of the straight run residue (as in the beer foam example). They start to rise with the vapor. To capture these droplets and to disperse the vapor evenly throughout the flasher, the vapor/droplet mixture encounters a *distributor*—a thick mesh screen or a tray of loose metal rings several inches thick. The distributor catches the droplets, which drip down to the bottom. Further up the flasher are two trays that operate the same as those in a distilling column. There may also be a reboiler, though it is not shown in the figure. Reflux, serving the same purpose as it does in a distilling column, is in the form of an atomized spray from the top of the vessel, using some of the cooled streams drawn off one of the trays. The droplets assure the rising vapors condense on one of the trays.

The *vacuum pump* at the top of the vessel maintains the low pressure in the vessel at about 25 mm Hg to 40 mm Hg (about 3% to 5% of atmospheric pressure) and continuously draws off any vapors that have not condensed.

They usually consist of water and some small amounts of hydrocarbon. Actually, most vacuum flashers use a device called a steam eductor to maintain the low pressure. While that is mechanically more appropriate, it does not conjure up as clear a picture for you. Either way, the vapors separating from the straight run residue at the reduced pressure have an equivalent end point of 1,000°F to 1,100°F.

The two streams drawn off the trays at the upper part of the flasher, *light flashed distillate* and *heavy flashed distillate*, are together called *flasher tops*. The two streams are often kept segregated. Refiners found through chemical analysis that the heavier part of the flasher tops contain most of the contaminants that poison catalysts in processing units further downstream. By keeping the streams segregated, they can treat the heavy flashed distillate and remove most of the bad actors.

Meanwhile, at the bottom of the flasher, the liquids drain through a pipe. Some flashers have an apparatus for one last pass at removing the good stuff. They pump superheated steam up through that pipe as the liquid comes down, releasing some lighter hydrocarbons that may have been entrained in the liquid. Because the superheated steam is at temperatures well above the cracking temperatures, the liquid coming out the bottom, the *flasher bottoms*, is quenched with some cooled liquids before the cracking has a chance to take place. (Later, in the chapter on residue reduction, you will find out that cracking requires a minimum *residence time* to get started.)

The flasher bottoms have several possible destinations—feed to an asphalt plant, a thermal cracker, or a coker, or as a blending component for residual fuel. But the real reason to run a flasher is to make the flasher tops in order to feed to a cat cracker.

## Adjusting the Distillation Curve

By careful calculation, the imputed distillation curve (the solid line in fig. 5-1) can be calculated to show the temperature/volume relationship as if there were no cracking to worry about. An apparatus in the lab uses a vacuum chamber to simulate what the vacuum flasher does. Crude oil assays show the imputed volumes at atmospheric pressure.

## Review

Flashing is the equivalent of distilling the straight run residue at a cut point in the neighborhood of 1,000°F to 1,100°F. Crude oil distillation curves show the temperature/volume relationship as if a theoretical distillation without cracking took place. That is, they assume the vacuum flasher is part of the distillation unit.

## Exercises

1. Fill in the blanks:

- a. Vacuum flashing is a technique to continue \_\_\_\_\_ of crude oil at high temperatures without encountering \_\_\_\_\_.
  - b. The lower the pressure around a liquid, the \_\_\_\_\_ (lower, higher) the boiling temperature.
  - c. The higher the pressure in a vacuum flasher, the \_\_\_\_\_ (lower, higher) the end point of the flasher tops, assuming the feed rate and feed temperature do not change.
  - d. Products from a flasher are \_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_.
  - e. To reduce the volume of flasher tops, holding the feed rate constant, you either \_\_\_\_\_ the pressure in the flasher or \_\_\_\_\_ the temperature of the flasher feed.
2. Use the data given to the operations manager in the previous chapter. In order to satisfy the need for feed to the asphalt plant, 35 M B/D of flasher bottoms must be made available.
- a. At what maximum cut point does the operations manager set the flasher to assure supply to the asphalt plant? Use the distillation curve temperatures, not the internal flasher temperatures, since you do not know at what pressure the flasher operates.
  - b. If the straight run residue was cut from the distilling column at 800°F, what would be the volume of the flasher tops?

# 6

## THE CHEMISTRY OF PETROLEUM

*It strikes me that Nature's system must be a real beauty, because in chemistry we find that the associations are always beautiful whole numbers—there are no fractions.*

—R. Buckminster Fuller

So far in most of the discussion of crude oil and refining, you have been able to avoid the basics of chemistry. The good times have come to an end. Distilling and flashing involve only physical separation, no chemical change. The rest of the refining processes, for the most part, involve chemical reactions. While you do not have to have taken Chemistry I and have gotten at least a C in Physical Chemistry, you will have to know something about the chemistry of hydrocarbons to go on from here.

Do not skip this chapter! You will have to keep a figurative thumb in these pages if you want a full appreciation of the next 13 chapters.

### Atoms and Molecules

Physicists are continually surprising the scientific world by finding smaller and smaller particles, even more esoteric than neutrons and electrons. Luckily, the smallest, useful notion in petroleum refining is the *atom*. Examples are carbon, hydrogen, sulfur, and oxygen, whose chemical symbols are C, H, S, and O.

The characteristics of matter depend on the types of atoms that make it up and how they are attached to each other in groups called *molecules*.

There are rules by which atoms can be arranged into molecules. The most important rules have to do with *valences* and *bonds*.

**Valences.** Each type of atom (element) has an affinity for other elements according to its atomic structure. For example, carbon atoms would always like to attach themselves to four other atoms. Hydrogen atoms would always like to attach themselves to only one other atom.

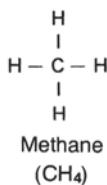
*Definition.* *The valence of an atom of any element is equal to the number of other atoms that the atom has a propensity to combine with.*

If you have been around refinery people, you will have noticed that whenever they refer to hydrogen as a separate compound, they never write it as H, but as H<sub>2</sub>, because that is how it exists—one hydrogen atom attached to a second, satisfying the valence rule of both atoms.

**Bonds.** The connection between two atoms is called a bond. You can think of it as an electrical force that ties the two atoms together.

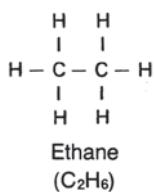
## Hydrocarbons

The simplest example of valence, bonds, and hydrocarbons is methane, CH<sub>4</sub>, which has one carbon and four hydrogen atoms. Look at the structure in figure 6–1 and see that all the valence rules are satisfied—each hydrogen is attached to one other atom, and the carbon is attached to four other atoms.

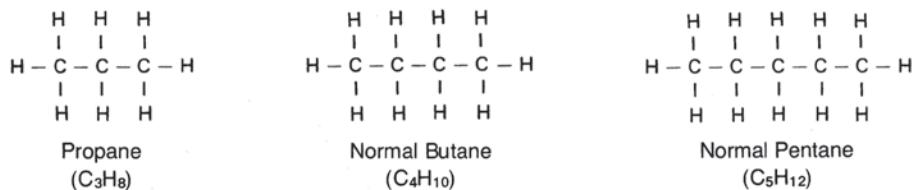


**Fig. 6–1.** Methane

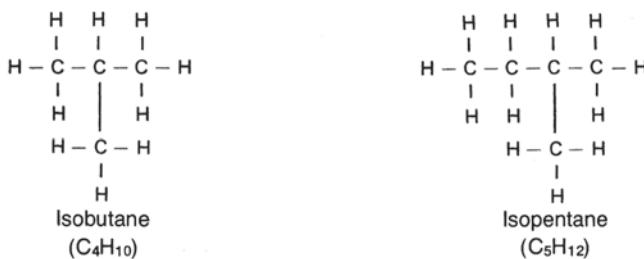
If you take the next simplest hydrocarbon, ethane, some further complications can be introduced. Ethane is C<sub>2</sub>H<sub>6</sub> (fig. 6–2). You can check that each carbon has four attachees; each hydrogen has one. Note that one carbon atom is attached to another carbon atom, and that is okay. Each one uses the same bond to satisfy its valence need.

**Fig. 6-2.** Ethane

A whole class of hydrocarbons can be defined by extending the relationship from methane to ethane and beyond. These molecules are *paraffins* or *straight chain compounds* and have the formula  $\text{C}_n\text{H}_{2n+2}$ . The examples in figure 6-3 are propane, normal butane, and normal pentane.

**Fig. 6-3.** Propane, normal butane, normal pentane

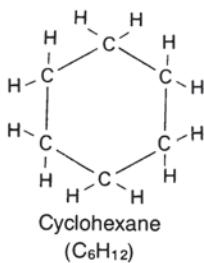
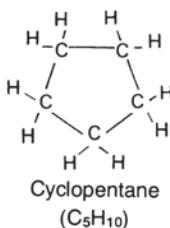
Why is the prefix *normal* used before butane and pentane? Well, there are several ways to arrange the carbon atoms in  $\text{C}_4\text{H}_{10}$  and  $\text{C}_5\text{H}_{12}$ . One of them is shown in figure 6-3. Another is to put a *branch* off of one of the inside carbons. In that case, the compounds  $\text{C}_4\text{H}_{10}$  and  $\text{C}_5\text{H}_{12}$  are called isobutane and isopentane (fig. 6-4).

**Fig. 6-4.** Iso-butane, iso-pentane

Isomerization and carbon's valence of four are the major reasons why there are almost a million identified different hydrocarbon compounds. Even though normal butane and isobutane have the same formula, they behave differently. They boil at different temperatures; they have different gravities (since they are packed differently); and they cause different chemical reactions, which will be important in a later chapter on alkylation.

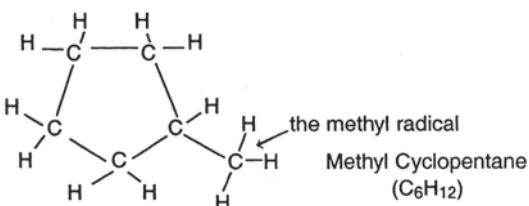
## Naphthenes

Another class of hydrocarbons found in petroleum is *naphthenes*. The two of most interest have either five or six carbons in them. The carbons are bent around into a ring or cyclic shape, as in figure 6-5, giving rise to the name cyclopentane ( $C_5H_{10}$ ) and cyclohexane ( $C_6H_{12}$ ). Note that there are less hydrogen atoms in cyclopentane than in normal or isopentane and the same for the cyclohexane.



**Fig. 6-5.** Naphthenes

Beyond the simple paraffins and cyclic hydrocarbons an infinite variety of possibilities can occur by connecting two or more types of compounds. The least complicated and simplest example is methyl cyclopentane, which is the connection of  $-CH_3$ , called a *methyl group*, and a cyclopentane at the spot where hydrogen ought to be. That forms  $C_6H_{12}$  as in figure 6-6. Actually, a more explicit chemical formula for methyl cyclopentane is  $C_6H_{10}CH_3$ , which better shows the methyl and the cyclopentane groups. Attach instead two methyl groups where hydrogens ought to be and you have *dimethyl* cyclopentane. Use an ethyl group,  $-C_2H_5$ , and you get *ethyl* cyclopentane. You can begin to see why there can be hundreds of thousands of compounds in a crude oil.



**Fig. 6-6.** Methyl cyclopentane

## Groups

*A group is a molecule wannabe. An ethyl group, for instance, would be  $-C_2H_5$ , which wants to be an ethane molecule but is missing one hydrogen. Instead, it is attached to another molecule or atom. Chemical engineers and chemists find it useful to refer to groups as if they were stand-alones to explain the structure of a molecule, and sometimes the intermediate steps of a process to get to that molecule.*

## Olefins and Aromatics

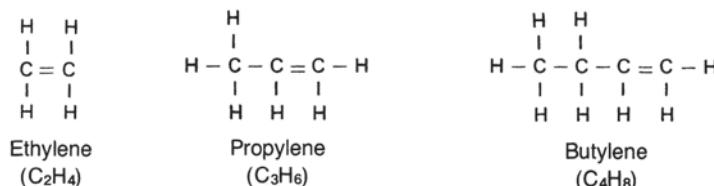
It is possible to have a compound with two carbons and only four hydrogens. That would seem to violate the valence rules you just spent six minutes learning. But in the chemical compound ethylene in figure 6–7, there is a *double bond* between the two carbon atoms to make up for the deficiency of hydrogen atoms. Ironically the double bond that holds the two carbons together is weaker, not stronger, than a single bond. You can think of it as two bonds squeezed into the space of one. Those carbons on either side desperately want to find some other atoms to satisfy the valence of four. A compound with double-bonded carbons is therefore more chemically reactive than its paraffin counterpart and can be reacted with some other reactive compound or atom with relative ease, eliminating the double bond. That is why ethylene is such a popular compound for making other compounds. For example, reacting a lot of ethylene molecules with each other makes polyethylene.

The key characteristic of the olefin is the double bond and the absence of two hydrogens from an otherwise *saturated* paraffin, i.e., a paraffin that has a full complement of hydrogens. The formula, therefore, is  $C_nH_{2n}$ .

Olefins are unnatural. It may be that only God can make a tree, but He or She could not handle olefins. They are not found in crude oil but are man-made in one of the several cracking processes that will be covered in later chapters. This seemingly irrelevant fact has implications in the design of refinery gas plants, which generally keep saturated gas and cracked gas segregated from each other. More on this is given in chapter 8.

The olefins that are of primary interest in petroleum refining are propylene ( $C_3H_6$ ) and butylenes ( $C_4H_8$ ) (fig. 6–7). Like ethylene, these compounds can be reacted with other chemicals relatively easily and so are suitable for applications in refinery (the alkylation process) and in

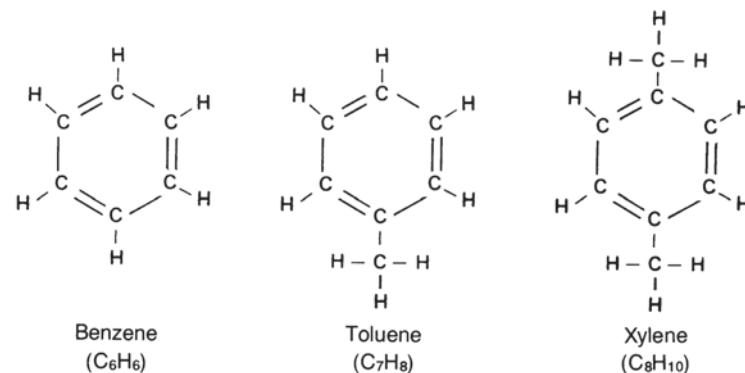
petrochemical applications (making polypropylene and polybutylene, to name just two). Still, there are many, many more olefins in the streams that come from cat crackers, thermal crackers, and cokers. There are never enough hydrogen atoms in these crackers to fill out the carbons of the smaller molecules that result from cracking larger ones.



**Fig. 6-7.** Olefins

*Aromatics* are another exception to the valence rules. Take the ring compound cyclohexane in figure 6-5. Each carbon has two hydrogens attached and is attached to two other carbons. If you removed one hydrogen from each carbon, you could bring the valence rules back to being satisfied by putting double bonds between some carbons. A double bond between every other carbon pair will do it (fig. 6-8). The resulting molecule is C<sub>6</sub>H<sub>6</sub>, *benzene*. Saying that every other bond around the benzene ring is a double bond is a simplification. The real description has to do with a resonating structure and hopping bonds, but that is a story for another time.

If one of the hydrogens of the benzene molecule is removed and a methyl group, -CH<sub>3</sub>, is put in its place, the result is C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, which is toluene. If two methyl groups are substituted for two hydrogens on the benzene ring, the result is C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>, which is xylene (pronounced “zi-leen”).



**Fig. 6-8.** Aromatics

Are there other ringed compounds with double bonds, like C<sub>7</sub>s or C<sub>8</sub>s? Not any that you will come across in petroleum refining. There are some in the petrochemicals business.

### **Refiners' Shorthand**

Refiners often use a shorthand convention that can baffle the outsider, especially if he or she does not realize that the notations leave off the hydrogens and indicate how many were left off by using little superscripts. For example:

- C<sub>3</sub><sup>o</sup> The zero means this is a paraffin, propane, C<sub>3</sub>H<sub>8</sub>.
- C<sub>3</sub><sup>-</sup> The dash means propane and lighter, i.e., propane, propylene, ethane, ethylene, methane, and hydrogen (C<sub>3</sub>H<sub>8</sub> C<sub>3</sub>H<sub>6</sub> C<sub>2</sub>H<sub>6</sub> C<sub>2</sub>H<sub>4</sub> CH<sub>4</sub> H<sub>2</sub>).
- C<sub>3</sub><sup>+</sup> The plus sign means propane and heavier, i.e., propane, butanes, butylenes, etc. (C<sub>3</sub>H<sub>8</sub> C<sub>4</sub>H<sub>10</sub> C<sub>4</sub>H<sub>8</sub> etc.).
- C<sub>3</sub><sup>=</sup> The double bar means this is an olefin with a double bond, such as propylene (C<sub>3</sub>H<sub>6</sub>).
- C<sub>3</sub><sup>s</sup> The s means plural, so this is propane (C<sub>3</sub><sup>o</sup>) and propylene (C<sub>3</sub><sup>=</sup>).

Benzene, toluene, and the xylenes happen to have high octane numbers, which makes them suitable for making gasoline. Also, as with ethylene, the double bonds make the benzene ring very chemically reactive. That makes the BTXs (benzene, toluene, and xylene) very popular building blocks in the chemical industry. The reactivity lent by the double bonds on the aromatics ring may be best illustrated by the numerous petrochemicals derived from them—polystyrene, epoxy, and polyesters such as PET or polyethylene terephthalate, the water bottle material.

The generic name “aromatics” includes *any compounds* that have the benzene ring in them. Many of the heavier compounds in crude oil have multiple benzene rings imbedded, and you will read later on that will determine the performance of the ultimate products, especially gasoline, jet fuel, diesel, asphalt, and lubricants. At the same time, many people use the term *aromatics* to refer to *only the BTXs*, the benzene, toluene, and xylenes. The name *aromatic*, by the way, comes from the characteristic smell of the BTXs, which is sort of sickly, sweet, hydrocarbonish odor. Chapter 21 deals with the special processing equipment for the extraction of aromatics in refineries.

You can see that once the number of carbons gets above six, the number of different variations in structure explodes, due both to the propensity

for carbon to hook up with four other atoms and to isomerization. For that reason, refiners pay much less attention to the individual compounds above the C<sub>6</sub>s (maybe a few C<sub>7</sub>s or C<sub>8</sub>s, but that is about it). Sometimes they will use the *PONAs*, the proportion of paraffins, olefins, naphthenes, and aromatics, to evaluate the suitability of a stream. At other times they will use the physical properties (gravity, viscosity, boiling temperatures, etc.) as a workable characterization.

## Exercises

1. Isobutane is the isomer of normal butane. Why is there not an isomer of benzene, C<sub>6</sub>H<sub>6</sub>?
2. How many different ways can isobutane be structured? Isopentane? Isobutylene?
3. Name the four types of structures generally referred to as the PONAs.
4. There are three different kinds of xylene. Can you draw the two not shown in figure 6–8?
5. Why is there only one type of toluene?

# 7

## REFINERY GAS PLANTS

*...and he shall separate them one from another,  
as a shepherd divideth his sheep from the goats.*

—Matthew 25:32

Almost all refinery processing units generate some volumes of butane and lighter gas. Gas processing is not a very colorful operation, but maybe that is why the engineers gave such exotic names to the parts. There are names such as *lean oil*, *fat oil*, *sponge oil*, and *rectified absorbers*, to mention a few. All are in the central location called the gas plant.

### Sats Gas Plant

The gas streams from some of the refinery process units have only *saturates* in them: methane, ethane, propane, butanes, and maybe hydrogen. The word *saturates* is a synonym for hydrocarbons with no double bonds; that is, all the carbon atoms are “saturated with hydrogen atoms.” These streams are usually handled in a facility called the *sats gas plant*. In contrast the *cracked gas plant* handles the streams that also contain the olefins (ethylene, propylene, and butylenes). Dealing with the even lighter gases, hydrogen and hydrogen sulfide, is so specialized that a separate chapter (chapter 16) is devoted to it.

The separation of the gases is a lot harder than the separations in the crude distilling unit. Remember that each of those gases is a single chemical and boils at a single temperature (table 7-1). That does not leave much tolerance for tail ends or any kind of sloppy separation. As a result, the gas separation columns have lots of trays and lots of reboiling and refluxing.

Another complication is the pressure/temperature relationships. The gas plants are just the inverse of the flasher. In order to get the streams to liquefy—an essential step in distillation—the mixture has to be either cooled below its boiling temperature (see table 7-1) or put under a lot of pressure. Gas separation usually uses both in combination.

**Table 7-1.** Some properties of light ends

Compound	Formula	Boiling Temperature*	Density**
		(°F)	(lb/gallon)
Hydrogen	H <sub>2</sub>	-423	—
Methane	C <sub>1</sub> H <sub>4</sub>	-258	2.5
Ethane	C <sub>2</sub> H <sub>6</sub>	-127	2.97
Ethylene	C <sub>2</sub> H <sub>4</sub>	-155	3.11
Propane	C <sub>3</sub> H <sub>8</sub>	-44	4.23
Propylene	C <sub>3</sub> H <sub>6</sub>	-54	4.37
Isobutane	iC <sub>4</sub> H <sub>10</sub>	11	4.69
Normal Butane	nC <sub>4</sub> H <sub>10</sub>	31	4.87
Isobutylene	iC <sub>4</sub> H <sub>8</sub>	20	5.01
N Butylenes ***	nC <sub>4</sub> H <sub>8</sub>	21	5.01
	nC <sub>4</sub> H <sub>8</sub>	34	5.09
	nC <sub>4</sub> H <sub>8</sub>	39	5.23

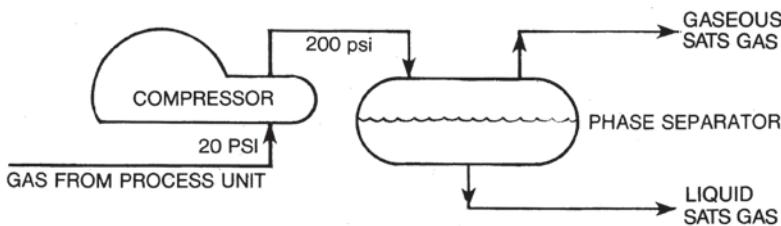
\*At atmospheric pressure

\*\*At atmospheric pressure and 60°F

\*\*\*There are three forms (isomers) of normal butylenes, each of them with the formula C<sub>4</sub>H<sub>8</sub>, each with a unique structure, and each with unique properties.

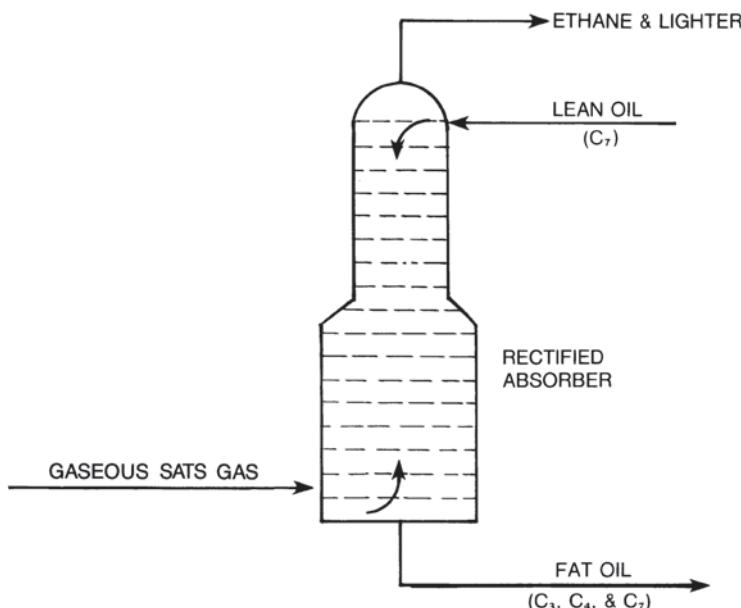
The sats gas coming from the processing units to the gas plant can go through the following typical steps:

1. *Compression and phase separation.* Low pressure gases are compressed to about 200 psi, as in figure 7-1. Because of the high pressure, the heavier gases, the propane and butanes, liquefy, allowing them to be drawn off. The liquid usually still has some of the lighter gases, ethane and methane, still dissolved in it, just like flat beer still has just a little carbon dioxide lingering around.



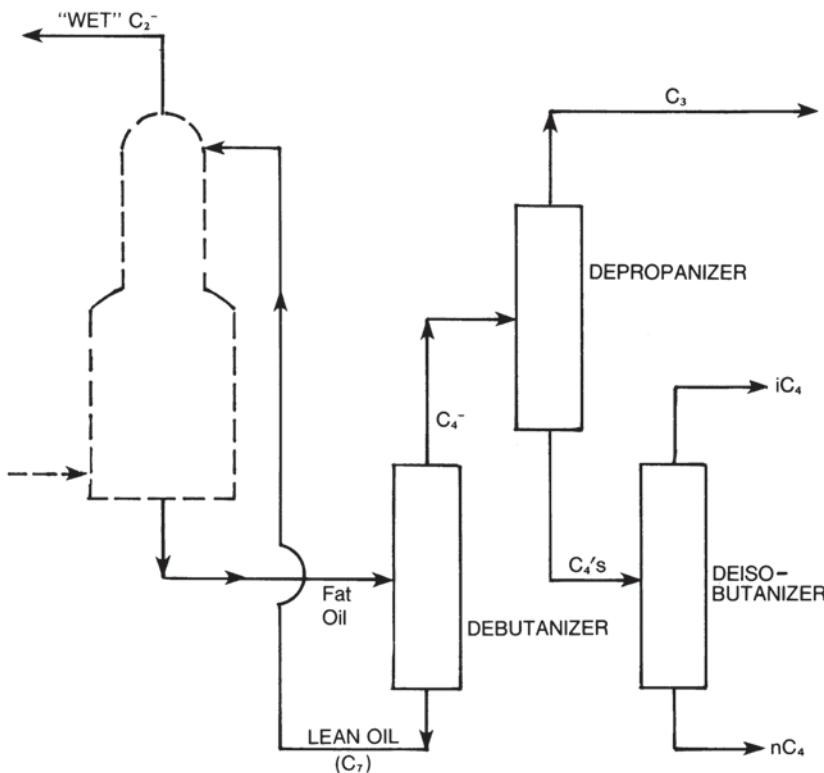
**Fig. 7-1.** Compression and phase separation

2. *Absorption*. The propane and butanes and the little bit of ethane and methane are depressurized and introduced to the lower section of the *rectified absorber* (fig. 7-2). This unusually shaped column is a fractionator with a special counterflow built in. *Lean oil*, a naphtha range liquid, usually heptane ( $C_7H_{16}$ ) or octane ( $C_8H_{18}$ ), enters the top tray of the absorber and trickles down the trays. As it does, it picks up (absorbs) almost all the propane and butane in the gas, but not the lighter gases, ethane, methane, and hydrogen. The naphtha now laden with the propane and butane is called *fat oil*, continuing the gastronomic analogy. The rocket ship design of the column has two different processes underway. In the top section, the absorption of the propane and butane takes place. In the bottom section, the remnant very light gases are given a last chance to exit the fat oil as it trickles down the wider trays.



**Fig. 7-2.** Absorption

**3. Debutanizing.** The fat oil is heated (heater not shown in fig. 7-3) and charged to a column, called a debutanizer, that separates the butanes and propane from the naphtha. Because the boiling range of the naphtha starts about 180°F and butane boils at about 31°F, the split is relatively easy. It is certainly easier than splitting butane and propane from ethane in a distilling column.

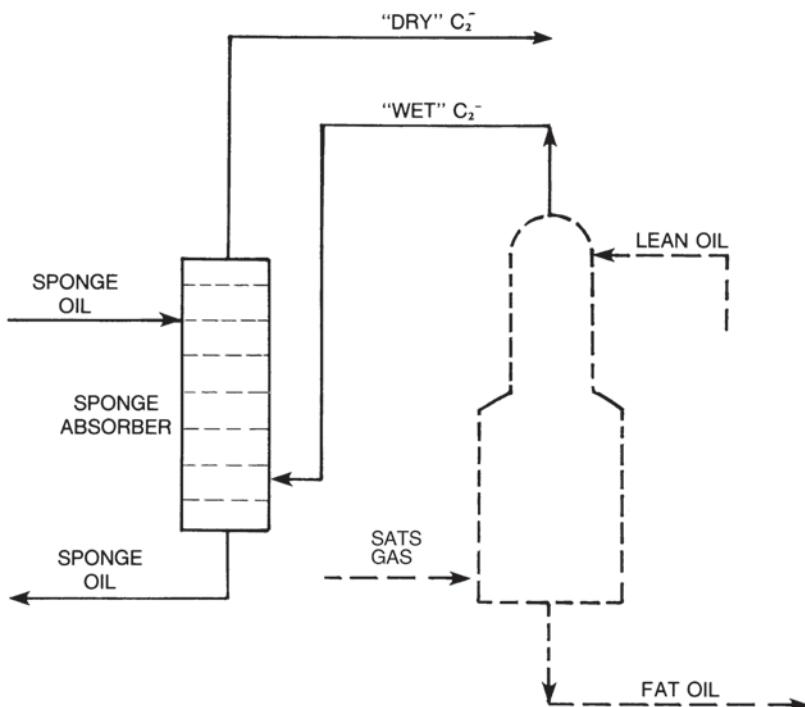


**Fig. 7-3.** Debutanizing, depropanizing, deisobutanizing

**4. Depropanizing.** The C<sub>3</sub>/C<sub>4</sub> stream is separated in a tall column that takes the propane overhead and the butanes out the bottom.

**5. Deisobutanizing.** Some refineries have a column that splits the butanes. Since the boiling temperatures of normal and isobutane are so close, many trays are needed to get good separation. Chillers and compressors are needed to liquefy the gas and reintroduce it as a reflux. The deisobutanizer is usually the tallest column in the gas plant.

6. *Sponge absorption.* In many refineries a further step might take place. When the lean oil is introduced to the rectified absorber, some of it may vaporize and go out the overhead with the ethane and lighter ( $C_2^-$ ). To recover the lean oil, the overhead is charged to the bottom of another absorber column and another, heavier lean oil, called *sponge oil*, is charged to the top. The overhead is almost all  $C_2^-$ , the bottoms (called *rich oil*), and has all the errant lean oil as shown in figure 7-4. Sponge absorption is very similar to rectified absorption, and sponge oil is typically kerosene range material. The rich oil plus fat oil stream is sent back to where it came from, probably the crude oil distillation column, for separation. But now you know all these colorful names and can toss them around with impunity.

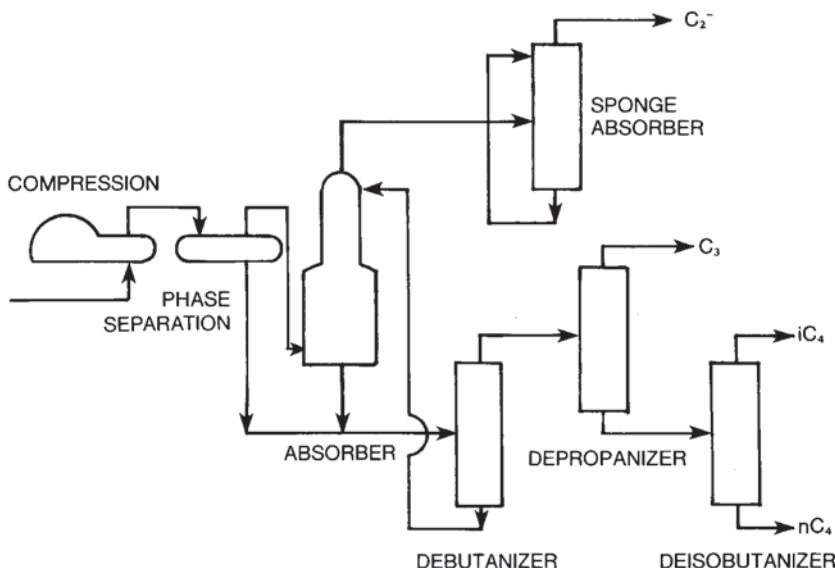


**Fig. 7-4.** Sponge absorption

Ethane is usually not split out in a refinery, since its primary use is refinery fuel. Sometimes, however, the ethane might be needed for feed to a chemical plant. Then the  $C_2^-$  is demethanized in another absorber column, separating the ethane and methane.

Where the propane market is strong, refiners sometimes want to squeeze the last bits of propane out of the  $C_2^-$  stream, the volume that would otherwise be considered tail ends. In that case they might put the  $C_2^-$  stream through another chiller to drop out some more liquid propane to add to the earlier propane stream.

All the main steps are put together in figure 7-5.



**Fig. 7-5.** Sats gas plant

## Cracked Gas Plant

The gas streams from the cat cracker and the other cracking processes contain olefins—ethylene, propylene, and butylenes. Keeping the cracked gases apart from the saturated gases eliminates the extra fractionating that would be required if they were commingled.

Usually ethylene stays with the  $C_2^-$  stream going to the *refinery fuel system*. It could be separated if there were a need for it in the chemical plant. But the propane/propylene and the butane/butylene streams can be separated from the  $C_2^-$  stream and from each other in fractionators much like those in the sats gas plant.

In most refineries, the propylene and butylenes are sent to an *alkylation plant*. For convenience the saturates, propane and butane, are sent along with the propylene and butylenes. The propylene and butylenes undergo reactions to become larger molecules; the propane and butanes do not react. As a result, the alkylation plant serves as the cracked gas plant because it separates out the propane and butane after reacting out the propylene, butylenes, and isobutane to form alkylate. (See chapter 9 to make sense of this.) In a few refineries, the propane/propylene stream or the butane/butylenes stream is sent off to a chemical plant as feedstock. The advent of MTBE plants in refineries also led to separating isobutylene, one of the two MTBE feedstocks, from the other C<sub>4</sub>s. But the demise of MTBE in many countries stopped that.

## Disposition

Why do refiners separate all these streams? Each of the different components has found a unique home in the refining business, and the highest value can usually be attained only when the stream is separated for disposition to this use.

**Isobutane.** This stream is used predominantly as one of the feedstocks to the alkylation process and is occasionally used as a motor gasoline blending component. In those areas of the world where MTBE is still acceptable, isobutane can be made into isobutylene in a dehydrogenation unit on the way to making MTBE.

**Normal butane.** This stream is used predominantly as a motor gasoline blending component. Due to its volatility, it is good for starting cold engines, but the rate at which it evaporates limits the amount that can be added. Some normal butane is also used as a chemical feedstock, as LPG mixed with propane, and as feed to a butane isomerization plant where it is converted to isobutane (chapter 12).

**Propane.** In the United States, most LPG (liquefied petroleum gas) is propane. About 10% of the LPG sales are butane or butane/propane mixes. Propane as a fuel has some unique characteristics that have found favor in many applications. It can be liquefied at reasonable temperatures and pressures for ease of transport, particularly in trucks. Yet at ambient temperatures, it will readily vaporize, making it easy to burn in stoves and home furnaces with no fuel pump and therefore no electricity. Propane has also widely been used as a chemical feedstock for making ethylene and propylene.

**Ethane.** The only application that gives rise to separating ethane in a refinery is its use as a chemical feedstock for making ethylene. (See chapter 19, “Ethylene Plants.”) Otherwise, the ethane is left with the methane and used as refinery fuel.

**Methane.** Refineries have a voracious appetite for fuel. Methane finds a ready home in all the process furnaces and steam boilers around the refinery.

**Hydrogen.** Several refinery processes require hydrogen—hydrocracking and a variety of hydrotreating units. Some of the gas streams, in particular the stream from the reformer, have high enough concentrations of hydrogen to warrant keeping them segregated through the compression stage. Compression then permits separation of a *hydrogen concentrate*, an H<sub>2</sub>/C<sub>1</sub> mix that can be used in the hydrogen applications. A supplementary supply of hydrogen can be specially made if the refinery has a *hydrogen plant*, sometimes called a *steam methane reformer*, which is a subject in chapter 16.

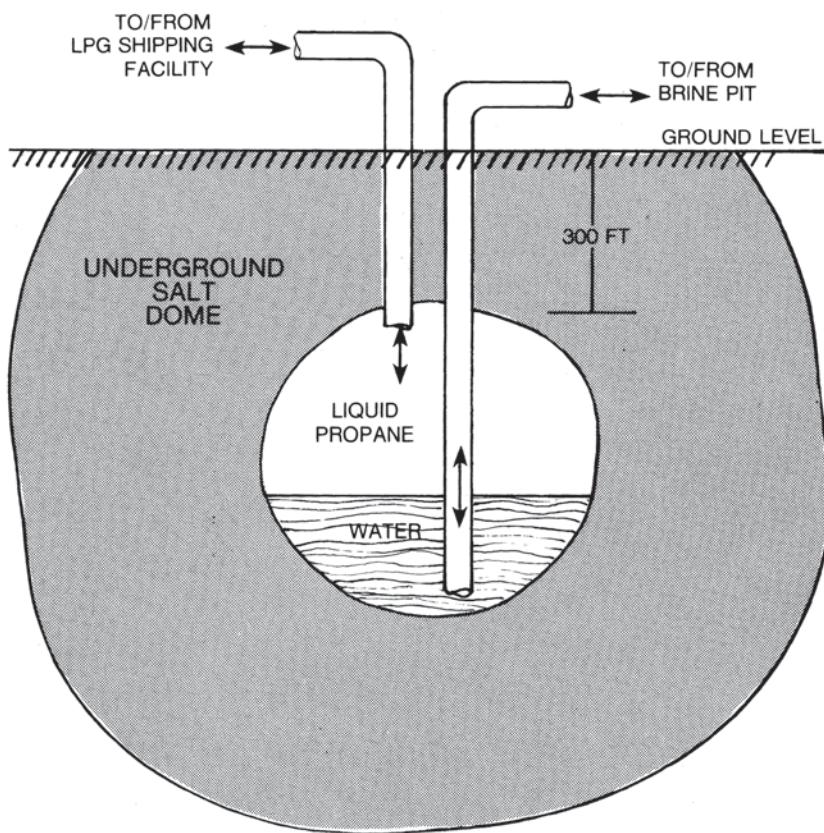
## Storage Facilities

This is a good place to talk about the rather specialized facilities needed to store the gases. Because of the volatility and boiling temperatures of these streams, high pressure containers are needed to store the streams in the liquid form.

Methane and ethane (when not used as chemical feedstock) are rarely ever stored in a refinery but are sent directly to the fuel system as they are produced. There are some *surge drums* in the system that can accumulate some of the gaseous methane for a short period of time during operating changes. Also those *tall flares* so characteristic of refineries are used to handle momentary surges in gas inventories by burning the excess.

Propane and butanes (and sometimes ethane) can be stored in steel storage or in underground storage. The characteristic of the propane and butane storage is the spherical shape. Steel storage is either in the form of *bullets* (cylinders on their sides with rounded ends) or large spheres. The round shape is due to an optimization of the cost of the steel and the structural strength necessary to accommodate the high pressure.

Underground storage generally takes one of two forms: *caverns* mined in rock, shale, or limestone; or *jugs* leached out of salt in underground *salt domes* as shown in figure 7–6.



**Fig. 7-6.** Underground storage for LPG

In the case of mined storage, the propane or butane is pumped in and out of the cavern in the liquid form, with the difference in the amount contained made up by more or less vapor being formed above the liquid.

In a salt dome, the ins and outs are handled in a more unusual fashion. The jug contains a combination of propane and salt water (brine). The two liquids, like any other oil/water combination, do not mix. To get the propane out, more brine is pumped in, forcing the propane out. To fill the jug, propane is pumped in, forcing the brine out, usually to a brine pit on the surface.

One advantage of salt dome storage is its expandability. By pumping fresh water instead of brine, more of the salt from the jug walls is dissolved, expanding the size of the jug at no cost. There is, of course, a practical limit to the size—the jug could get so wide it could collapse or breach the integrity of the salt dome and leak out the edges.

The other advantage is the original construction cost. Salt dome jugs are much cheaper than mined storage, which is much cheaper than steel storage. Unfortunately, nature limits the availability of salt domes, suitable rock, shale, and limestone to only a few areas around the world.

Where they are available, such as along the U.S. Gulf Coast, salt domes are widely used to store all sorts of petroleum and petrochemical products, particularly ethane, propane, butanes, ethylene, propylene, and even crude oil for a country's strategic petroleum reserve.

## Review

The gaseous hydrocarbons, hydrogen, ethane, methane, propane butanes, ethylene, propylene, and butylenes, are separated from each other by a variety of schemes besides fractionators. Compressors liquefy them, rectified absorbers separate them without resorting to ultra-low temperatures, and in the alkylation plant olefins are reacted into larger molecules, making them easier to fractionate them from the other gases.

## Exercises

1. Fill in the blanks:

- a. The two sections of the gas plant are called the \_\_\_\_\_ gas plant and the \_\_\_\_\_ gas plant.
- b. The naphtha used to strip out the heavier gases in the rectified absorber is called \_\_\_\_\_ . The liquids-laden lean oil is called \_\_\_\_\_ .
- c. A stream that can be used to absorb a lot of some parts of another stream is called a \_\_\_\_\_ .

2. Match up the following streams with the usual uses:

<b>Streams</b>	<b>Used in</b>
Methane	
Ethane	Hydrotreating
Propane	Blended to motor gasoline
Normal butane	Refinery fuel
Isobutane	Alkylation feed
Propylene	Chemical feed
Butylenes	Commercial fuel
Ethylene	
Hydrogen	

3. Draw a set of distillation columns that could be used to separate a stream coming from a cat cracker that has ethane, ethylene, propane, propylene, normal butane, isobutane, and butylenes. Use table 7-1 that has the boiling temperatures of each compound. Assume each column has only tops and bottoms, no side draws. What special problem does the butane/butylenes split present?

# 8

## CAT CRACKING

*What cracker is this same that deafs our ears  
With this abundance of superfluous breath?*

—King John, William Shakespeare

In the adolescent years of the petroleum industry, the proportion of the crude oil barrel that consumers wanted in the form of gasoline increased faster than fuel oil. It became apparent to refiners that distilling enough crude to make the straight run gasoline to satisfy the market would result in a glut of fuel oils. That would reverse the situation in the 19th century before automobiles, when they literally dumped gasoline into open pits as they processed enough crude oil to make the fuel oils. The new economy saw increasing prices of gasoline and declining prices of the heavier cuts.

To cope with this physical and economic problem, the inventive process engineers developed a number of cracking techniques, the most popular of which eventually was *cat cracking*.

### The Process

In the chapters on distilling and vacuum flashing distilling, you read about the phenomenon of cracking and you saw a little about the chemistry of cracking in figures 5-1 and 5-2. Here is the process of cracking in a cat cracker: straight run heavy gas oils are contacted with a *catalyst* at elevated temperatures and pressures to promote cracking to smaller, more valuable molecules.

**Definition.** A catalyst is a substance added to a chemical reaction that facilitates or accelerates the reaction; but when the reaction is complete, the

catalyst comes out just like it went in. In other words, the catalyst does not change chemically. It promotes reactions between other chemicals.

Catalysts are like some redheaded 10-year-old boys you know. They never get into trouble; it is just that wherever they go, trouble happens. Catalysts can be liquids, gelatins, or solids, and those solids can be powders, beads, or shaped pieces.

The feed to the cat cracking process is usually straight run heavy gas oil and flasher tops. The boiling range cat feed can be anywhere in the 650°F to 1,100°F range. Heat is required to make the process go; temperatures in the cat cracker where the cracking takes place can be about 900°F or higher, even approaching 1,100°F depending on the catalyst and the results desired. The heat can partly come from preheating the feed in a heat exchanger and always from the hot catalyst that has just gone through a heat-generating chemical reaction to clean it up.

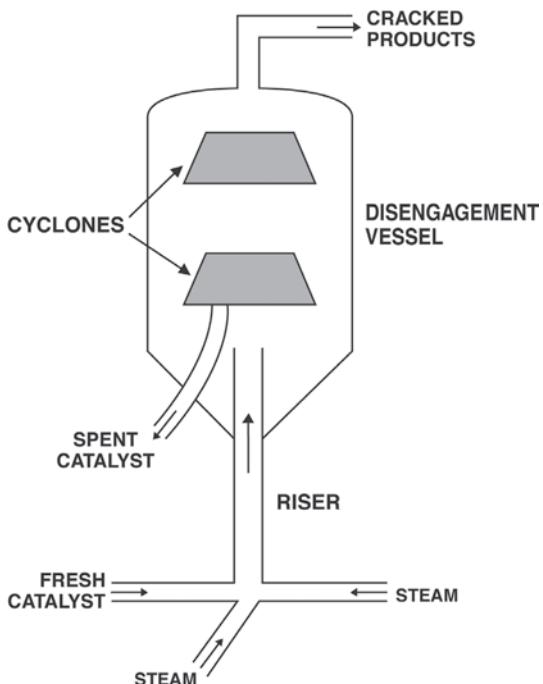
The process is designed to promote cracking in a specific way. The object is to convert the heavy cuts to gasoline. Ideally, all the product coming out of the cat cracker would be in the gasoline range, but the technology is not that good. During the cracking process, lots of phenomena occur:

- As the large molecules crack, there is not enough hydrogen to go around, so some small amounts of carbon form *coke*, which is virtually pure carbon atoms stuck together.
- As the large molecules break up, a full range of smaller molecules from methane on up are formed. Due to the deficiency of hydrogen, many of the molecules are olefins (those double-bonded paraffins).
- Where the large molecules in the feed are made up of several aromatic or naphthalene rings stuck together, smaller aromatic or naphthenic compounds plus some olefins can result.
- Finally, the large molecules, made up of several aromatic or naphthenic rings plus long side chains, are likely to crack where the side chains are attached. The resulting molecules, though lower in carbon count, may be more dense or heavier; that is, their specific gravity is higher and their API gravity is lower. They also tend to have higher boiling temperatures. Ironically these molecules can form a product heavier than the feed.

The products of cat cracking are the full range of hydrocarbons, from methane through to residue, plus coke. Three main parts make up the cat cracking hardware: the reaction section, the regenerator, and the fractionator.

## Reaction Section

The guts of the cat cracker is the reaction section (fig. 8-1), consisting of the cat feed heater and the riser, which is a pipe from ground level up to a water tank-like vessel called a *disengagement chamber*. The heater (not shown in fig. 8-1) raises the temperature of the cat feed to about 700°F. The feed mixes with hot catalyst being fed into the riser, and steam is introduced with the catalyst to give the whole mixture enough lift to climb up to the bottom section of the disengagement chamber. All that raises the temperature to 900°F to 1,100°F, promoting the cracking. Almost all the cracking reactions take place in the riser, even though *residence time* in the riser is only about a second. (In the older cat crackers, the disengagement chamber was called the *reactor* because it was thought that was where most of the cracking took place. The newer crackers use this vessel only to separate the catalyst from the hydrocarbon.)



**Fig. 8-1.** Cat cracker riser and disengagement vessel

As the hydrocarbon/catalyst mixture hits the disengagement chamber, it encounters a *cyclone*, a mechanical device that spins the mixture. The catalyst being heavier, the centrifugal motion slaps it against the walls of

the cyclone, where it slides to the bottom and out the piping, exiting the disengagement chamber via gravity. The hydrocarbon, mostly in vapor form but with some liquid droplets, rises from the cyclone to the top of the chamber, encounters another cyclone that does a final catalyst separation, and then exits the top.

Refiners had a purpose in switching to a design where all the reactions take place in the riser instead of in the reactor—to lengthen the contact time between the feed and the catalyst. However, on some *riser crackers*, as the new vintage of CCUs is sometimes called, the hardware is set up to allow some feed to be introduced further up the riser to reduce the contact time. That allows refiners to segregate the feed from different crudes, since feeds with different compositions often respond to the catalysts at different rates.

## Catalysts

The catalyst used in modern cat crackers is a marvel of evolution. It used to be made of natural alumina-based clay, but now refiners buy only the much-improved synthetically produced cat cracking catalysts called *zeolytes*. The particles have three unusual characteristics. If you had a jar of cat cracker catalyst and shook or tilted it, the powder, which looks like off-white baby powder, would slosh around just like a fluid. This behavior, so important to the design of the whole process, gave rise to another name refiners often use, *fluid cat cracking*.

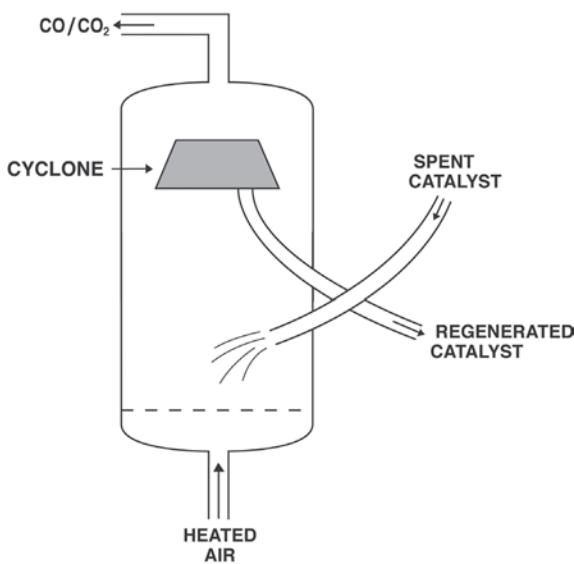
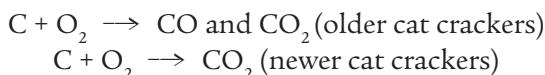
The second characteristic is not apparent to the naked eye. Using an electronic microscope, you would be able to see that each catalyst particle has a large number of pores and, as a consequence, a tremendous *surface area*, especially in relation to the size of the particle. If the particles were the size of the planet Earth, the pores would be deeper than the Grand Canyon and spaced every few miles or so over the surface. The influence of the catalyst depends on contact with the cat feed, so the huge surface area is vital to the process.

The third characteristic in the modern cat cracker catalysts comes from technology leaps. The old alumina-based clay catalyst already had the minerals necessary to promote the cracking reactions. Nowadays the catalysts are synthesized to exacting dimension and mineral content. The pores are designed and fabricated so minutely that they will let in just one molecule at a time, and only molecules of a certain size, at that. That way the types of molecules that are catalyzed can be controlled and refiners can end up with designer outturns (well, almost). The catalyst suppliers can

furnish refiners with catalysts that will favor (but not deliver 100%) the creation of high octane gasoline components or, perhaps, the light olefins (propylene and butylenes). Other catalysts are designed to permit the use of heavier feeds, or not to create so much coke, or to reduce the temperature of the reaction to save energy, and so on.

## The Regenerator

During the cracking process, some portion of hydrocarbon cracks all the way to coke and ends up as a deposit on the catalyst. As the catalyst surface is covered up, the catalyst becomes inactive (or *spent*), which reduces its effectiveness. To remove the carbon, the spent catalyst flows by gravity to a vessel called a regenerator (fig. 8-2). Heated air, about 1,100°F, is mixed with the spent catalyst, and a chemical reaction takes place that removes the coke from the catalyst:



**Fig. 8-2.** Catalyst regeneration

This process, *oxidation of coke*, is similar to burning coal or briquettes in that carbon unites with oxygen and gives off carbon dioxide ( $\text{CO}_2$ ),

perhaps carbon monoxide (CO), and a large amount of heat. Part of the heat transfers to the catalyst, which leaves the regenerator as hot *regenerated catalyst*, en route to the riser. The rest leaves as hot CO<sub>2</sub>, which can be used as source for heating the feed or elsewhere. In the older cat crackers, the CO/CO<sub>2</sub> is sent to a CO furnace, where oxidation of the rest of the CO to CO<sub>2</sub> is completed.

The regenerator has its own cyclone at the top that separates the catalyst from the CO/CO<sub>2</sub>. The regenerated catalyst flows from the cyclone, again by gravity, out of the regenerator, ready to be mixed with cat feed and steam and sent up the riser once more. Thus the catalyst is in continuous motion going through the cracking/regeneration cycle.

### **What Is Burning?**

*Burning almost anything has a simple formula. Take natural gas, for example:*



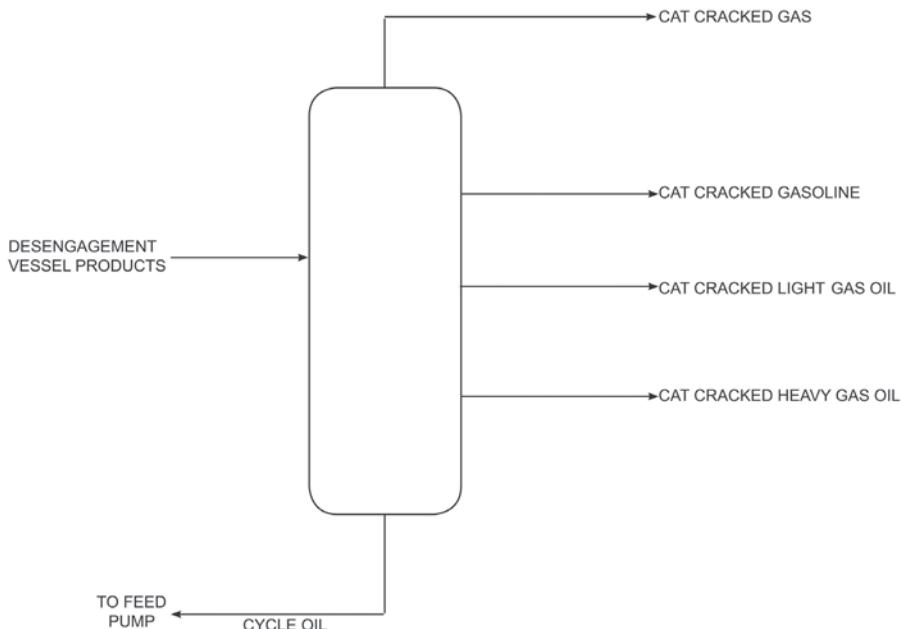
*This chemical reaction gives off heat—it is exothermic. (See chapter 22 to learn how much heat is given off.) More complicated molecules than methane, such as coal, wood, trash, or gasoline, have the same result: the formation of carbon and water and the generation of heat.*

*Elements besides carbon and hydrogen can result in ash or smoke. Also some of the carbon may not completely combust and may appear as smoke. If there is insufficient oxygen around, carbon monoxide (CO) may form in addition to the carbon dioxide. The CO can subsequently be further oxidized to CO<sub>2</sub> to give off more heat.*

Small amounts of brand new, fresh catalyst are continually added. Some of the circulating catalyst will have ended not on the catalyst side of the cat cracker but as catalyst fines in the bottom of the cat cracker fractionator. Also some escapes with the CO<sub>2</sub> stream. In addition, some crude oils have metals in them that deactivate some catalyst particles, which then need replacement.

## The Fractionator

Meanwhile, back on the hydrocarbon side, when the cracked product leaves the disengagement vessel, it is charged to a fractionating column (fig. 8–3) dedicated to the cat cracker products. The products separated generally are the gases ( $C_4$  and lighter), cat-cracked gasoline, cat-cracked gas oil, and the fractionator bottoms, called *slurry oil* because it contains some of the catalyst that did not get caught by the cyclones. A variety of things can be done with the slurry oil, but the most popular is to mix it with the fresh cat feed and run it through the reaction again. Some of the slurry oil may crack each time through the reactor. By recycling enough, all the slurry oil may be made to disappear. The process has the ominous designation *recycling to extinction*. Sometimes the most stubborn molecules just keep going around in a circle with no further cracking, so a small amount of cycle oil can be drawn off continuously.



**Fig 8–3.** Fractionation

After sitting in a settling tank where the catalyst settles to the bottom, the *clarified slurry oil* can be blended off to heavy fuel oil.

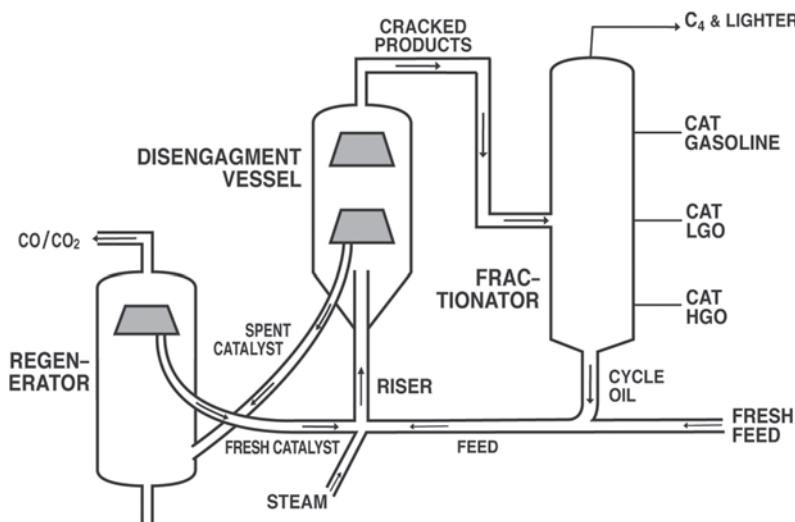
The cat-cracked gas oil may be separated into light and heavy gas oil. Both are sometimes called cycle oil (light cycle oil, heavy cycle oil). In the past both have sometimes been recycled to the reaction section also. Nowadays most refiners send the gas oil streams elsewhere. The cat-cracked heavy gas oil can be used as feed to a hydrocracker or as a residual fuel component. The light gas oil makes a good blending stock for distillate fuel (but not diesel fuel). The cat-cracked gasoline is a good motor gasoline blending component.

There is quite a bit of latitude in the cut point between the gasoline and light gas oil stream. Refiners use this as one way to regulate the balance between gasoline and distillate as the seasons change. As the winter heating oil season comes on, many refineries go into a *max distillate mode*. They make adjustments to the CCU fractionator to lower the end point of the cat-cracked gasoline to push more volume into the cat light gas oil. In the summer, during a *max gasoline mode*, the shift is in the other direction.

The products from the fractionator are different in composition than those from the crude distilling column light ends. The cracking process results in the creation of olefins, so the C<sub>4</sub> and lighter stream contains not only the four paraffins (methane, ethane, propane, and butanes) but also ethylene, propylene, and butylenes. Because of these extra components, this stream is sent to be separated at the *cracked gas plant*. This is in contrast to the gas from operations like distilling (and, as discussed later, the hydrotreater, hydrocracker, reformer, and others), where the gases contain only saturated compounds. These end up in the *sats gas plant* for separation. The isobutane, propylene, and butylenes from the cat cracker will be of special interest when discussing alkylation, a process that converts these compounds into gasoline blending components.

The other heavier products also differ in composition. During the cracking process, many of the heavy, complex molecules will crack at the connection between the aromatics rings and the side chains. Consequently, the cat cracker products tend to be rich in aromatics, the molecules replete with benzene rings somewhere in their structure. That is good news for boosting octane numbers and making gasoline, but as you will find out later, bad news for making jet fuel and diesel fuel.

All pieces fit together as shown in figure 8-4. You can see there are two circular flows going on. On the left side, the catalyst goes through the reaction, is regenerated, and gets charged back to the reaction again. On the right side, hydrocarbon comes in and goes out, but the slurry oil provides continuous circulation of at least some of the hydrocarbon components.



**Fig. 8-4.** Cat cracking unit

## Yields

The object of the cat cracking process is to convert heavy gas oil to gasoline and lighter yields. A set of typical yields will demonstrate how successful the process is.

**Table 8-1**

<b>% Volume</b>		
Feed:	Heavy Gas Oil	40.0
	Flasher Tops	60.0
	Cycle Oil	<u>(10.0)*</u>
		100.0
Yield:	Coke	8.0
	C <sub>4</sub> and Lighter	35.0
	Cat-cracked Gasoline	55.0
	Cat-cracked Light Gas Oil	12.0
	Cat-cracked Heavy Gas Oil	8.0
	Cycle Oil	<u>(10.0)*</u>
		118.0

\*Recycle stream not included in feed or yields total.

Since the cycle oil is recycled to extinction, a simple diagram for cat cracking does not even show it as entering or leaving the process. Something more important does show up, however: the phenomenon of *gain*. In the yield structure shown above, the products coming out add up to 118% of the feed going in. That has nothing to do with the recycle stream but only with the gravities of the products coming out compared to the gravities of the feeds. If you measured the yields in percent weight instead of percent volume, the yields would come out to 100%. But since most U.S. petroleum products are sold by the gallon, U.S. refiners measure everything in volume. And since cracking plays games with the densities, cat cracking yields show a substantial gain. Gain is the bane of the accountants but sometimes becomes an obsession with refiners as they attempt to “fluff up the barrel” with their cracking processes.

## Process Variables

Cat crackers usually make so much money by converting heavy feed to light products that refiners almost always try to run them to their capacity. The limit could be set by *coke burning capacity* (the rate at which the catalyst is regenerated), by feed rate, or by fractionator capacity, if the reaction makes too much of one of the products. The bottlenecks become apparent when the yields of gasoline fall off and either heavy gas oil or C<sub>4</sub> and lighter yields start to increase. Some of the things that affect cat cracker yields are the quality of the feed, the reaction temperatures, the feed rate, the recycle rate, and, incredibly enough, the time of day and temperature outside the control room, as explained below.

**Feed quality.** The cracking reaction is very complex, and lots of data are available to predict yields from feed with different characteristics. The gravity of the feed and the paraffin, naphthene, and aromatic contents are important indicators.

**Reaction temperature.** The higher the temperature, the more cracking will occur; but at some point, the generation of C<sub>4</sub> and lighter gases will really take off, at the expense of the cat gasoline or cat light gas oil.

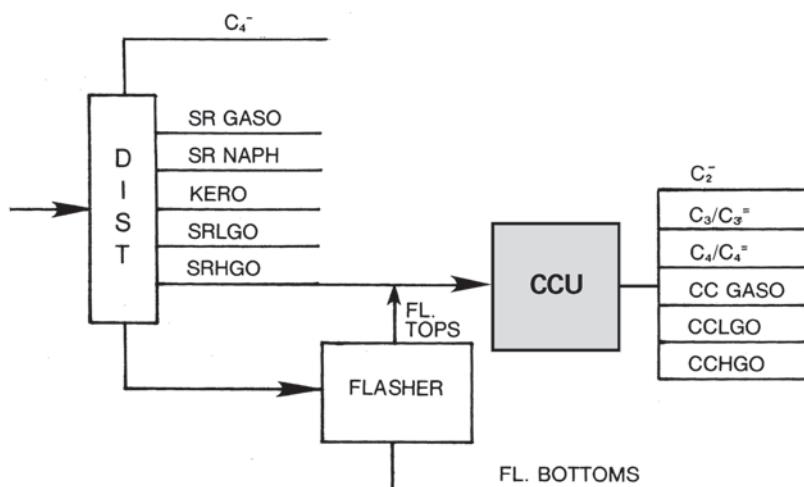
**Feed rate and recycle rate.** The yields will suffer at higher feed rates since the contact with the catalyst will be diluted. So refiners watch the *fresh feed rate* and the volume of fractionator bottoms being recycled.

**Time of day and temperature.** Cat crackers have better yields at night than during the day. Are the swing shift and graveyard shift operators better? Do tinkering engineers come around only during the day and mess things

up? Not really; in order to regenerate the spent catalyst, fresh air is heated and blown into the regenerator continuously. As the temperature of the air outside goes down, the air gets denser. Since the blowers that pump the air are always operated at maximum speed, more oxygen is actually pumped into the regenerator when it is cold than when it is hot. The more oxygen, the more coke is burned off the catalyst. The fresher the catalyst, the better the reaction; the better the reaction, the more gasoline is produced. From the operator's data logs, the swings can actually be plotted, and as night comes and the temperature drops, the yield gets better. With the heat of the afternoon, the yield falls off. Summer and winter have the same effects, which is too bad because usually the demands for gasoline go up in the summer when the yields go down.

## Review

From a process point of view, you can sketch the cat cracker as a feed-in/product-out box in a refinery flow diagram. Thus far, you have covered distilling, flashing, and cat cracking. Figure 8-5 shows the way these come together. This diagram uses the shorthand notation that will be used in building the entire refinery flow diagram from here on.



**Fig. 8-5.** Refinery flows with a cat cracker

## Exercises

1. What is the difference between a cat cracker, a fluid cat cracker, and a riser cracker?
2. Fill in the blanks:
  - a. There are two circulating flows in a fluid cat cracker. On the one side is \_\_\_\_\_; on the other is \_\_\_\_\_.
  - b. Spent catalyst has \_\_\_\_\_ deposited on it. The regeneration process removes it by reacting it with \_\_\_\_\_ to form \_\_\_\_\_ and \_\_\_\_\_.
  - c. The purpose of cat cracking is to convert \_\_\_\_\_ to \_\_\_\_\_.
  - d. Cat cracker feed usually comes from the \_\_\_\_\_ and the \_\_\_\_\_.
  - e. \_\_\_\_\_ are found in the cracked gas stream but not in the sats gas streams.
  - f. The cat cracker fractionator bottoms, called \_\_\_\_\_, are usually \_\_\_\_\_ by injecting them in the feed.
3. Use the data and answers from the previous chapters and the cat cracker yields from this chapter. Assume feeds to the cat cracker are all the flasher tops and all the straight run heavy gas oil (the cut between the straight run light gas oil and flasher feed). How much cat light gas oil is produced?
4. An indicator of how complicated refining operations can get is the number of alternatives to make a downstream volume change. Name six ways to increase the volume of cat light gas oil.

# 9 ALKYLATION

*Yield who will to their separation,  
My object in living is to unite.*

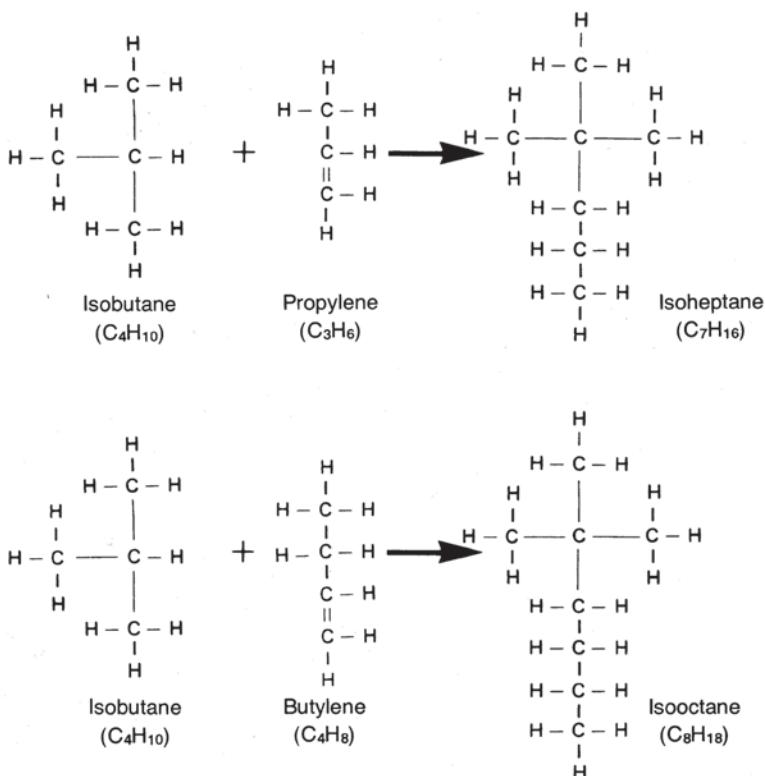
—“Two Tramps in Mud Time,” Robert Frost

After the engineers were so clever about the invention of cat cracking, they attacked the problem of all the light ends the process created. The objective was to maximize the volume of gasoline being produced, but butylenes and propylene were too volatile and plentiful to stay dissolved in the gasoline blends. So they devised a process that was the inverse of cracking, *alkylation*, which starts with small molecules and ends up with larger ones.

## The Chemical Reaction

To a chemist, alkylation covers a broad range of reactions that stick molecules together when one of them is a paraffin (*alkane*). But to a refiner, alkylation is the reaction of propylene or butylene with isobutane to form an isoparaffin called an alkylate (fig. 9-1).

Under ideal conditions, alkylate would consist of isoheptane and isooctane, two excellent, high octane gasoline blending components. Propylene and butylenes are so reactive, however, that other, not-so-high-octane components in the gasoline range form as by-products. But not enough are formed to undermine the attractiveness of an alky plant.



**Fig. 9-1.** Alkylation of propylene and butylene

Alkylation has a volumetric effect on refining operations that is the inverse of cracking because there is a significant amount of *shrinkage*. With propylene as the feed, 1 bbl of propylene and 1.6 bbl of isobutane go in, and 2.1 bbl of product come out; 1 bbl of butylene and 1.21 bbl of isobutane yield 1.8 bbl of product. As in cracking, the weight in equals the weight out. Nothing gets lost. Only the densities and volumes change.

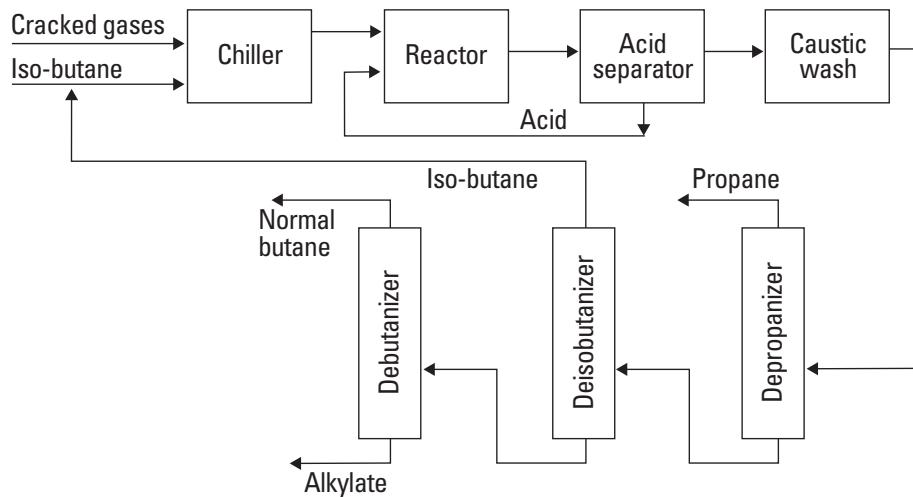
## The Process

Propylene and butylenes are hyper enough that the chemical reaction could be made to take place by just subjecting the isobutane and olefins to high pressures. But the equipment would be very expensive to handle this route to alkylation. Like a lot of other processes, catalysts have been developed to facilitate the process and simplify the hardware. Alkylation plants use either sulfuric acid or hydrofluoric acid as catalyst. In this case

the catalyst is liquid, in contrast to the solids in cat cracking. The processes using both catalysts are basically the same. Those plants that use hydrofluoric acid are called HF plants; the others are called sulfuric plants. Both have safety concerns because hydrofluoric and sulfuric acids are seriously nasty items, corroding all but specially lined vessels and piping around them. Hydrofluoric has an additional concern. If it escapes, it floats in a cloud and can travel great distances, to the annoyance of refinery neighbors. Sulfuric acid will form droplets if it escapes and quickly settles down to the ground, though that is not much consolation to anyone working in the immediate vicinity.

Sulfuric plants work better for butylene alkylation; HF plants are better for propylene. Sulfuric acid seems to be slightly more popular, so this chapter describes only the sulfuric route. However, the HF route to alkylation is not much different.

The *alky plant* consists of seven main parts: the chiller, the reactors, the acid separator, the caustic wash, and three distilling columns, all shown in figure 9–2.



**Fig. 9–2.** Alkylation plant flows

**The chiller.** Alkylation with sulfuric acid catalysts works best at temperatures in the neighborhood of about 40°F. The olefin feed, a propane/propylene and/or butane/butylene stream comes from the cat cracker, thermal cracker, or coker, but not the hydrocracker, which makes no olefins. The stream is mixed with isobutane and sulfuric acid and pumped through a chiller. The pressure is high enough to keep the mixture in liquid form. Sometimes the chilling is done right in the reactor.

**The reactors.** The reaction time for the alkylation process is relatively long, so the mixture is pumped through a large reactor. The reactors hold so much total volume that by the time the contents turn over once, the *residence time* of any one molecule is quite long, about 20 to 25 minutes. As the liquid passes through the reactors, it encounters mixers to assure that the olefins come in good contact with the isobutane and the acid catalyst, promoting the reaction.

**Acid separator.** The mixture then moves to the *acid settler*. The acid and hydrocarbons separate like oil and water. The hydrocarbon is drawn off the top; the acid is drawn off the bottom. The acid is then recycled back to the feed side.

**Caustic wash.** The hydrocarbon from the acid separator will have some traces of acid in it, so it is treated with *caustic soda* in a vessel. Caustic soda does to the hydrocarbon what Alka-Seltzer does to your stomach when you have indigestion—it neutralizes the acid. What is left (in the alky plant, not your stomach) is a mixture of hydrocarbons and some salts from the caustic treating, ready to be separated.

**Fractionators.** Three standard fractionators separate the alkylate and the saturated gases. Any unreacted isobutane is recycled to the feed.

## Yields

During the alkylation process, a number of *side reactions* occur, some of which are more or less undesirable. Because there are a lot of molecules forming and reacting, there are small amounts of propane, butane, and pentane formed, which are not too bad; but a small amount of *tar* forms, as well as a thick, brownish oil containing a mixture of complex hydrocarbons. The molecules are so heavy they usually build up in the acid and exit the scene when the acid is sent back to the supplier for regeneration.

The volumetric balances for propylene and butylene feed are as follows:

**Table 9-1**

	Volume Balances	
	Propylene	Butylene
<i>Feeds</i>		
Propylene	1.0	—
Butylene	—	1.0
Isobutane	1.6 — 2.6	1.2 — 2.2
<i>Products</i>		
Propane	0.3	
Normal Butane	—	0.1
Alkylate	1.8 — 2.1	1.7 — 1.8

What the feeds and the yields do not show is the propane and normal butane that just pass through the plant untouched. As a matter of fact, the alky plant provides significant capacity to the refinery for making segregated propane and butane streams. The reactors take out the propylene and butylene, converting it to alkylate. The fractionators separate the propane, butane, and unreacted isobutane from the alkylate. When the alky plant is down for one reason or another, the butane/butylene stream might find another home in gasoline blending. The propane/propylene stream is too volatile to put in gasoline, so it is usually routed to the refinery fuel system instead, and LPG production (propane only) drops significantly.

## Process Variables

The alky plant manager has to watch a number of key variables to keep too many side reactions from occurring that could cause the quality of the alkylate to deteriorate, as evidenced by such things as lower octane number, poor color, and high vapor pressure.

**Reaction temperature.** Temperatures too low cause the sulfuric acid to get syrupy. That inhibits complete mixing and the olefins do not completely react. High temperatures cause compounds other than isoheptane and isoocetane to occur, lowering the alkylate quality.

**Acid strength.** As the acid circulates through the process, it gets diluted with water that inevitably comes in with the olefins, and it also picks up tar. As the acid concentration goes from 99% down to about 89%, it is drawn off and sent back to the acid supplier for fortifying.

**Isobutane concentration.** Propylene and butylenes are very reactive, particularly in the presence of the acid catalyst. They will react with each other as well as with isobutane. For that reason, excess isobutane is mixed in, as much as 10 times the amount needed for the reaction. That way the propylene and butylenes are 10 times as likely to react with isobutane as with each other.

**Olefin space velocity.** The length of time the fresh olefin feed resides in the reactor causes alkylate quality to vary.

## Poly Plants

Some refineries do not have enough isobutane to alkylate all their propylene and butylenes. They may choose to put all the butylenes in an alky plant, utilizing what isobutane they have. Then they build a polymerization plant for the propylene.

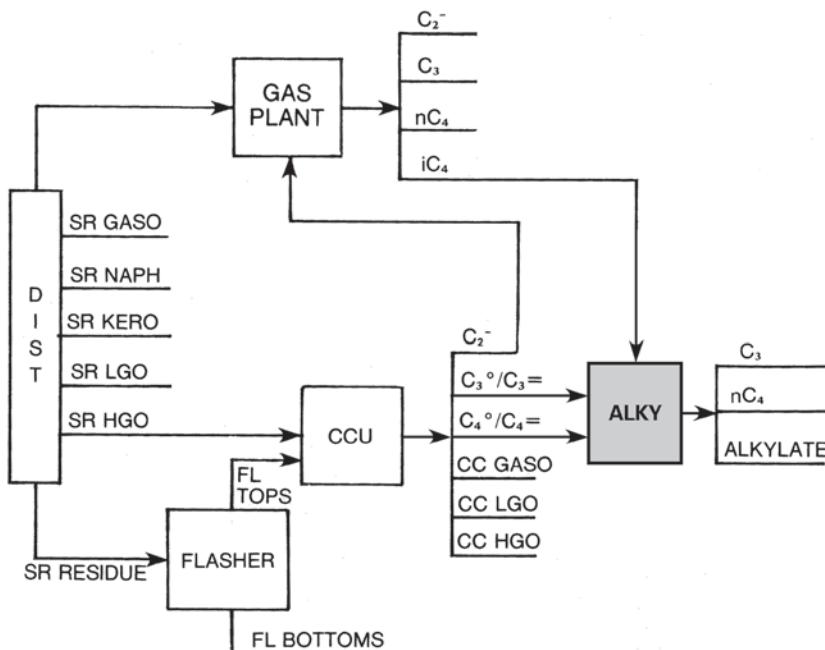
A poly plant, sometimes called a *dimer* plant, is a poor man's alky plant. Propylene is reacted, not with isobutane but with itself, to form isohexene,  $C_6H_{12}$ , or  $C_6^+$ , also called *dimate*. This olefin (with a double bond and a branch) will fit nicely into the gasoline blending pool. It does not have the octane number of propylene alkylate (88 versus 92), but it does make a home for the otherwise refinery fuel-value propylene.

In one version of the process similar to alkylation, the catalyst is phosphoric acid. In another version, the dimersol process, a liquid catalyst based on nickel carboxylate/ethyl aluminum dichloride does the job. There are only a few of these plants operating. In both versions the propane passes through the process and is separated from the dimate at the end by distillation.

## Review

Alkylate has emerged as a hero in the past few years as refiners struggle to improve the environmental qualities of gasoline and still maintain octane number levels. Since you have not gotten to chapter 12 on gasoline blending yet, you may not fully appreciate the attributes of alkylate. It has a low vapor pressure, zero sulfur, zero olefin content, zero benzene, and a high octane number—a blender's dream. And all this comes from working with some otherwise low-valued cats and dogs around the refinery—propylene, butylene, and isobutane.

In the big refining picture the alky plant can be represented by a box with propylene, butylene, and isobutane in, along with propane and normal butane, and alkylate out, along with the propane and normal butane. To put alkylation in perspective, figure 9–3 shows the refinery processing units covered so far, plus alkylation. How complicated it quickly gets!



**Fig. 9–3.** Refinery flows with an alkylation plant

## Exercises

1. Fill in the blanks.

- a. Alkylation is the inverse of \_\_\_\_\_.
- b. The catalyst in alkylation is either \_\_\_\_\_ or \_\_\_\_\_, depending on the process chosen.
- c. The five main parts of an alky plant are: \_\_\_\_\_, \_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_.
- d. Alkylate is made up mostly of two isoparaffins, \_\_\_\_\_ and \_\_\_\_\_.
- e. Because of the high \_\_\_\_\_, low \_\_\_\_\_, and zero \_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_ content, alkylate makes an ideal \_\_\_\_\_.

2. The cracked gas stream coming to an alky plant has the following composition:

	Volume
Propane	0.15
Propylene	0.25
Isobutane	0.10
Normal butane	0.20
Butylenes	0.30
	1.00

If the volume is 3,000 B/D and the alky plant yields are those shown in this chapter, how much isobutane is needed from the sats gas plant to convert all the propylene and butylenes to alkylate? What are the alky plant outturns?

# 10

## CATALYTIC REFORMING

*Nothing so needs reforming as other people's habits.*

—Pudd'nhead Wilson, Mark Twain

Cat reforming has provided more controversy in the refining business than all the other units combined. What started out as an engineering solution to market needs ended up in the middle of debates between refiners and environmental protectors.

### The History

The tortuous history began when refiners created cat reformers as a method of raising both the volume and quality of gasoline. In the first half of the 20th century, the demand for gasoline grew at twice the rate of fuels oils. Coupled to that, the specifications of the gasoline that car manufacturers designed into their vehicles increased incessantly. America built four- and six-lane highways across the continent, and consumers moved beyond Henry Ford's Model T to big, fat comfortable passenger cars. The engines in them needed cheap, higher octane gasoline.

As the refiners scrounged around their refineries looking for suitable blending components, they found heavy naphtha that was being left in kerosene. Catalytic reforming could upgrade the quality of these naphthas, some with octane numbers in the range of 35 to 40, to as much as 90 octane, increasing the quality and quantity of the gasoline making capacity at the same time.

**The Golden Years.** In 1949 UOP introduced a novel plant design and a catalyst that has endured since. They arrived just in time for the so-called

Golden Years, the quarter century following World War II of sustained 7% economic growth in the United States. Throughout this period, refiners found themselves in an *octane race*, competing by advertising gasoline with ever-higher octane numbers. The gas pump with 100 octane premium gasoline seemed hydrocarbon's Holy Grail. As a way to manage the truth in advertising, more refiners built new and improved cat reformers, boosting the quality of their gasoline even further.

**The environment.** In the 1970s, enough concern about the environment reached the public agenda that governments began requiring refiners to reduce the amount of lead they put in gasoline. For decades, refiners had exploited the mysterious fact that the addition of tiny amounts of tetraethyl lead could substantially increase the gasoline octane. They had always known that the lead compounds spewing from the tailpipes were toxic, but in the mid-1970s the government published a schedule to phase out over 10 years the already-restricted amount of lead allowed. Refiners built new cat reformers, debottlenecked old ones, and introduced tweaked versions of catalysts into their existing ones to increase the amount of aromatics, which were high octane gasoline blending components.

Beddour's law came into effect as lead phased out in the 1980s and the benzene content of gasoline became a big issue. (Dr. Robert F. Beddour, professor of chemistry at the University of Texas, once said, "You cannot eliminate a pollutant without creating another one.") By then benzene was well-known as a carcinogen, and even the few percent that came primarily from the cat reformers became the focus of concern and eventually phase-down regulation. Once again the refiners went to work to change the feeds and modify the catalysts in the reformer to eliminate this pollutant, replacing it with some other benign, albeit mutated (cat-reformed) molecules. Complicating the effort were the limits put on the total aromatics content, since these compounds, with the characteristic benzene ring imbedded in them, were suspect as well.

**The by-product workhorse.** Coincidentally, throughout the evolution of cat reforming, refiners became increasingly aware that one of the reformer by-products, hydrogen, emerged as an essential workhorse in the refinery. They increasingly used hydrogen in hydrotreaters to help remove sulfur and other contaminants from various dirty streams and to change the structure of some others. And even more, hydrocrackers had become a black hole for hydrogen. When a cat reformer shuts down for maintenance or has an emergency shutdown, major parts of the refinery are affected by the shortage of hydrogen and have to shut down as well.

## The Chemical Reactions

You may want to use that figurative finger stuck in chapter 6 that covered chemistry to move through this chapter without getting too lost.

Unlike some of the previous processes discussed, the boiling range of the feed to a cat reformer differs very little from the product of a catalytic reformer. What does change is the chemical composition.

Refiners originally designed the cat reformer to run on straight run naphtha. Naphtha from hydrocracking can also benefit from the changes that take place in the cat reformer. These naphtha streams typically have a high concentration of normal paraffins and naphthenes. The cat reformer causes many of these components to be *reformed* into isoparaffins and aromatics that have much higher octane numbers.

Table 10–1 shows a typical cat reforming material balance.

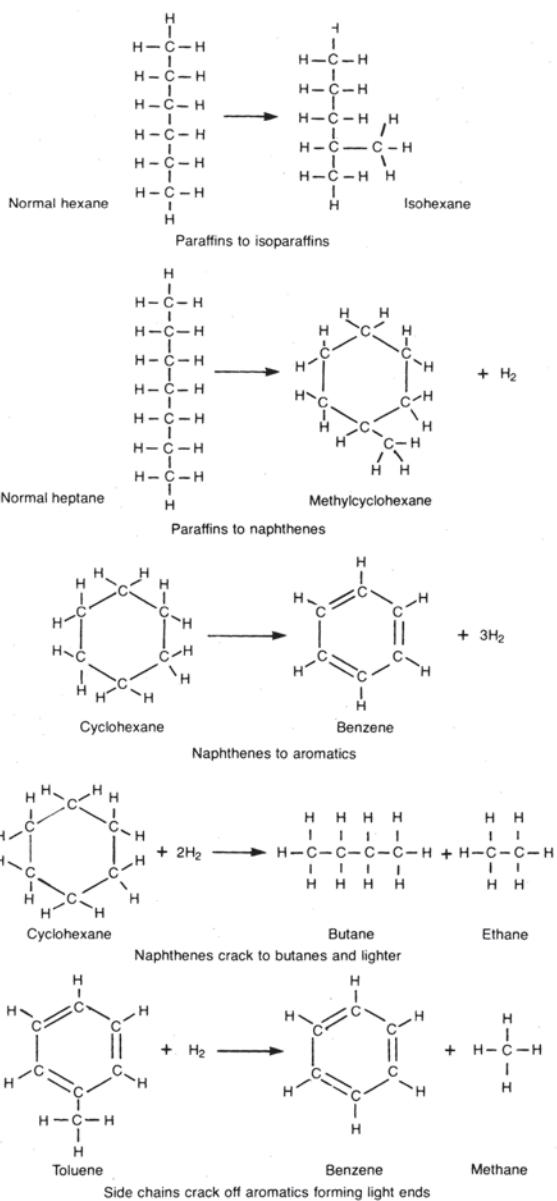
**Table 10–1.** Reformer material balance

	% Volume	
	Feed	Product
Paraffins	45	20
Isoparaffins	5	15
Olefins	0	0
Naphthenes	40	10
Aromatics	10	53
Hydrogen	0	2

Examples of the good reactions, shown in figure 10–1, that take place in the cat reforming process are mainly the following:

- Paraffins are converted to isoparaffins.
- Paraffins are converted to naphthenes, releasing hydrogen.
- Naphthenes are converted to aromatics, releasing hydrogen.

Why are these good? Because isoparaffins and naphthenes have much higher octane numbers than normal paraffins, and aromatics have much higher octane numbers than naphthenes.



**Fig. 10-1.** Reformer reaction

And some not-so-good reactions, from an octane point of view, also take place:

- Some of the paraffins and naphthenes crack and form butanes and lighter gases.
- Some of the side chains get broken off the naphthenes and aromatics and form butanes and lighter gases.

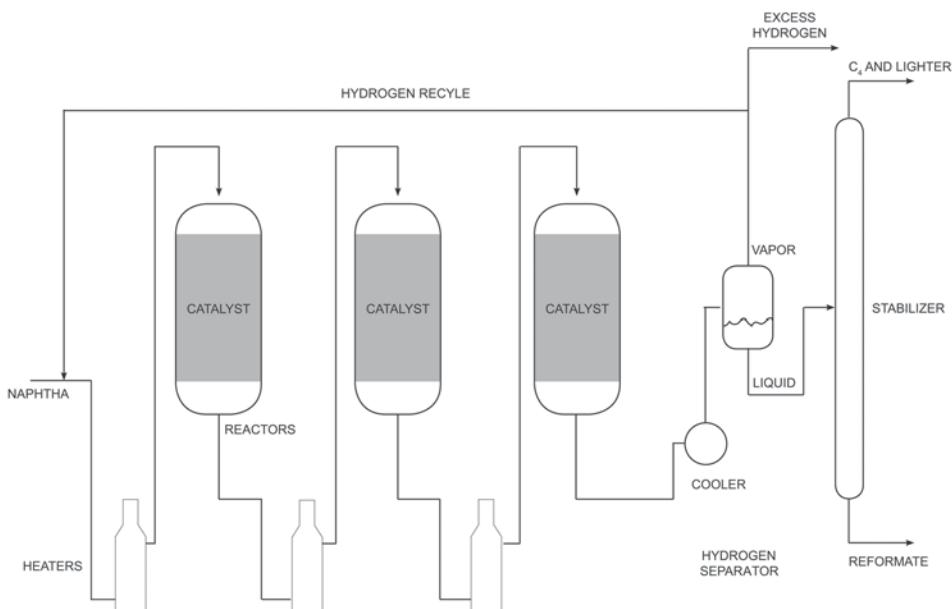
Both these results deteriorate the quality of the naphtha by forming gases that cannot be blended into gasoline.

The important thing to remember is *paraffins and naphthenes get converted to aromatics and isomers*, as shown in the reactions in figure 10–1. Of course naphthas from different crude oils vary considerably in PNA composition, and therefore so does the effectiveness of the cat reformer in raising octane numbers.

## The Hardware

You might expect some unusual hardware would be required to cause these complicated reactions to take place. On the contrary, what is needed is an unusual catalyst, and in this case it is made of platinum, and sometimes rhenium or palladium. Sometimes chlorine is present and acts as a *promoter*, something that enhances the ability of a catalyst to perform. The platinum is present in no small amounts (millions of dollars' worth in one process unit), so great care is taken to keep track of it. The platinum is the key ingredient that does the wonderful job of causing paraffins to wrap themselves around in circles and to lose their extra hydrogens and to poke side chains out where none existed before. For that reason, cat reformers are sometimes called *platformers*, and their product, *reformate*, is sometimes called *platformate*.

There are two basic ways of putting the naphtha molecules in contact with the catalyst. In the *fixed bed* design in figure 10–2, naphtha is dribbled through the catalyst, which stays put in a vessel, or actually several vessels that are used in series. The other, more recent design has the catalyst in constant motion, like in a cat cracker, merging with and then separating from the naphtha for regeneration.



**Fig 10–2.** Semi-regenerating cat reformer

## Semiregenerative Cat Reformers

The reforming reactions are *endothermic*—they need to absorb heat. For that reason, semiregenerative or fixed bed cat reformers typically have at least three reactors, with furnaces to heat or reheat the naphtha to the proper reaction temperature in front of each one. The reactors typically operate at 40 psia to 100 psia pressure and about 500°F.

The naphtha feed is pressurized, heated in a furnace, and charged to the top of the first reactor, through the catalyst and out the bottom. This process repeats in the next two reactors. The product then runs through a cooler where most of it is liquefied. The purpose of the liquefaction at this point is to permit separation of the hydrogen-rich gas stream for recycling. This process is important enough to warrant a few sentences.

Look back at the chemical reactions in figure 10–1. The ones that create cyclopes and aromatics result in the production of extra hydrogen because aromatics do not need as many hydrogens as naphthenes and paraffins. But reforming is also a modest user of hydrogen in the reactors. In the chaos that takes place in the reformer, some miscellaneous carbon atoms crack off bigger molecules. To keep the carbon from depositing on the catalyst as

it does in cat cracking, excess hydrogen is kept in the reactor. The carbon reacts with the hydrogen and forms methane and ethane.

Meanwhile downstream of the reactors at the hydrogen separators, part of the hydrogen stream is recycled to the feed, while the other part is sent to the gas plant. The liquid product from the bottom of the separator is sent to a fractionator called a *stabilizer*, a column that is nothing more than a debutanizer. Most of the reactor product comes out the bottom as reformate; butanes and lighter go overhead and head towards the sats gas plant.

## Regeneration

As the process proceeds, some carbon in the form of coke inevitably deposits on the catalyst anyway, causing a decline in performance. Symptoms of the deterioration of *catalyst activity* are either reduced octane numbers, lower reformate yield per barrel of feed, or both, as shown in table 10–2.

**Table 10–2.** Fixed bed reformer yields

	Yields—% Volume	
	Fresh or Regenerated Catalyst	Catalyst after a Long Run
H <sub>2</sub>	2	2
C <sub>1</sub> /C <sub>2</sub>	2	3
C <sub>3</sub>	2	3
iC <sub>4</sub>	3	4
nC <sub>4</sub>	3	4
Reformate	88	84
Octane number	94	92

After about 12 months catalyst activity in the early vintage reformers declined so severely that refiners shut them down for 20 or 30 days to regenerate the catalyst. By the 1960s refiners figured out that if they added a fourth reactor, they could take one reactor off-line at a time and regenerate it, creating the so-called semiregen cat reformer. Since the catalyst in each reactor could be regenerated as frequently as they wanted, the regeneration could be much milder and as short as 30 hours. That kept the reformer going for as much as 36 months without a shutdown. Beside the shutdown costs, that saved refiners a lot of upset in the rest of the refinery, especially from the loss of hydrogen. They could have built up stocks of high octane

components to last during a reformer shutdown, but it was impractical to store hydrogen.

So, in the later vintage fixed bed reformers, at any one time three reactors are in operation, with the fourth in a regeneration mode. Regeneration is accomplished by blowing hot air into the reactor to remove the carbon from the catalyst by forming carbon dioxide. A small amount of chlorine in the hot air will also remove some of the metals deposits. Then, by cycling in a reactor with freshly regenerated catalyst, the process is virtually continuous.

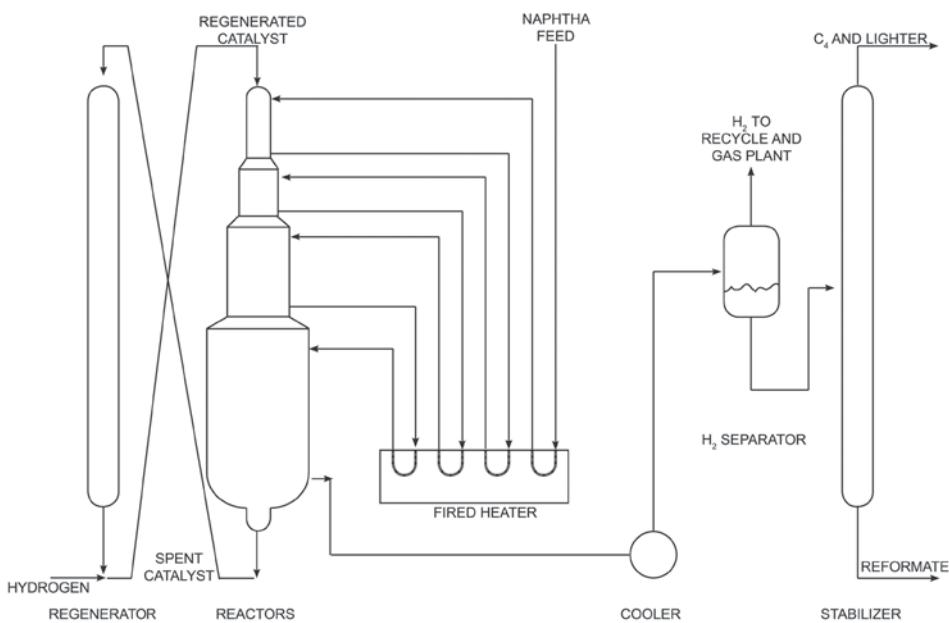
**Catalyst replacement.** Despite the continuous regeneration, over a long period of time the activity of the catalyst will decay. The high temperatures required for regeneration cause the catalyst's pores to collapse; some metals like vanadium or nickel deposit on the catalyst. Consequently, every three years or so a semiregen reformer must be shut down to swap out the catalyst for some fresh stuff. The platinum and rhenium in the catalyst are the expensive parts. The refiners either own or lease these precious metals; the processors just do the refurbishment for a fee, returning the same amount of metal to the refiners.

## Continuous Cat Reforming

In 1971 UOP, and subsequently other imitators, introduced the continuous cat reforming (CCR) design. They aimed to improve the efficiency of cat reforming by lowering the operating pressures and temperatures, extending the run life between shutdowns, and reducing maintenance problems. They did all this with the unit shown in figure 10-3.

The reactors are stacked atop each other. The continuously moving catalyst circulates down the center of the reactors by gravity. It drops from the top to the bottom in the annular space between two concentric pipes made of a fine mesh. The naphtha passes through the mesh (and the catalyst) to the center space. The naphtha then exits the bottom of each reactor section to be reheated and reentered to the next reactor.

After exiting the last reactor, the flow of the naphtha, now reformate, is more or less the same as the semiregen reformer—it goes through a hydrogen separation and a stabilizer to separate reformate and the butane and lighter by-products.



**Fig. 10-3.** Continuous cat reformer

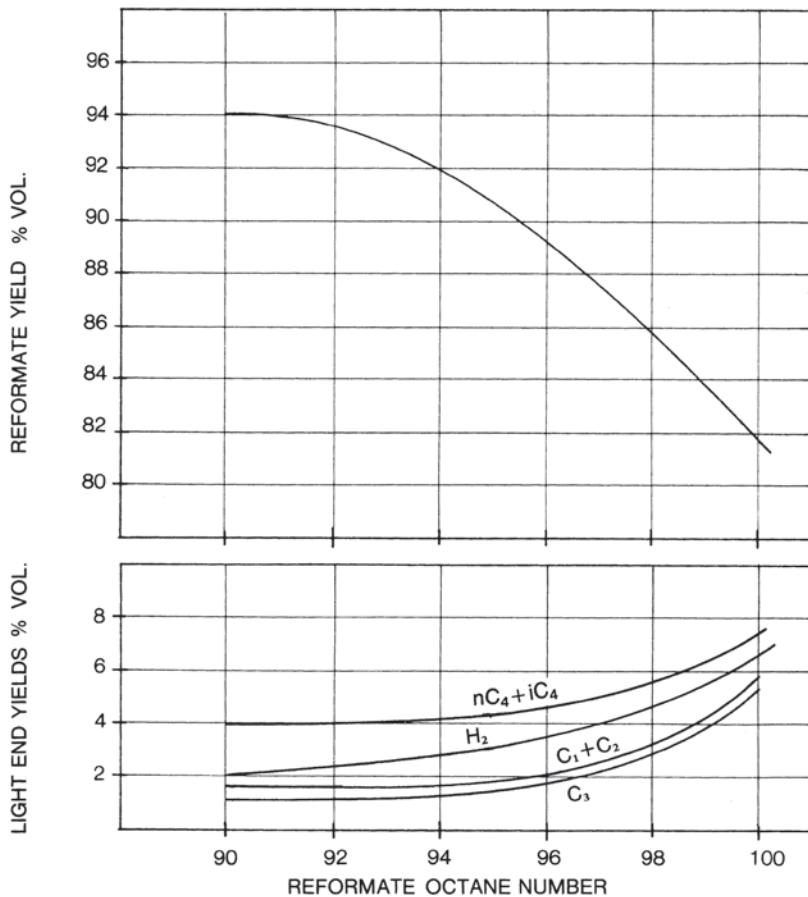
The catalyst flow from the bottom of the reactor is, of course, different. It has some carbon and maybe small amounts of metals all over it. This *spent catalyst* is scooted up to the top of the regenerator. There, gravity flow drops it through several sections where it is treated with oxygen and chlorine to remove the coke and metals. The treatment is much less severe than in a semiregen unit because the catalyst has had only a small exposure to the naphtha reactions. That allows lower temperatures in both the reactors and the regenerator.

From the bottom of the regenerator hot hydrogen drives the regenerated catalyst back to the top of the reactor stack.

**Catalyst replacement.** Since catalyst is always on the move, it is not hard to take a slipstream out to remove small amounts of catalyst and replace them with equal amounts of fresh catalyst. Over a few months the entire complement of catalyst can be turned over and sent to the supplier for heavy duty reconstitution. In that way, shutdowns are extended to as much as six years apart, and then only for a general maintenance turnaround.

## Process Variables

The operators play with a variety of dials and buttons when they run the reformer—temperature, pressure, residence time, feed quality, feed cut points, and more. The game is really a balance between the volume of reformate produced and its quality. Figure 10–4 shows one of the relationships: *as the octane number goes up, the percent volume of reformate goes down.*



**Fig. 10-4.** Cat reformer yields vs. octane number

Correspondingly, the yield of butanes and lighter goes up. That happens because more reforming of the heavier molecules inevitably leads to side chains breaking off or free carbon atoms forming methane or ethane. So the operation of the cat reformer must be tuned very closely to the gasoline

blending operations and the gasoline component yields of the other processing units.

The properties of the naphtha feed, as measured by the paraffin, naphthene, and aromatic (PNA) content, affect the yields and quality also. The PNA analysis of naphtha is an important component in the analysis of a crude oil's value. If you hold a lot of other things constant, the more naphthenes in the feed, the more aromatics are likely to be in the product; the more normal paraffins, the bigger the shift to isoparaffins and aromatics.

**Benzene issues.** So what is a refiner to do with a reformer that makes benzene out of naphthenes in a world that does not want benzene in gasoline? Refiners have several options:

- Remove from the reformer feed the types of molecules that readily form benzene. The precursors to benzene include cyclohexane and normal hexane. By fractionating out the 177°F and lighter fraction, the cyclohexane and normal hexane can be removed and the benzene content of the reformate drops. (Some other components come out with the benzene precursors and the octane boost at the reformer suffers.)
- Remove the benzene from the reformate. Maybe the refinery happens to be near a petrochemicals center. Petrochemicals producers lust after benzene, which they use as a building block for polystyrene, polyurethane, nylon, and other petrochemicals. Many refiners make as much benzene as they can. Then they run the reformate through a BEU, benzene extraction unit, and sell the benzene. (See chapter 21 to learn how that works.)
- Refiners strapped for capital who do not want to build a fractionator to split out the benzene precursors or are logically removed from benzene markets may have to reduce the severity of their reformers (lower the pressure and temperature or use different catalysts) to make less benzene, do less reforming, and to avoid increasing the octane of the naphtha as much.
- Hydrotreat the reformate to add hydrogen to the benzene, converting it back to cyclohexane. That also converts the toluene and xylenes to naphthenes, which also undermines the octane number of the reformate. Other octane-enhanced components such as isoparaffins are not affected. Still, this option seems rather circular, but a refiner with spare hydrotreating capacity may use it.

## Review

Catalytic reforming is an important process for upgrading low octane naphtha to a high octane gasoline blending component, reformat. Normal paraffins are converted to isoparaffins and naphthenes, and naphthenes are converted to aromatics to capitalize on their higher octane numbers. Unfortunately, the higher the octane number of the reformat, the lower the yield and the more light ends produced.

## Exercises

1. Fill in the blanks:

- a. The basic purpose of catalytic reforming is to increase the \_\_\_\_\_ of naphtha.
  - b. The expensive components of the reforming catalyst are \_\_\_\_\_ and \_\_\_\_\_.
  - c. Reformate has a much higher concentration of \_\_\_\_\_ than the reformer feed.
  - d. An important by-product of cat reforming is \_\_\_\_\_.
  - e. The other by-products of cat reforming are \_\_\_\_\_, \_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_.
  - f. To keep the catalyst from getting coked up, the reactors are kept filled with \_\_\_\_\_.
  - g. Symptoms of aging catalyst are the decline of the reformat \_\_\_\_\_ or \_\_\_\_\_, and the increase in yield of the \_\_\_\_\_.
2. Suppose the reformer feed is 15 M B/D and the operating conditions are set to produce 91 octane reformat. The 91 octane reformat is worth 100¢/gal and the C<sub>4</sub> and lighter streams are worth 50¢/gal. Each increase in octane number increases the reformat value by 1¢/gal. Does it make sense to increase the severity of the reformer, that is, run it to produce higher octane reformat? Use the yield versus octane number chart in figure 10-4. (Hint: check the economics at 91, 95, and 100 octane.)
  3. Draw an additional example of each of the five types of reactions that take place in the catalytic reformer.
  4. Draw the refinery configuration covered so far, including the cat reformer in its correct place.

# 11

## HYDROCRACKING

*Cancel and tear to pieces that great bond...*

*—Macbeth, Shakespeare*

Hydrocracking is a process of more recent vintage than cat cracking. It can stand alone in a refinery as the only cracking unit. It can also work in concert with a cat cracker or coker to extend the flexibility and capability of a refinery.

Plopped in the middle of a refinery, *hydrocracking* can take care of many of the headaches that refiners experience as the market changes from month to month or season to season. Hydrocrackers can produce gasoline components from light or heavy gas oils, cracked gas oils, or straight run gas oils from the crude distilling unit. They can produce light distillates (jet fuel and diesel fuel) from heavy gas oils. Hydrocrackers produce isobutane, a handy supply for the alky plant. Maybe best of all, hydrocrackers produce no bottom-of-the-barrel leftovers (coke, pitch, or resid). The outturn is all light oil, gasoline, jet fuel, and/or distillate fuel. Refiners use hydrocrackers to move from max diesel and distillate fuels in the winter to max gasoline and maybe even jet fuel in the summer. In the refineries where they reside, hydrocrackers have become refiners' swing units.

### The Process

Hydrocracking is simple—it is catalytic cracking in the presence of hydrogen. Various combinations of hydrogen, catalyst, and operating conditions permit cracking a wide range of feedstocks, from kerosene to straight run residue or the cycle oils from the cat cracker, coker, or thermal

cracker. Hydrocrackers run in one, two, or three stages, with the latter ones sequentially upgrading: heavy stuff to middle distillates, and middle distillates to gasoline range components.

With some irony, hydrocracking makes excellent distillate blending stocks but lower quality gasoline blending stocks. The hydrocracker products have lower aromatics-type molecules and higher naphthenes and paraffins. Lower aromatic gas oil burns cleaner and has a higher diesel index. Low aromatics gasoline has a lower octane number.

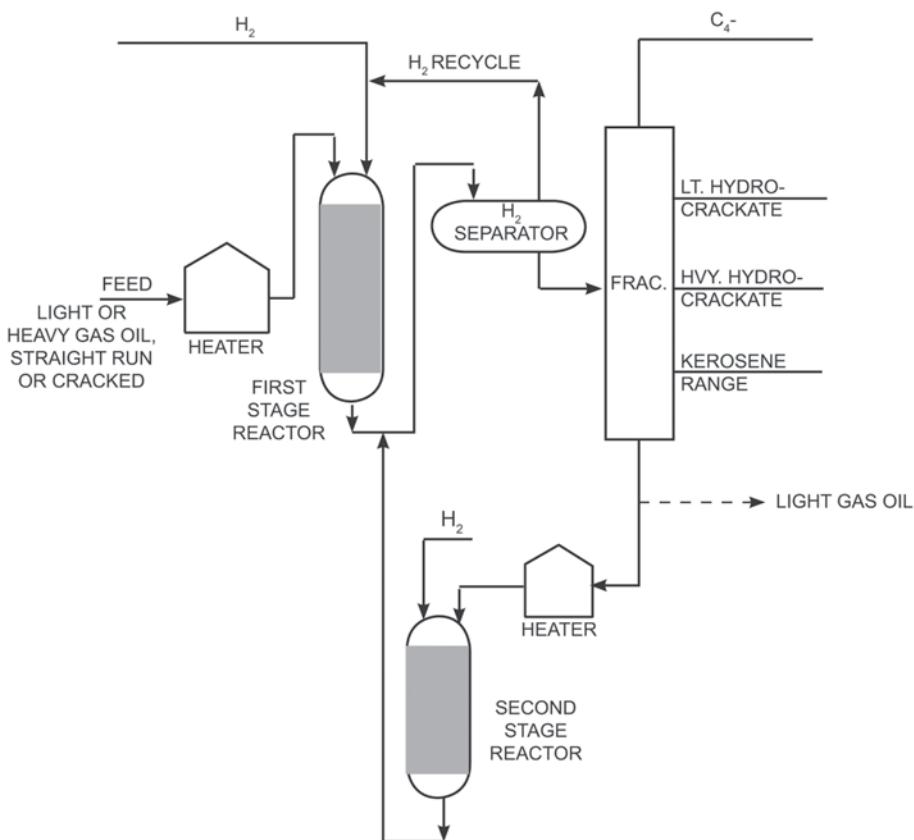
Why does every refinery not have one of these machines? Even though about a dozen different types of hydrocrackers are presently popular, they all are expensive to build and operate. The units described below are typical of most of them.

## The Hardware and the Reactions

Hydrocracking catalysts are fortunately less precious and expensive than reforming catalysts. Usually they are compounds of sulfur with cobalt, molybdenum, or nickel plus alumina. (You may always have wondered what anyone used those metals for.) In contrast to cat cracking but like cat reforming, most hydrocracker designs have their catalysts in a fixed bed. Just a few units such as the H-Oil, Hycon, LC-Fining, and OCR models have fluidized beds with moving catalyst. The unit described here and in figure 11-1 has two fixed beds, as do more than 75% of the world's hydrocrackers.

Feed (in this example, cracked heavy gas oil) is mixed with hydrogen vapor, heated to 550°F to 750°F, pressurized to 1,200 psi to 2,000 psi, and charged to the first stage reactor. As it passes through the catalyst, about 40% to 50% of the feed is cracked to gasoline range material (below the 400°F end point).

Why is the unusually high pressure used? The gas oils that are most suitable for hydrocracking are from other cracking processes, cat cracking and coking. These gas oils are normally replete with benzene-ringed compounds. To crack these tough molecules apart needs high pressure and moderate temperature.



**Fig. 11-1.** Two stage hydrocracker

The hydrogen and the catalyst are complementary in several ways. First, the catalyst causes long chain molecules to crack and the rings in aromatic compounds to open up. Both these reactions need heat to keep them going. They are *endothermic processes*. On the other hand, once the cracking takes place, momentarily creating an olefin, the excess hydrogen floating around saturates (fills out) the molecules, a process that gives off heat. This process, called *hydrogenation*, is *exothermic*. Thus, hydrogenation gives off the heat necessary to keep the cracking and ring opening going.

The catalyst and hydrogen also complement each other in the formation of isoparaffins. Cracking forms olefins, which could join together to form normal paraffins. Hydrogenation rapidly fills out all the double bonds, often forming isoparaffins, preventing reversion to less desirable molecules. (Isoparaffins have higher octane numbers than normal paraffins.)

After the hydrocarbon leaves the first stage, it is cooled enough for virtually all but the methane and hydrogen to liquefy. In the *hydrogen*

*separator*, the hydrogen/methane stream is split out for recycling to the feed. The liquid is charged to a fractionator. Whatever products are desired (gasoline components, jet fuel, and gas oil), the fractionator cuts them out of the first stage reactor effluent, leaving a bottoms stream ready for the next, second stage, reactor. In other words, kerosene range and light gas oil range material could be taken as separate side draw products from the fractionator. They could instead be included in the fractionator bottoms if further conversion to gasoline range material is the object.

The bottoms stream is again mixed with a hydrogen stream and charged to the second stage. Since this material has already been subjected to some hydrogenation, cracking, and reforming in the first stage, the operations of the second stage are more severe (higher temperatures and pressures). Like the outturn of the first stage, the second stage product is separated from the hydrogen and charged to the (same) fractionator.

Some hydrocrackers are configured in three stages, either by stacking different catalysts in one reactor or by having three reactors. Different reactions take place in each stage. In the first stage, the catalyst opens up the rings of complicated molecules where the contaminants, sulfur and nitrogen, might be embedded. The hydrogen forms  $H_2S$  and  $NH_4^+$ , hydrogen sulfide and ammonia. At the same time the hydrogen fills out many of the opened double bonds, forming simpler, lighter compounds.

In the second stage, run more severely, the catalyst opens up more rings of the heavy, complicated molecules and cracks others, forming light products. In the third stage, a kind of polishing job takes place where the olefins and aromatic compounds are saturated, forming naphthenes, paraffins, and especially isoparaffins.

Since hydrocracker reactors operate at really severe conditions—up to 2,000 psi and 750°F—imagine the hardware necessary to contain the reactions. The 6-inch specialty-steel reactor walls have to resist hydrogen intrusion, which can lead to stress fractures. The possibility of *runaway cracking* creates further critical worry. Since the overall process is exothermic, the temperature can rise rapidly, accelerating the cracking rates dangerously, which only gives off more heat as hydrogenation then takes place. Elaborate quench systems are built into most hydrocrackers to control runaway.

**Yields.** Another satisfying feature of the hydrocracker is a 10%–20% gain in volume, again what refiners sometimes call “fluffing up the barrel.” The cracking/hydrogenation combination results in products whose average gravity is 10°–20° API higher than the feed. The table below shows typical yields from hydrocracking cat-cracked cycle oil and cat-cracked gas oil. The primary products, blending components heading for the gasoline blending pool, are called *hydrocrackate*.

**Table 11–1.** Hydrocracker yields

	% Volume	
Feed		
Cat-cracked cycle oil	1.00	
Cat-cracked light gas oil		1.00
Product		
Propane	0.02	0.03
Isobutane	0.02	0.02
Normal butane	0.06	0.08
Hydrocrackate	0.75	0.80
Kerosene range	0.15	0.17
Light gas oil range	<u>0.15</u>	<u>0.00</u>
Total	1.15	1.10

Not shown is the hydrogen requirement, which is measured in standard cubic feet per barrel of feed. Cracking heavier feed requires more hydrogen than lighter feed. The hydrogen-to-carbon ratio in larger molecules is lower than smaller molecules. Larger molecules tend to have more hydrogen-deficient aromatic rings. For the same gasoline yield, 20°API heavy gas oil may require twice the hydrogen consumption as 33°API light gas oil.

The heavier part of the hydrocrackate contains a lot of aromatics *precursors* (types of molecules that easily convert to aromatics in a reformer). Refiners often split out this naphtha and feed it to the reformer for upgrading. The kerosene range material makes a good jet fuel or a distillate blending stock because of its low aromatic content, a consequence of hydrogen saturating those double bonds. More on why that is good will be covered in chapter 15 on distillate fuels and chapter 16 on hydrotreating.

**Residue hydrocracking.** A handful of hydrocrackers have been designed and constructed to use straight run residue or flasher bottoms as feed. Many of them are operated as hydrotreaters, as described in chapter 14. The yields are more than 90% residual fuel. The purpose of the operation is to remove sulfur by the catalytic reaction of the hydrogen and the sulfur compounds, forming H<sub>2</sub>S, hydrogen sulfide. Residue with a sulfur content of about 4% or less can be converted to heavy fuel oil with less than 0.3% sulfur.

Only a few, real residue hydrocrackers that produce predominantly light products have been built. They pump enormous amount of hydrogen into the reactions to break up the very heavy molecules and

require lots of recycling of the heavy ends back through the reactor to make them go away.

A residue hydrocracker costs a relatively large bundle of money just to convert high sulfur residual fuel to low sulfur residual fuel, and even more to convert it to light products. Special circumstances including location, access to cheap, heavy crude oil, and lack of any high sulfur residual fuel market might make this economically viable.

## Review

With the addition of the hydrocracker to the refinery processing scheme, the compelling requirement for integrated operations becomes apparent. The hydrocracker is a pivot point since it can swing refinery yields between gasoline, distillate fuel, and jet fuel and simultaneously improve the quality. How the hydrocracker runs depends somewhat ironically on the feed rates and operating conditions of other units, the cat cracker, the coker, and the thermal cracker, and the streams they produce. In addition, the hydrocracker generates isobutane for the alky plant and naphtha for the cat reformer and gets hydrogen back from the cat reformer.

## Exercises

1. Contrast hydrocracking, cat cracking, and thermal cracking in terms of feed, what promotes the reaction, and what the products and product PONAs are.
2. How is a hydrocracker complementary to a cat cracker? A reformer to a hydrocracker?
3. Draw the refinery flow diagram with the hydrocracker added.

# 12 ISOMERIZATION

*“My dear Bilbo! Something is the matter with you.  
You are not the hobbit that you were.”*

*—The Hobbit, J. R. R. Tolkien*

Isom plants are molecule rearrangers somewhat like the cat reformer, except that they only convert normal paraffins to isoparaffins. Curiously, the C<sub>4</sub> isomerization unit is built for very different reasons than the C<sub>5</sub>/C<sub>6</sub> isomerization unit.

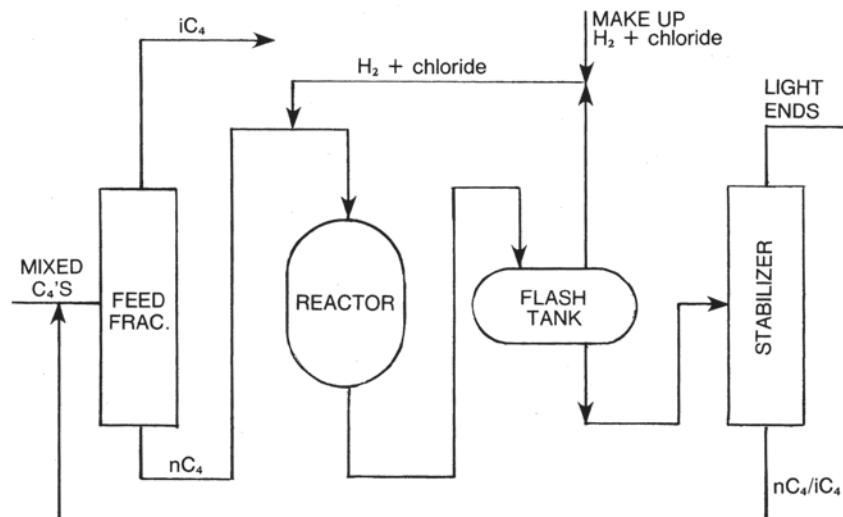
## Butane Isomerization

A refinery that has an alkylation plant is not likely to have exactly enough isobutane to match the propylene and butylene feeds. If the refinery has a hydrocracker, there is likely to be surplus isobutane that is probably blended off to gasoline. Without a hydrocracker, but with a cat cracker and alky plant, a refiner may have to supplement the iC<sub>4</sub> supply. Refiners usually have two choices—buy it or make it in a butane isomerization (BI) plant.

**The process.** The feed to the BI plant is normal butane or mixed butanes (normal and isobutane), which are sometimes called *field grade butanes* if they come from a gas processing plant. If they come from refinery operations, the butanes are processed to remove any trace of olefins because they tend to deactivate the catalyst.

The butanes are fed to a feed preparation column (fig. 12-1) where isobutane is separated, which is marginally cheaper than pumping it around and taking up space in the BI plant. The high purity normal butane is then mixed with a small amount of hydrogen and charged at 220°F to a reactor

containing a platinum catalyst. At this temperature some of the  $nC_4$  would convert to  $iC_4$ , even without the catalyst. But add the presence of platinum and the conversion jumps to a commercial rate. The hydrogen does not really enter into the isomerization reaction. It is there just to minimize coke formation, reacting with any freed carbon to form methane, ethane, or propane.



**Fig. 12-1.** Butane isomerization

The stream coming from the reactor contains about 60% isobutane, 40% normal butane, and a minor amount of propane and lighter gases. In a fractionator, the latter are split out and sent to the fuel system; the butanes are recycled to the feed fractionator so that the normal butane can be separated from the isobutane and rerun.

**Yields.** After accounting for the once-through 60% conversion, the normal butane recycle, the small amount of by-products, and the fact that isobutane is less dense than normal butane, the yield of isobutane **on a volume basis** is slightly more than 100%. In essence, it's normal butane in, isobutane out, and that's it.

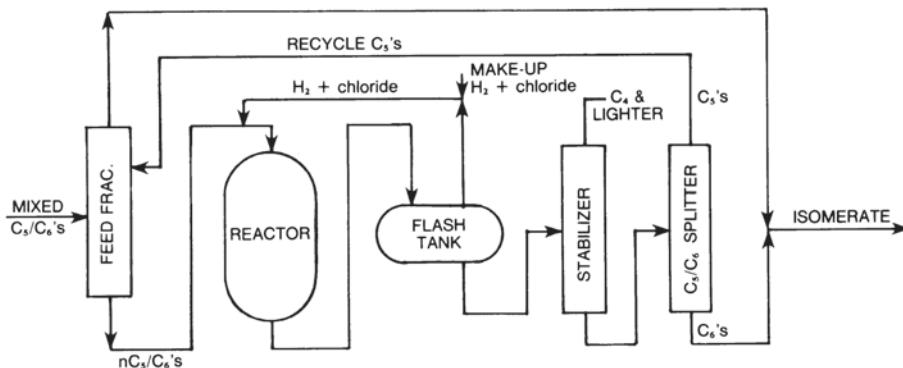
## C<sub>5</sub>/C<sub>6</sub> Isomerization

For a refinery that has problems meeting the gasoline octane targets and has a lot of straight run gasoline around, C<sub>5</sub>/C<sub>6</sub> isomerization has appeal. Normal pentane, which has an octane number of 62, can be converted to isopentane with an octane number of 92. Normal hexane goes from an untenable low 25 octane to about 75.

**The process.** The boiling points of the four compounds involved, the two normal paraffins and their isomers, are annoying:

Isopentane	50°F-82°F
Normal pentane	97°F
Isohexane	129°F-142°F
Normal hexane	156°F

Isopentane and its variation, neopentane, boil at the lowest temperatures. As in the BI plant, the C<sub>5</sub>/C<sub>6</sub> isom plant probably has a feed fractionator that separates the isopentane from the feed, as shown in figure 12-2. There is no sense in carrying the extra baggage that will not be involved in the reaction. But because the isohexane boils between normal pentane and normal hexane (there are several isomers, which boil from 129°F to 142°F), it is often left in the feed. It would take two columns or a very tall single column with lots of reflux and reboil to get it out.



**Fig. 12-2.** C<sub>5</sub>/C<sub>6</sub> isomerization

Like the BI plant, a small amount of hydrogen is mixed with the feed, which is then charged to a reactor at about 250°F. At this temperature, the catalyst will promote conversion of about half the normal paraffins feed to the corresponding isomers, creating an *isomerate stream*. The reactor product can be fractionated to recycle the normal pentanes to extinction. The C<sub>5</sub>s are split from the C<sub>6</sub>s and fed back to the feed prep column, where the isopentane is split out and the normal pentane is left in the feed. Again the boiling points of the iso- and normal mix present themselves as a pain in the column bottoms. Some refiners put in another finishing column to recycle the normal hexanes also. Some just let the normal hexanes stay with the isohexane and remain content passing the normal hexanes through the process only one time, as in figure 12–2.

**Yields.** C<sub>5</sub>/C<sub>6</sub> isomerization is a little more chemically complex than C<sub>4</sub> isomerization, so about 2% to 3% light ends (C<sub>4</sub> and lighter) get created in the process. But again, with the iso versus normal density trick, the C<sub>5</sub>/C<sub>6</sub> outturn is about 100% on a volume basis.

Depending on the extent of recycle, the octane number of the isomerate can vary from 80 to 91 octane, with the cost of energy (fractionation, pumping) increasing with the octane number (see table 12–1). The conversion of the normal paraffins to their isomers on a once-through basis with no recycle runs 70% to 90%.

**Table 12–1.** Octane improvement in a C<sub>5</sub>/C<sub>6</sub> isomerization plant

	% Feed	% Product	Octane number
nC <sub>5</sub>	33	15	62
iC <sub>5</sub>	22	40	92
nC <sub>6</sub>	20	6	26
iC <sub>6</sub>	25	27	74–96
Typical feed octane number			67
Typical product octane number			80

## Review

Butane isomerization is used to satisfy the feed needs of alkylation by converting normal butane to isobutane. C<sub>5</sub>/C<sub>6</sub> isomerization is a method of increasing the octane number of the light gasoline components, normal pentane and normal hexane, that are found in abundance in light straight run gasoline.

## **Exercises**

1. How are refiners motivated differently in having a BI plant compared to having a C<sub>5</sub>/C<sub>6</sub> isom plant?
2. What must be added to figure 12–2 to show recycling of normal hexane?
3. The isoparaffins have the same hydrogen-to-carbon ratios as the normal paraffins. Why is hydrogen added to isom plant feeds?
4. Why do isopentane and isohexane have a range of boiling temperatures?

# 13

## RESIDUE REDUCTION

*The very ruins have been destroyed.*

—*Civil War*, Luca

Residue reduction, residue destruction, residue conversion—they all mean the same, and they all started about 100 years ago. Motor gasoline had begun its spectacular growth and refiners struggled to keep up with demand by running more crude oil to yield straight run gasoline. They started to drown in the coproduced residual fuel.

Along came William Burton of Standard of Indiana and his innovation in 1912—cracking residual fuel to produce light products. Those refineries that adopted his thermal crackers doubled their gasoline yields from 12% to 24% and cut residual fuel production by even more. In the process, coke formation quickly fouled the vessels, requiring laborious removal every 48 hours. Shortly after came Jesse Dubbs, a man so preposterously committed to petroleum research he named his son Carbon Dubbs (who in turn named his daughters Methyl and Ethyl). Together the father and son found that adding steam to the cracking reactor (later the Dubbs Unit) mitigated the amount of coke formed.

Decades later other advanced technologies—cat cracking, hydrocracking, and coking—eclipsed thermal cracking as a gasoline generating unit. Today a mild form of thermal cracking, *visbreaking*, is still in use around the world as a way of upgrading flasher bottoms or straight run residue to residual fuel specifications. In the United States, nearly every visbreaker and thermal cracker has been scrapped in favor of the newer processes.

A few high capital cost units around the world have extended the capabilities of cat cracking and hydrocracking to very heavy feeds. They are collectively called residue fluid cat cracking (RFCC) or residue hydrocracking units (RHCUs).

Hydrocrackers cost more than cat crackers, which cost more than cokers, which cost more than thermal crackers. Those units also convert different types of feed into different percentages of light oils—gasoline and distillates (kerosene, diesel, and heating oil blend stocks). So the selection of which processes unit belongs in a refinery depends on the original capital cost, the market for the different products, and the price and qualities of the accessible crude oils.

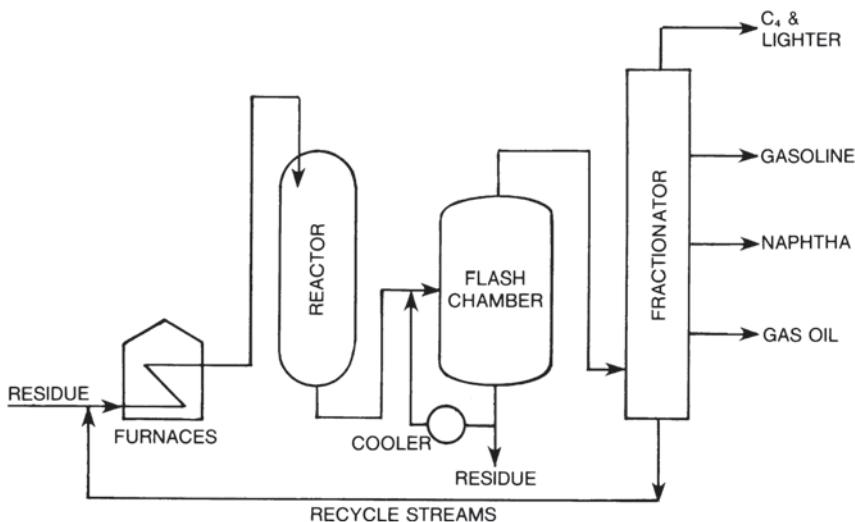
## Thermal Cracking and Visbreaking

What nobody wants to do in a crude oil distilling unit—heat the crude oil so high that it begins to crack—they now do in a thermal cracker. However, just using heat to generate cracking can also result in coking up the heater tubes. The tubes have to be of small enough diameters as they run through the furnace to pass the heat quickly to the heavy feed inside. Carbon atoms can crack off by themselves and adhere to the inside of the heater tubes and clog them. The coking problem is managed by the addition of steam, which drops the partial pressure in the tubes, by high velocities of the feed going through the tubes, and by quick pressure drop at the tail end of the furnaces to stop the cracking and coke formation.

**The process.** Either straight run residue from the crude oil distilling unit (*long residue*) or flasher bottoms (sometimes called *short residue*) are primary feeds to a thermal cracker. Sometimes cat cracker heavy cycle oils are used.

The furnaces (fig. 13-1) heat the feed to about 1,000°F. Space velocity in the furnace in the heater tubes is short to prevent much reaction from taking place there. The furnace effluent goes to a reaction chamber for just a few minutes. Pressure in this vessel is kept at about 140 psi, which favors cracking but not coking.

The product from the reaction chamber passes through a quench to stop the cracking by mixing it with a somewhat cooler recycle stream. The effect is similar to throwing a bucket of water on two amorous dogs.



**Fig. 13-1.** Thermal cracker

The stream is then charged to a *flash chamber* where the lighter products go overhead because the pressure is reduced as in a vacuum flasher. These lighter products go to a fractionator. The C<sub>4</sub> and lighter streams, which are laden with propylene and butylenes, are sent for processing where cracked gases are handled, usually the alky plant. The thermal cracked gasoline and naphtha are used for gasoline blending. The gas oils can be used as a distillate fuel. The residue from the bottom of the flash chamber is the same type of heavy hydrocarbon as flasher bottoms. It is, of course, a smaller volume than the feed, but it will still need a diluent such as gas oil to reduce its viscosity to make it marketable as residual fuel, a heavy industrial fuel oil. (See the material balance in table 13-1.)

**Table 13-1.** Typical yields cracking flasher bottoms (percentage weight)

	Visbreaker	Thermal Cracker	Delayed Coker	Fluid Coker	Flexicoker
C <sub>4</sub> & lighter gas	3	5	8	10	10
Light oils	15	45	60	70	70
Residual fuel	82	70	—	—	—
Heavy gas oil*	—	(20)	12	7	7
Coke	—	—	20	8	—
Low Btu gas	—	—	—	5	13

\* The thermal cracker bottoms need cutter stock in the form of straight run or cat-cracked gas oil. The cokers generate heavy gas oil that might be processed elsewhere into light oils or used as fuel oil.

**Visbreaking.** A visbreaker is a poor man's thermal cracker. On paper it sounds like a thermal cracker, but the hardware is simpler and cheaper to build and operate. On the other hand, it only converts 15% or so of the feed to light oils. A refinery that has no vacuum flasher or even one that does may not be able to market the bottoms products because it does not meet the residual fuel specification for viscosity. In that case a more valuable stream like straight run or cat-cracked heavy gas oil may have to be added as *cutter stock* or diluent. The visbreaker is an alternative because it creates its own cutter stock by cracking just enough of the heavy bottoms product to loosen it up. You might think of a visbreaker as refinery Ex-Lax.

Most visbreakers are one of two designs, the *coil* or furnace type or the *soaker*. The difference is mostly the trade-off between space velocity (residence time) and temperature.

In the coil design, the feed is heated in two stages, reaching about 900°F for one to three minutes. Coming out of the heaters, it is quenched to stop the cracking. In the soaker design, the furnace heats the feed to about 800°F, but the feed passes through a soaker drum for a few minutes to allow cracking. In both cases the system is kept at high pressure, sometimes up to 750 psi, to control coking. Both systems have a reduced pressure flash drum to allow light products to vaporize and use injected steam to help drive off these fractions.

The heavier gas oils stay with the heavy ends from the bottom of the flash chamber and provide the self-made diluent that reduces the viscosity. The net result is a little bit of light products but residual fuel with no cutter stock requirement.

## Coking

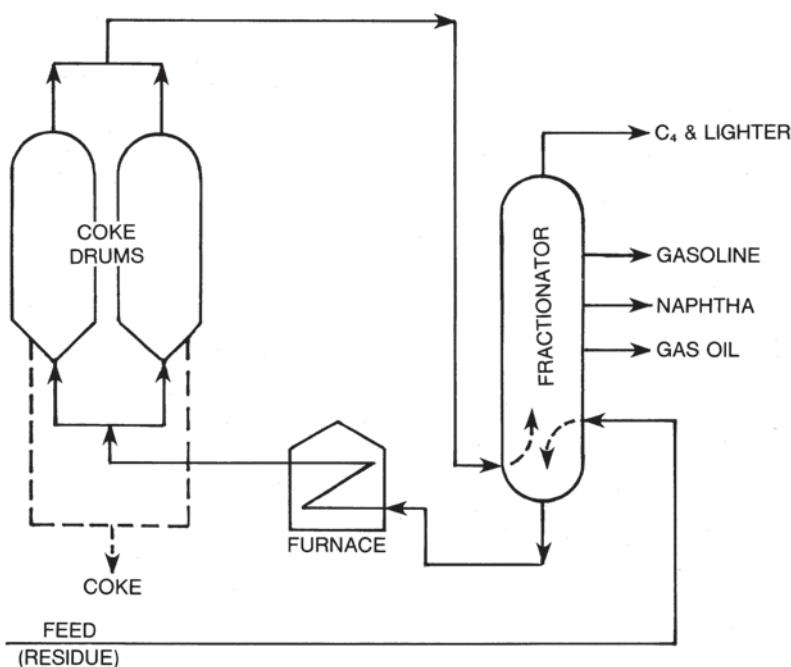
Coker design has gone down three paths: *delayed cokers*, *fluid cokers*, and *flexicokers*. Not many of the last two have been built, so this chapter will concentrate on the first, delayed cokers, and just describe the main differences with the other two at the end of the section.

**Delayed coking.** If thermal cracking is like throwing a hamburger on a hot grill for a few minutes, coking is like Texas barbecue—slow cooked all the way through. Over the years, as refiners gathered more knowledge about thermal cracking, they found that they could raise heavy feedstocks to high temperatures without coking up their furnace tubes if they used high velocities just in the tubes to postpone the formation of coke. That gave rise to the term *delayed coking*.

The furnace tubes through which the feed passes to be heated up are fairly narrow diameters to allow efficient heat exchange. Coking up these tubes is always a mess for refinery maintenance people. It is better if the coke formation takes place where it can be more easily dealt with.

Using a wider diameter vessel called a *coke drum* made the removal of the coke feasible. Still, the hardware is mechanically more complicated than refiners like since they are, for the most part, fluids handlers. Coke is a solid and the *coke handling* facilities presented some unique challenges. Eventually they developed designs to handle the whole process efficiently on a continuous flow basis.

**The process.** The feed to the delayed coker (flasher bottoms, heavy cat-cracked cycle oil) is quickly heated to about 1,000°F and then charged to the bottom of a coke drum (fig. 13-2). As the material sits in this insulated vessel, it keeps cooking. The lighter cracked product in vapor form rises to the top of the drum and is drawn off and sent to a fractionator for separation.



**Fig. 13-2.** Delayed coker

The heavier product fills up the insulated coke drum, cracking all the while, until virtually all the molecules containing any hydrogen crack off. The carbon left behind, called coke, is in solid form.

**Coke removal.** Back in the old days, even the thermal cracker reaction chambers sometimes got coked up because of some upset or accident. The only way to get the coke out was to send workers into the vessel with chipping hammers and respirators. Surely this is what inhibited the enthusiasm for coke production in refineries.

Nowadays, *decoking* is a routine, daily occurrence and is usually accomplished by using a high pressure water jet (about 2,000 psi). First, water is poured into the drum to cool it down, ironically like pouring the soft drink Coke into a cup filled with all that ice that fast-food places like to add. The Coke just fills the empty spaces. In a refinery operation, a hole is drilled in the (petroleum) coke from the top to the bottom of the drum. A rotating stem is lowered through the hole, spraying a water jet sideways. The high pressure water jet cuts up the coke into small lumps that drop out the bottom of the drum into a bunker or into trucks or rail cars for shipment or hauling to the *coke barn*.

Coke drums typically come in groups of two or more and run on a 48-hour cycle. Filling a drum with coke takes about 24 hours. Switching, cooling, decoking, and emptying take about 22 hours, during which time the other drum is filling. Alternating drums makes delayed coking seem like a continuous process.

**Coke.** The unique characteristics of coke warrant a few words. Most refineries produce *green coke*, so called because of the slightly green hue when the sun shines on it. Most green coke ends up as fuel in cement kilns or in power plants where it is mixed with coal, crushed to a powder, and burned.

Coke from any coker is nearly all carbon, but not quite. A small percentage of very heavy, very complex hydrocarbons may wrap themselves around the coke. A higher grade of coke comes from removing these hydrocarbons in a *calciner*. In that process the coke is heated to as high as 2,400°F, which drives off the hydrocarbons, leaving behind *sponge coke*, so called because of its spongelike appearance under a microscope. Sponge coke is suitable for making electrodes for steel and aluminum manufacture. *Calcinable coke* used for industrial applications usually needs to be low in contaminants, especially sulfur and heavy metals such as vanadium and nickel, which are common in many crude oils.

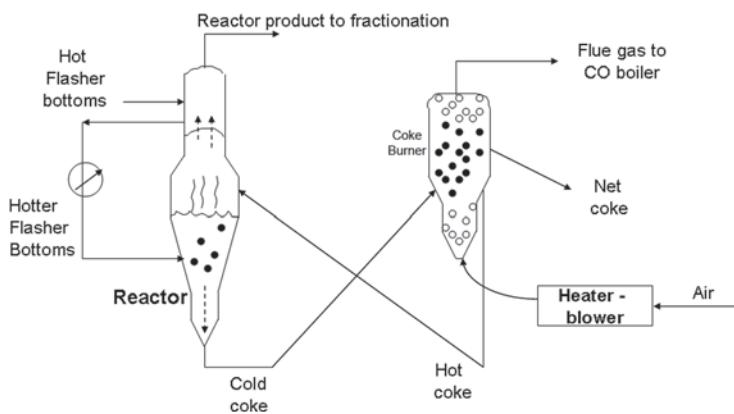
Only a few crude oils can be used to make an exotic-sounding variety of calcined coke called *needle coke*. The name comes from the elongated crystalline structure. Needle coke is used to make anodes for electric arc furnaces, mostly for steel making. The special structure of needle coke lets it handle temperatures up to 5,000°F without falling apart. Since the suitable crude oils are few and the process is touchy, needle coke commands a big

price premium over regular calcined coke, which itself sells for a premium over sponge coke.

Petroleum coke from coking (as opposed to coke from coal) is seldom added to iron in steel making. It does not have the structural strength.

Different refiners run their cokers to make money in their own ways. Most run them to maximize the production of light oils and end up with green coke, the cheapest of the varieties. Some run them to make the more valuable calcinable coke, and so they take care to select the right crude oils and run the operation at higher pressures. Only a few refiners select crude oils and operate their cokers to produce needle coke. Even then, the refiners can be so selective as to produce *intermediate, premium, or super premium grade* needle coke, all commanding the elevated prices their names imply.

**Fluid coking.** In a process that looks like cat cracking on paper, the fluid coker makes coke “on the fly” and separates fine particles of coke from the hydrocarbon using cyclones, *à la* the cat cracker (fig. 13–3). Coke also falls to the bottom of the reactor and is drawn off. All the coke is then sent to a gasifier and hit with heated air. The reaction is exothermic (it gives off heat) and also creates a low Btu gas made up of C<sub>4</sub> and lighter, including hydrogen, carbon monoxide, and carbon dioxide. This gas can be burned to generate steam or electricity.

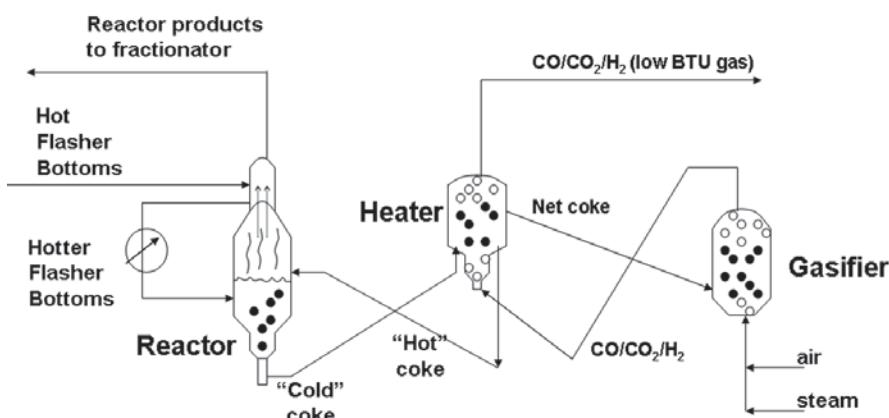


**Fig. 13–3.** Fluid coker

The rest of the coke, which is now super hot, is recycled to the main reactor and acts as the heat transfer medium to crack the incoming fresh feed. As the hot coke gives up its heat in the reactor, it is drawn off with the freshly made coke and goes to the gasifier. A fluid coker still makes some net coke, but converts the rest of the coke to the low Btu gas, a result refiners like.

The process is difficult to control and most refiners have chosen to go the delayed coker route. As you might imagine, moving the hot solids from one vessel to another is tricky and the process is difficult to control.

**Flexicoking.** Another design that has not yet captured the imagination of most refiners is flexicoking, an extension of fluid coking. The process adds a second gasifier to the sequence to convert all the coke to low Btu gas (fig 13-4). Ironically, for many of the flexicokers that have been put in service, engineers have found ways to debottleneck them in order to convert more fresh feed. The result has been to overwhelm even the second gasifier, resulting once more in net coke being produced, just the result that the flexicoker was designed to eliminate.



**Fig. 13-4.** Flexicoker

## Cat Cracking and Hydrocracking

**Residue cat cracking.** A few refiners have built cat crackers designed to use residue as feed (RFCCs). Relative to a conventional cat cracker feeding straight run heavy gas oil and flashed distillate, everything is larger in a residue cat cracker. The risers have to be wider and longer to allow more residence time, and the regenerators are larger because the relative amount of coke laid down on the catalyst is higher. The catalysts are designed to handle more complex molecules in their pores, and the crude oils are chosen to assure they do not have contaminants that poison the catalyst.

**Residue hydrocracking.** Hydrocrackers designed to reduce residue (RHCUs) have the same scale issue—much larger heaters and reactors are required. In some such as the catalytic hydrofining process, the catalyst is kept in constant motion in an *ebulating bed* reactor by blowing it in along with the hydrogen and the feed. In the H-Oil version, catalyst enters the top of the reactor and passes countercurrently by the feed and hydrogen, and then it is drawn off the bottom for recycling. Again, these are difficult processes to control.

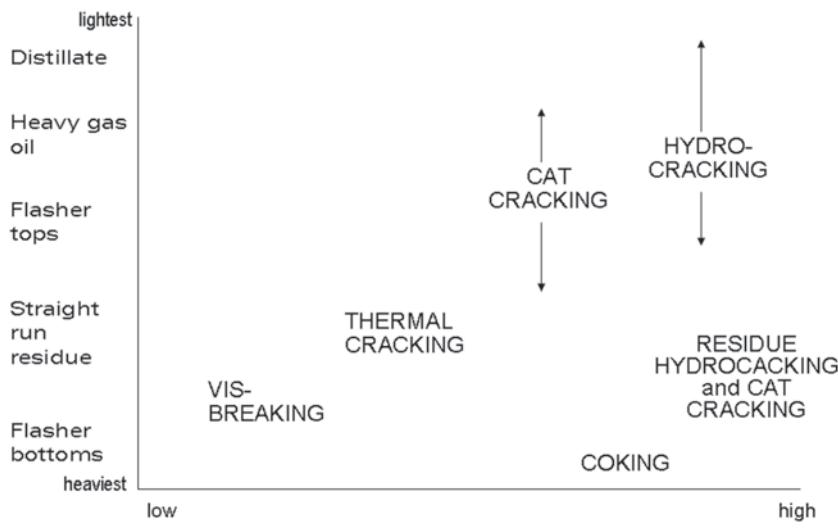
With the presence of hydrogen, residue hydrocrackers produce virtually no coke. Carbon reacts with the added hydrogen to form methane and other gases. But, like the RFCC, 80% to 90% of the heavy feed gets converted, leaving a thick pitch product behind that has to be blended with diluent to make residual fuel.

## The Conundrum

How does a refiner choose which residue reduction process to put in a refinery? The selection depends on many factors, including the value of residual fuel, the value of the light products, the value of coke, the capital and operating costs of the various hardware configurations, and the properties of the crude oil being run in the refinery. High metals content, high carbon-to-hydrogen ratio, and high coke prices push a refiner in the direction of delayed coking and away from RFCC and RHCUs. Poorer coke prices but better residual fuel prices relative to light oil prices, such as in many lesser developed countries, push refiners towards thermal cracking and visbreaking.

As a first approximation, figure 13–5 shows what kind of feeds and how much conversion to light oils from each of the conversion units might be expected. Coincidentally, the capital and operating cost of each of the units could also have been the measure on the horizontal axis.

### Feedstock quality:



**Fig. 13-5.** Conversion of feedstocks

## Review

Delayed coking is by far the technology refiners have preferred in recent years to eliminate the bottom of the barrel from the refinery product slate. Heating flasher bottoms or other sources of pitch to cracking temperatures and delaying the cracking to coke until the hydrocarbon gets into a coker drum permits the cracked products to escape the top and the coke to accumulate in the drum. The quality of the coke produced depends mostly on the quality of the crude oil being run and the post coker processing of the coke.

## Exercises

1. Fill in the blanks.

- a. The main difference between thermal cracking and cat cracking is that the former uses no \_\_\_\_\_ to promote cracking.
  - b. The main difference between thermal cracking and coking is the production of \_\_\_\_\_ and \_\_\_\_\_.
  - c. To prevent coking in a thermal cracker reaction chamber, the feed is \_\_\_\_\_.
  - d. To promote coking in a coke drum, the feed is \_\_\_\_\_.
  - e. The various names refiners give to different types of coke are \_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_.
  - f. The thermal-cracked and coker C<sub>4</sub> and lighter gas is sent to the \_\_\_\_\_ plant because it contains \_\_\_\_\_.
  - g. The three main parts of thermal crackers or cokers are the \_\_\_\_\_, \_\_\_\_\_, and the \_\_\_\_\_, which in a coker is called a \_\_\_\_\_.
2. The refinery manager in chapters 4 and 5 has to tell the sales manager how much coke to sell. He runs all the flasher bottoms to the coker. Use the yields in this chapter and answers to problem 2 in chapter 3 to do the calculation. Assume the gravity of the flasher bottoms is 10°API or 350 lb/bbl. (Remember—the coke yield is given by percent weight, and the units of sale for coke are short tons, 2,000 lb/ton.)

# 14 GASOLINE

*The good things of life are not to be had singly, but come to us with a mixture.*

—Charles Lamb

Finally you get to gasoline, the subject everybody knows a little about. Gasoline is the product almost everyone buys and occasionally spills on their shoes. They know what today's gasoline price is because it is posted on every other corner. They understand that higher octane is better than lower octane, but they may not know why. That is all okay for most people because a competitive marketplace delivers gasoline grades that will work just fine in their cars. So most people do not need to understand much more—except you.

It used to be, in early editions of this book, that understanding how to make gasoline was a fairly simple matter. However, since the 1980s, governments and institutions have learned how bad "old-fashioned" gasoline is for your health. Governments, especially in the United States, have put successively more restrictions on the content of gasoline, giving progressively bigger headaches to refiners. The best way to cover the accumulated complexities is a historical tour, starting with what refiners think of as "the good old days" and environmentalists consider the "dirty past." So this chapter will start with gasoline blending circa 1965 and work its way to the 21st century, covering these questions:

- What happens when gasoline is burned in a car engine?
- What are octane and the equally important property, vapor pressure?
- Whatever happened to tetraethyl lead, and what did that do?
- How does gasoline affect the environment?

- How do refiners blend gasoline now to mitigate environmental harm?
- What effect does gasoline blending have on the way a refinery is operated?

## Gasoline Engines

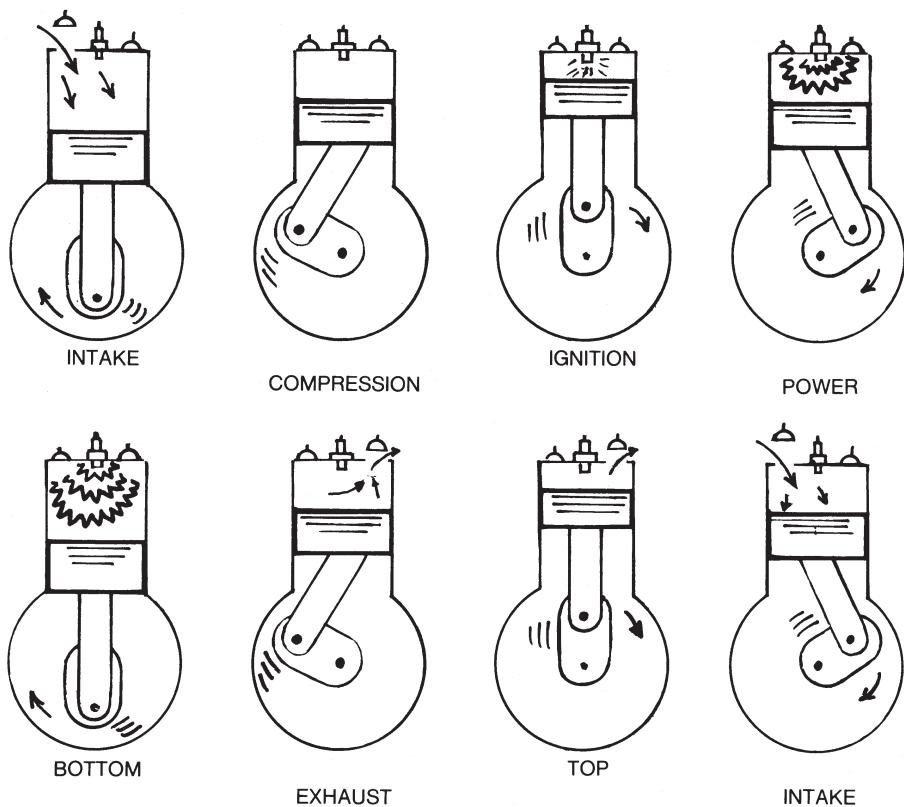
To understand how gasoline gets used requires some knowledge of how an automobile engine works. The essential parts of a gasoline engine, at least for the next few paragraphs, are the gas tank, the fuel pump, fuel injection, the cylinders, the pistons, the exhaust valves, and the spark plugs. Engines without the last item (spark plugs) follow in the next chapter because they are diesels.

You might say the whole motive process in a car starts at the gas tank when you fill it at a gas station. As you start the engine to leave, the fuel pump pushes gasoline out of the tank and sends it to the fuel injection apparatus. The purpose of fuel injection is to get the gasoline to the right state and in the right place to burn, releasing its chemical energy.

Gasoline, like other hydrocarbons, does not burn in its liquid state. It has to be vaporized and mixed with oxygen to ignite. For example, when you throw charcoal lighter on the coals in your barbecue grill and then toss in a match, the vapors ignite, not the liquid. That is why some dummies can get away with squirting charcoal lighter directly on a lit fire without barbecuing themselves. The liquid stream does not ignite. Unless the charcoal lighter has been sitting in the sun or next to the grill and is warm, the stream does not vaporize in the air, only when it hits the hot coals.

The fuel injection apparatus mixes the gasoline with air as it pumps it up to a high pressure and then squirts it into the cylinder. The sudden release of pressure is enough to vaporize the mixture, filling the cylinder with a gasoline/air mixture, ripe for ignition. The nitrogen that is also in the air just passes through the process, more or less unaffected. (More is bad, as you will read in a few pages.)

The sequence of happenings illustrated in figure 14-1 shows one full round of a four-stroke engine's cycle. Keep in mind you may have four, six, or eight cylinders doing this in your car, cycling at 2,000 to 3,000 times per minute.



**Fig. 14-1.** Four stroke internal combustion engine

The downward movement of the piston works together with the fuel injection apparatus to suck the gasoline/air mixture into the cylinder. At the bottom of the stroke, the space in the cylinder reaches its maximum and is filled with the fuel/air vapor. The fuel injection apparatus closes and in the next step, *compression*, the piston moves up the cylinder, compressing the vapor. When the piston reaches the top of the stroke at the point of *ignition*, the spark plug gives off a powerful flash, igniting the gasoline vapor. The gasoline burns rapidly, just short of an explosion. The gases expand and put huge pressure on the piston, forcing it down the cylinder in the *power* stroke. Power is transmitted to the crankshaft as the piston is forced down the cylinder. At the *bottom* of the power stroke, the exhaust valve at the top of the cylinder opens. The combustion gases (in a perfect world, comprised totally of water, carbon dioxide, and nitrogen) are pushed out in the *exhaust* stroke as the piston moves up the cylinder. At the *top* of the stroke, the outlet valve closes, the injector opens up again to squirt the fuel in, and the process is ready to be repeated.

Note that each cycle requires two trips of the piston up and down the cylinder, which is not the reason why it is called a *four-cycle engine*. The four cycles are intake, compression, power, and exhaust, which are not really cycles, but nobody ever said automotive engineers were all that articulate.

Some small two-cycle engines (lawn mowers, outboards, etc.) use gasoline. Big two-cycle engines run on diesel fuel or the heavier residual fuel, which you can read about in chapter 15.

## Vapor Pressure

A crucial step in the engine cycle is the vaporization of the gasoline. When the engine is warm, there is no problem—the engine heat assures that 100% of the gasoline will enter the cylinder in vapor form. But when the engine is being started from cold, the injector may spit some droplets instead of vapor into the cylinder, making ignition difficult at worst, less smooth at best.

The trick in handling cold starts is to have enough volatile hydrocarbons in the gasoline to get a vapor/air mixture that will ignite. The measure of volatility is vapor pressure, and more specifically *Reid vapor pressure (RVP)*, immortalizing the man who designed the test apparatus.

**Definition.** Vapor pressure is a measure of the surface pressure it takes to keep a liquid from vaporizing.

A light hydrocarbon like propane has a very high vapor pressure—it is very volatile. A heavier hydrocarbon like gas oil has nearly zero vapor pressure—it vaporizes very slowly...at normal temperatures. If you think for a moment, you will realize that any vapor pressure is a function of temperature. RVP is measured at 100°F, an arbitrary number Reid chose.

**Engine conditions.** Definitions out of the way, we can return to the vaporization problem. The RVP of gasoline must meet two extreme conditions. On cold starts, enough gasoline must vaporize to provide an ignitable mixture. Once ignition occurs, the rest of the gasoline in the cylinder will vaporize and burn too. The other extreme happens when the engine is running while completely warmed up or, even more extreme, is being restarted when it is hot. At that point, the gasoline vapor must not expand in the injection apparatus so much that no air can be mixed with it. Again, the mixture must be ignitable.

Refiners have found that there is a direct correlation between a gasoline's ability to meet those conditions and the RVP. Furthermore, they have found that the ideal RVP for gasoline varies with the seasons. In the dead of winter

in a place like Bemidji, Minnesota, cold starts need a gasoline with a 12 RVP or more. During the dog days of August in Brownsville, Texas, cars will not restart if the gasoline has a higher RVP than about 5 or 6.

Environmental regulations have a good deal to do with *the right* RVP, but more will be given concerning that later.

**Vapor lock.** One other constraint on vapor pressure is worth mentioning—vapor lock. Car engines can shut down if they encounter an unexpected high altitude or high temperature. At high altitudes, the atmospheric pressure is lower, and high RVP gasoline will tend to vaporize anywhere in the system. High temperatures aggravate the problem. The fuel pump tries to pump a combination of vapor and liquid when it is designed to handle only liquid. Consequently, the whole system will starve, and the engine will quit and will not start again until the temperature of the gasoline is lowered, which could take hours.

To avoid vapor lock, gasoline RVP is customized to accommodate the temperature and pressure conditions in the area, including seasonal temperature and barometric swings.

**Blending gasoline to meet RVP requirements.** So much for what cars need—how do refiners get there? If you look at the list of gasoline blending components in table 14-1, you will see that several have RVPs outside the limits just mentioned. The answer might jump right out at you: as the industry evolved, butane became the pressuring agent of choice.

**Table 14-1.** Vapor pressures

Blending Components	RVP (psi)
iC <sub>4</sub>	71.0
nC <sub>4</sub>	52.0
Reformate	2.8
Hydrocrackate	2.5
Alkylate	4.6
Straight Run Gasoline	11.1
Straight Run Naphtha	1.0
Cat-cracked Gasoline	4.4
Coker Gasoline	4.0

If you sat down to design the scheme for the refining industry to blend gasoline, you would probably reject the thought that there would be enough butane around to be the marginal component used for all vapor pressure control. But for many years and places that is the way it was. Butanes are

made in refineries as a by-product of conversion processes. They also come into the refinery mixed with some crudes and are recovered from natural gas in gas processing plants. Somehow these three rather inelastic supplies end up providing all the butane that is needed for gasoline blending.

Getting down to nuts and bolts, the procedure for calculating the amount of butane needed to pressure up the gasoline involves only algebra and weighted averages. Vapor pressure calculations are not exactly related to the volumetric weighted averages, but for the purposes of this drill, they are close enough. Suppose the RVP specification is 10 psi and you have five components available. Table 14-2 shows how much normal butane is needed. Use that old, vexing mantra from high school, "Let X equal the amount."

**Table 14-2.** Blending for vapor pressure

Component	Volume in Barrels	RVP	Volume × RVP
Straight run naphtha	4,000	1.0	4,000
Reformate	6,000	2.8	16,800
Hydrocrackate	1,000	2.5	2,500
Cat-cracked gasoline	8,000	4.4	35,200
	19,000		58,500
Normal butane	X	52	52X

If X = the amount of butane you need, after blending, the volume will be 19,000 plus X. For a spec of 10 psi RVP:

$$\begin{aligned} 10 \times (19,000 + X) &= 58,500 + 52X \\ 190,000 + 10X &= 58,500 + 52X \\ X &= 3,131 \text{ bbl of normal butane required} \end{aligned}$$

Total gasoline production is 19,000 bbl + 3,131 bbl = 22,131 bbl.

So the calculation is pretty simple, but some of the implications might be mentioned. Since the specification for RVP is higher in the winter than in the summer, the capacity to produce gasoline is higher in the winter. The higher the RVP spec, the more butane refiners can blend in, and the more total volume of gasoline they make. Unfortunately, in most markets, except those like Miami Beach, Florida, or Vail, Colorado, the demand for gasoline is lower in the winter than the summer. The additional winter gasoline blending capacity does, however, give some flexibility to increase distillate fuels production without having to undermanufacture gasoline.

Also, in the hotter climates, local environmental regulations set such a low maximum on RVP in the summer (perhaps as low as 6.5–7.0) that no butane can be added to the gasoline without exceeding the spec. That can exasperate refiners' efforts to meet market demand during the peak demand season.

**Normal versus isobutane.** Why would refiners use normal butane instead of isobutane to pressure gasoline? There are several good reasons. First, the RVP of normal butane is 19 psi less than isobutane (71 versus 52), which means that more normal butane can be blended in. Second, normal butane is more “normal” and plentiful in nature. Third, isobutane has another welcome home, alkylation. Very often, refineries do not even have enough isobutane to satisfy the appetite of the alky plant. Either they have to buy some or if they have one, they can use a *butane isomerization plant* (see chapter 12) to convert normal butane to isobutane. All this results in isobutane prices higher than normal butane prices and that gives an incentive to blend as much normal butane as allowed.

Do you recall back in the “good old days” watching a car gas tank as you filled it and seeing a wavy-looking vapor appear around the gas cap? That was butane escaping from the gasoline blend. If you recall correctly, you probably saw more vapors in the winter than in the summer. That was the result of the higher vapor pressure spec and more butane in the winter versus the summer. Since those times, the escaping butane and other hydrocarbons have been identified as major contributors to air pollution, and lower RVPs have been mandated to restrict those emissions. Many places also have clumsy vapor recovery systems on the nozzle to capture and recycle the vapors.

## Octane Number

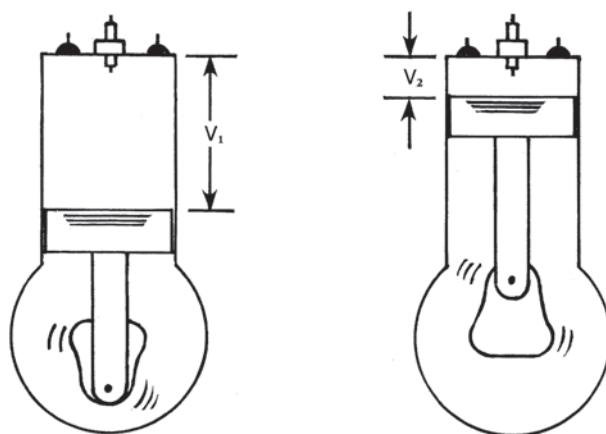
Everyone knows that bigger and more powerful cars need higher octane gasoline, and they accept that higher octane gasoline should cost more. This section will give you a clue why that is, in fact, true.

Octane numbers are measures of whether a gasoline will *knock* in an engine. That is a fine definition, but it requires an explanation of another almost universally obscure phenomenon, knocking.

**Knocking.** You will find it helpful to refer back to figure 14–1, the diagram of the engine cycle. After the gasoline/air vapor is injected into the cylinder, the piston moves up to compress it. As the vapor is compressed, it heats up. (Have you ever felt the bottom of a bicycle pump after you have pumped up a tire? It is hot—the same effect as in an engine cylinder.) If

the gasoline/air vapor is compressed enough, it will get so hot that it may *self-ignite*, without the aid of a spark plug. If this happens before the piston reaches the top of the stroke, the engine will knock and push the piston in the wrong direction, against the crankshaft instead of with it. Typically, knocking occurs only momentarily before the spark plug flashes so knocking is usually perceived as a click, ping, or...well...*knock* coming from the engine. Clearly knocking is bad for an engine since it not only works against the engine's motive power and lowers mileage efficiency, but it is also tough on the mechanical parts.

At the very early stages of engine development, refiners discovered that the various types of gasoline blending components had different knock behavior. A consistent way to measure when a blending component would knock used the *compression ratio*. In figure 14-2 the compression ratio is shown as the cylinder's volume at the bottom of the stroke divided by the volume at the top of the stroke. A big compression ratio is more likely to cause a gasoline to preignite than a small one. The test apparatus for measuring knocking uses this thought. The smallest compression where a gasoline starts to knock is measured against an arbitrary scale called *octane numbers*.



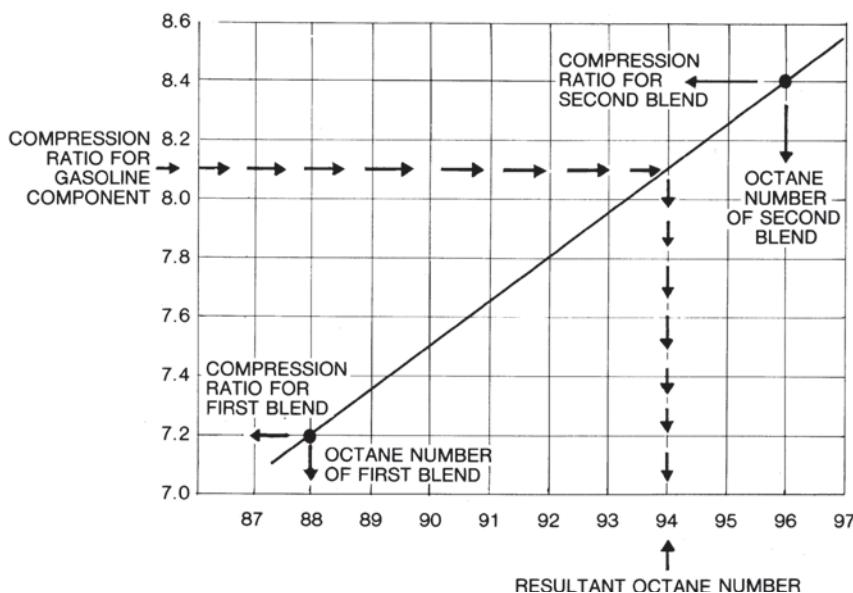
**Fig. 14-2.** Compression ratio equals  $V_1 : V_2$

Early on, refiners agreed to define isoctane,  $C_8H_{18}$ , as 100 octane gasoline and normal heptane,  $C_7H_{16}$ , which knocks at a much lower compression ratio, as zero octane gasoline. By using a test engine, any gasoline component can be matched with blends of isoctane and normal heptane.

**Definition.** The octane number of any gasoline blend or blending component equals the percent of isoctane in the isoctane/normal heptane blend that knocks at the same compression ratio as the gasoline or component being evaluated.

**Testing for knock.** An explanation of the test procedure might help with that seemingly convoluted definition. In its most basic form a test engine is used that has a movable cylinder top that can be screwed up or down to vary the compression ratio. The gasoline whose octane number is to be measured is fed into the engine. As the engine is running, the head is turned down, increasing the compression ratio. At some point, knocking will occur. Originally testers sat next to the engine with their heads cocked and listened for the knock by ear. But now they have a little more interesting life because they can use electronic detonation meters. After noting the compression ratio when knocking started, they shut down the engine and return the cylinder head to the top.

Two blends of iso-octane and normal heptane are concocted, one that the tester guesses will knock at a higher compression ratio and one at a lower ratio. The octane numbers of these blends are known by definition—the percent iso-octane. The tester runs each through the same test procedures noting the compression ratio when knocking occurs. That calibrates the test engine. By plotting the three data points, the octane number of the gasoline component can be read off a graph like that in figure 14-3.



**Fig. 14-3.** Plotting the octane number test

In that example, on a test engine, a gasoline component knocked at a compression ratio of 8.1:1. Two test blends were made up, one with 88% iso-octane (88 octane) the other with 96% iso-octane (96 octane). In the

test engine, they knocked at 7.2:1 and 8.4:1, respectively. Since the octane number of the gasoline component knocked at a compression ratio of 8.1, its octane number must be 94.0.

**Octane requirements.** So now you know what octane numbers measure. Why are they important? The design of an engine demands that the fuel behave in a certain way. The compression ratio of an engine determines the amount of power it can deliver. The higher the compression ratio, the longer the power stroke, and the more powerful the engine. So different size cars have different engine designs, and therefore, requirements for gasolines of different octane numbers. You don't get to vary the compression ratio of your car by turning the head up or down, so you have to buy the quality of gasoline that accommodates the car and compression ratio you have. You play the hand you're dealt (or for golfers, play it as it lies).

**Types of octane numbers.** You need to know two more sets of nomenclature about octane numbers: the different kinds and their uses. First, the *tests* for octane numbers are run under two sets of conditions. The *Research Octane Number (RON)* test simulates driving under mild, cruising conditions; the *Motor Octane Number (MON)* test is run under more severe conditions and simulates operations under load or accelerating. The two measures, RON and MON, give an indication of a gasoline's performance under the full range of conditions. (Perversely, the Research Octane Number measures conditions when you are "motoring along," while the Motor Octane Number measures conditions when you are *not*, such as when you are pulling a trailer or driving up a steep hill.)

In the 1960s there was a controversy among the U.S. Federal Trade Commission (FTC), U.S. refiners, and the car manufacturers about posting octane numbers on gasoline pumps. (They were not posted at that time. There was just "regular" and "premium.") The FTC wanted octane numbers posted. The refiners had been advertising "100 octane gasoline" as their premium product, which referred, of course to the RON. They wanted to post only the RON. They did not want to confuse the public (or embarrass themselves) by putting the lower MON on the pump. The car manufacturers favored the MON as a better measure of how their products performed, and they were happy to sell cars that needed the "lower" MONs. The FTC advocated posting RON and MON. "Too confusing," said the refiners and car manufacturers. The FTC finally arrived at a compromise by ordering the following be posted on gasoline pumps:

$$\frac{\text{RON} + \text{MON}}{2}$$

That measure did not have any particular meaning other than the fact that the controversy was over.  $(R + M)/2$  remains the nominal industry standard. The 87, 89, 91, or higher and lower numbers you see on gas pumps in the United States are the result.

The second piece of information about octane numbers relates to how they behave. When two gasoline components are mixed together, the octane numbers do not blend linearly. That is, the resulting octane is not always the simple, weight-averaged octane. However, and most fortunately, there is such a thing as a *blending octane number* for the RON and MON of every component and that does blend nearly linearly, at least close enough. Gasoline blenders learn through experience how the blending octane numbers relate to the “neat” octane numbers of the blending components they use. When references are made to RONs or MONs of components, they can mean either the true or blending octane number. To make things simple here, all references to octane numbers will mean the blending octane number, not the true number.

**Blending for octane number.** Nowadays, almost all refiners have made life easy for themselves and migrated to using  $(R + M)/2$  rather than the individual RON and MON to blend their gasoline. An example may help pull these ideas together. Take the blend of gasoline in the previous example where butane was added to achieve the vapor pressure spec. Calculate the  $(R + M)/2$  of the blend using the typical (but not universal) octane numbers in table 14-3. The octane number of that blend is 82.4  $(R + M)/2$ .

**Table 14-3.** Blending for octane number

	Barrels	$(R + M)/2$
Straight run gasoline	4,000	63
Reformate	6,000	89
Hydrocrackate	1,000	74
Cat-cracked gasoline	8,000	85
Normal butane	3,131	92.5
Total	22,131	82.7

Now calculate how much alkylate would have to be added to meet a minimum octane specification 87.0  $(R + M)/2$ . You have to know the octane number of alkylate, which for this example is 96.5  $(R + M)/2$ . Let Y = the amount of alkylate to be added. Here is what you know so far in table 14-4:

**Table 14-4.** Octane numbers

	Volume	(R + M)/2
Gasoline blend	22,131	82.7
Alkylate	Y	96.5
Specification (minimum)		87.0

In order to bring the 22,131 bbl blend with an 82.4 (R + M)/2 up to the spec of 87, the following amount of alkylate with (R + M)/2 must be added:

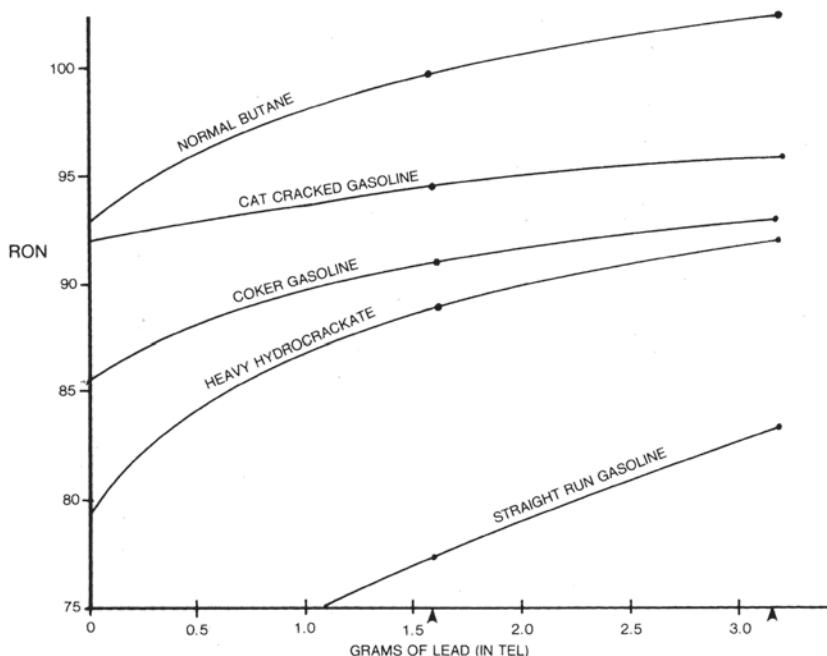
$$(22,131 + Y) (87.0) = (22,131) (82.7) + Y (95.9)$$

$$Y = 10,692.5 \text{ bbl}$$

What is wrong with this picture? Well, if you add 10,692.5 bbl of alkylate to the blend to meet the minimum octane specifications, you no longer meet the RVP specification. Going back and recalculating how much more butane to put in won't help. Then the octane number will be off again. You could solve the butane and alkylate dilemma by using two equations and two unknowns. But of course, on any given day, the refiner probably has to blend up two grades of gasoline, 87 octane and 92 or so. (Most refiners nowadays do not blend an intermediate grade but rather mix the higher and lower octane grades together to achieve the midgrade.) To solve for two grades and two specifications, octane number and vapor pressure, would require four equations and four unknowns. That is more algebra than anyone wants to handle with a pencil and paper. So, refiners employ a computerized mathematical technique called *linear programming* to do it for them, described in a few paragraphs.

## Leaded Gasoline

Until the 1970s refiners added lead to gasoline as a simple and economical way to increase the octane number. Lead, in the form of tetraethyl lead (TEL), increases the octane number of gasoline (that is, it suppresses the tendency to self-ignite) without affecting any other performance characteristics, including vapor pressure. Adding a small amount of lead, say about 3 grams per gallon in the form of tetraethyl lead, could increase the octane number of a gasoline blend by as much as 5 RON. You can see that in figure 14-4 from the effects on the various blending components.



**Fig. 14-4.** Effect of lead (TEL) in gasoline

Unfortunately, TEL is terribly toxic and even in low concentration in vapor form can cause...er...ah...oh, memory loss, blindness, or death. Because of this hazard, as late as the 1960s the Surgeon General of the United States set the maximum amount of TEL allowed in gasoline sold in the United States at 4 grams per gallon. The U.S. Environmental Protection Agency then acceded to the authoritative position of the Surgeon General. When the pressure to do something about the poor air quality in many U.S. cities became unforgettably unbearable, the EPA mandated the use of catalytic mufflers in all new cars to improve the exhaust characteristics. It turns out that lead poisons the catalyst in these mufflers. To deal with both the health effects of airborne lead and the detrimental impact on the catalytic mufflers, the EPA then ordered a gradual phaseout of the lead content in U.S. gasoline, starting in 1975. The use of lead in gasoline in the United States and most (but not all) countries around the world is now just a memory, at least for those who never had a personal encounter with lead vapor.

## Petrochemical Blending Components

With the advent of lead phase down, refiners began a desperate search for ways to maintain the octane level of their gasoline pool. They took the most obvious and readily available step—crank up the severity of the cat reformer, making higher octane reformate. Of course that reduced the volume of gasoline they could produce, as you saw in the chapter on cat reforming. So they added more reforming capacity and raised the cut point of naphtha to increase the feed to their reformers. As a consequence they made more benzene, just at a time when the EPA mandated a substantial reduction in the allowable benzene content in gasoline, since benzene is a carcinogen. Refiners faced the dilemma of building more refining capacity or looking for other ways to expand volume and octane at the same time. Oil company connections to the petrochemicals industry led them to experiment in the 1980s with a handful of readily available commodities: MeOH, EtOH, TBA, MTBE, ETBE, TAME, and the nearly unpronounceable THxME, THpME, THpEE, and THxEE. Only some of them made the final cut (Table 14-5).

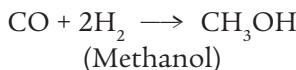
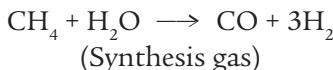
**Table 14-5.** Blending characteristics of ethers and alcohols

	RVP, psi	RON	MON	(R + M)/2
Methanol	40	135	105	120
Ethanol	11	132	106	119
TBA	6	106	89	98
MTBE	9	118	101	110
ETBE	4	118	102	110
TAME	1.5	111	98	105

**Methanol.** One of the oldest industrial chemicals around is methanol (MeOH or  $\text{CH}_3\text{OH}$ ), also known as methyl alcohol or sometimes wood alcohol because of the historic practice of making it by processing fresh-cut lumber from hardwood trees. Since 1923, chemical companies have used a more efficient process that starts with natural gas. Some companies in some parts of the world use naphtha as a starter.

With a casual look at the formulas for methane and methanol,  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$ , you might think that the route from one to the other would involve something like a catalyst and some water, maybe a little pressure and temperature. Unfortunately chemists have been searching for the silver bullet, the catalyst that would promote that reaction. They have found some,

but none that have proved commercial. Instead, the route from methane to methanol involves a complicated, intermediate step: the creation of synthesis gas, a mixture of carbon monoxide (CO) and hydrogen (H<sub>2</sub>):



The formulas are deceptively simple. The process and hardware are complicated and pricey, and they involve expensive catalysts, temperatures of 500°F to 800°F, and pressures of 4,000 psi to 5,000 psi. For that reason, almost all refiners chose to buy their methanol from chemical companies that specialized in the commodity and just blended it in.

Methanol has some properties that eventually undermined the enthusiasm for its continued use. First, it is corrosive and toxic and really bad if it gets on your person. Second, it has an affinity for water in the same way your favorite bourbon or scotch whiskey does. Unlike oil/water mixtures, methanol will not settle out of water and has to be separated by distillation, which is not at all practical if water and methanol mix anywhere but in a refinery or chemical plant. But to make matters worse, if methanol as a blendstock in gasoline picks up enough water, the methanol/water mixture will *phase separate*. It will remove itself from the rest of the gasoline blend. That makes handling difficult enough in refineries but even more so in pipelines and terminals, which are not meant to be water free. (They did not need to be because the water is removed at the terminals by drawing it off the bottoms of the tanks as *BS&W, bottom sediment and water*.) Worst of all, if a methanol blend leaks out of an underground storage tank, which almost all gas stations have, the *hydrophilic* (water-loving) methanol can get into the underground water supply much more easily than the hydrocarbon.

In the 1980s oil companies tried to commercialize a methanol blend in the United States, called M-85, made of 85% oil gasoline and 15% methanol. During the process they discovered more bad news about methanol. When it is burned in an internal combustion engine, it emits formaldehyde, a scary carcinogen, in the exhaust. Eventually the health hazards and water affinity caused M-85 and all other blends of methanol and gasoline to fail under their own weight.

**TBA.** At about the same time the chemical companies started promoting another chemical, tertiary butyl alcohol. TBA originated as a by-product from making propylene oxide. It can also be made on purpose by reacting butane with water or isobutylene and propylene. Refiners were attracted

to TBA because it worked in sympathy with methanol as a *cosolvent*. TBA dissolved easily in both methanol and conventional gasoline blending components. So it helped methanol stay in solution in the gasoline blend, even as it picked up water. With the demise of M-85, most of the hype around TBA vaporized too.

**MTBE.** Methyl tertiary butyl ether (with a name like that, no wonder it is called MTBE) became an expensive but more user friendly successor to methanol. Like methanol, MTBE has affinity for water. But it is an ether, not an alcohol, and it does not phase separate like methanol. Like methanol, it gives a big octane boost at 109 (R + M)/2 to the gasoline pool and has an RVP of only 8. (Both octane and RVP depend on what other components are blended in the gasoline.) Unlike methanol, it will not make you any sicker than the rest of the gasoline pool. On balance, refiners found MTBE attractive and started building their own MTBE plants.

The route to MTBE starts with isobutylene and, ironically, methanol. Refiners still had an aversion to building methanol plants, and in a serendipitous stroke of insight, continued to buy the commodity from chemical companies. Isobutylene was available from cat cracking and other cracking processes, but sometimes in limited supply. That created a market for isobutylene and an incentive to build plants that would create isobutylene from isobutane or even normal butane.

MTBE happens to also be soluble in water, which did it in. During the period of rapid increase in the use of MTBE, numerous underground gasoline storage tanks still exhibited minor leaks. Leaked gasoline often sinks in the ground until it reaches an aquifer, but it will sit atop that underground layer of water. MTBE will not. It will be leached into the water, similar to methanol. Environmental testing found numerous examples of MTBE in drinking water in the late 20th century, and that led to the demise of MTBE as a gasoline blending component in the United States and most other places in the world.

**ETBE.** For a while, refiners bought some ethyl tertiary butyl ether from chemical companies. Some have built ETBE plants, or use modified MTBE plants. ETBE has a higher octane number (109) and lower RVP (4) than MTBE, but about the same water affinity and toxicity. However it is more expensive to make and is not a big item on refiners' to-do lists.

**Ethanol.** To the surprise of traditional oil refiners along came a strong contender, both politically and commercially, for winning the octane enhancer race in the 1980s and 1990s. Ethanol, or ethyl alcohol, comes from the natural fermentation of vegetables. For millenia when farmers fermented grapes they got wine; from potatoes they got vodka; and from grain or corn they got whiskey. Ethyl alcohol,  $\text{CH}_3\text{CH}_2\text{OH}$ , is the operative

ingredient in all these beverages. During the 1970s and 1980s, farm lobbies around the world successfully convinced their national or local governments that growing and fermenting corn, sugar cane, and some other crops and using it for automotive fuel would be good for their energy independence and their economies. Government subsidies have brought on large amounts of natural ethanol capacity and created a consumer market for a blend of 90% conventional motor gasoline and about 10% ethanol. Ethanol also has an affinity for water, as any imbiber can tell you. Surely it leaks into aquifers in the same way methanol and MTBE did. Curiously, no one seems to care if they get a few parts per million of this pick-me-up in their drinking water.

Petrochemical companies also make ethanol from ethylene by reacting it with water in the presence of a phosphoric acid catalyst. The low conversion rate of 4% to 6% requires a lot of ethylene recycling through the reactor to get the job done. Consequently, ethanol from the petrochemical industry does not compete with ethanol from the agricultural sector, especially when government subsidies for only the renewable version are in place.

Ethanol's research octane number of 114 gives a real boost to the gasoline pool, but the RVP of 19 means that other lighter hydrocarbons have to be backed out of the pool to meet the vapor pressure limitations. In warm weather, that forces refiners to displace all the butane from ethanol-enhanced gasoline and even some of the C<sub>5</sub>s in the various blending components. Refiners have to run their fractionation columns differently and look for a home for the rejects. The pentanes are sometimes sent to the reformer to be converted to cyclic compounds or sold to chemical companies for ethylene plant feeds. The C<sub>5</sub> olefins can be made into the next group of exotics.

**TAME, THxME, THpME, THxEE, and THpEE.** This group of tongue-strangling chemicals emerged when refiners needed to remove C<sub>5</sub>, C<sub>6</sub>, and C<sub>7</sub> olefins from the gasoline pools to meet the eventual specifications, as you will read in a few paragraphs. TAME is tertiary amyl methyl ether (*amyl* is a synonym for a C<sub>5</sub>, as in amylene, C<sub>5</sub>). THxME is tertiary hexyl methyl ether; THpME is tertiary heptyl methyl ether; THxEE is tertiary hexyl ethyl ether; and THpEE is tertiary heptyl ethyl ether. All these chemicals have high octane numbers, low RVPs, and no other bad stuff like sulfur in them. However, refiners are loath to build these expensive plants unless regulators back them into a corner.

## Combating Smog and Ozone

As governments developed more science about air pollution, they found more bad actors. They connected carbon monoxide, oxides of nitrogen, and the hydrocarbons floating around in the air to the smothering ozone and thick layers of brownish smog that hung over the big cities. (The oxides of nitrogen include NO, NO<sub>2</sub>, and NO<sub>3</sub>, and are termed NO<sub>x</sub>.) In the 1990s governments started mandating that gasoline must have a minimum oxygen content of several percent. Since hydrocarbons from crude oil have no oxygen content, that meant of course the need for feedstocks from nontraditional sources. Refiners had by that time already been blending the *oxygenates*—ethanol, MTBE, and some of the other ethers—all of which have an oxygen atom in each molecule. Now they had to accelerate the program to meet the government proscriptions.

The theory behind the mandate involved introducing oxygen to the combustion process to assure more complete burning of the hydrocarbons to CO<sub>2</sub> and H<sub>2</sub>O, with virtually no CO. It also reduced the amount of unburned hydrocarbons coming out of the engines.

The change was intended to enhance the operation of the catalytic mufflers (that were already supposed to be doing the same thing) and improve those old cars that had old-fashioned mufflers.

## TOX, NO<sub>x</sub>, VOCs, and SO<sub>x</sub>

This unsavory group, which sounds like the name of a law firm formed by the children of itinerant circus performers, was the next show that came into town. Extensive, invasive engineering research found these culprits were spewing out the tailpipes of cars, vaporizing out the gas tank fill pipes, or generally leaking throughout the distribution systems. Governments, oil companies, and environmentalists adopted a shorthand clarion call, TOX, NO<sub>x</sub>, VOCs, and SO<sub>x</sub>, which stands for toxic compounds, nitrogen oxides, volatile organic compounds, and sulfur oxides.

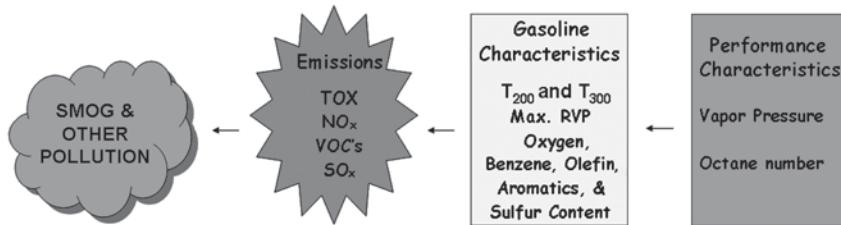
The conventional wisdom deemed a number of givens. The heaviest parts of the gasoline blending components, those at the high end points, contributed to hydrocarbon getting all the way through the combustion system unburned. The lightest of the hydrocarbons such as butane were evaporating or leaking out of the gas tanks, the engine seals, and the gas pumps before they could even get to the combustion chamber. Benzene in small concentrations was positively identified as a carcinogenic threat

and therefore one of the toxic compounds. Other aromatics compounds could result in unburned emissions, including benzene. Nitrogen oxides and VOCs reacted with sunlight to create smog and ozone. Sulfur oxides contributed directly to smog formation and caused the catalyst in mufflers to work poorly, emitting more VOCs and CO. Furthermore, olefins, with their reactive double bonds, tended to form gums and mess up the efficiency of the engines. And when they ended up as unburned tailpipe emissions, they facilitated smog formation—and on and on and on.

The consequence of all this good news/bad news was a succession of rules for the content and behavior of gasoline under the banner of *reformulated gasoline* for fuel sold in densely populated areas where ambient conditions do not disperse pollutants very effectively.

The complexity of gasoline blending now reaches art form, as you can see in figure 14-5. On the rightmost panel, gasoline blending has to provide fuel that meets the technical requirements of car engines: octane number and vapor pressure. The other three panels address the impact on the environment.

## Blending Gasoline



**Fig. 14-5.** Blending gasoline to meet environmental specifications

The object of the regulations is to prevent air pollution, but TOX, NO<sub>x</sub>, VOCs, and SO<sub>x</sub> coming out of cars contribute to different forms of pollution in mysterious, nonlinear ways. Refiners control those indirectly by the components they put into gasoline. In the United States, the EPA has devised a complex model that predicts the emissions of those four culprits based on just a few characteristics of each batch of gasoline. Refiners have to assure that their blends, on average, do not exceed various combinations of the four *emitants* (a term emerging from the pollution-speak community) in panel 2 by trading off various combinations of the independent variables in panel 3. The inputs to the model include distillation data (the percent vaporized at 200°F and 300°F), RVP, and the percent aromatics, oxygen, olefins, benzene, and sulfur. Refiners have to run this model for all the gasoline they ship, tally the results, and report them.

## Gasoline Blending: Impact on Operations

Do refiners have a clue how to deal with all these constraints? How do governments know if they are complying? There is no pretending that optimizing the blending of gasoline is simple. Consider for a moment the ever-increasing levels of complexity as refiners set the operating conditions in the processing units:

- a. Given the demands for three grades of gasoline and the availability of components, blend up the volumes that meet all the specifications—octane, RVP, pollutability—with no leftover components.
- b. Now think about varying the operating conditions of some of the process units. Change the severity on the reformers to adjust yields versus octane numbers, but be mindful of the benzene and aromatics content; increase the temperature in the cat cracker to generate more olefins and ultimately more alkylate, etc.
- c. Finally, what about diverting streams in and out of units? Send cat-cracked light gas oil to be blended to furnace oil rather than hydrocracked; remove the light ends from straight run gasoline to reduce RVP; cut the benzene precursors out of reformer feed; cut the bottoms off the straight-run naphtha (reformer feed) to make more kerosene/turbine fuel; and so on.

**Linear programming.** Incredibly enough, each of these conundrums can be represented by an algebraic equation. In a typical refinery, there can be as many as 500 equations and 2,000 variables. But who can deal with that morass of equations and variables?

During World War II, two mathematicians working for the U.S. government, George Danzig and John von Neumann, developed a technique called linear programming (LP) to allocate scarce resources to their highest uses. In 1947 they quietly published their astoundingly relevant algorithm. Not only will the LP method find solutions (there are many) to all the simultaneous equations in a refinery model, it will find the one solution that maximizes profit! How great is that?

Input to the LP model requires the variable costs of each operation, from distilling to blending; crude oil availabilities, distillation curves, and costs; and product demands, quality specifications, and prices. The LP searches through the equations to find the optimal solution, the one that generates the most money.

Every refinery has a model that the planners use to set operating instructions for the coming weeks and months. After all, a purchase of crude

oil might require a lead time of weeks before it arrives, and product demands vary seasonally. Still, the solution from the LP is but an approximation, for several reasons:

- The process unit yields fed into the model are only estimates. Depending on any number of things (time since the last shutdown, catalyst activity, air temperature, cooling water temperature, etc.) the yields and octane numbers could stray from the estimates.
- The inevitable unscheduled shutdowns of units, pumps, exchangers, and other equipment in the refinery will interrupt orderly flow.
- The crude composition could vary over the period. Crude prices undoubtedly will change, both in absolute levels and relative to each other.
- The product demands and prices will vary in the same way.

Nonetheless, as an analytical technique to develop a model or a plan, the linear program is the essential tool for organizing thoughts about how to run the refinery.

## Review

The subject of gasoline blending brings into focus most of the operations in a refinery. The rudiments of meeting octane and RVP specs are simple enough, but optimizing gasoline blending implies optimizing the entire refinery.

As a gesture of conciliation to you after reading this exhausting litany of refiners' problems, no TOX, NO<sub>x</sub>, VOCs, and SO<sub>x</sub> blending problem will be included in the exercises.

## Exercises

1. Define the following terms:

vapor pressure	oxygenates
RVP	compression ratio
power stroke	RON and MON
vapor lock	leaded gasoline
pressuring agent	TOX, $\text{NO}_x$ , VOCs, and $\text{SO}_x$
knocking	

2. a. Calculate the amount of normal butane needed to produce a 10.0 psi RVP for a mixture of 3,000 barrels of alkylate, 2,500 barrels of reformate, 1,000 barrels of hydrocrackate, and 3,600 barrels of cat-cracked gasoline. (Use the octane numbers in table 14-3.)  
b. How much alkylate [with  $(R + M)/2$  of 96.5] needs to be added to bring the blend up to 87  $(R + M)/2$ ?  
c. What problem with the blend occurs when you add the alkylate?

# 15

## DISTILLATE AND RESIDUAL FUELS

*Warmth, warmth, more warmth! For we are dying of cold and not darkness. It is not the night that kills, but the frost.*

— *The Tragic Sense of Life*, Miguel de Unamuno

This chapter covers the industrial and transport fuels in the middle and the bottom of the barrel:

- Kerosene
- Jet fuel
- Heating oil
- Diesel fuels
- Residual fuels

About 95% of the hydrocarbons that boil between 350°F and 800°F and that are not cracked into gasoline blending components end up as one of these fuels.

### Kerosene and Jet Fuel

Kerosene has a tradition of being the favorite fuel for exurban situations, especially rural cooling, lighting, and heating—not so much in the United States any more, but in many other countries. The attraction has always been its relative ease of transport in cans, drums, or trucks and its easy ignition. The spectacular rise of John D. Rockefeller's Standard Oil Company in

the early years of the oil era was based on the refining and marketing of kerosene, a fuel renowned ever since for “lighting the lamps of China.”

Kerosene is the cut between naphtha and gas oil, but the actual boiling range can run well into both, anywhere from 350°F to 600°F. It depends on whether the refiner has a market for the lighter or heavier end of the cut.

Commercial jet fuels are hardly more than hydrotreated kerosene. But given the sensitive, 35,000-foot nature of the product use, the specifications of the kerosene feed to the hydrotreater are considerably tighter. Commercial jet fuel (*Jet A* in the United States, *Jet A-1* elsewhere) has a boiling point specification of 205°C to 300°C. (The 205°C is actually the 10% recovered point, so the initial boiling point is slightly lower.)

Besides the constricting boiling points, commercial jet fuel must meet a score of other specifications, the most important of which are the freeze point, the smoke point, and the aromatics content. The freeze point measures the temperature at which crystals start to form in the fuel, potentially clogging the fuel filters. Airline passengers flying at 35,000 feet should take comfort that the specification is set at -40°C.

The smoke point and aromatics content are related to each other. The smoke point measurement uses a device much like a kerosene lantern—turn the wick up too high and the flame starts to smoke, blocking the light. The smoke is merely unburned hydrocarbon. The smoke point is equal to the length of the wick in a standard test apparatus when smoke starts to appear. Kerosene with a high aromatics content smokes sooner. The aromatics have a smaller hydrogen-to-carbon ratio than paraffins or naphthenes and are therefore more prone to incomplete combustion.

Military jet fuel (JP-5 and JP-8) has a lower 10% recovery point to allow more naphtha cut. The partial reason for this is to expand the capacity of domestic refineries to produce military jet fuel during emergencies. Many countries have weaned themselves away from JP-4 in favor of JP-8, which has a higher flash point specification, meaning it is safer to handle.

## **Heating Oil**

The numbering system for fuel oils is almost lost in history. Originally refiners established six grades of fuel oils, which more or less related to their cut points and consequently their applications.

- Number 1 oil, sometimes called stove oil, white oil, or just kerosene, is used for lighting, heating, and cooking.

- Number 2 oil, in the light gas oil range, is used as domestic heating oil but cannot easily be vaporized and used for lighting and cooking.
- Number 3 oil was an intermediate grade that died an early death.
- Number 4 oil is a light gas oil/heavy gas oil mix that is used in marine diesel engines and as industrial fuel oil.
- Number 5 oil is an industrial fuel oil and marine diesel fuel that has to be heated to move and burn it. It has also been rebranded extensively to road oil, poured directly on dirt roads for a semipermanent hard surface that helps keep down dirt and dust.
- Number 6 oil is a residual fuel oil used in industrial boilers and power plants and in ships' boilers as bunker fuel. It has to be heated to move it and burn it.

For safety reasons, each of these fuel oils has its own flash point specification, the temperature at which the fuels start to give off enough vapors to form a combustible mixture. (See the accompanying box, "Liquids Do Not Burn.") Numerous recorded tragedies have come from situations where gasoline inadvertently got mixed with heating oil. The gasoline vapors escaping from a basement storage tank found an ignition source in a nearby hot water heater and exploded (fig. 15-1).



**Fig. 15-1.** Flash points dangers

## Liquids Don't Burn

Burning is an exothermic chemical reaction—it releases heat. In the simplest form when it comes to hydrocarbon, burning methane creates carbon dioxide and water:



Burning more complex molecules such as a residual fuel,  $\text{C}_{20}\text{H}_{24}$ , gives corresponding amounts of carbon dioxide and water. In each case, to get a complete reaction, the hydrocarbon has to be in intimate contact with oxygen. For that reason,

*Liquids don't burn. Vapors burn.*

That explains the mechanics behind flash points. The still liquid allows insufficient infiltration of the oxygen. If virtually no vapors come off below the flash point temperature, nothing can ignite.

In the case of coal, the solid is pulverized to tiny particles to allow large surface areas to be exposed to oxygen to get the carbon/oxygen content and the chemical reaction:



However, even with coal, some heavy hydrocarbons always accompany the pure carbon, giving rise to some water formation. The cloud of vapor coming from a “smoke” stack is generally water vapor condensing into water droplets as it hits the colder air.

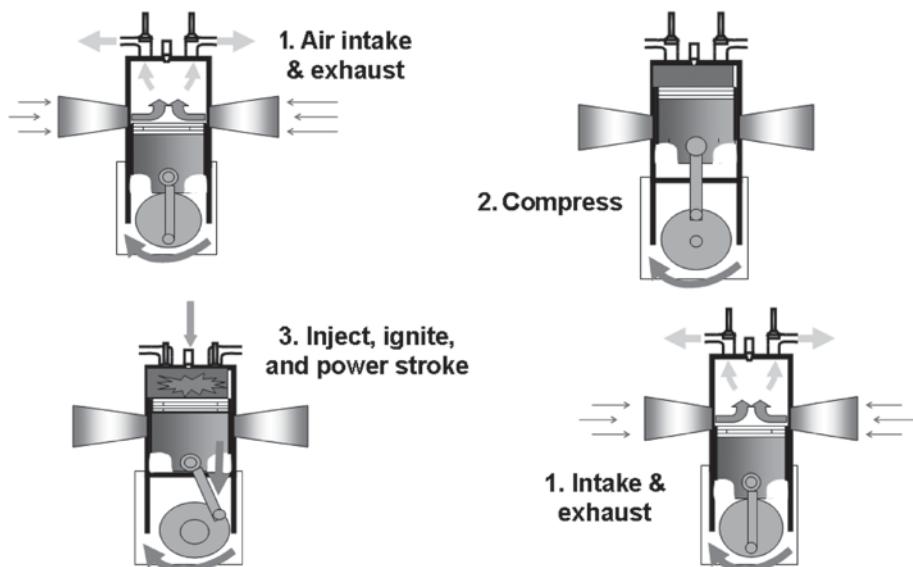
Finally, if there is insufficient oxygen available, either carbon monoxide may also form, as in a cat cracker catalyst regenerator, or the hydrocarbon may not completely burn, leaving the firebox, cylinder, or turbine as a dark vapor, otherwise known as smoke.

That explains why wood fires are hard to start and may give off smoke initially. Wood (cellulose) is mostly carbon, hydrogen, and oxygen and needs to be heated up to vaporize and burn cleanly.

Other specifications for these fuels include sulfur content, metals content (which can deposit on preheaters and burner tips), acidity, viscosity, and sediment content.

## Automotive Diesel Fuel

To understand the art of making diesel fuel, you have to forget half of what you learned about blending gasoline. Diesel engines and gasoline engines may look alike, but they work on two different principles. In one up-and-down cycle, the diesel engine does all that a gasoline engine does in two cycles. Unlike the gasoline engine, the diesel engine (fig. 15-2) has no spark plug, but it does have an air compressor. Also, the boiling point of diesel fuel is so high, it does not readily vaporize. The fuel injector sprays the fuel into the cylinder as atomized droplets.



**Fig. 15-2.** Two stroke diesel engine

As shown in figure 15-2, in the first step the piston drops below the air intakes from the compressor, allowing the compressed air to blow the combustion gases out the top exhaust valves. The piston moves past the air intake, compressing the air, making it hotter; so hot, in fact, that when the diesel fuel is injected as atomized droplets, they immediately vaporize and ignite. The expansion of the combusting gases pushes the piston down in a power stroke, past the air intakes from the compressor. The exhaust valves open, and the cycle repeats.

Outside the United States, automotive diesel fuel is known as *gas oil*. The name implies that the fuel has been boiled out of the crude oil and then condensed back to liquid oil, as opposed to residual fuel that never has

been vaporized. Automotive diesel engines power cars, trucks, construction equipment, and stationary engines for pumps and compressors. Larger diesel engines use heavier fuel, as discussed below.

**Cetane number.** For gasoline engines, preignition is an abomination. For diesel engines, it is the essence of operation—the droplets have to self-ignite. Refiners use cetane number as a measure of the self-ignitability of diesel. Reminiscent of octane number and its derivation, the cetane number is determined using two test fluids, in this case normal cetane ( $C_{16}H_{34}$ ) and alpha-methylnaphthalene ( $C_{11}H_{12}$ ). The cetane number of a fuel equals the percent  $C_{16}H_{34}$  in a mixture with  $C_{11}H_{12}$  that self-ignites at a compression ratio just like the fuel being evaluated.

To make testing easier, a simpler procedure for evaluating diesel fuel quality uses a *cetane index*, which is closely correlated with the cetane number. The cetane index can be taken from a nomogram (a multilined chart) or a formula involving the gravity and the 50% boiling point of the diesel fuel.

**Blending components.** All the light gas oil components can be used for diesel blending, but as in gasoline, some are better than others. Paraffins have a higher cetane number (higher is good). Aromatics have lower cetane numbers. This is just the opposite of octane numbers! The cracked light gas oils tend to have higher aromatic content (and cetane numbers of 32 to 35) mostly because they come from cracking large, complex molecules with lots of aromatic ring structures. Straight run light gas oils tend to be paraffinic and have cetane numbers of 50 to 55. Gas oils from a hydrocracker cracking heavy gas oil have higher cetane numbers. Generally, pumping in hydrogen during the cracking process produces paraffins and also saturates much of the aromatics into more cetane-friendly naphthenes.

The gas oils from *natural gas to liquids* (GTL) plants are strictly paraffins, mostly straight chained. They have such high cetane numbers and other good properties that they are generally not used neat as diesel fuel but only to blend up poorer quality blend stocks.

Refiners would like to use all the straight run light gas oil to make diesel fuel and use the cracked gas oils as furnace oil or hydrocracker feed. If the market does not allow that, sometimes a refiner will use an *ignition accelerator* additive to boost the cetane number by as much as 10. In cold weather, kerosene is often added to lower the pour point of furnace oil and at the same time raise the cetane number. (Kerosene is about 55 cetane.) Kerosene and jet fuel sulfur levels are generally too high to be used as an additive to the ultra-low diesel fuel now on the market.

**Quality.** In a drive across America you might find diesel fuel quality at “gas” stations varying from 40 to 50 cetane. In Europe, where diesel vehicles predominate, cetane numbers generally exceed 50.

One of the unintended consequences of lowering the maximum allowable sulfur content of diesel fuel to so-called ultra low levels is higher cetane numbers. Due to the more severe hydrotreating, more aromatics are converted to naphthenes and paraffins.

Diesel fuels can have numerous additives to improve performance:

- Organic nitrates for cetane improvement
- Pour point depressants
- Viscosity improvers to reduce wear
- Biocides to reduce slime
- Polymeric additives to reduce wax buildup for flow improvement
- Antioxidants to reduce varnish formation
- Copper deactivators
- Dispersants to reduce asphaltene deposition and fouling
- Antistatic additives to reduce explosions

## Residual Fuels

The end of the road for the bottom of the barrel, when a refiner runs out of coker or other residue reduction capacity, or does not have an asphalt operation, is resid (residual fuel). This last resort generally returns less money per barrel than the crude oil costs. It is called *residual fuel* because it is the leftover after a refiner has done all that can be done to make money out of crude oil—but enough disparaging remarks.

The basic constituent of resid is flasher bottoms, which by themselves are too viscous to market. Typically a refiner will dilute the flasher bottoms with *cutter stock*, perhaps cat-cracked heavy gas oil or other heavy cracked streams that might otherwise go to a hydrocracker.

The lower price of residual fuel inevitably attracted consumers' efforts to find ways to use it after all, as you can see from reading chapter 22, "Fuel Values—Heating Values."

**Boiler fuel.** The traditional use for residual fuel has been boiler fuel, the simplest way to burn hydrocarbon. The heated residual fuel is sprayed through a specially designed burner tip or nozzle into the firebox section of a boiler where the constant fire vaporizes the fuel droplets, igniting them

instantly. A maze of tubes in the heat transfer section of the boiler brings in water, which is heated to steam. The steam is then directed into electricity generators, ships' propulsion turbines, or another mechanical apparatus to use the energy.

**Marine diesel fuel.** Eventually the mechanical engineers developed diesel engines that could use the heavier, cheaper residual fuels. Diesels have the advantage over steam boilers in that more of the energy generated during combustion gets harnessed and does not go out the stack (used to be *smoke* stack but no one says that any more) and gets lost.

Marine diesel fuels come in a dozen or more grades, depending on the market and vendor. They fall into three categories:

1. Marine diesel, which is similar to automotive diesel but may have a lower cetane number and other looser specifications
2. Heavy marine diesel, which is residual fuel
3. Intermediate marine diesel, a blend of the two, and sometimes called *number 4 oil*, as mentioned above

Marine diesels use both two- and four-stroke mechanisms. Many of these mammoth machines have 8–12 pistons and cylinders 2–3 feet in diameter, with strokes 5–8 feet long. Because the fuel burns more slowly when heavy marine diesel fuels are used, they operate at much slower rates than automotive diesels, turning at perhaps 100 rpm to 135 rpm, compared to the thousands that register on the dash of a diesel car.

**Blending and quality.** Depending on where the fuel is combusted, emissions controls can determine the maximum sulfur content of the residual fuel. A power plant in a sensitive air quality area may require a maximum of 0.1% to 0.5% sulfur; a ship at sea may be able to burn 5% sulfur resid, but probably not in port.

Flasher bottoms usually have the highest concentration of sulfur and metals of all the cuts coming from crude oil. At the same time, the lighter diluents have to be added to the flasher bottoms to get the viscosity and the pour points down. Those usually have lower contaminant levels or are more easily desulfurized in a hydrotreater, so diluent tends to improve the properties of the flasher bottoms. Some might even say that "the solution to pollution is dilution."

Residual fuels tend to be a garbage dump where off-spec or otherwise bad streams can be disposed. Flash point often limits some volatile components from being blended into residual fuels.

## Review

Fuel oils originate in a variety of places around the refinery. Kerosene and jet fuel come from the distilling unit, and perhaps the hydrocracker. Diesel and heating oil come from the distilling unit and from the middle distillates fractions of the various crackers. Residual fuels are the dump site of the refinery, and have leftover flasher bottoms plus whatever diluent in the form of heavy gas oil can be spared from other units. The specifications of these fuels vary markedly, with the distillation cut points being the most prominent differentiator. Related to that is another crucial specification, flash point.

## Exercises

1. Explain how gasoline and diesel fuels differ in the following:
  - How ignition occurs
  - How octane and cetane numbers are measured
  - Components that favor higher quality
2. What is the difference between furnace oil and diesel?
3. What two designs can shipbuilders use to power a ship with residual fuel?

# 16

## HYDROGEN, HYDROTREATING, AND SULFUR PLANTS

*Neither to smell rank nor to smell sweet pleases me.*

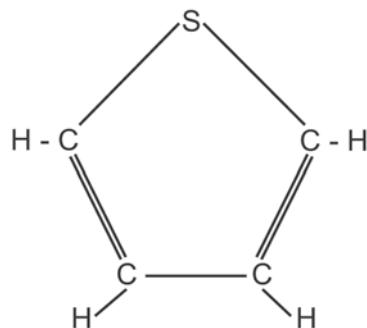
*—Epigrams, Decimus Magnus Ausonius*

Crude oils have all sorts of contaminants. As the petroleum fractions travel through the refinery processing units, these impurities can have detrimental effects on the equipment and the catalysts. When they come out the refinery gate in finished products, they can pollute the environment. Consequently governments or the refiners themselves may impose limits on the content of some impurities, like sulfur.

Hydrotreating does an effective job of removing many of the contaminants from many of the streams. Hydrogen is the operative input to the hydrotreating process.

### Hydrotreating

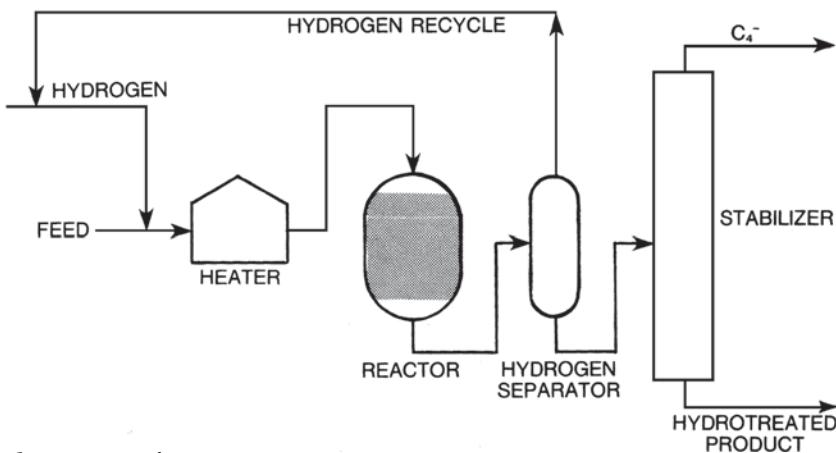
Any refinery streams that have C<sub>6</sub> and heavier hydrocarbons in them are likely to have some sulfur hidden in the mixture in the form of obscure compounds, even if they come from sweet crude. These are not little pieces of yellow material floating around in the oil. The sulfur atoms are attached or imbedded in various molecules such as the thiophene in figure 16–1, and therefore mechanical processes like distillation cannot remove them. It has to be done chemically. Hydrotreating is the normal process used to break the sulfur away.



**Fig. 16-1.** Thiophene, a hydrocarbon with a sulfur atom

In the hydrotreating process, the stream is mixed with hydrogen and chlorine and heated to anywhere between 500°F and 750°F, depending on the stream being hydrotreated and the purpose of the hydrotreating. The oil/hydrogen stream is then charged to a vessel filled with a catalyst in pellet form as in figure 16-2. The catalyst promotes several reactions:

- In the main reaction, hydrogen combines with the sulfur atoms to form hydrogen sulfide,  $\text{H}_2\text{S}$ .
- Nitrogen compounds are converted to ammonia,  $\text{NH}_4$ .
- Metals entrained in the oil react with the chlorine to form chlorides.
- Olefins and aromatics get saturated with hydrogen.
- As the contaminants crack away from the hydrocarbon, some methane, ethane, propane, and butanes form.



**Fig. 16-2.** Hydrotreater

The most popular catalysts being used these days are based on cobalt, tungsten, or molybdenum oxides. These exotic metals have proven to be resistant to poisoning from contaminants and easier to regenerate.

The stream coming from the reactor is sent to a flash tank where most of the propane and lighter products, including the unused hydrogen, the H<sub>2</sub>S, and the tiny bit of ammonia, go overhead. To completely strip out these light ends, a small fractionator is generally tacked onto the tail end of the process. Hydrotreating generates only a few percent of light gases, but the heavier the feed, the higher the percent.

The importance of hydrotreating has been gradually increasing for many years for three reasons:

1. Pretreaters in front of the cat reformers, cat crackers, and hydrocrackers protect the increasingly sensitive catalysts from getting fouled by sulfur, nitrogen, and metals.
2. Governments are continually lowering the allowable sulfur content in gasoline and fuel oils.
3. Hydrotreating will change the PONA composition of fuels, reducing the olefins and aromatics and increasing the paraffins and naphthenes. Sometimes this cuts some slack for other parts of the refinery that might have been constrained by having to meet olefins or aromatics limits in the finished products.

Some specific examples of all three of these drivers follow.

**Jet fuel hydrotreating.** Hydrotreating will improve the burning characteristics of distillates, especially jet fuel. The kerosene fraction can contain a large percentage of aromatic compounds that have higher carbon-to-hydrogen ratios. When these compounds burn, the deficiency of hydrogen can cause smoke. As a matter of fact, one of the specifications on jet fuel is the *smoke point*. Smoke is nothing more than unburned hydrocarbons, molecules that did not make it all the way to H<sub>2</sub>O and CO<sub>2</sub>. Nowadays you can sometimes see a darkish trail behind jet passenger planes as they rise from takeoff at maximum power, a mode in which unburned hydrocarbons are likely to make it through the jet engines.

The apparatus used to measure smoke point is similar to a kerosene lantern. A reservoir of fuel is fitted with a wick that can be cranked up or down to vary the length and the flame size. Size matters: the smoke point is a measure of how far the wick can be cranked up before smoke is visible above the flame. Smoke point equals the wick length, in millimeters.

Kerosene with a low smoke point (low is bad) can be improved by hydrotreating. During the process, the aromatic rings get saturated with hydrogen, converting them to naphthenes with more hydrogen-to-carbon ratios that burn cleaner.

**Distillates hydrotreating.** Distillate and jet fuel hydrotreaters can be and often are used interchangeably, running each stream on a *blocked-out* basis (one at a time) or running them together and splitting them afterwards. Distillates used for diesel fuel need at least some treating to get the sulfur levels on-spec, especially the ultra-low levels mandated in many places. In addition, hydrotreating the cracked light gas oils reduces the amount of aromatics compounds and raises the cetane number.

**Gasoline hydrotreating.** While hydrotreating effectively reduces the sulfur in gasoline blendstocks, it also reduces the olefins and aromatics content by saturating the double bonds with hydrogen. The bad news is that it also reduces the octane number as the aromatics compounds get saturated to naphthenes.

**Pyrolysis gas hydrotreating.** One of the coproducts of making ethylene from naphtha or gas oil is pyrolysis gasoline (covered in chapter 19). This gasoline stream has a high content of aromatics, olefins and *diolefins* or *dienes*, all molecules that have one or more sets of double-bonded carbons. *Alkynes*, molecules missing so much hydrogen they have a triple bond, like acetylene, may also be around. Often, pyrolysis gasoline is only suitable for gasoline blending in small concentrations. It smells bad, has a funny color, and forms gum in fuel injectors.

**Cat feed and reformer feed hydrotreating.** To protect the catalyst and improve conversion rates, cat reformer feed is almost always hydrotreated. Hydrotreaters in front of cat crackers have a triple purpose. They protect the catalyst; they result in lower contaminant CCU products; and the conversion of some of the aromatics in the cat feed also enables better conversion rates. The hydrotreating catalyst not only protects the CCU catalyst, it works in sympathy with it.

**Residual hydrotreating.** Residual fuels are likewise under environmental pressure, and, somewhat belatedly, residual desulfurization facilities have been commercially developed. Although the flow diagrams are similar to lighter stream hydrotreaters, the hardware and yields are different. Residual streams have much lower hydrogen-to-carbon ratios. In addition to needing a larger presence of excess hydrogen in the reactor, resid hydrotreaters operate at higher pressures to minimize coke formation. So a residual hydrotreater must be built as sturdily as a hydrocracker, an expensive proposition.

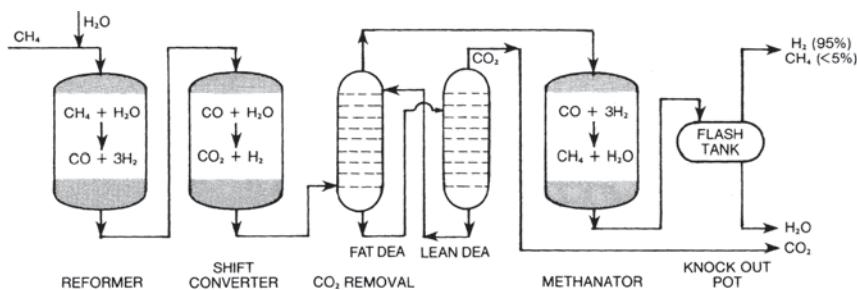
The yield from hydrotreating residuals has higher light end production. In the large molecules prevalent in residual fuels (especially the “trimethyl chickenwire” compounds), sulfur, nitrogen, and metals cannot be removed without literally destroying the molecule to spring the imbedded pollutant. In the process the smaller molecules result.

## Hydrogen Sources

The first stop in a refinery to get hydrogen is the cat reformer. The light end by-products of the reforming process contain a high percent of hydrogen, so the stream is deethanized or depropanized to get a methane/hydrogen stream with a high concentration of hydrogen. But refiners may still have to resort to other sources.

**Hydrogen plant.** Usually the reformer cannot satisfy all the hydrogen requirements in a refinery if there is an H<sub>2</sub>-hungry hydrocracker in operation. Hydrogen can be produced on purpose (not as a by-product) in a plant called a *steam methane reformer (SMR)* as shown in figure 16-3.

As the process engineers considered ways to make hydrogen, they looked for chemical compounds with a high proportion of hydrogen in order to waste as little as possible of the remaining material or the energy used to process it. The two compounds they finally chose were almost too obvious: methane (CH<sub>4</sub>) and water (H<sub>2</sub>O).



**Fig. 16-3.** Steam methane reformer

The trick in the SMR is to spring as much of the hydrogen from methane and water as possible, but with a minimum amount of energy (fuel) consumed in the process. With the aid of some very useful catalysts,

some high temperatures and pressures, and heavy duty equipment, the typical SMR operates in four stages:

1. *Reforming.* Methane and steam (the H<sub>2</sub>O) are mixed and passed over a catalyst at about 1,500°F, resulting in the formation of carbon monoxide and hydrogen:

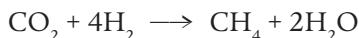
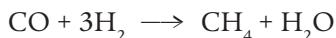


But in a refinery, not much use can be found for CO, carbon monoxide. That may not be so in a chemical plant, where they call this combination of CO and H<sub>2</sub> gases *synthesis gas*, and they use it to make some alcohols and aldehydes. But in a refinery they take a next step.

2. *Shift conversion.* Not content with the hydrogen already formed, the process exploits the carbon monoxide. More steam is added over another catalyst at 650°F to form carbon dioxide and hydrogen:



3. *Gas purification.* In order to provide a concentrated hydrogen stream, the carbon dioxide can be separated from the hydrogen by a solvent extraction process.
4. *Methanation.* Since the presence of carbon monoxide or dioxide in the hydrogen stream can mess up some of the applications, a cleanup step converts any traces to methane. A catalyst at 800°F is used.



In some places, a sulfur-free methane stream (natural gas) is not available. In that case, refiners substitute heavier hydrocarbons such as propane or naphtha. The equipment design and catalysts are somewhat more elaborate and the process is less fuel efficient, but it works.

**Scavenging.** The gas streams from hydrocrackers and hydrotreaters usually have moderate amounts of hydrogen that are not swept up in the separation for the recycle streams. To capture these volumes, the gas streams can be sent to one of three schemes to recover the hydrogen.

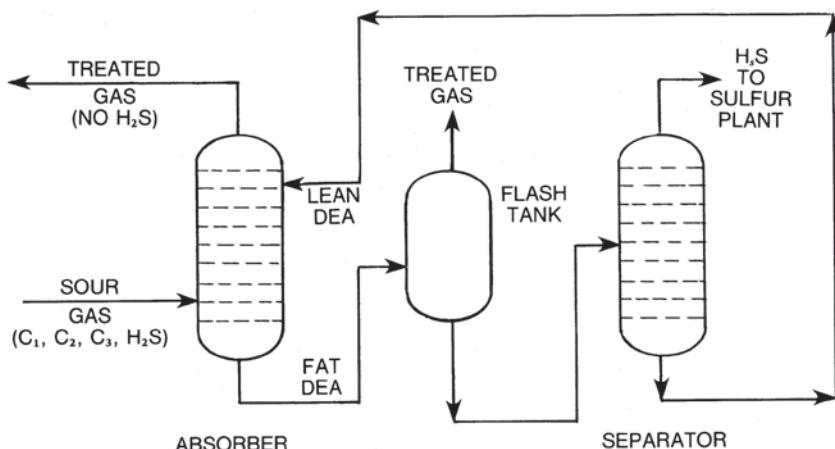
1. *Pressure swing adsorption.* In this simple process, the gas stream is passed through a vessel with an adsorbent (metal particles that act like flypaper). The hydrocarbons will stick to the adsorbent, but not the hydrogen, which comes out the back end at high purity, an appealing attribute of this alternative. After the adsorbent gets covered up with hydrocarbons, the operation is switched to a parallel vessel and the adsorbent is cleaned off by heating it, driving off the gases.
2. *Cryogenic separation.* By cooling the gas stream to about  $-250^{\circ}\text{F}$  under 200 psi pressure, almost all the methane and heavier will liquefy, leaving a hydrogen vapor stream. Large volume applications make this alternative attractive.
3. *Diffusion.* This process uses a membrane that allows hydrogen to pass through, but not the larger hydrogen molecules. This technique applies where the volumes of hydrogens are small.

## Sulfur Facilities

Hydrotreating creates hydrogen sulfide ( $\text{H}_2\text{S}$ ) streams—a deadly, toxic gas that needs careful disposal. The usual process involves two steps: first, the removal of the  $\text{H}_2\text{S}$  stream from the hydrocarbon streams; second, the conversion of the lethal  $\text{H}_2\text{S}$  to elemental sulfur, a harmless chemical.

**$\text{H}_2\text{S}$  recovery.** Until about 1970, much of the  $\text{H}_2\text{S}$  in refineries was used, along with the other light ends, as refinery fuel. The product of burning  $\text{H}_2\text{S}$  is  $\text{SO}_2$ , sulfur dioxide, which stinks like rotten eggs, but it does not kill anyone (immediately). Air quality regulations now limit  $\text{SO}_2$  emissions to the extent that almost 100% of the  $\text{H}_2\text{S}$  must be kept out of the fuel systems.

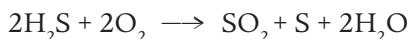
Recovery of the  $\text{H}_2\text{S}$  can be done by a number of different chemical processes. The most widely used is solvent extraction using diethanolamine (DEA). A mixture of DEA and water trickles down a vessel with trays or packing that will distribute the liquid (fig. 16-4). The gas stream containing the  $\text{H}_2\text{S}$  enters at the bottom. As the streams circulate, the DEA selectively absorbs the  $\text{H}_2\text{S}$  gas. The rich DEA is then fractionated to separate the  $\text{H}_2\text{S}$ , which is sent to a sulfur recovery plant. The stripped DEA is recycled. This process is similar to the lean oil/fat oil process for separating  $\text{C}_2^-$  gas from  $\text{C}_3^+$  gas described in chapter 7 on gas plants. The difference is that DEA selectively picks up  $\text{H}_2\text{S}$ , but not any hydrocarbons.



**Fig. 16-4.** H<sub>2</sub>S removal

**Sulfur recovery.** The conversion of H<sub>2</sub>S to plain sulfur is done in a process first developed by Karl Friedrich Claus in 1885. There are variations on the process today suited to various H<sub>2</sub>S/hydrocarbon ratios, but they mostly use a basic two-step, split stream process (fig. 16-5):

1. *Combustion.* Part of the H<sub>2</sub>S stream is burned in a furnace, producing SO<sub>2</sub>, water, and sulfur.

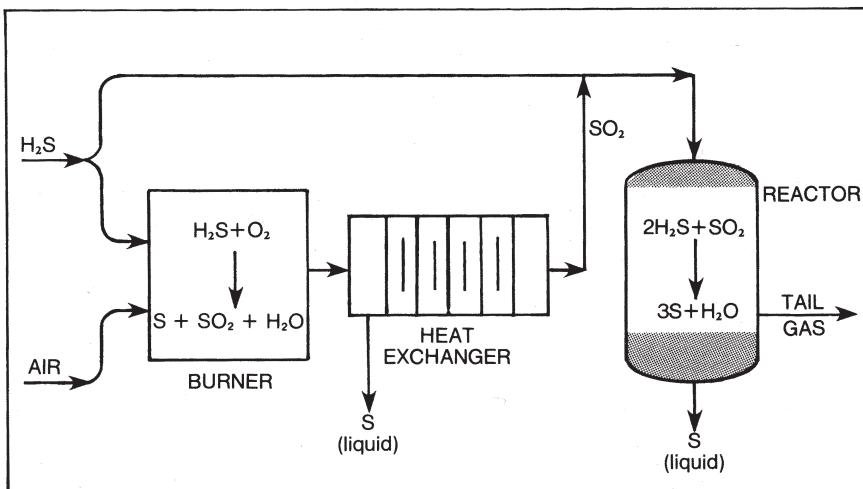


SO<sub>2</sub> and elemental sulfur, S, are formed instead of just SO<sub>2</sub> because the air (oxygen) admitted to the furnace is limited to one-third the amount needed to make all SO<sub>2</sub>. All the gases from the furnace are captured so that no SO<sub>2</sub> escapes to the atmosphere.

2. *Reaction.* The remainder of the H<sub>2</sub>S is mixed with the combustion products and passed over a catalyst. The H<sub>2</sub>S reacts with the SO<sub>2</sub> to form sulfur and water.



The sulfur drops out of the reaction vessel in the molten (hot liquid) form. Most refineries store and ship sulfur in the molten state, although some companies store it by pouring it on the ground in forms, letting it solidify. Sulfur can be stored indefinitely in this dry state, called a *sulfur pile*.



**Fig. 16-5.** Sulfur plant

Claus plants convert about 95% of the  $\text{H}_2\text{S}$  to sulfur. Some local environmental regulations may permit the balance of the  $\text{H}_2\text{S}$ , known as the *tail gas*, to be burned in the refinery fuel system, but not in the United States. The tail gas can be processed for  $\text{H}_2\text{S}$  removal in more elaborate facilities like Sulfreen, Stretford, or SCOT.

**SCOT (Shell Claus offgas treating).** The Claus plant tail gas contains small amounts of  $\text{H}_2\text{S}$ , plus two other pesky sulfur compounds created in the Claus plant, carbonyl sulfide ( $\text{COS}$ ) and carbon disulfide ( $\text{CS}_2$ ). In the SCOT unit, the  $\text{COS}$  and  $\text{CS}_2$  are converted to  $\text{H}_2\text{S}$  using yet another catalyst, a cobalt-molybdenum combination. The  $\text{H}_2\text{S}$  is then extracted and recycled to the Claus unit for conversion to sulfur. Between the two units, Claus and SCOT, virtually all the  $\text{H}_2\text{S}$  is recycled to extinction.

## Review

Hydrotreaters are second in number in a refinery only to fractionators. The hydrotreaters, the hydrogen plant, and the sulfur plant are intimately related. Hydrotreating relies on the hydrogen plant for its operative feed,  $\text{H}_2$ , to remove sulfur atoms and in the process creates  $\text{H}_2\text{S}$ , which has to be processed in the sulfur plant to segregate the S into a benign form before it reaches the environment.

## Exercises

1. Identify which of these streams are feeds, products, or internal streams in hydrotreating, DEA treating, Claus plants, and an SMR: H<sub>2</sub>S, CH<sub>4</sub>, S, CO, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, and SO<sub>2</sub>.

# 17 ASPHALT

*Muddy, ill-seeming, thick, bereft of beauty.*

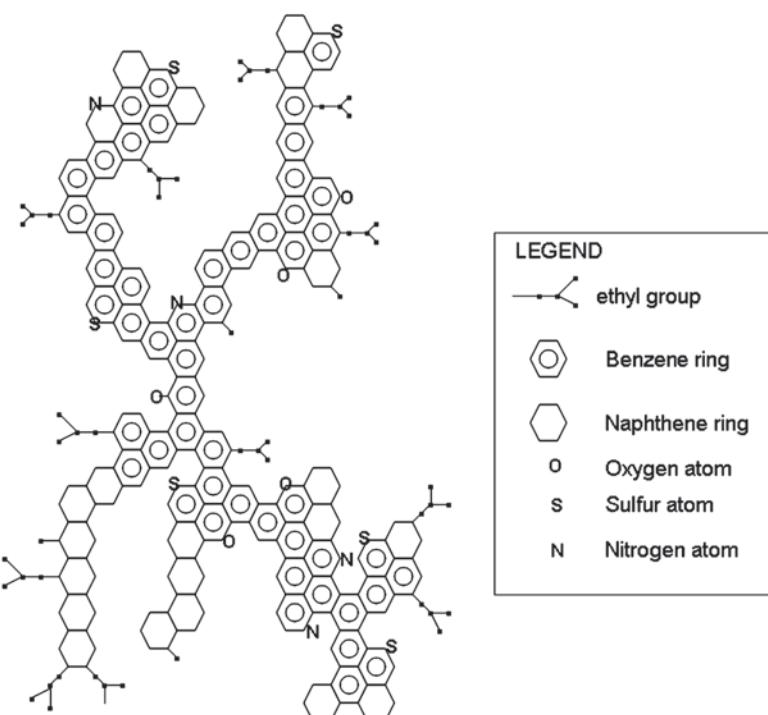
—*The Taming of the Shrew*, Shakespeare

Many refiners find manufacturing asphalt to be a rewarding option for the bottom of the barrel—as long as governments have money coming in to pay for roads. The business model for a few refiners, most of them with no more than 10,000 to 15,000 barrels per day distilling capacity, even focuses on asphalt as their primary product. The lighter cuts, gasoline through gas oil, are by-products for them, often sold to other refiners or product blenders. But most asphalt comes from larger refiners that think of asphalt as a higher value use of the bottom of the barrel than making residual fuel.

## Composition

Some crude oils, especially the heavier ones such as Arab Heavy, Boscan (from Venezuela), or Maya (Mexico) have a high concentration of asphaltenes in their straight run residue. Most of them then end up in the flasher bottoms. Asphaltenes, yet another classification of hydrocarbons, have a high carbon-to-hydrogen ratio. They have numerous six-carbon rings, many with double bonds, called *aromatic rings* after the benzene ring they resemble. Organic chemists sometimes nudge each other in the ribs, giggle, and refer to them as “trimethyl chicken wire.”

The 2-D representation in figure 17-1 does not even do justice to the complexity of asphaltenes. In a 3-D world, they are more like multiple layers of balled-up chicken wire, often wrapped around other asphaltenes.



**Fig. 17-1.** Asphaltene-resin complex (from Altamirano, et.al.; IMP Bulletin, 1986)

Besides asphaltenes, straight run residue may contain resins, which are a poorly understood class of hydrocarbons that are smaller but similar to asphaltenes. Scientists think resins have a peculiar, “groupielike” affinity for asphaltenes. Both asphaltenes and resins have small amounts of sulfur, nitrogen, vanadium, nickel, other metals, and oxygen as minor parts of their cyclic structures.

## Asphaltic Crude Oils

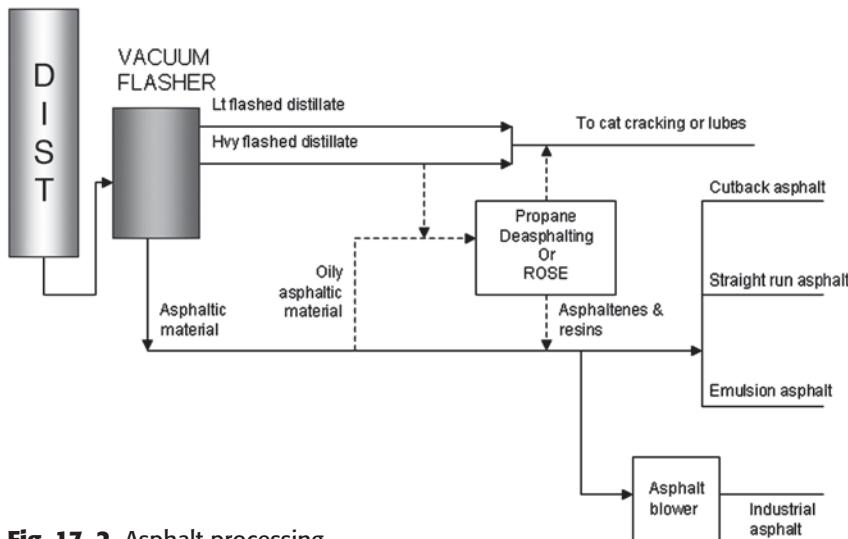
Asphaltenes come in hundreds of thousands of varieties, more than can be catalogued. Consequently, choosing a crude oil to make asphalt is close to black art, pun intended. Much of the knowledge about the quality of asphalt produced from various crude oils comes not from an examination of the crude oil assay but from experimentation—running the crude oil and testing the resulting asphalt for properties.

## Asphalt Products

Asphalts can be categorized into four groups, reflecting both the customer and the process (fig. 17-2):

1. Straight run asphalt
2. Cutback asphalt
3. Emulsion asphalt
4. Industrial asphalt

The first three are used essentially for paving roads and parking lots. Industrial (or blown) asphalt is used for pipe coating, roofing shingles, roof coating, and other waterproofing applications.



**Fig. 17-2.** Asphalt processing

## **Straight run asphalt**

Deep flashing at the vacuum flashing unit of straight run residue of some “asphalt-suitable” crude oils will yield flasher bottoms that can be used directly as asphalt. The bottoms are a black or dark brown material, more or less solid at room temperature. The higher the operating temperature in the flasher, or more importantly the deeper the vacuum, the more solid the asphalt. Too high a temperature, however, will lead to some cracking and will undermine the quality of the asphalt.

The most important characteristics of paving asphalts are measured by the softening point test and the penetration test. The softening point is the lowest temperature at which an object with a standardized weight and shape will start to sink into the asphalt. The most popular test method uses a ring and ball apparatus. Commercial grades of paving asphalt have softening points in the 80°F to 340°F range.

The hardness of asphalt, once it is applied, is measured by its penetration (“pen”). The apparatus for the test has a long needle with a weight on top. The depth to which the needle penetrates into the asphalt over time at a specified temperature is its penetration. Commonly, very hard asphalt has a penetration of 30 millimeters, while the softer grades range up to 300 millimeters.

A wide variety of grades of asphalt can be dispensed from a refinery by making blocked out runs. For a period of time the flasher can be run with a very low vacuum, producing 40 pen asphalt. Then at a less severe vacuum, 300 pen asphalt can be run down to another tank. By blending the two grades into trucks, tank cars, or barges, any grade in between can be supplied.

The composition of the straight run residue, of some crude oils may not allow asphalt manufacture directly from the vacuum flasher. Sometimes very long chain paraffins or naphthenes end up in the flasher bottoms. In that case, some refiners use a solvent extraction process to separate those oils from the asphaltic materials.

Also, running some crude oils can result in some asphaltenes and resins to exit the flasher at the top in the heavy flashed distillate (the heavier part of the flasher tops). Some refiners will just allow that stream to go to the cat cracker and hope the asphaltic molecules will crack apart. If they do not, they end up in the cat cracker cycle oil. Other refiners, especially those that use flasher tops as lube base stocks, will extract the asphaltic materials with propane deasphalting or the *residual oil supercritical extraction (ROSE) process*.

## Propane extraction

Propane has the unusual property that at certain temperatures it will dissolve paraffins and some naphthenes, but not asphaltenes and resins. Then at higher temperatures, the propane separates from the heavier oils. To exploit this, liquid propane is introduced into a mixture of flasher bottoms and/or heavy flashed distillate at the bottom of a column. The asphaltic material precipitates to the bottom and the lighter propane/oils mixture moves to the top of the column. The asphaltic material comes out the bottom as a slurry in propane; the mixture is heated and the propane is flashed off, leaving asphalt. The propane/oil combination warms up as it reaches the top of the column and the propane separates from the oil, which is then referred to as *DAO*, or *deasphalted oil*.

## ROSE process

A few refineries use the ROSE process to separate asphaltic material from oils used for cracking or lubes. ROSE takes advantage of the physical properties of propane, butane, or pentane in a series of extraction columns to separate out, at different pressures and temperatures and sequentially, the asphaltenes, the resins, and then the other oils.

## Cutback asphalts

When paving companies put asphalt down on a parking lot, they have to apply it hot, to assure the asphalt completely mixes with the aggregate. Asphalt is the binder that holds all the materials together. The temperatures at which the asphalt is fluid enough depend on the asphalt composition. To accommodate the trade-off between the desire for hard asphalt and the temperature limitations of the construction equipment, diluents can be added to the asphalt (the asphalt is cut back) to lower the flow temperature. After the asphalt is put on the ground, raked, and rolled, it sits for a few days, curing (hardening) as the diluent evaporates. That leaves behind a hard asphalt and durable road or parking lot at ambient temperatures.

The several grades of cutbacks are classified according to the rate at which they cure—RC cutbacks (rapid cure), MC cutbacks (medium cure), and SC cutbacks (slow cure). These are diluted with, correspondingly, naphtha, kerosene, and gas oil.

Of course, in many parts of the world, particularly in populated areas, just letting diluents evaporate into the atmosphere is totally out of the question. Cutbacks are prohibited in these places—environmental authorities see to that. Refiners have not been that unhappy about prohibitions against cutback asphalts. The thought had long nagged them that using valuable hydrocarbons as asphalt diluent, only to have them evaporate into thin (sometimes not so thin) air was a waste. So they created a benign alternative, emulsion asphalts.

## **Emulsion asphalts**

So what could be added to asphalt to make it flow at reasonable temperatures, that would be cheap, and that would not disturb the environment? Water, you say? How could that be? Water and oil do not mix.

Emulsion asphalts have about 30% to 50% water and 50% to 70% asphalt plus a tiny bit of an agent that creates the emulsion. The emulsifying agent behaves just like soap. One end of its molecule is *hydrophilic*; it has an affinity for water. The other end is *oleophilic*; it loves oil. Dishwashing soap works the same way to remove grease and oils from plates. After using a sinkful of soapy water for a while, all the soap molecules get attached to oil molecules and will not remove any more from the plates.

To make the emulsion, the heated liquid asphalt and water are put into a mixer called a colloidal mill where the asphalt particles are sheared, forming tiny droplets, only about 10 microns (0.0000001 meters) in diameter. The addition of about 1% emulsifier keeps asphalt suspended in the water. In this state, the emulsion has the consistency of heavy cream, more or less. After transport and laying, the water evaporates and the asphalt particles bond to each other, binding the aggregate.

Early in the ascension of emulsions, researchers painfully discovered that some emulsifiers react with the water to create a negatively charged emulsion. That makes them *anionic*. Many aggregates used as mixes are also negatively charged and will somewhat repulse the asphalt, especially in damp weather when the electricity can flow more easily. To combat this problem producers now use emulsifiers that are positively charged, giving asphalt emulsions (*cationics*) that readily grab on to the negatively charged aggregates. Most paving asphalt emulsions are now cationics.

## Blown asphalt

This is not slang for a batch of off-spec asphalt. Asphalt used primarily for industrial applications, mostly where waterproofing is involved, often must be a harder asphalt than can be achieved at a vacuum flasher. A refiner can harden a grade of asphalt by changing the asphalt composition in an asphalt blower, sometimes called an air rectification unit. Air bubbles are blown through hot asphalt. Only a moderate amount of the oxygen actually becomes part of the new molecules. The oxygen does, however, stimulate chemical reactions that cause asphaltenes to bond to each other, increasing the penetration and hardness. The asphalt also becomes more brittle. That is why asphalt blowing is used much less than it used to be for making paving asphalts.

## Review

Experience trumps analysis in asphalt. Refiners learn that deep vacuum flashing of some crude oils yields good asphalt. Flasher bottoms from other crude oils might need to be further processed in propane deasphalting or ROSE units to remove hydrocarbons that undermine the quality of the asphalt. In most paving applications, asphalts need a diluent to allow lower temperature handling. The traditional use of naphtha, kerosene, and gas oil cutbacks is environmentally unfriendly. Making emulsions using water and an emulsion agent has replaced cutbacks in many crowded parts of the world.

## Exercises

1. What new classes of compounds were introduced in this chapter that make asphalt possible?
2. What constituency vigorously objects to cutbacks being used and why?
3. What is the difference between anionic and cationic emulsions?

# 18 LUBRICANTS

*No one means all he says, and yet very few say all they mean,  
for words are slippery and thought is viscous.*

—Henry Adams, historian

Most people, when they hear the terms *lubricants* or *lubes*, conjure up an image of quart containers of motor oil, the amber fluid they may have once poured into their car's crank case or the black liquid they emptied out. Indeed, motor oil accounts for more volume than any other lube oil. But still, the applications include a bewildering array of products for numerous applications, including:

- |                       |                     |
|-----------------------|---------------------|
| Auto gasoline engines | Auto diesel engines |
| Railroad engines      | Stationary engines  |
| Marine diesel engines | Bearings            |
| Steam turbines        | Gears               |
| Refrigeration units   | Hydraulic equipment |
| Electric transformers | Metal working       |
| Switch gear           | Textile coating     |
| Capacitors            | Cable pulling       |
| Corrosion protection  |                     |

Engine oils account for about one-half the total volume of lubes. Another 20% of lube oils are also used in nonlubricating applications such as:

- |                       |                   |
|-----------------------|-------------------|
| Electrical insulation | Heat transmission |
| Rubber extending      | Food processing   |
| Tire manufacturing    | Pharmaceuticals   |

Each of these applications has unique products with precise specifications, making the lube department's book of lube specs run to hundreds of pages.

Over the last decades, the nitty-gritty of lube manufacture has, in large part, migrated away from refineries to specialized blending and compounding enterprises. The refineries do what they do best, process a small number of large volume base oils, usually less than a dozen. (Large is a relative term. All in all, lube base oils account for only 1% to 2% of refinery output, although the production at individual refineries varies widely from none to as much as 10%.) These base oils are manufactured to a variety of performance requirements with processing steps and additives to achieve them.

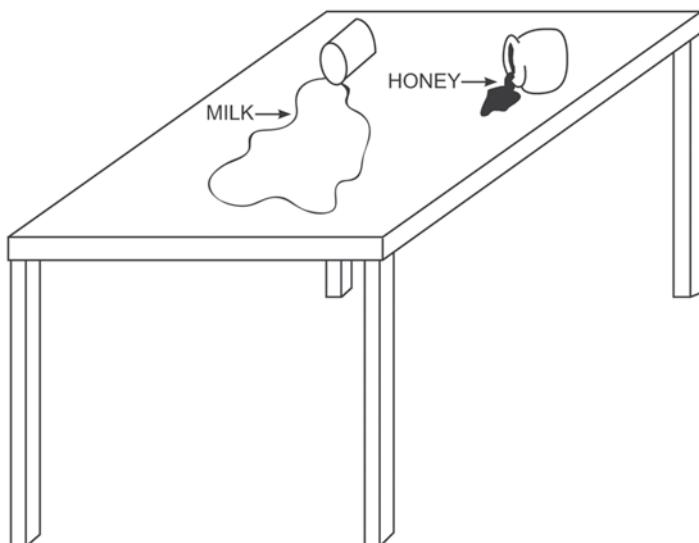
Warning: the rest of this chapter may be more focused and technical than the average reader might want to take on. But if you are interested in lubes, here it is.

## Properties and Specifications

As knowledge of lubricants and things to be lubricated became more technologically advanced, scientists and engineers upgraded recognition of their field by renaming it *tribology*. (The Greek word for rubbing is *tribos*.) Tribologists had learned, long before they had that title of course, that viscosity is the crucial property of lubricating oils.

**Definition.** When two parts rub against each other, *viscosity* is the property that determines whether a film of oil will stay between the parts without being squeezed out. Viscosity is measured by how fast a liquid will flow through a small hole in a container.

Highly viscous oils are thick and slow flowing. Low viscosity oils flow rapidly. The difference is apparent if a jar of (high viscosity) honey and a glass of (low viscosity) milk get tipped over simultaneously (fig. 18-1).



**Fig. 18–1.** Viscosity differences

The viscosity of most fluids changes with temperature. (Heat honey in the microwave for a few seconds and watch it pour more easily.) So temperature measurement accompanies any viscosity properties. Different lube oils change viscosities at different rates as they are heated, depending on the makeup of the oil. To deal with this, the *viscosity index* (VI) measures the change in viscosity between two standard temperatures, 100°F (40°C) and 212°F (100°C). The Society of Automotive Engineers deemed these two temperatures to be standards long ago; they established measurement methods and set up a definitive scale to classify lube oils. Now lubes are either low, medium, high, or (of later vintage as applications demanded even better performance) extra high viscosity index as follows:

LVI	< 35 Saybolt Universal Seconds (SUS)
MVI	35–80 SUS
HVI	80–110 SUS
XHVI	> 110 SUS

LVI and MVI base oils are usually called *naphthenics*, owing to the types of crude oil utilized to produce them. They are characterized by their very low wax content that eliminates the need for further processing to remove wax and by their excellent solvency (not present in higher viscosity index paraffinic oils).

The measure SUS (often inexplicably written SSU) refers to Saybolt Universal Seconds. A unit of SUS equals the time in seconds for 60 milliliters

of oil to empty out of a Saybolt viscometer through a calibrated tube orifice at a given temperature. (Saybolt is the now-international company that Edward Saybolt founded in 1898 to offer independent measurement services to the oil industry. They invented and coined both the procedure and device.)

Viscosity actually comes in two flavors—kinematic and dynamic. Physical chemists would state *dynamic viscosity* in centipoises (pronounced cent-ih-pwaz), a unit abbreviated *cp*. This unit was devised by Jean Louis Marie Poiseuille (1799–1869) to immortalize his otherwise totally unpronounceable name.

The same scientists would measure *kinematic viscosity* in centistokes, abbreviated *cs* and named after its inventor, the more enunciable Sir George Gabriel Stokes (1819–1903). Kinematic viscosity is equal to the dynamic viscosity divided by the density of the fluid being measured. These otherwise arcane terms are essential to engineering calculations that track performance of liquids. SUS, by the way, is a measure of kinematic viscosity, stated in its own unique units. Table 18-1 offers some palpable insight to viscosity measures.

**Table 18-1.** Typical viscosities of some fluids

	Centipoise <i>cp</i>	Centistokes <i>cs</i>	Saybolt Universal Seconds (SUS)
Water	1	1	31
Milk	3	4	40
Olive oil	35	43	200
SAE 30 oil	352	440	2,000
Honey	1,760	2,200	10,000

In recent years, the International Standards Organization has weighed in on the subject of viscosity. ISO has a grading system used for lubes that denotes the kinematic viscosity (in centistokes) for small ranges ( $\pm 10\%$ ), so that, for example, 30 cp viscosity covers 27–33 cp. ISO measurements are taken at 40°C (104°F), while the American Society of Testing Materials still measures viscosity at 100°F.

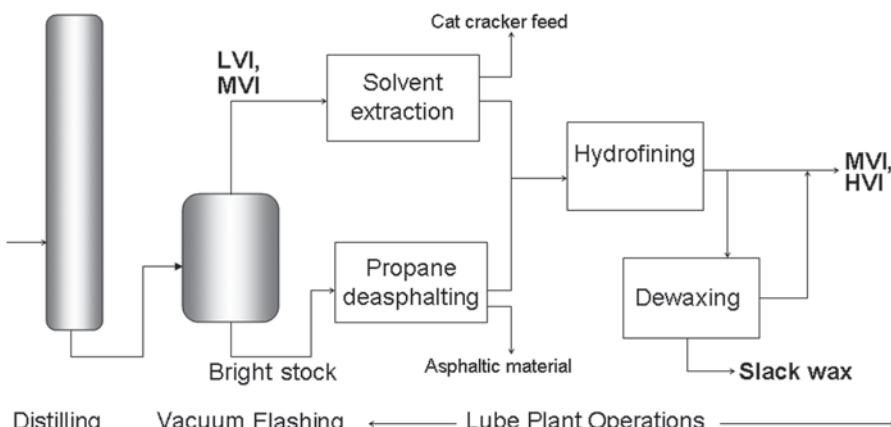
Regardless of all this interbureau intrigue and engineering perplexity, viscosity and viscosity index are the most important of many variables as refineries prepare lube oil base stocks.

## Refinery Operations

Most lube oil base stocks come from the bottom of the crude oil distillation unit—straight run residue. This residue stream is then fed to a vacuum flasher. Sometimes the lubes department has its own, smaller unit dedicated to lube base oil preparation. In other refineries, the vacuum flasher makes special, blocked-out runs to generate lube base oil feed stocks. In some cases, where a suitable crude oil is used, the flasher bottoms, puzzlingly called *bright stock*, can be used to make heavy, severe-duty lube oils. Bright stock can also come from the propane deasphalting unit described below where the lube bright stock is separated from asphaltic materials.

The performance of lubes, especially the viscosity, is sensitive to the types of molecules in the base oils. Branched chain paraffins work the best, and as second best, naphthenes do also. Aromatic compounds do not work because they have poor VI and oxidation characteristics. Long, straight chain paraffins, commonly called waxes, have high VIs, but at low temperatures they tend to solidify, drop out, and cause flow problems. Different crude oils, of course, can have different concentrations of these three molecule types, and their proportions are well-known from crude oil assays. Because of this, selection of lube-suitable crude oils often conflicts with the economics of general refining crude oils. That gives an extra cost burden for the lube business units to recover in the marketplace.

Typically the lube base oils coming from the flasher fall into the LVI, maybe MVI range. They contain enough pesky molecules to limit the viscosity performance. Further processing can improve them by removing or modifying the bad actors, using the schemes in figure 18-2.



**Fig. 18-2.** Lube processing

Asphaltenes are a major culprit. These molecules, depicted in figure 17–1 in the asphalt chapter, can have numerous aromatic rings, some imbedded sulfur, nitrogen, and oxygen atoms, and side chains of 20 or more carbon lengths. The rendition in figure 17–1 does not even do justice to the complexity because it shows only a 2-D view. Asphaltenes look more like pieces of balled-up chicken wire, wrapped around themselves and other molecules. That hardly suggests a slippery lubricant.

Another lubricity-detracting type of molecule, found particularly in bright stock, is the vaguely defined *resin*. Chemists have a hard time describing resins that reside in these process streams, other than that they are complex combinations of mostly carbon and hydrogen (as opposed to asphaltenes, which have some oxygen, nitrogen, and sulfur as well). Some scientists pragmatically differentiate resins from asphaltenes on the basis of what solvents will or will not dissolve each. Asphaltenes will not dissolve in gasoline or ether, but resins will. Fortunately these mysterious molecules, resins, are eliminated in the same way as the asphaltenes.

## **Propane deasphalting**

This process can separate almost all the asphaltenes and resins from the lube base oils and bright stock. For the bright stock base oils from the bottom of the vacuum flasher, the traditional solvent has been propane, though sometimes butane or pentane is used. In the extraction vessel, liquid propane is introduced to the bottom, the bright stock to the top. As the propane moves up the vessel, it preferentially dissolves the paraffins and most of the naphthenes, but not the asphaltenes and resins, which are predominantly aromatic compounds.

The lube base oil, which is the extract, moves out of the extraction unit with the propane. The raffinate has the asphaltenes, the resins, some of the naphthenes, and other aromatic compounds. The raffinate ends up in residual fuel blending, the asphalt plant, or coker feed. The propane is separated from the lube base oil by heating.

## Aromatics removal

For the lube oils from the top of the flasher, less attention can be paid to the small amount of asphaltenes and resins that make it out the top. Still there are aromatics included in these streams that depress viscosity measures, and they can be removed.

Solvent extraction might do the trick, but this time using NMP (n-methyl-2-pyrollidone), or sometimes furfural or phenol. These solvents all have cyclic structures, so in this case, with some modicum of irony, the extract is the unwanted aromatic constituents and the raffinate is improved lube base oils, just the opposite of propane deasphalting. The solvent also pulls out other bad actors, compounds containing oxygen, nitrogen, and sulfur atoms.

## Dewaxing

Pour point can be a critical specification. For example, motor oils have to perform during cold starts before the engine heats up, sometimes below 0°F. Base oils often have long, waxy, paraffin chains that will start to crystallize as the temperature drops below a level called the *cloud point*. The crystals in this cloudy mixture can plug up any filter in the system meant to catch sludge or other solid junk. At lower temperatures, typically another 10°F to 30°F less, the lubricant approaches a honeylike state (the *pour point*) and will not readily flow. That can cause moderate to intolerably severe damage to engines on cold starts. While many lubricants are designed to endure low temperature exposures, for some, such as sewing machine oil or trombone oil, pour point is not an issue.

To eliminate these waxes and lower the pour point and the cloud point temperatures of the lube base oils (lower is good), they can be processed in the dewaxing unit. In one incarnation of this process, the base oil is mixed with a solvent, typically *methyl ethyl ketone* (MEK) and toluene and then chilled. The solvent acts like antifreeze for everything but the waxes, which eventually solidify as the temperature falls. Filtering separates the wax from the rest. By distillation, the solvent is easily separated from the base oil and recycled.

Even with solvent extraction and dewaxing, the base oil may not achieve the XHVI properties necessary for some applications such as those high performance auto engines that have severe operating conditions. Some lube oil plants achieve these higher viscosity indexes and other properties by further treating HVI base oils with acids or by more severe hydrofinishing. Also, lube oil plants can start with slack waxes and subject them to hydrocracking and hydroisomerization to get molecules with branch chains instead of just straight chains.

## **Hydrofinishing**

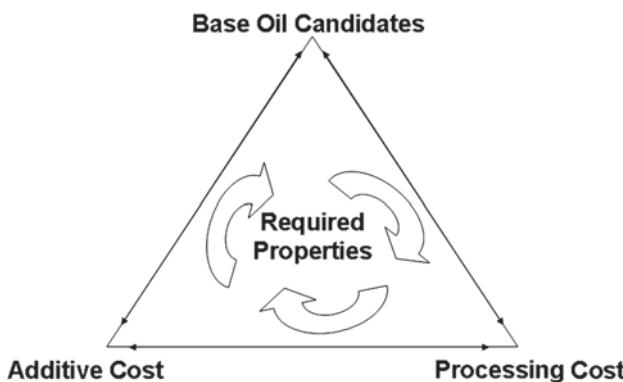
The base oils coming from the solvent extraction operation may still have some olefins (double-bonded compounds) or even some aromatics that can cause color issues. These compounds also tend to break down chemically in applications sooner rather than later by reacting with oxygen and other compounds. In the old days of refining, these streams were subjected to clay and acid treatment using sulfuric acid to remove the double bonds.

Nowadays, treatment with hydrogen does an even better job at less expense. The hydrofinishing unit looks like any other refinery hydrotreater, albeit smaller. It uses hydrogen over a catalyst to attack double-bonded compounds (olefins and aromatics) that tend to form carbon deposits. Hydrofinishing also removes oxygen, nitrogen, and sulfur. The plant processes each of the base oils on a blocked-out basis, running down to segregated storage until the next batch is started.

Hydrofinishing combined with hydroisomerization can also be used to dewax, destroying the waxes by cracking them into smaller molecules then changing the straight chains into branched chains. A hydrodewaxing unit is essentially a hydrocracker that uses a catalyst specifically designed to attack long chain paraffins. The cracked remnants from these two processes that are out of the range of lube base oils are removed by distillation.

## Blending

Meeting the specifications of 100 different lubricants calls for juggling the costs of three things: the cost of the various base oils, the cost of prospective additives, and the cost of blending the two together (fig. 18-3). The base oils can go through all the steps mentioned above, or not. Additives can compensate for processing. Blending various base oil grades plus additives has a cost.



**Fig. 18-3.** Blending lubricants

The hundreds of additives available that can improve performance characteristics aim to achieve the following, among other things:

- Improve the viscosity index (VI improvers)
- Depress the pour point or cloud point (depressants)
- Increase the resistance to oxidation (antioxidants)
- Prevent foaming (antifoaming agents)
- Prevent emulsifying (antiemulsion agents)
- Prevent rust or corrosion (anticorrosion agents)
- Prevent lacquers and deposits (detergents)
- Reduce friction (friction modifiers)
- Prevent scuffing (extreme pressure or EP agents)
- Keep contaminants in suspension (dispersants)
- Prevent wear by neutralizing acids from fuel combustion

They all cost money, of course, but they can make less costly base oils perform without, say, a dewaxing step. Additives typically comprise less than 10% of the total volume of a finished lubricant. A blender/compounder facility can have on hand hundreds of drums or small tanks of additives to satisfy an operation that behaves more like a drugstore than a refinery.

## Synthetic Lubes

A first cousin to petroleum lubricants comes from the petrochemicals sector—synthetic motor oils. These lubes generally have properties superior to oil-based lubricants because of the way they are derived. They start with ethylene, which of course comes from cracking oil in an olefins plant. The ethylene is then *oligomerized*, that is, made into straight chains of 10 or so ethylene molecules, called alpha olefins. Then the alpha olefins are also oligomerized, but not necessarily in straight chains, which would be paraffin wax. These *polyalpha olefins* are mostly branched chain paraffins.

Because of the extra steps to get to the end product, particularly the olefin plant, polyalpha olefins are generally pricier than oil-based lubes. But they are also totally free of any contaminants such as sulfur, nitrogen, oxygen, and metals. They are also a more consistent mixture of branched chain molecules, giving them their superior properties of viscosity and lubricity (the ability to reduce friction).

## Grease

When a part is to be lubricated but it is not in a closed container, lubricating oil will not do the job—it will run off. In those cases, a lubricant held in suspension by some thickening agent, i.e., grease, is used. Thickening agents include lithium/fatty acid compounds, clay materials, and some polymers. Sometimes other special purpose materials such as asbestos, graphite, molybdenum, silicones, and talc are added to provide insulation or lubricity. As with lubricants, other additives enhance the performance of greases.

## Waxes

Lube plants, like slaughter houses, let nothing go to waste. Having removed the waxy material from the base oils, further processing can make waxes suitable for market. Candles and polishes still show slight market growth. Wax for waterproofing and wax paper is nearly dormant, but numerous small applications, from cosmetics to rat poisons, keep the wax market lively. The product of the solvent dewaxing process described above is *slack wax*. In some dewaxing plants, slack wax is then further treated to remove the residual oil by *deoiling* to yield a high quality finished wax. Some other plants use a dedicated slack wax mild hydrotreater to improve the critical properties of wax—odor, color, taste, melt point, and the carcinogenic compound content.

## Review

The crucial property of lubricants is viscosity, and the flasher bottoms and flasher tops of different crude oils differ in this and other properties. In large part meeting lube specifications depends on the isoparaffins/naphthene/normal paraffin/aromatic content and the presence of asphaltenes and resins. Further processing can eliminate or convert the bad actors (the last four of the five) to give lube base stocks that can be blended with each other and with additives to give an extensive range of lube products.

## **Exercises**

1. What are the preferred molecular shapes of lubricants?
2. Where do lubricant base stocks come from?
3. What is the similarity between propane deasphalting and solvent dewaxing?
4. What two routes to the superior properties of XHVI are available?

# 19

## ETHYLENE PLANTS

*Soone hot, soone cold, nothing violent is permanent.*

—*A Petite Pallace of Pettie His Pleasure*, George Pettie

The closest refiners come to becoming chemical companies happens when they build ethylene plants. That is the reason why integrated oil/chemical companies built so many large ethylene plants: they bridged the gap between the two. Ethylene plants are better called *olefins plants*. However they are variously referred to as ethylene crackers (a misnomer—they do not crack ethylene), steam crackers (another misnomer, although steam *is* mixed with the feed) or “something”-crackers, with the first term denoting the feed, as in ethane cracker.

Olefin plants can be designed to crack a number of feedstocks. They usually fall into the following categories:

- Ethane
- Ethane/propane mix
- Propane
- Butane
- Naphtha
- Gas oil

The original olefin plants were built to produce ethylene to supply the growing appetite of the chemical industry for this basic building block. The propylene coming from an olefin plant attracted less interest. Propylene in abundant amounts was always readily available to be filched from refinery alkylation plants. Many early U.S. olefins plants were designed to

crack ethane or ethane and propane, first because ethane was abundantly available from natural gas, and second, because of the high yield of ethylene from ethane (table 19–1).

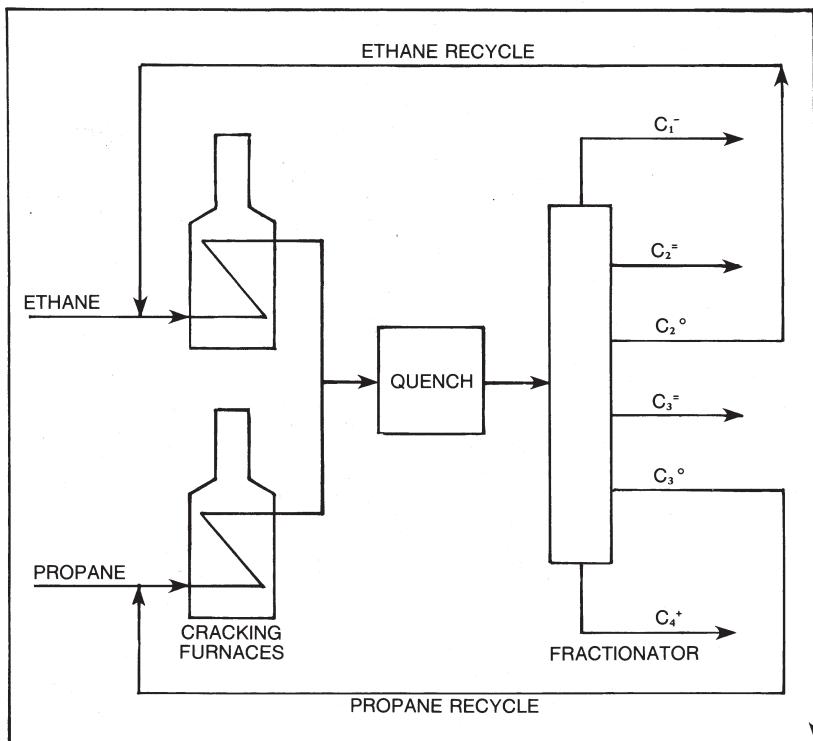
**Table 19–1.** Ethylene plant yields

	Pounds of Product per Pound of Feed				
	Ethane	Propane	Butane	Naphtha	Gas Oil
Ethane/Ethylene	0.77	0.40	0.36	0.23	0.18
Propane/Propylene	0.01	0.18	0.20	0.13	0.14
Butanes/Butylenes	0.01	0.02	0.05	0.15	0.06
Butadiene	0.01	0.01	0.03	0.04	0.04
Fuel Gas	0.20	0.38	0.31	0.26	0.18
Gasoline	—	0.01	0.05	0.18	0.18
Gas Oil	—	—	—	0.01	0.12
Fuel Oil	—	—	—	—	0.10

In other parts of the world where natural gas resources were scarce, naphtha emerged as the preferred flavor of feed. The demand for gasoline has always grown much slower outside the United States. That left lots of naphtha available to the chemical industry at relatively attractive prices. A few olefin plants have been built to crack gas oil, producing as by-products some high octane gasoline blending components. Those olefin plants, as large as medium-sized refineries, were integrated into refineries and produce a significant amount of the gasoline.

## The Process

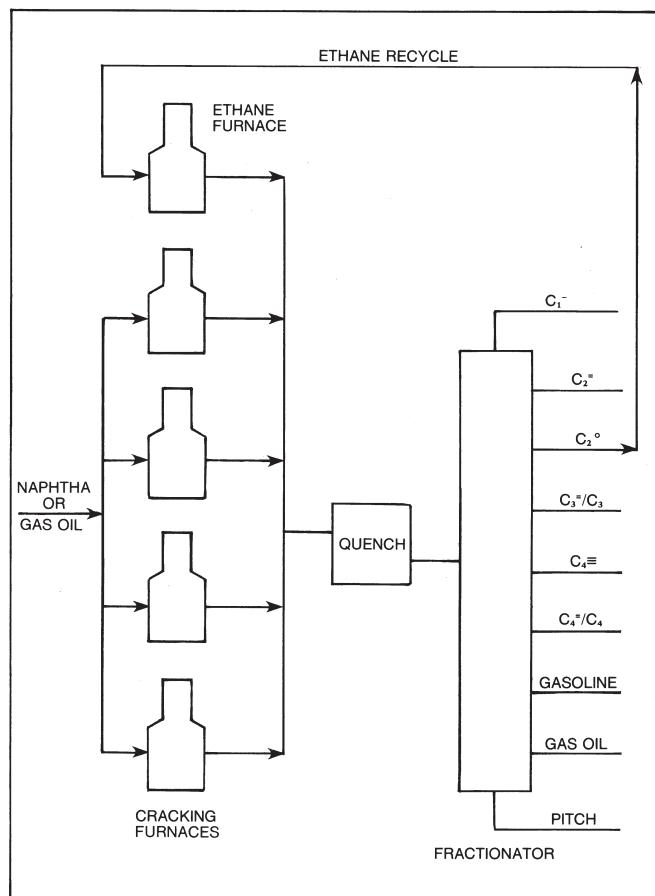
Ethane/propane crackers, as shown in figure 19–1, are the simplest design, but they demonstrate the fundamentals. The ethane and propane can be fed separately or as a mixture to the cracking furnaces where the short residence time (one-tenth of a second) and 1,200°F–1,500°F temperature yield a high volume of ethylene. The quench downstream of the cracking furnaces stops the cracking process from taking the feeds all the way to methane. But for the operating conditions and feeds and a few bells and whistles, olefin plants are just plain old thermal crackers.



**Fig. 19-1.** Olefins plant: ethane-propane cracker

In one pass through the cracking furnace, only about 60% to 70% of the ethane and propane disappear (crack). Downstream in the product fractionator, the ethane and propane are split out and recycled to the feed. Generally, the ethane is recycled to extinction, but some of the propane goes with the propylene.

The olefin plants designed to crack heavier feedstocks need extra separation facilities. Table 19-1 shows that ethylene and propylene make up only about 35% of the yield from cracking naphtha and gas oil. The rest has to be separated in a series of columns and a cryogenic unit to recover the ethylene. Figure 19-2 greatly simplifies the scheme by showing only a single fractionator. The yield in table 19-1 assumes that the ethane is recycled to an ethane furnace.



**Fig. 19–2.** Olefins Plant: Heavy Liquids Cracker

## Refinery Interactions

Olefin plants sometimes provide a home for a number of “junk” streams in a refinery. For example, the dry gas stream from a cat cracker is usually sent to the fuel system, even though it contains ethane, ethylene, some propane, and propylene. These components can be recovered by commingling them with the furnace outturns of the olefin plant before they head for the separation section.

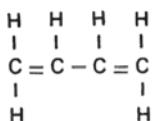
As another example, some of the naphthas in the gasoline pool are of such low octane they get shut out of the gasoline pool as a blending component. A normal pentane (RON of 62) or normal hexane (RON of 26) stream in refineries that have no  $C_5/C_6$  isomerization unit could be examples. These streams can make attractive feedstocks for refiner-owned olefins plants, turning trash into treasures.

On the outturn side of the olefin plant, refiners find some other complementary opportunities too. Beside the gasoline range products, called *pyrolysis gasoline* or *pygas*, the butanes and butylenes can generally find a home in the refinery processes.

## Products

Ethylene is normally sold as a stream with 99% or greater purity. Deliveries are almost always by pipeline. Propylene is bought and sold in three different commercial grades that differ by the accompanying amount of propane mixed in. Polymer grade propylene is 97% to 99% propylene; chemical grade is 92% to 95%; and refinery grade is 50% to 65%. Refinery grade propylene is the propane/propylene mixture coming from cat crackers, the biggest source of propylene in a refinery. Chemical grade propylene comes out of naphtha and gas oil at about 92%, with 8% propane. Either of these two grades can be fractionated to get the polymer grade.

A commercial chemical product that turns up in the olefin plant outturns but rarely in the refinery sector is butadiene (fig. 19-3). This chemical is in the *diolefin* family and has two double bonds with the formula  $C_4H_6$ . The two double bonds make it doubly reactive, especially for creating plastics and rubber compounds. This extra reactivity, however, makes it prone to gum formation and other undesirable reactions when it is used in gasoline, so if it is in small quantities, it is hydrotreated to butylenes. Otherwise it is used as a chemical feedstock.



**Fig. 19-3.** Butadiene

## Review

Olefin plants, the makers of the petrochemical base products ethylene and propylene, can have an affinity for refineries. Naphthas and gas oil from a refinery can feed an olefins plant, producing these two petrochemicals. A handful of by-products also come out of the olefin plants cracking these heavy feedstocks, including butylenes, which can be used in the refinery's alky plant, and pyrolysis gasoline, which the refinery can use in gasoline blending. Gas plants process natural gas to remove ethane, propane, butanes, and natural gasoline, all of which can also be used as feed to olefin plants.

## Exercises

1. How much feed, in barrels per day, do you need to run a typical worldscale olefins plant producing 1 billion lb/year of ethylene from the following feeds:
  - Ethane (3.2 lb/gal)
  - Propane (4.24 lb/gal)
  - Naphtha (6.4 lb/gal)
  - Gas oil (7.3 lb/gal)
2. A company has an ethane/propane cracker with a capacity of 500 MM lb/year of ethylene. Presently it is cracking a mixture of 70% (by volume) ethane and 30% propane, running the plant at capacity. Suddenly the propylene market turns sour, and the company wishes to produce only 20 MM lb/year of propylene. How much feed were they cracking, how much propylene were they producing, and how much ethane should they substitute for propane?

20

## SIMPLE AND COMPLEX REFINERIES

*Aevo roussimo nostro, Simplicitas. (Simplicity, most rare in our age.)*

—*Ars Amatoria*, Publius Ovidius Naso

A look at the economics of simple and complex refineries offers one way to tie the essential parts of this book together. After all is said and done, refineries are about making money, and some refineries make more than others, just because of the assembly of processing units in them. This chapter discusses why.

### Measuring Profitability

In the 1980s the businessmen running refineries made an intellectual breakthrough that coincided with the revolution underway in information technology. They recognized that the prices for crude oil, gasoline, distillates, and residual fuels connected to each other in a profound way. The kinds of hardware in refineries around the world not only had impact on the profitability of refineries. They set, in large part, the margins between crude and products and the *differences* between crudes and products themselves.

The constellation of relationships tying crude to products had a prerequisite. Prices had to be free to respond to market forces—the changing preferences of consumers, the sometimes capricious wishes of crude producers, and the influence of other fuels, especially natural gas and coal. The rise in spot markets during the 1970s provided the necessary setting.

The essence of the structure around crude and products pricing and profitability was the relative ability of a refinery to produce various slates of products. The key concept was simple—*the more valuable products a refinery makes, the more it can pay for crude oil*. The more valuable products are, of course, the light oils, gasoline, jet fuel, and distillate fuels. The less valuable products are the heavy oils or black oils, i.e., residual fuel. From this theorem refiners adapted an old set of nomenclature: simple, complex, and very complex refineries.

### ***Origins of “Complexity”***

*In the 1960s, when refiners were still building refineries as fast as they could, Wilbur Nelson of the Oil & Gas Journal devised a shorthand for characterizing how much plant and equipment a refinery had. He measured the cost and throughput of every refining unit (cat cracking, reforming, alkylation, etc.) relative to distilling. Then he calculated an index that captured both relative costs and throughput and called it the complexity factor.*

*For example, a simple refinery with a distilling column, a cat reformer to upgrade the heavy naphtha, plus some treating of gas and distillates might have a complexity factor of 2.2. Distilling would make up 1.0; the cat reformer had only 15% as much throughput, but cat reforming capacity per barrel costs 4 times as much as distilling. That adds  $0.15 \times 4.0 = 0.6$  to the complexity factor. The treating might add another 0.6 for a total of 2.2.*

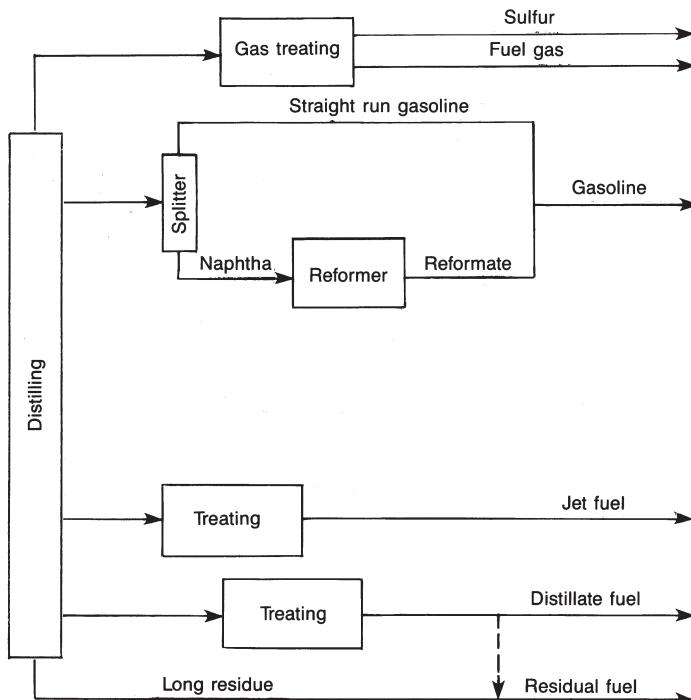
*A more elaborate refinery that also has a cat cracker, alky plant, maybe a thermal cracker, a gas plant, and hydrotreating might have a complexity factor of 9 or 10. Nelson thought of refineries with a complexity factor of 2 to 5 (variations of the so-called hydroskimming refinery shown in fig. 20–1) as simple refineries. Complex refineries, as in figure 20–2, had complexity factors in the 8 to 12 range. Refineries that had cokers or ethylene plants pushed their complexity factors up to 15 or more—very complex.*

*Nelson’s intent was to provide a scheme to compare various investment options. Keep in mind, the name of the game in the 1960s was “keeping up with demand.” Even though his idea dealt with only the investment side of the equation, it set out the framework for later analysis of operating costs, revenues, and profitability. The complexity factors are still used today to estimate construction costs and replacement costs and are kept up-to-date and published by the Oil & Gas Journal.*

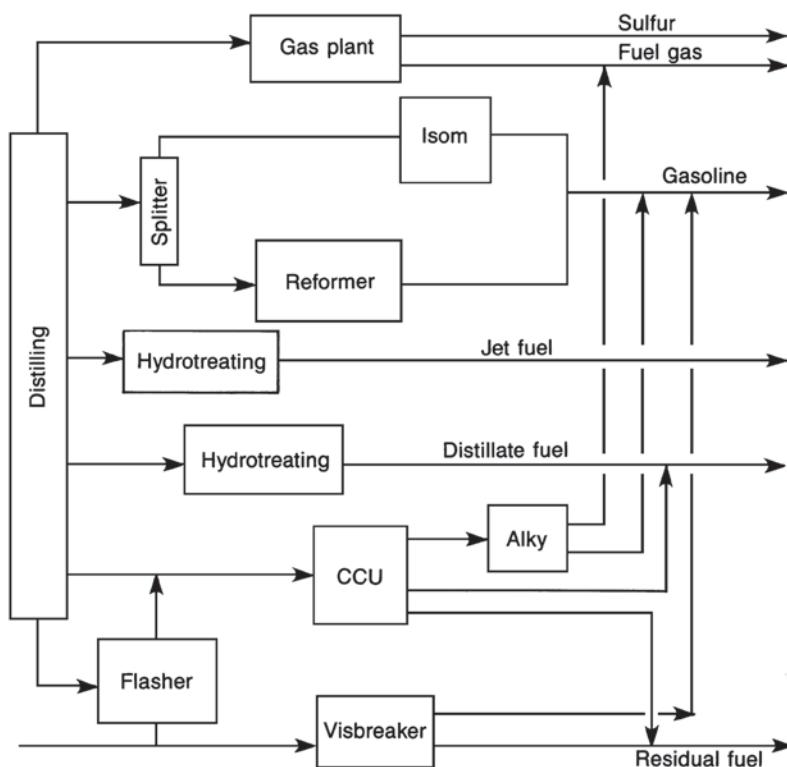
**Definitions.** The three types of refineries are defined as follows:

- *Simple refinery.* Crude distillation, cat reforming, and hydrotreating distillates.
- *Complex refinery.* Simple refinery plus a vacuum flasher, cat cracker, alky plant, and gas processing.
- *Very complex refinery.* Complex refinery plus a coker, which eliminates residual fuel production.

The simple refinery looks more or less like figure 20–1. The addition of a cat cracker in figure 20–2 redefines it as a complex refinery. (The cat cracker dominates that refinery even though it has a visbreaker and an isom plant. On the margin it will behave economically like a complex refinery.) To get to a very complex refinery, you need only add a coker to figure 20–2.



**Fig. 20–1.** Simple or hydroskimming refinery

**Fig. 20-2.** Complex or gasoline refinery

As you move from simple to complex to very complex, the gasoline yield (and gain) goes up and the resid yield goes down. Table 20-1 shows the typical yields from running a medium sulfur and medium weight crude like West Texas Sour or Arab Light.

**Table 20-1.** Percent refinery yields from medium crude

	Simple	Complex	Very Complex
Gasoline	30	50	60
Jet Fuel	10	10	10
Distillate Fuel	20	25	25
Residual Fuel	35	10	—
LPG	—	3	4
Coke	—	—	3
Refinery Fuel	8	12	13
Gain	(3)	(10)	(15)

To begin to understand how refinery configuration can influence the relationships between crude prices and between crude and product prices, start with the calculation in table 20–2 for just simple and complex refineries. (There are more than enough numbers there without adding very complex refinery data.) The sum of the product yields times the refinery gate prices gives the total revenue. (In earlier editions of this book, exhibits of crude prices ranged from \$15/bbl to \$30/bbl, depending on the publication date. Who knows what the crude price will be when *you* read this chapter.) Subtract the operating cost and the crude cost and you get the refining margin. The percent volumes here are the *marginal yields*, the yields from running the last few barrels per day through the refinery as it approaches capacity. That makes the last line the “margin on the margin,” which you may have learned in Economics 101 or 102 is what sets prices in the marketplace.

**Table 20–2.** Refining \$65 medium crude

	Simple Refinery			Complex Refinery		
	% Volume	\$/bbl	\$/bbl	% Volume	\$/bbl	\$/bbl
Gasoline	30	90	27.00	50	90	45.00
Jet Fuel	10	85	8.50	10	85	8.50
Distillate Fuel	20	80	16.00	25	80	20.00
Residual Fuel	35	55	19.25	10	55	5.50
Refinery fuel	8	—	—	12	—	—
(Gain)	<u>(3)</u>	—	—	<u>(7)</u>	—	—
Total Outturn/Revenue	100		70.75	100		79.00
	% Volume	\$/bbl	\$/bbl	% Volume	\$/bbl	\$/bbl
Medium Crude Cost	100	65	65.00	100	65	65.00
Operating Cost		1	1.00		2.50	2.50
Refining Margin			4.75			11.50

You can note the following things about processing the same type of crude in two different refineries:

1. The light oil yield is lower in the simple refinery.
2. This lower yield gives lower revenue.
3. The simple refinery’s operating costs are lower.
4. The profitability of the simple refinery is also lower.

The extra margin, of course, is what the owner of the complex refinery hopes for and expects as compensation for spending all that money for additional processing units. It does not always turn out that way, as you will see in a few pages.

Now, move on to table 20-3 where the same two refineries are now processing a (cheaper) heavy crude, like Mayan from Mexico or Arab Heavy, instead of the medium crude. You can make the following observations about this example:

1. Compared to running the medium crude, the light oil yield goes down big time in the simple refinery.
2. The complex refinery has sufficient conversion capacity to turn the heavy part of the heavy crude into light products, and it will want to run heavy crude oil.
3. The heavy crude price is lower than the medium crude price, but not low enough to keep the simple refinery interested. The simple refinery simply does not have enough conversion capacity to take advantage of the price difference between the light oils and residual fuel (the *light/heavy differential*). It will want to run light crude oil.

**Table 20-3.** Refining \$60 heavy crude

	Simple Refinery			Complex Refinery		
	% Volume	\$/bbl	\$/bbl	% Volume	\$/bbl	\$/bbl
Gasoline	10	90	9.00	50	90	45.00
Jet Fuel	5	85	4.25	5	85	4.25
Distillate Fuel	17	80	13.60	30	80	24.00
Residual Fuel	63	55	34.65	10	55	5.50
Refinery Fuel	10	—	—	15	—	—
(Gain)	(5)	—	—	(10)	—	—
Total Outturn/Revenue	100		61.50	100		78.75
Heavy Crude Cost	100	60	60.00	100	60	60.00
Operating Costs		1	1.00		2.50	2.50
Refining Margin			0.50			16.25

Now think of a hypothetical world with only these two refineries, running at capacity and running only these two crudes, 50% each. The market forces make the world unstable. One or more of the following has to happen:

1. The positive margins of both refineries indicate that this world needs to have both the simple and the complex refinery stay in business.
2. The complex refinery has incentive to switch to more heavy crude oil, but the simple refinery has incentive to switch to more light crude oil.
3. As they do, the amount of light products increases on the margin, pushing the light oil price down and the residual fuel price up. That hurts the complex refinery more than the simple refinery and reduces the incentive for the complex refinery to run as much heavy crude oil.
4. That reduces the demand (and the price) for heavy crude oil and increases the price for light crude oil, which reduces the incentive for the simple refinery to run as much light crude oil.

Any or all of the above changes, and more, put continuous but volatile pressure on the crude and products market and cause crude prices to *change relative to each other*, and the product prices to do the same thing.

## Tracking Profitability

The world is not composed of two refineries and two crudes. The numbers are more like thousands. To bring some order to the chaos, refiners try to follow the relationships setting the prices of crude and products. For example, they may want to look at how competing refiners are faring. They model the simple, complex, and very complex refineries and calculate the results of running a selection of light, medium, and heavy crudes. The results might look like table 20–4, three sets of crudes in all three refineries in one market. The calculation uses the same set of product prices and crude oil, but the yields are unique to each refinery/crude combination.

**Table 20-4.** U.S. Gulf Coast refining margins

	Crude Price* \$/barrel	Refining Margins—\$/barrel		
		Simple	Complex	Very Complex
Light Crudes				
Louisiana Sweet	—	0.75	6.50	9.80
Nigerian Light	0.50	0.30	6.80	10.00
Medium Crudes				
West Texas Sour	(2.00)	(2.35)	8.85	15.25
Arab Light	(1.50)	(1.95)	8.45	14.75
Isthmus (Mexico)	(1.75)	(1.50)	7.40	
Heavy Crudes				
Mayan	(7.20)	(0.59)	3.27	17.50
Arab Heavy	(7.60)	(0.90)	3.80	18.00
Venezuelan	(7.00)	(0.95)	3.00	17.00

\* Crude prices relative to NYMEX light sweet crude

What does this table, which reflects a hypothetical point in time, say about prices and margins?

1. From the first column, the light/heavy crude oil differential is about \$7.50 per barrel.
2. Refiners with cat crackers and cokers are making lots of money.
3. The marginal crude seems to be light, which provides the least margin for everyone. The marginal refinery seems to be the simple refinery, which is just about breaking even running light, sweet crude, but not the heavier crudes.
4. There is a big incentive for refiners to add more coking capacity and buy more heavy crude oils to run. There is also incentive to build more cat cracking capacity and run medium crude oils.
5. Any more coking or cat cracking capacity will probably drive the simple refineries out of business.

Suppose the refiners follow their economic noses and start construction on more coking and cat cracking capacity. Five or six years later, when that capacity all comes on, the array of margins might look like table 20-5.

**Table 20–5.** U.S. Gulf Coast refining margins

	Crude Price* (\$/bbl)	Five Years Later		
		Simple	Complex	Very Complex
<b>Light Crudes</b>				
Louisiana Sweet	—	(0.75)	5.50	4.80
Nigerian Light	0.50	(0.30)	5.80	4.00
<b>Medium Crudes</b>				
West Texas Sour	(1.00)	(1.35)	4.85	5.25
Arab Light	(0.50)	(0.95)	4.35	4.75
Isthmus (Mexico)	(0.75)	(0.50)	5.00	5.35
<b>Heavy Crudes</b>				
Mayan	(3.20)	(1.59)	4.27	6.50
Arab Heavy	(3.60)	(1.90)	4.80	7.00
Venezuelan	(3.00)	(1.95)	4.00	6.00

\* Crude prices relative to NYMEX light sweet crude

From that array, the following conclusions pop out:

1. The additional conversion capacity has driven up the demand (and the price) for heavy crude oils, and the light/heavy crude oil differential has shrunk to about \$3.00/bbl.
2. The extra capacity has driven simple refinery margins negative—their capacity is just not needed.
3. The more complex refineries are making a lot less money and shareholders are looking for the executives who approved the AFEs for the additional capacity. (They, of course, have all retired by then.)
4. Everyone swears they will never spend that much money on cokers and cat crackers again.

This phenomenon has been a painfully observable behavior in the refining industry over the last 30 years (check the light/heavy differentials over the period).

Nonetheless, any refiner can look at this array of margins and conclude where the forces are that will affect his own economics—future crude price movements, the viability of various refinery configurations, and timing.

Of course, every day or week or month the revenues change as the product prices change, which gives rise to changes in the margins. But this analysis gives the basis for understanding who may have the competitive advantage for making money in the future.

## Same Refinery—Different Modes

Why even think about simple refineries when they seem to be unprofitable anachronisms? They seem to be less configured to make money than any other refining layout. The facts are that there are not very many simple refineries in the world and hardly any in the developed countries where gasoline is a big part of the market. Product yields and crude composition need conversion capacity in refinery configurations. However a closer look at how refiners put together the refining jigsaw reveals a subtle observation: at high utilization rates, almost every refinery operates like a worse refinery than it does on the average.

The units downstream of distilling all have fixed capacities. They fill up as a refiner increases crude runs. The cat cracker and coker, the critical conversion units in complex and very complex refineries, might be matched to the distilling capacity. But then again, the amount of cat feed for the cracker and pitch for the coker depend on what type of crude a refiner feeds to the distilling unit. The heavier the feed, the more quickly those two units fill up.

On top of the other breakthroughs about refinery economics came the realization that any complex or very complex refinery might itself run in two or three modes from time to time. Figure 20-3 illustrates how that might come about. The plot shows how the marginal yields of three main products change as distilling capacity utilization increases.

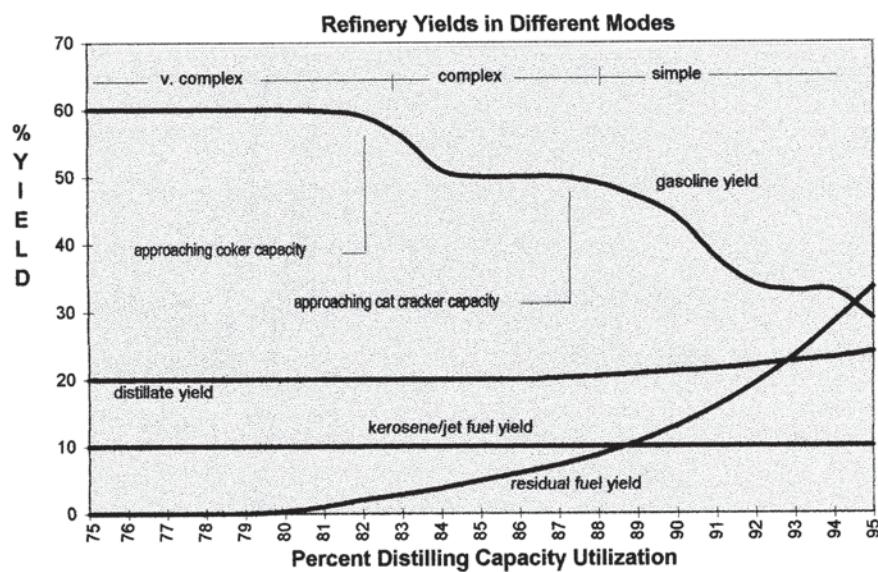


Fig. 20-3.

As a refiner runs the distilling unit at ever-higher rates, typically the coker fills up first. It is the most profitable unit in the refinery because it converts low-valued heavy oil to high-valued light oil. When that happens, the next increment of crude does not return the same profit as the previous volume. There is no room in the coker, but there may well be some in the cat cracker. So the refinery running the last few barrels per day behaves, on the margin, like a complex (cat cracker) refinery. The refinery slips from a very complex mode to a complex mode.

As the distilling unit processes more crude and the cat cracker fills up, the returns slip again. The last increment of crude run through the distilling unit gets simple yields and lower margins. The sequence, from left to right, is reflected in the changing margins in tables 20–4 and 20–5.

So a very complex refinery can operate *on the margin* in any of the three modes, simple, complex, and very complex. When a refiner looks to buy that last cargo of crude, the current capacity utilization dictates the incentive.

## What Sets Prices

By this time you are mumbling exasperatingly, “So what *does* set the product and crude prices?” You have seen how different types of refineries simultaneously enjoy different margins (table 20–2). You have seen how the crude and product prices change in relationship to each other over time (table 20–5). Now you can extrapolate figure 20–4 to the whole industry to understand what sets prices.

Industry product demands and crude supply fill up industry’s capacity just as refiners fill up their own plants. If product demands increase, the most profitable (very complex) refineries fill up first, then the complex refineries and the simple. If product demands are high enough, the refining margins have to increase to keep the simple refineries in business. In table 20–4, that is barely happening. It looks like the very complex refineries have filled up and the marginal refineries are the complex ones. (The complex refinery margins are less than the very complex ones, which means the very complex refineries have not forced the complex out of business, but they are forcing the simple refinery operations out of business.) All types of crudes give a reasonably positive margin in the complex refinery. At the same time, the very complex refineries are making a relatively large bundle of money just because they have a coker that turns resid into gasoline. They just keep on refining crude and making money. But they do not, in this case, set the margins. Their cokers are full and if they have not filled their cat crackers, they are undoubtedly heading that way.

What do tables 20–4 and 20–5 say about setting crude prices? There are times when the complex and very complex refineries make big margins running heavy crudes. That suggests that at that time there was plenty of heavy crude around. At the same time, the complex and very complex refineries make puny margins on light crudes, which suggests light crudes are in short supply or are overpriced, or both. Medium crudes, making medium margins in complex and very complex refineries, are the marginal crudes and will put pressure on the light crude producers to increase production or reduce their prices, or both.

Suppose something changes—heavy crude production drops. Heavy crude prices would rise in reaction. Resid from complex and simple refineries would decline as medium or light crudes replace heavy crude. Resid prices would rise. Cokers and very complex refineries would no longer look as attractive. They may be full but their margins would decline as heavy crude and resid prices go up (and light oil prices decline, keeping medium crude/complex refinery margins about the same). Margins for medium and heavy crudes in complex and very complex refineries would converge. If the heavy crude shortage becomes severe enough, the complex margins would rise above very complex refineries. Together with heavy crudes, they would become the combined price setters.

All that requires you keep a multitude of moving parts in mind simultaneously, which is not easy to do without careful thought. As the dynamics of the oil market change the relationships every day, the frantic business of crude selection requires continuous, rigorous analysis of industry margins to get the best combination.

And all the while the general level of crude oil prices moves up and down, virtually independently of all these margin changes. But that is another story.

## Review

A refiner's margins are a function of his own refinery's processing units, the crudes he buys, and the prices he receives for his products. But the prices and costs are set by an elaborate constellation of industry refinery economics that mimic his own. The relationship between product prices and crude prices has more moving parts than the refineries themselves. And that makes complexity watching vital as refiners try to catch early warning signals for significant profitability changes.

## **Exercises**

1. Why do some people say the light/heavy differential is the bid price of a coker?
2. If light oil prices are going down faster than crude oil prices are going down, and resid prices are staying the same, what happens to the margins in simple, complex, and very complex refineries?

# 21

## SOLVENT RECOVERY OF AROMATICS

*We, we only are left!*  
—“Rugby Chapel,” Matthew Arnold

In 1907 Lázar Edeleanu developed a process by which aromatic compounds could be preferentially removed from a hydrocarbon mixture. The process worked even in cases where the boiling points of the aromatic compounds were virtually the same as the other compounds in the mixture. Distillation under those conditions would not work, so Edeleanu’s innovation made a major breakthrough.

### Applications

Removal of aromatic compounds can be desirable for two different reasons. Either the aromatics have detrimental effects on the quality of the mixture they are in, or the aromatics are worth more if they are separated than if they are not. You have already seen a couple of examples:

- Gasoline now has a max benzene spec.
- Aromatic compounds in kerosene can cause unacceptable smoke points.

Other more specialized applications include:

- Kerosene range solvents that are aromatics-free or aromatics-laden have various industrial applications.

- Separated benzene, xylene, and toluene have numerous chemical applications.
- Removing aromatics from heavy gas oil stocks can improve the lubricating oil characteristics.

## Processes

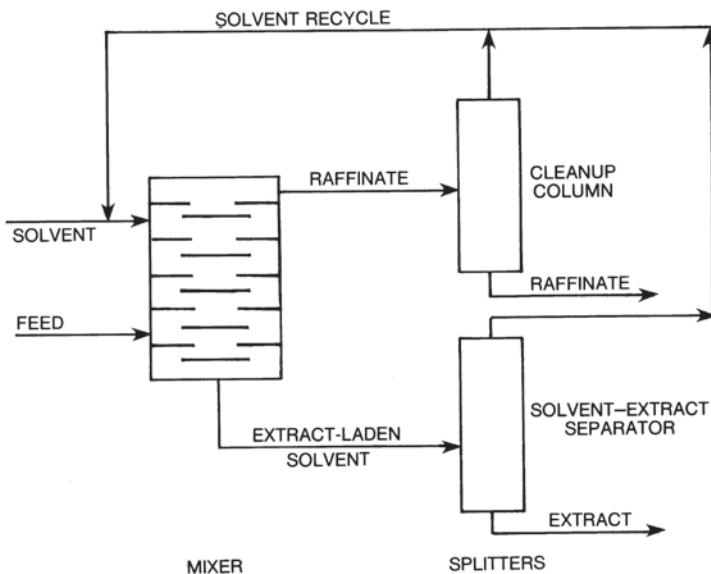
The solvent recovery process is based on the ability of certain compounds to dissolve selectively certain classes of other compounds. In this case, certain solvents will dissolve aromatics but not paraffins, olefins, or naphthenes. The reasons the process works are a story you will not read here.

The first corequisite that makes this approach successful is that the solvent with the extracted compounds dissolved in it readily separates itself from the starting hydrocarbon mixture. The second corequisite is that the solvent and the dissolved extract can easily be split in a fractionator.

Take kerosene as an example, one that has a lot of aromatic compounds in it. To one-half a beaker of kerosene add one-half a beaker of a solvent—in this case, liquid sulfur dioxide. After mixing, the liquid will separate into two phases with the kerosene on the bottom and the sulfur dioxide on top. The kerosene on the bottom will fill less than one-half the beaker. The sulfur dioxide, because the aromatic compounds have dissolved in it, will take up more than one-half the beaker.

If the sulfur dioxide is poured off, the aromatic compounds can be “sprung” from it by simply heating the mixture to the aromatics boiling temperature. This two-step process is *batch solvent processing*.

Knowing how a simple batch process works, a continuous flow process is easy to conceptualize. Figure 21–1 shows a three-column system. The feed is introduced as a vapor into the lower part of a vessel or column with a labyrinth of mixers inside. (Sometimes the mixers are mechanically moved, such as in a *rotating disc contactor*.) The solvent is introduced as a liquid near the top. The solvent works its way towards the bottom of the vessel, dissolving the *extract* as it goes along. The rest of the hydrocarbon, which emerges from the top, is called *raffinate*.



**Fig. 21-1.** Solvent recovery process

Two columns handle the streams coming out of the mixer. One column cleans up any small amounts of solvent that may have followed along with the raffinate. The other column separates the solvent and the extract. The solvent from both columns is recycled to the top of the mixer.

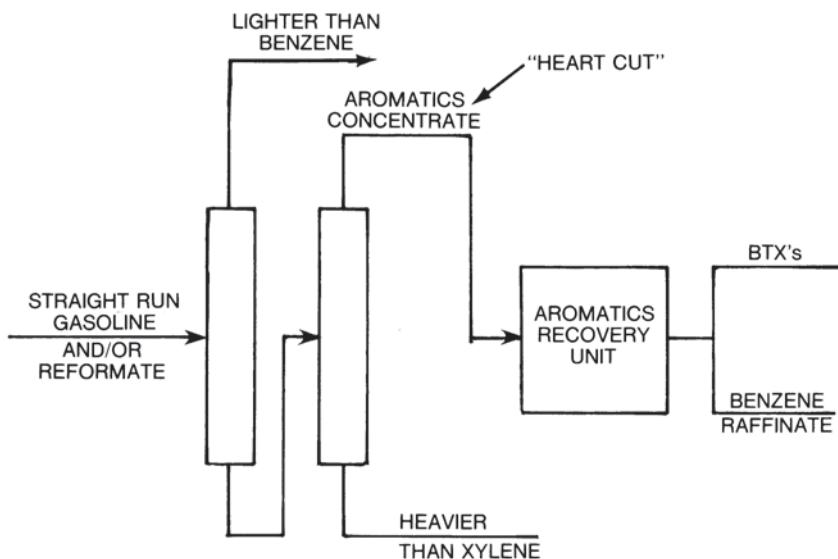
Some of the solvents used in various applications are listed below:

- Kerosene treating: liquid SO<sub>2</sub>, Furfural
- Lubricating oil treating: liquid SO<sub>2</sub>, Furfural, phenol, propane (separates paraffins from asphaltenes)
- Gasoline: Sulfolane, phenol, acetonitrile, liquid SO<sub>2</sub>

A good solvent has a boiling temperature sufficiently higher than the targeted extract so that separating the two in a fractionating column is easily accomplished.

## Benzene and Aromatics Recovery

The most widespread application of solvent extraction is used in BTX recovery, especially for benzene. To make the process efficient, the feed to the process is pared down to an *aromatics concentrate* by making a *heart cut* from a reformate or straight run gasoline stream as shown in figure 21-2. The aromatics concentrate then has a larger benzene content, making the extraction process more efficient.



**Fig. 21-2.** BTX recovery

One bit of nomenclature is often misleading. *Benzene raffinate* contains no benzene. It is the leftover of the aromatics concentrate after the goodies (benzene) are removed. Benzene raffinate is still an acceptable gasoline blending component and the separated benzene becomes a chemical feedstock.

## Review

Benzene can be recovered from a stream of mixed hydrocarbons using a special solvent. The solvent has three special properties. It can selectively absorb aromatics compounds (i.e., benzene) and not paraffins, naphthenes, or olefins; it separates itself easily from those compounds with the aromatics dissolved in it; and its boiling temperature is sufficiently different from benzene that the two can easily be separated by heating until one boils off.

## Exercises

1. Which has a higher concentration of benzene in it as it leaves the solvent extraction vessel, the benzene raffinate or the solvent?
2. What are the three essential features of a good solvent for extraction?

# 22

## FUEL VALUES— HEATING VALUES

*If you can't stand the heat, get out of the kitchen.*

— Harry S. Truman

Many of the economic forces on the various petroleum products are tied to the amount of energy in the form of heat the individual products yield when they are burned. Indeed, the choice of which streams to use as refinery fuel must take into account the market value of the streams and the heating value.

### Thermal Content

When a hydrocarbon is burned, two things happen: a chemical reaction takes place and heat is generated. Typically the chemical is a transformation of the hydrocarbon into H<sub>2</sub>O and CO<sub>2</sub>.



Each type of molecule gives off a unique amount of heat. The usual measure of heat in the petroleum industry is the British thermal unit (Btu).

**Definition.** The amount of heat required to raise the temperature of 1 pound of water 1°F is equal to 1 Btu.

Table 22-1 gives the heating values for some commercial petroleum products.

**Table 22–1.** Heating values

Product	Higher Heating Value
Natural gas	1,000–1,050 Btu/scf
Ethane	66,000 Btu/gal
Propane	91,600 Btu/gal
Butane	103,300 Btu/gal
Distillate fuel	140,000 Btu/gal
Residual fuel (2.5% sulfur)	153,000 Btu/gal
Residual fuel (0.3% sulfur)	151,500 Btu/gal

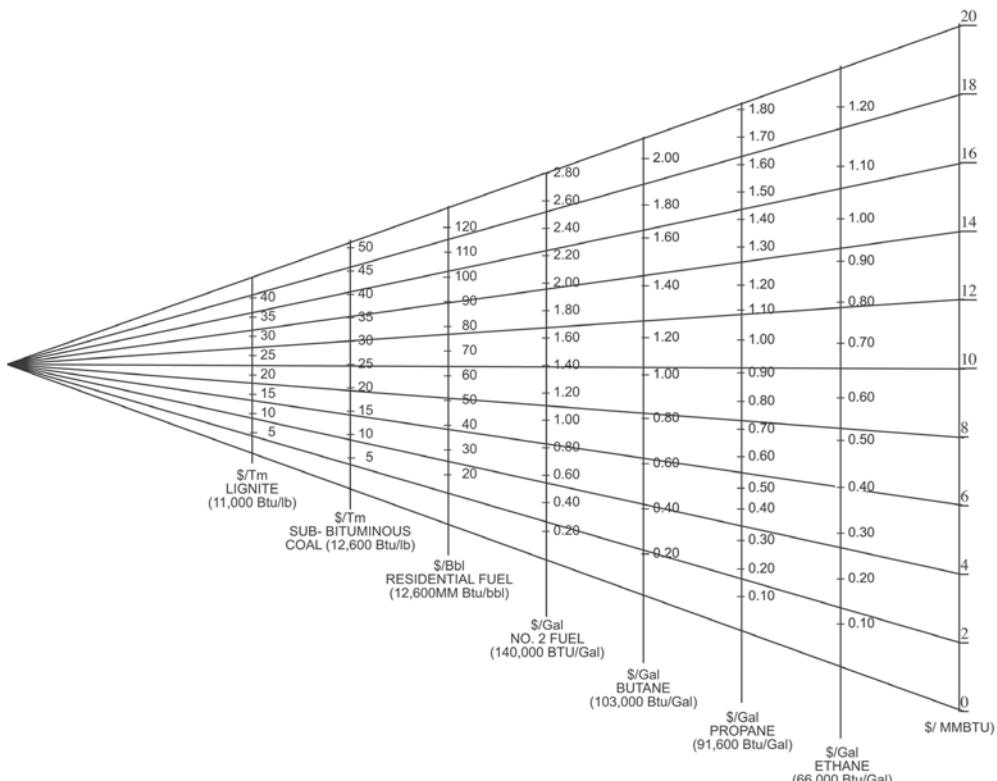
There are two types of heating values. The so-called higher heating value represents the gross amount of heat given off, called the *heat of combustion*, by burning the hydrocarbon. The lower heating value takes into account what happens to the water created during the chemical reaction, burning. A portion of the heat of combustion is absorbed to vaporize the water. Not all that heat is recovered or is usable as the heat goes through a furnace and the exhaust. As a general rule, the heavier the fuel, the lower the ratio of hydrogen to carbon, so the less H<sub>2</sub>O gets formed during combustion. Typical results of this inability to capture the heat of vaporization are measured by the thermal efficiency (table 22–2), the recoverable heat divided by the gross heating value, that is, lower ÷ higher heating value.

**Table 22–2.** Thermal efficiency

Product	Thermal efficiency, %
Natural gas	84
Propane	85
Distillate	88
Residual fuel	89

## Competitive Fuel Value Nomogram

A handy way to relate the values of the various products and their heating values is shown in the nomogram in figure 22–1. That “peephole” diagram first appeared in the *Oil & Gas Journal* in 1972 and was updated to put higher scales on it in 1977 and then again in 1980 as energy prices escalated.



**Fig. 22–1.** Equivalent fuel values for selected hydrocarbons

As an example of nomogram use, assume you want to find the fuel values equivalent to \$5/MM Btu natural gas. First go to the vertical scale on the right and find the line that intersects the natural gas scale at \$5. Next, read along that line, right to left, to find the equivalent values of the other fuels: \$0.33/gal for ethane, \$0.46/gal for propane, \$0.52/gal for butane, and so on.

Similarly, the value for any fuel can be equated to the value of any other fuel by extending a straight line from the vertex on the left through the first fuel's value until it intersects the second fuel. For example, by laying a straight edge from the vertex through the high sulfur residual fuel scale at \$30/bbl, you can see the equivalent values are \$104/ton for lignite, 66¢/gal for No. 2 fuel, 43¢/gal for propane, and \$4.71 for natural gas.

## **Exercises**

1. Which is better for a refiner to use as refinery fuel, natural gas (1,000 Btu/scf) at \$7/MM Btu, residual fuel at \$50/bbl, or butane at 60¢/gal?

# 23 ANSWERS AND SOLUTIONS

*What is the answer? ...In that case, what is the question?*

*—The Autobiography of Alice B. Toklas, Gertrude Stein*

## **Chapter 2: From the Oil Patch to the Refinery**

1. LPG is either propane, butane, or a mixture of the two, depending where in the world it is. LNG is liquefied natural gas, methane that has been cooled to very low temperatures until it liquefies, so it can be transported by LNG tanker and stored in a more compact form. NGLs are the mixture of ethane, propane, butane, and natural gasoline that is the product of a gas plant before it goes through fractionation to separate the four from each other.
2. The heavier components of the wet gas stream, butane and natural gasoline, may condense to liquids during pipeline transport; also the four components may have a higher market value as individual streams than as components of natural gas.

## **Chapter 3: Crude Oil Characteristics**

1. a. Calculate the cumulative percent volumes and plot.
- b. The Oklahoma Sweet has 9.7%. The heavy California crude only starts to boil somewhere between 260°F and 315°F, and so it does not even have the full range of naphtha. The volume is only 4.2%.

2. Because of the peculiar formula for API gravity (it has a  $y$  intercept), you cannot add them and divide by two. You have to convert the API gravities to specific gravities, add them, divide by two, then convert them back to API gravity:

$$11^{\circ}\text{F} = 0.9930 \text{ sp. gr.}$$

$$50^{\circ}\text{F} = \underline{0.7796 \text{ sp. gr.}}$$

$$1.7726 \div 2 = 0.8813 = 28.05^{\circ}\text{F}$$

## Chapter 4: Distilling

1. a. cooler  
b. batch, continuous  
c. end point, initial boiling point  
d. decreases  
e. decreases, increases
2. There are several ways to solve the problem. One simplifying assumption you can make is that the distillation curve is a set of straight lines between the cut point/percent volume plots. Then calculate a composite distillation curve by figuring the volume in each cut from the two crudes.

Volume—M B/D	
IBP-113	31.5
113-260	25.8
260-315	35.1
315-500	21.5
500-750	37.6
750-1,000	20.0
1,000+	<u>28.5</u>
	200.0

The next step can be done either by algebra or by plotting the distillation curve. The algebraic method is as follows. The IBP of the SRLGO is  $525^{\circ}\text{F}$ . That means that some of the  $500^{\circ}\text{F}$  to  $750^{\circ}\text{F}$  cut goes into jet fuel. To determine how much, let  $X$  be the amount. Then,

$$\frac{525 - 500}{750 - 500} = \frac{X}{37.6}$$

$$X = 3.76$$

That means the 525°F–750°F cut has in it:

$$37.6 - 3.76 = 33.84 \text{ M B/D}$$

To get only 20 MB/D, starting at 525°F, let Y = the end point. Then,

$$\frac{Y - 525}{750 - 525} = \frac{20.0}{33.84}$$

$$Y = 658^{\circ}\text{F}$$

## Chapter 5: Vacuum Flashing

1. a. distillation, cracking  
b. lower  
c. lower  
d. light flashed distillate, heavy flashed distillate, flasher bottoms  
e. increase, lower
2. a. To get 35 M B/D flasher bottoms, start at the “bottom of the barrel” on the distillation curve and work up. In problem 2, chapter 4, the volume of 1,000°F + material is 28.5 M B/D. So, all that must be flasher bottoms. The 750°F–1,000°F cut (20 M B/D) will cover the remainder of the requirement of  $35.0 - 28.5 = 6.5$  M B/D. Calculate as follows:

Let X equal the IBP of the flasher bottoms (also known as the *flasher temperature* and the *end point of the flasher tops*).

Then,

$$\frac{1,000 - X}{1,000 - 750} = \frac{6.5}{20.0}$$

$$X = 918.75^{\circ}\text{F}$$

Of course the operations manager would probably be fired for doing this because flasher tops, used as feed to the cat cracker, are worth considerably more than asphalt, so he just downgraded the profitability of the refinery.

- b. The flasher tops come from the 750°F–1,000°F cut, and go from 800°F–918.75°F.

Let Y = Volume of flasher tops.

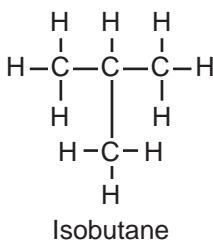
Then,

$$\frac{Y}{20} = \frac{918.75 - 800.0}{1,000.0 - 750}$$

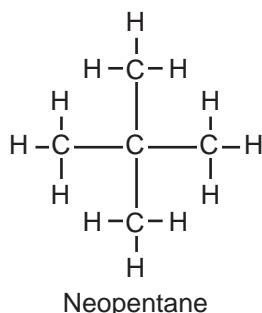
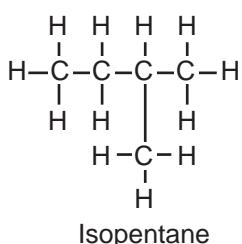
$$Y = 9.5 \text{ M B/D}$$

## Chapter 6: The Chemistry of Petroleum

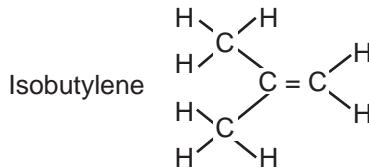
- Any way you build  $C_6H_6$ , to get the hydrogens down to six, the carbons have to be connected to each other in a cyclical shape with double bonds in alternate carbon connections. Otherwise, the carbon and hydrogen valences will not be satisfied. (There are no known molecules that have triple bonds that will do the trick. They are probably too unstable to exist.)
- There is only one structure for isobutane, a branch off the middle of three carbons.



There are two isomers of pentane. The first isopentane has a branch off either of the two inside carbons in the string of four. It does not matter which one; they are symmetrical if you turn them around. The other isomer, neopentane, has four carbon branches off the inside carbon.

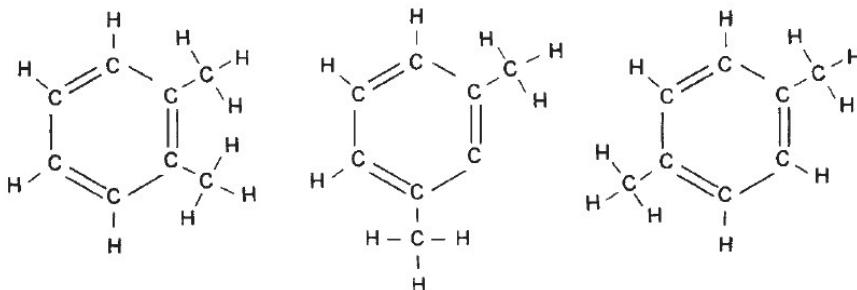


Drawing the carbons slightly cockeyed can best depict the one isomer of butylene. Then, no matter how you rotate it, it looks the same (fig. 23-3).



3. Paraffins, olefins, naphthenes, and aromatics.

4. The three types of xylene, called *para*, *meta*, and *ortho*xylene, depend on where the methyl radicals are attached.



5. It does not matter where a single methyl radical is attached since the benzene ring is symmetrical.

## Chapter 7: Refinery Gas Plants

1. a. sats, cracked  
b. lean oil, fat oil  
c. sponge oil

2. Methane—Refinery fuel

Ethane—Refinery fuel or chemical feed

Propane—Commercial fuel or chemical feed

Normal butane—Motor gasoline blending

Isobutane—Aklylation feed

Propylene—Alkylation

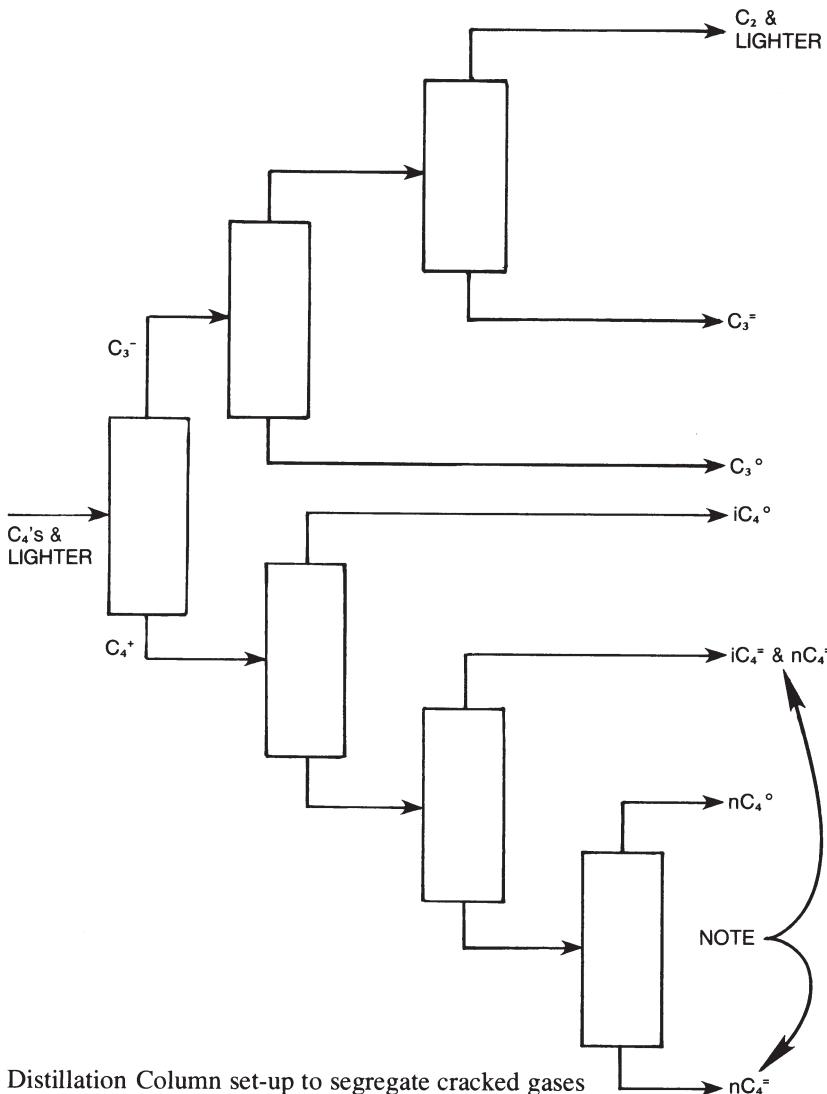
Butylenes—Alkylation

Ethylene—Refinery fuel or chemical feed

Hydrogen—Hydrotreating

3. One of the forms of butylenes and the isobutylene boils at lower temperatures than normal butane; the other two normal butylenes boil at temperatures higher. So the butylenes get split from each other to get the normal butane out.

One distilling column configuration is given below. Several other schemes are possible as well. The important factor is to understand what goes overhead and what does not.



## Chapter 8: Cat Cracking

1. Currently, riser crackers are fluid cat crackers, and both are cat crackers.
2. a. catalyst, hydrocarbon  
b. coke or carbon, air, CO, CO<sub>2</sub>  
c. heavy straight run cuts, gasoline  
d. distilling column, flasher  
e. olefins  
f. cycle oil, recycled to extinction
3. From the question on flashing, flasher tops, with cut points 800°F–918.75°F, are 9.5 M B/D. The cut points of the straight run heavy gas oil must be the end point of the straight run light gas oil, 658°F (from the question on distilling) and the initial boiling point of the straight run residue, 800°F. The nasty job of calculating the volume of this 658°F–800°F cut goes as follows:

Volume of 500°F–750°F = 37.6 (Distilling problem)

500°F–525°F = 3.76 (Distilling problem)

525°F–658°F = 20.0 (Distilling problem)

Therefore,

$$\begin{aligned}\text{Volume of } 658^{\circ}\text{F} &- 750^{\circ}\text{F} = 37.6 - 20 - 3.76 \\ &= 13.84\end{aligned}$$

Volume of 750°F–1,000°F = 20.0 (Distilling problem)

Volume of 800°F–1,000°F = 16.0 (Flasher problem)

Therefore,

$$\text{Volume of } 750^{\circ}\text{F} &- 800^{\circ}\text{F} = 4.0$$

Therefore,

Volume of straight run heavy gas oil =

$$658^{\circ}\text{F} - 800^{\circ}\text{F} = 13.84 + 4.0 = 17.84$$

Yield of cat light gas oil is 12%; cat cracker feed is the straight run heavy gas oil and flasher tops, so the cat light gas oil volume is  $0.12 \times (17.84 + 9.5) = 3.28$  M B/D.

4. (1) Decrease the initial boiling point; (2) increase the end point of the cat light gas oil; (3) increase the feed to the cat cracker by increasing the crude distilling column feed rate; (4) change the cut points of the

straight run heavy gas oil and the flasher tops; (5) increase the cycle oil volume by lowering the end point of the cat heavy gas oil; (6) change the operating conditions in the cat cracker reactor; or (7) change the operating conditions in the regenerator to change the cracking yields.

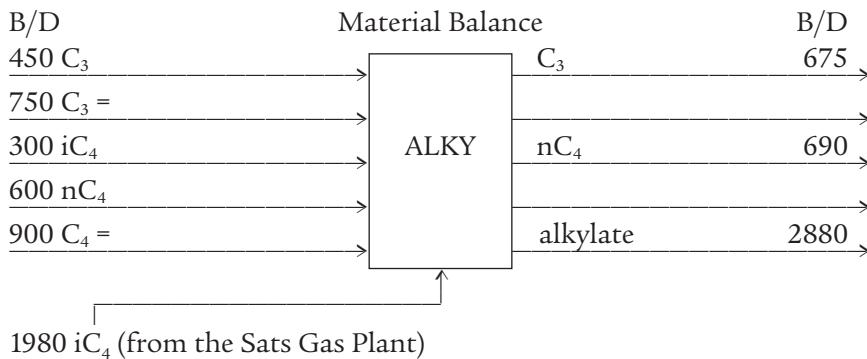
## Chapter 9: Alkylation

1. a. cracking  
b. sulfuric acid, hydrofluoric acid  
c. cooler, reactor, acid separator, caustic wash, and fractionators  
d. isoheptane and isooctane  
e. octane number, vapor pressure, sulfur, benzene, olefins, gasoline blending component
2. First  $iC_4$  needed for the following:

$$C_3 \text{ alkylation: } 3,000 \times 0.25 \times 1.6 = 1,200 \text{ B/D}$$

$$C_4 \text{ alkylation: } 3,000 \times 0.30 \times 1.2 = \frac{1,080 \text{ B/D}}{2,280 \text{ B/D}}$$

less the 300 B/D in the feed is  $1,980 \text{ B/D}$



Then, alkylate production:

$$\begin{array}{ll} \text{From } C_3: & 3,000 \times 0.15 \times 1.8 = 810 \text{ B/D} \\ C_4: & 3,000 \times 0.30 \times 1.7 = \frac{1,530 \text{ B/D}}{\text{Total alkylate}} \\ & 2,340 \text{ B/D} \end{array}$$

The propane and butane out of the plant equals the propane and butane in plus what gets created during the process.

## Chapter 10: Cat Reforming

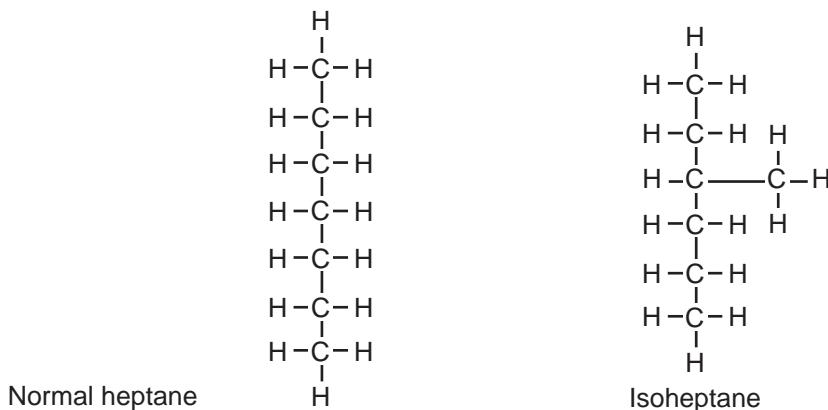
1. a. octane
- b. platinum, palladium
- c. aromatics
- d. hydrogen
- e. methane, ethane, propane, butanes
- f. hydrogen
- g. yield, octane number, butanes and lighter

2. The values of the yield are computed as follows:

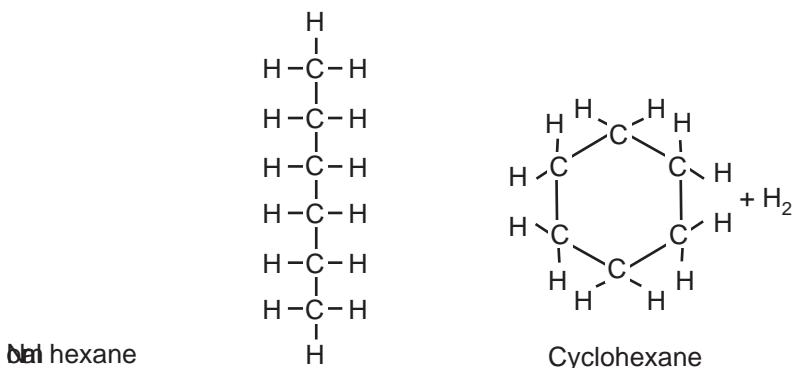
From the chart:	91 Oct.	95 Oct.	100 Oct.
Reformate Yield , % volume	88.0	84.6	75.0
C <sub>4</sub> and Lighter Yield, % volume	8.7	10.4	25.2
Reformate Value, ¢/gal	100.0	104.0	109.0
C <sub>4</sub> and Lighter Value, ¢/gal	50.0	50.0	50.0
Reformate value	8,800.0	8,800.8	8,175.0
C <sub>4</sub> and lighter value	435.0	525.0	1,260.0
Total Value	9,235.0	9,333.8	9,435.0

The total value keeps going up—only slightly, but up—as the octane number is raised despite the falling yield of reformate. So it makes sense to increase severity.

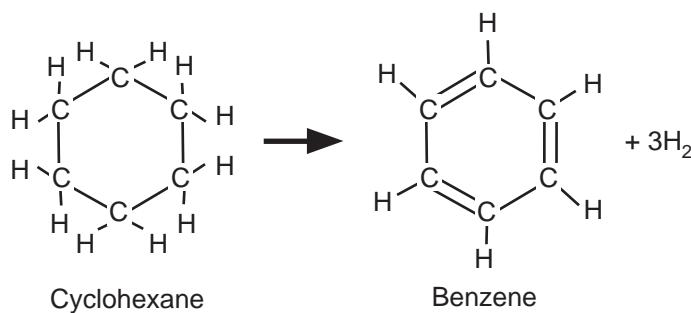
3. Paraffins to isoparaffins:



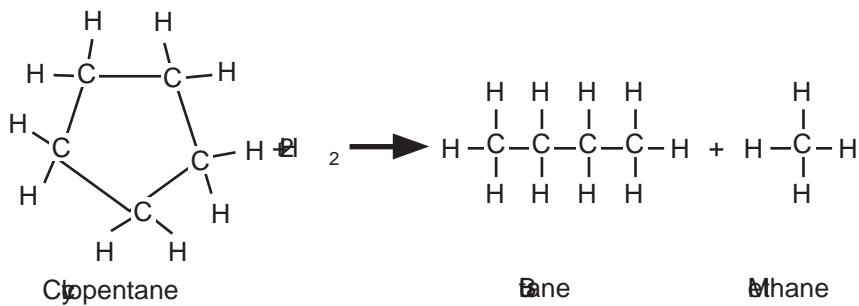
Paraffins to naphthenes:



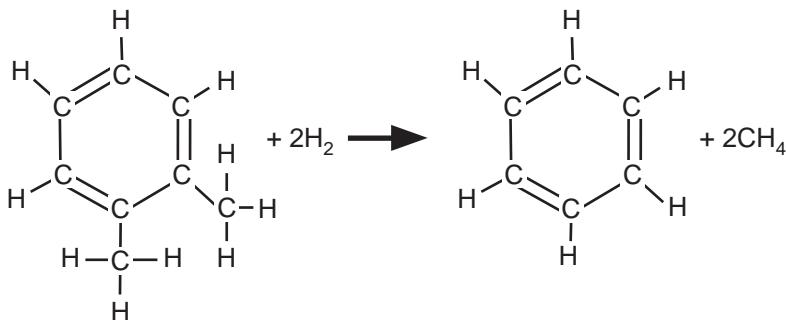
Naphthenes to aromatics:



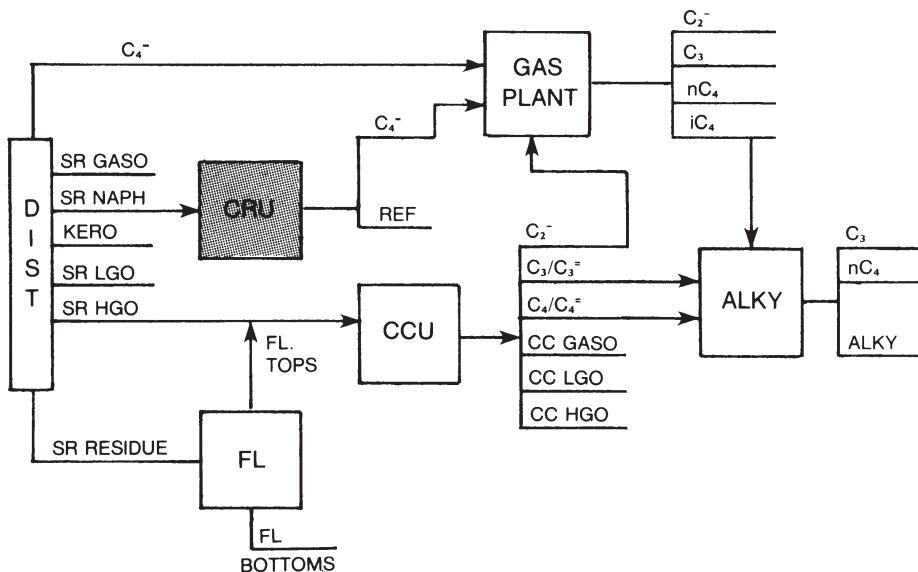
Naphthenes crack to butanes and lighter:



Side chains crack off aromatics:



4. Refinery configuration:

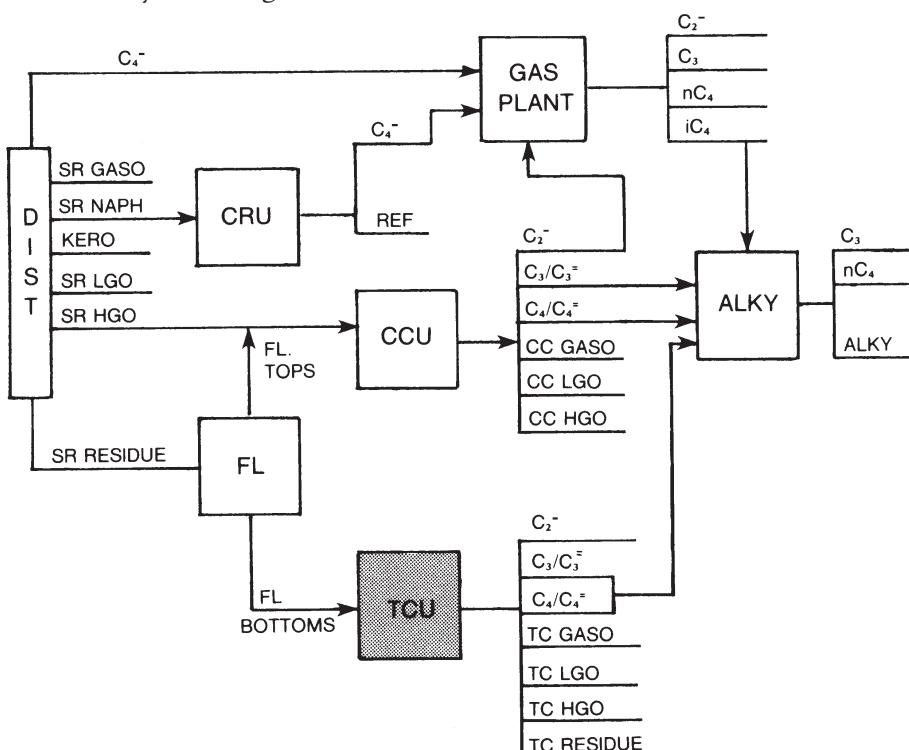


### Refinery Operation with Catalytic Reformer

## Chapter 11: Hydrocracking

	Hydrocracking	Cat Cracking	Thermal Cracking
Feed	gas oils	heavy straight run gas oil	CCHGO flasher bottoms
Process promoter	catalyst, hydrogen	catalyst	heat
Product quality	paraffinic, naphthenic	naphthenic, aromatic olefinic	paraffinic, naphthenic, aromatic olefinic

2. Cat cracker gas oils make good feed to hydrocrackers. Hydrocrackate makes good feed to reformers.
3. Refinery flow diagram:



## Chapter 12: Isomerization

1. Refiners include a BI plant in their configuration because they are short of isobutane needed for their alky plant. They have a  $C_5/C_6$  isom plant because they need to upgrade the octane numbers of their  $C_5$ s and  $C_6$ s, most of which are in their straight run gasoline.
2. To get the normal hexane split out for recycling to extinction, you must add a deisohexanizer downstream of the  $C_5/C_6$  splitter and route the bottoms to the reactor. You would probably want to then configure all three fractionators so all the isohexane is split out of the feed to avoid passing it through the reactor.
3. The hydrogen helps prevent carbon formation and deposition on the catalyst, which would deactivate it.
4. These isoparaffins can have any of several structures, each of which has its own properties.

## Chapter 13: Residue Reduction

1. a. catalyst  
 b. coke, residue  
 c. cooled with a recycle steam  
 d. “cooked” until it cracks all the way to coke  
 e. Any three of the following: sponge coke, green coke, calcinable coke, anode grade coke, needle coke  
 f. alky (plant) or the cracked gas, olefins  
 g. furnace, distillation column, reactor, coke drum
2. Flasher bottoms are 35 M B/D.  

$$\text{Coke yield} = \frac{35,000 \times 350 \times 0.30}{2,000} = 1,837.5 \text{ tons/day}$$

## Chapter 14: Gasoline

1. *Vapor pressure* is a measure of the surface pressure necessary to keep a liquid from vaporizing.

*RVP* stands for Reid vapor pressure and is the numerical result of measuring vapor pressure using Reid's method.

*Power stroke* is the downward motion of a piston that occurs after ignition as the fuel combusts and expands.

*Vapor lock* is the phenomenon of insufficient gasoline flow from a fuel pump due to its inability to pump the mixture that results from low pressure or high temperature, which has high volatility.

*Pressuring agent* is the hydrocarbon, usually normal butane, used to bring gasoline blends up to an acceptable vapor pressure.

*Knocking* is the preignition of gasoline in a cylinder during the compression stroke.

*Oxygenates* are ethers or alcohols used as gasoline blending components. They have at least one oxygen atom connected to the other carbons and hydrogens.

*Compression ratio* is a measure of the amount of compression that takes place in an engine's cylinder and is equal to the volume of the cylinder at the bottom of the intake stroke to the volume at the top of the compression stroke.

*RON* and *MON* are measures of octane numbers under conditions simulating mild and severe conditions, respectively.

*Leaded gasoline* is gasoline that has TEL (tetraethyl lead) added to boost the octane number.

*TOX*,  $NO_x$ , *VOCs*, and  $SO_x$  are toxic compounds such as formaldehyde, oxides of nitrogen, volatile organic compounds such as pentene, and oxides of sulfur.

2. a. To get the amount of butane necessary to meet the RVP spec:

	Barrels	RVP	(R + M)/2
Alkylate	3,000	4.6	96.9
Reformate	2,500	2.8	89.0
Hydrocrackate	1,000	2.5	74.0
CC gasoline	3,600	4.4	85.0
Subtotal	10,100	3.4	
Normal butane	X	52.0	92.5
$(10,100)(3.8) + 52.0X = (10,100 + X)(10.0)$			
$X = 1,490 \text{ bbl to meet the RVP spec.}$			
Blend, including the butane	11,473	10.0	84.8

- b. To get the amount of alkylate to meet the octane spec:

	Barrels	RVP	(R + M)/2
Pressured gasoline	11,590	10.0	84.8
Alkylate	Y	8.0	96.5

Let Y = the amount of alkylate to meet the spec of 87.0:

$$(11,590)(84.8) + 96.5 Y = (11,590 + Y)(87.0)$$

$$Y = 2,684 \text{ bbl}$$

So 2,684 bbl of alkylate have to be added to meet the octane spec.

- c. When the alkylate is added in, the vapor pressure of the gasoline blend goes down a tad, making room for more butane. To get the balance between butane and MTBE, you have to use a two equation/two unknown calculation.

## Chapter 15: Distillate and Residual Fuels

1. Gasoline and diesel fuel differences:

- In a gasoline engine, the spark plug ignites the gasoline/air mixture. In a diesel engine, the fuel self-ignites when it hits the hot, compressed air and vaporizes.
- Octane numbers are measured against mixtures of normal heptane and iso-octane. Cetane numbers are measured against mixtures of normal cetane and alpha-methylnaphthalene.

- Higher octane comes from aromatics and isoparaffins. Higher cetane numbers come from normal paraffins and naphthenes.
2. Diesel fuel and heating oil come from light gas oils, but diesel fuel has to meet a cetane number specification. The two products may also have different sulfur and other specifications and different packages.
  3. Shipbuilders could use a diesel engine or a boiler with a turbine.

## **Chapter 16 Hydrogen, Hydrotreating, and Sulfur Plants**

1.

	Hydrotreating	DEA treating	Claus Plant	SMR
H <sub>2</sub> S	P	F, P	F, I	—
S	—	—	P	—
CO	—	—	—	I
CO <sub>2</sub>	—	—	—	I
CH <sub>4</sub>	—	—	—	F, P
H <sub>2</sub>	F	—	—	F, P
O <sub>2</sub>	—	—	F	—
SO <sub>2</sub>	—	—	I, P	—

P—Product

F—Feed

I—Internal steam

## **Chapter 17: Asphalt**

1. The classes of compounds that make asphalt possible are asphaltenes and resins.
2. Anyone concerned about the environment would object to the diluents used in cutbacks because they end up polluting the atmosphere.
3. Anionic emulsions have a negative charge; cationics have a positive charge. Both need aggregates (gravel and sand) that have the opposite charge.

## Chapter 18: Lubricants

1. The best lubricants are branched-chained paraffins, but naphthalene-based molecules will do.
2. Lubricant base stocks come from the tops or the bottoms of a vacuum flasher.
3. Both use an absorption process with a solvent, an extract, and a raffinate.
4. Two routes to XHVI are intense hydroprocessing or using synthetic lubes (polyalpha olefins made from alpha olefins).

## Chapter 19: Ethylene Plants

$$\begin{array}{lll} \text{1. Ethane: } & 1 \times 10^9 \div (0.77 \times 3.2 \times 42 \times 365) & = 26 \text{ M B/D} \\ \text{Propane: } & 1 \times 10^9 \div (0.40 \times 4.24 \times 42 \times 365) & = 38 \text{ M B/D} \\ \text{Naphtha: } & 1 \times 10^9 \div (0.23 \times 6.4 \times 42 \times 365) & = 44 \text{ M B/D} \\ \text{Gas Oil: } & 1 \times 10^9 \div (0.18 \times 7.3 \times 42 \times 365) & = 50 \text{ M B/D} \end{array}$$

2. Let X equal the feed in B/D of the 70/30 mix. To make 500 MM lb of ethylene, the feed rate is as follows:

Calculate the weighted average ethylene yield from the ethane and propane. The yield from ethane is X times the percent ethane times the pounds per gallon ethane times the yield of ethylene from ethane times 42 gallons per barrel times 365 days per year. The same calculation process is used for ethylene from propane.

$$\begin{array}{lll} \text{From ethane} & \text{From propane} & \text{Ethylene} \\ (X)(0.7)(3.2)(0.77)(42)(365) & + (X)(0.30)(4.24)(0.40)(42)(365) & = 500 \times 10^6 \\ X = 14.6 \text{ M B/D of ethane/propane feed} & & \end{array}$$

The propylene production was:

$$\begin{array}{lll} \text{From ethane} & \text{From propane} & \text{Propylene} \\ (14.6)(0.7)(3.2)(42)(365)(0.1) & + (14.6)(0.3)(4.24)(42)(365)(0.18) & = 101.2 \times 10^6 \end{array}$$

To find out how much ethane and propane must be cracked to make 500 MM lb of ethylene but only 20 MM lb of propylene, use simultaneous equations:

Let Y equal the ethane feed rate in B/D.

Let Z equal the propane feed rate in B/D.

Then:

	From ethane	From propane
Ethylene:	$500 \times 10^6 = (Y)(3.2)(42)(365)(0.77)$	$+ (Z)(4.24)(42)(365)(0.40)$
Propylene:	$20 \times 10^6 = (Y)(3.2)(42)(365)(0.01)$	$+ (Z)(4.24)(42)(365)(0.18)$
	$500 \times 10^6 = 37,773 Y + 26,000 Z$	
	$20 \times 10^6 = 490 Y + 11,700 Z$	
	$Y = 12.4 \text{ M B/D ethane}$	
	$Z = \frac{1.2}{13.6} \text{ M B/D propane}$	
	$\text{M B/D of 91/9 mix}$	

## Chapter 20: Simple and Complex Refineries

1. Since a coker converts heavy oil to light oil, the difference in price between the two is what pays for the capital invested in a coker.
2. Simple refinery margins will rise, complex refinery margins will fall, and very complex refining margins will fall even faster.

## Chapter 21: Solvent Recovery of Aromatics

1. The solvent will have a higher concentration of benzene than the benzene raffinate; benzene raffinate is what is left over after the benzene has been taken out.
2. A good solvent for extraction will selectively dissolve the target compound, readily separate itself from the original mixture, and can easily be separated from the target compound by distillation.

## Chapter 22: Fuel Values—Heating Values

1. The lines through natural gas at \$7 per MM Btu, residual fuel at \$50/bbl, or butane at 60¢/gal indicate that butane has the lowest cost per Btu.

## GLOSSARY

*The world's no blot for us,  
Nor blank; it means intensely, and means good:  
To find its meaning is my meat and drink.*

—*Fra Lippo Lippi*, Robert Browning

**absorbent.** The material that can selectively remove a target constituent from another compound by dissolving it.

**absorption.** A variation on fractionation. In a distilling column the stream to be separated is introduced in vapor form near the bottom. An absorbing liquid, called *lean oil*, is introduced at the top. The lean oil properties are such that as the two pass each other, the lean oil will selectively absorb components of the stream to be separated and exit the bottom of the fractionator as fat oil. The fat oil is then more easily separated into the extract and lean oil in conventional fractionation.

**adsorbents.** Special materials like activated charcoal, alumina, or silica gel, used in an adsorption process that selectively cause some compounds, but not others, to attach themselves mechanically as liquids.

**adsorption.** A process for removing target constituents from a stream by having them condense on an adsorbent, which is then taken off-line so the target constituents can be recovered.

**alkylation.** 1. A refining process in which propylene or butylene is reacted with isobutylene to form a high octane gasoline blending component, alkylate. 2. Any chemical process in which an alkyl group (a group derived from a paraffin) is connected to another organic compound.

**American Petroleum Institute (API).** An association which, among many other things, sets technical standards for measuring, testing, and other types of handling of petroleum.

**API.** An acronym for the American Petroleum Institute.

**API gravity.** An arbitrary scale used for characterizing the gravity of a petroleum product. The degrees API (written °API) are related to specific gravity scale by the formula: °API = [141.5/(sp.gr. @ 15°C / 15°C)] - 131.5

**aromatics.** 1. A group of hydrocarbons characterized by having at least one benzene ring type structure of six carbon atoms with three double and three single bonds connecting them somewhere in the molecule. The simplest is benzene itself, plus toluene and the xylenes. Aromatics in gas oils and residuals can have many, even scores, of rings. 2. The three aromatics compounds—benzene, toluene, and xylene.

**asphalt.** 1. A heavy, semisolid petroleum product that gradually softens when heated and is used for surface cementing. Typically brown or black in color, it is composed of high carbon-to-hydrogen hydrocarbons. It occurs naturally in crude oil or can be distilled or extracted. 2. The end product used for area surfacing consisting of refinery asphalt mixed with aggregate.

**asphaltenes.** Polyaromatic materials in heavy residues characterized by not being soluble in aromatic-free, low boiling point solvents. They are soluble in carbon disulfide.

**associated natural gas.** Natural gas that is dissolved in crude in the reservoir and is coproduced with the crude oil.

**barrel.** A standard of measurement in the oil industry; equivalent to 42 U.S. gallons, 35 Imperial gallons, or 159 liters.

**benzene.** The chemical C<sub>6</sub>H<sub>6</sub>, consisting of a six-carbon ring connected by double and single bonds. Benzene has excellent octane characteristics but is carcinogenic and therefore its content in gasoline is limited severely by regulation. Benzene is used in a large number of chemical processes, including those to make styrene and nylon.

**bitumen.** The British term for asphalt or the heavy asphalt extracted from tar sands.

**black oil.** Residual fuel or more generally the very heavy residues in the refinery.

**blown asphalt.** A special grade of industrial asphalt made by oxidizing flasher bottoms by blowing heated air through it.

**boiling point.** The temperature at which a liquid will boil. See also **end point** and **initial boiling point**.

**boiling range.** The lowest temperatures between which a hydrocarbon mixture will begin to boil and completely vaporize.

**bottoms.** 1. The product coming from the bottom of a fractionation column. 2. The liquid level left in a tank after it has been pumped “empty” and the pump loses suction.

**bottom sediment and water (BS&W).** The bottom sediment and water that settle out of petroleum stored in a tank.

**bright stock.** A lubricating oil component with high viscosity. Usually made by vacuum distillation of paraffinic crude oil, deasphalting, and solvent extraction of aromatics.

**British thermal unit (Btu).** A standard measure of energy; the quantity of heat required to raise the temperature of 1 pound of water by 1°F.

**BS&W.** An abbreviation for bottom sediment and water.

**Btu.** An abbreviation for British thermal unit.

**bubble cap trays.** The trays in a fractionator consisting of a plate with holes and bubble caps. The bubble caps cause the vapor coming from the bottom to come in intimate contact with the liquid sitting on the tray.

**bunker fuel.** Fuel oil or diesel used as ship fuel. Originally coal stored in the ship's bunkers.

**butadiene.**  $C_4H_6$ . A diolefin with two double bonds and two isomers. A colorless gas resulting from cracking processes. Traces result from cat cracking; made purposefully by catalytic dehydrogenation of butane or butylene and in ethylene plants using butane, naphtha, or gas oil as feeds. Butadiene is principally used to make polymers like synthetic rubber and acrylonitrile butadiene styrene (ABS) plastics.

**butane.**  $C_4H_{10}$ . Commercial butane is typically a mixture of normal butane and isobutane, predominantly normal. To keep them liquid and economically stored, butane must be maintained under pressure or at low temperatures.

**butylene.**  $C_4H_8$ . Hydrocarbons with several different isomers in the olefin series, used in refining in an alkylation plant or in petrochemicals to make solvents and some polymers.

**catalyst.** A substance present in a chemical reaction that will promote, accelerate, or selectively direct a reaction but not take part in it by changing chemically itself. Sometimes a catalyst is used to lower the temperature or pressure at which the reaction takes place.

**catalytic cracking.** A central process in refining in which heavy gas oil range feeds are subjected to heat in the presence of a catalyst and large molecules crack into smaller molecules in the gasoline, diesel, and surrounding ranges.

**catalytic reforming.** The process in refining in which naphthas are changed chemically to increase their octane numbers. Paraffins are converted to isoparaffins and naphthenes; naphthenes are converted to aromatics. The catalyst is platinum and sometimes palladium. Also referred to as *cat reforming*.

**caustic soda.** The name used for sodium hydroxide ( $NaOH$ ); used in refineries to treat acidic hydrocarbon streams to neutralize them. The term is derived from the corrosive effect on skin.

**cavern.** Underground storage either leached out of a natural salt dome or mined out of a rock formation.

**centipoise.** A measure of viscosity, related to centistokes by adjusting for density.

**centistoke.** A measure of viscosity.

**cetane number.** A measure of the ignition quality of diesel fuel and set by the percent of cetane in a mixture with alpha-methylnaphthalene.

**clarified oil.** Cycle oil from the cat cracker fractionator that has settled in a tank where errant catalyst has dropped out.

**coke.** 1. A product of the coking process in the form of mostly solid, densely packed carbon atoms. 2. Deposits of carbon that settle on catalysts in cat crackers, cat reformers, hydrocrackers, and hydrotreaters and degrade their effectiveness.

**coker.** A refinery process in which heavy feed such as flasher bottoms, cycle oil from a cat cracker, or thermal cracked gas oil is cooked at high temperatures. Cracking creates light oils; coke forms in the reactors and needs to be removed after they fill up.

**compression ratio.** The ratio of volumes in a internal combustion cylinder when the piston is at the bottom of the stroke and the top of the stroke, giving a measure of how much the air or air/fuel mixture is compressed in the compression stroke.

**condensate.** 1. The relatively small amount of liquid hydrocarbon, typically C<sub>4</sub>s through naphtha or gas oil, that gets produced in the oil patch with unassociated gas. 2. The liquid formed when a vapor cools.

**cracked gas.** The C<sub>4</sub>-stream coming from a cat cracker, coker, or thermal cracker containing olefins in addition to the saturated paraffins.

**cracked gas plant.** The set of columns and treaters in a refinery that handle separation and treating of the cracked, olefinic gases.

**cracking.** Refining processes in which large molecules are broken into smaller molecules of uneven sizes. It can be promoted by heat and pressure alone, such as in thermal cracking or coking, or enhanced by the use of catalysts as in cat cracking or hydrocracking.

**cut.** A refinery term referring to a stream obtained from a fractionation unit with a specific initial boiling point and end point.

**cutter stock.** Diluent added to residue to meet residual fuel specifications for viscosity and perhaps sulfur content. Typically cracked gas oil.

**cyclic compounds.** See **ring compounds**.

**cyclics.** Cyclic compounds. See **ring compounds**.

**deasphalting.** A process in which the asphaltic constituents of a heavy residual oil are separated by mixing with liquid propane. Everything will dissolve in the propane but the asphaltics, which can then be subsequently removed.

**decocking.** The process of removing coke from catalysts in a cat cracker, cat reformer, hydrocracker, or hydrotreater. Usually heated air will oxidize the coke to carbon monoxide or carbon dioxide.

**delayed coker.** A process unit in which residue is cooked until it cracks to coke and light products.

**diene.** Same as a diolefin.

**diesel.** 1. An internal combustion engine in which ignition occurs by injecting fuel in a cylinder where air has been compressed and is at a very high temperature, causing self-ignition. 2. Distillate fuel used in a diesel engine.

**diolefin.**  $C_nH_{2n-2}$ . A paraffin-type molecule except that it is missing hydrogen atoms, causing it to have two double bonds somewhere along its chain.

**distillate.** 1. The liquid obtained by condensing the vapor given off by a boiling liquid. 2. Any stream, except the bottoms, coming from a fractionator. 3. The products or streams in the light gas oil range such as straight run light gas oil, cat-cracked light gas oil, heating oil, or diesel.

**distillation.** A separation process that results in separated products with different boiling ranges. Distillation is carried out in a way that the materials being separated are not subjected to conditions that would cause them to crack or otherwise decompose or chemically change.

**distillation range.** See **boiling range**.

**distributor.** A device in a vessel that disperses either liquid or vapor to promote better circulation.

**dry gas.** Natural gas or refinery gas streams that are in the  $C_4$  and lighter range.

**effective cut points.** Cut points that can be considered a clean cut, ignoring any tail ends.

**end point.** The lowest temperature at which virtually 100% of a petroleum product will boil off to vapor form.

**ethane.**  $C_2H_6$ . A colorless gas; a minor constituent of natural gas and a component in refinery gas that, along with methane, is typically used as refinery fuel. An important feedstock for making ethylene.

**ethylene.**  $C_2H_4$ . A colorless gas created by cracking processes. In refineries it is typically burned with the methane and ethane. In chemical plants it is purposefully made in ethylene plants and is a basic building block for a wide range of products including polyethylene and ethyl alcohol.

**extract.** The target constituent in a solvent extraction process. See also **solvent extraction**.

**fixed bed.** A place in a vessel for catalyst through or by which feed can be passed for reaction; as opposed to a fluid bed, where the catalyst moves with the feed.

**flash chamber.** A wide vessel in a vacuum flasher, thermal cracking plant, or similar operation into which a hot stream is introduced, causing the lighter fractions of that stream to vaporize and leave by the top.

**flash point.** The lowest temperature at which any combustible liquid will give off sufficient vapor to form an inflammable mixture with air. Flash points are used to specify the volatility of fuel oils, mostly for safety reasons.

**flue gas.** Gas from the various furnaces going up the flue (stack).

**fluid bed.** Contrast with **fixed bed**.

**fluid cat cracking.** By far the most popular design of cat cracking in which a powdery catalyst that flows like a fluid is mixed with the feed and the reaction takes place as the feed/catalyst is in motion.

**fractionation.** The general name given to a process for separating mixtures of hydrocarbons or other chemicals into separate streams or cuts or fractions.

**freeze point.** The temperature at which crystals first appear as a liquid is cooled, which is especially important in aviation fuels, diesel, and furnace oil.

**fresh feed rate.** The feed going into a reaction without counting the amount of recycling of any reaction products.

**fuel oil.** Usually residual fuel but sometimes distillate fuel.

**furnace oil.** A distillate fuel made of cracked and straight run light gas oils, primarily for domestic heating because of its ease of handling and storing.

**gain.** The volumetric expansion resulting from the creation of lighter, less dense molecules from heavier, compact molecules, even given that the weight remains the same before and after.

**gas cap.** An accumulation of natural gas at the top of a crude oil reservoir. The gas cap often provides the pressure to rapidly evacuate the crude oil from the reservoir.

**gas oil.** A fraction of hydrocarbon in the range of approximately 450°F to 800°F. Sources are crude oil distilling and cracking.

**gasoline.** A light petroleum product in the range of approximately 80°F to 400°F for use in spark-ignited internal combustion engines.

**gum.** A complex, sticky substance that forms by the oxidation of gasolines, especially those stored over a long period of time. Gum fouls car engines, especially the fuel injection ports.

**heat exchanger.** An apparatus for transferring heat from one liquid or vapor stream to another. A typical heat exchanger will have a cylindrical vessel through which one stream can flow and a set of pipes or tubes in series in the cylinder through which the other can flow. Heat transfers through the tubes by conduction.

**heating oil.** Any distillate or residual fuel.

**HF alkylation.** Alkylation using hydrofluoric acid as a catalyst.

**hydrocarbon.** Any organic compound comprised of hydrogen and carbon, including crude oil, natural gas, and coal.

**hydrocrackate.** The gasoline range product from a hydrocracker.

**hydrocracking.** A process in which light or heavy gas oils or residue hydrocarbons are mixed with hydrogen under high pressure and temperature and in the presence of a catalyst to produce light oils.

**hydrodesulfurization.** A process in which sulfur is removed from the molecules in any refinery stream by reacting it with hydrogen in the presence of a catalyst.

**hydrogenation.** Filling in with hydrogen the “free” places around the double bonds in an unsaturated hydrocarbon molecule.

**hydrophilic.** Having an affinity for water. For example, bourbon has an affinity for water because it mixes easily with it. Olive oil is not hydrophilic because it does not. (It is hydrophobic.) A single molecule can have both a hydrophilic and hydrophobic sites, such as soap.

**hydrophobic.** Contrast with **hydrophilic**.

**hydrotreating.** A process in which a hydrocarbon is subjected to heat and pressure in the presence of a catalyst to remove sulfur and other contaminants such as nitrogen and metals and in which some hydrogenation can take place.

**IBP.** An abbreviation for initial boiling point.

**initial boiling point (IBP).** The lowest temperature at which a petroleum product will begin to boil.

**isomerization.** A refinery process in which compounds are changed to their isomer form using a catalyst. For example normal hexane to isohexane or normal butane to isobutane.

**isomers.** Two compounds composed of the identical atoms, but with different configurations, giving different physical properties.

**isoctane.**  $C_8H_{18}$ . The liquid used with normal heptane to measure the octane number of gasolines.

**jug.** A salt dome storage cavern for hydrocarbon or chemicals.

**kerosene.** A petroleum product made from crude oil with a boiling range of approximately 315°F to 450°F, used as domestic heating oil.

**lean oil.** See absorption.

**light ends.** In a refinery, the  $CH_4$  and lighter gases.

**light oil.** Generally gasoline, kerosene, and distillate fuels.

**liquefied petroleum gas (LPG).** Propane and butane meeting market specifications.

**long residue.** Straight run residue from a distilling unit.

**LPG.** An abbreviation for liquefied petroleum gas.

**mercaptans.** A group of sulfur-containing compounds found in some crude oils having a skunklike odor. Mercaptans are manufactured and injected into natural gas and LPG as an odorant for safety purposes.

**methane.** CH<sub>4</sub>. A light, odorless, flammable gas that is the principal component of natural gas.

**methanol.** CH<sub>3</sub>OH. Methyl alcohol, also known as wood alcohol. Methanol can be made by the destructive distillation of wood or through a process starting with methane or a heavier hydrocarbon, decomposing it to synthesis gas, and recombining it to methanol.

**MON.** An abbreviation for Motor Octane Number.

**Motor Octane Number (MON).** One of two standard measures of gasoline knock, this one simulating more severe operating conditions. Contrast with Research Octane Number; see also octane number.

**naphtha.** Hydrocarbon fractions in the range of approximately 220°F to 315°F. Naphtha is generally not suitable for direct blending to gasoline and is usually further processed in a cat reformer or used as feed to an ethylene plant.

**naphthenes.** Hydrocarbons with saturated ring structures with a general formula C<sub>n</sub>H<sub>2n</sub>.

**naphthenic acids.** Organic acids occurring in petroleum that contain a naphthene ring and one or more carboxylic acid groups. Naphthenic acids are used in the manufacture of paint driers and industrial soaps.

**natural gas.** Naturally occurring gas consisting predominantly of methane, sometimes in conjunction with crude (associated gas) and sometimes alone (unassociated gas).

**natural gasoline.** A gasoline range product separated at a location near the point of production from natural gas streams and used as a gasoline blending component.

**nonassociated gas.** Natural gas that exists in a reservoir alone and is produced without any crude oil.

**octane number.** An index measured by finding a blend of iso-octane and normal heptane that knocks under the identical conditions as the gasoline being evaluated. It is a measure of the ease of self-ignition of a fuel without the aid of a spark plug. The higher the octane number, the more resistance to preignition or self-ignition. See also **Motor Octane Number** and **Research Octane Number**.

**olefins.** A class of hydrocarbons similar to paraffins, but that has two hydrogen atoms missing and a double bond replacing them. The general formula is C<sub>n</sub>H<sub>2n</sub> for monoolefins and C<sub>n</sub>H<sub>2n-2</sub> for diolefins, those having two sets of double bonds.

**organic compounds.** Compounds that includes carbon and hydrogen. Generally organic compounds can be classified as either aliphatics (straight chain compounds), cyclics (compounds with ring structures), and combinations of aliphatics and cyclics.

**paraffins.** Straight chain hydrocarbons with the general formula  $C_nH_{2n+2}$ .

**penetration.** A measure of the hardness and consistency of asphalt in terms of the depth that a special pointed device will penetrate the product in a set time and temperature.

**petroleum coke.** See **coke**.

**pitch.** Residue coming from the bottom of a flasher.

**platformer.** Archaic name for a reformer.

**pour point.** The temperature at which an oil starts to solidify and no longer flows freely.

**precursor.** Compounds that are suitable or susceptible to specific conversion to another compound. For example, methyl cyclopentane is a good precursor for making benzene in a cat reformer.

**propane.**  $C_3H_8$ . A hydrocarbon gas that is a principal constituent of the heating fuel, LPG. Propane is used extensively for domestic heating and as a feed to ethylene plants.

**propylene.**  $C_3H_6$ . A hydrocarbon in the olefin series resulting from olefin plant operations and refinery cracking processes and used as alkyl plant feed or chemical feedstock.

**pygas.** See **pyrolysis gasoline**.

**pyrolysis.** Heating a feedstock to high temperature to promote cracking, as in an ethylene plant.

**pyrolysis gasoline.** The gasoline created in an ethylene plant cracking gas oil or naphtha feedstocks. Sometimes called *pygas*, it has high content of aromatics and olefins and some diolefins.

**quench.** Hitting a very hot stream coming out of a reactor, with a cooler stream to stop immediately the reaction underway.

**radical.** A group of atoms that separate themselves from a compound momentarily and are highly reactive. For example, two methyl radicals, written as  $\cdot CH_3$  can come from cracking an ethane atom, but they will rapidly attach themselves to some other atom or compound.

**raffinate.** The leftover from a solvent extraction process. See also **solvent extraction**.

**reactor.** The vessel in which the chemical reaction takes place.

**reboiler.** A heat exchanger used towards the bottom of a fractionator to reheat or even vaporize a liquid and introduce it several trays higher to help purify the incoming stream or to get more heat into the column.

**reflux.** A heat exchanger, which takes vapor from the upper parts of a fractionator, cools it to liquefy it, and reintroduces it lower on the column. The purpose is to help purify the incoming stream and to remove heat from the column.

**reformate.** The high octane, primary product of reforming naphtha.

**reforming.** See **cat reforming** or **steam methane reformer**.

**regenerator.** The vessel in a catalytic process where a spent catalyst is cleaned up before being recycled back to the process. An example is the cat cracker regenerator where coke is burned off the catalyst.

**Reid vapor pressure.** The pressure necessary to keep a liquid from continually vaporizing, as measured in an apparatus designed by Reid himself. Used as a standard measure for gasoline specifications.

**Research Octane Number (RON).** One of two standard measures of gasoline knock, this one simulating less severe operating conditions like cruising. Contrast with **Motor Octane Number**; see also **octane number**.

**resid.** See **residual fuel**.

**residence time.** The amount of time a hydrocarbon spends in a vessel where a reaction is taking place.

**residual fuel.** Heavy fuel oil made from long, short, or cracked residue plus whatever cutter stock is necessary to meet market specifications. Also called *resid*.

**residual oil supercritical extraction (ROSE) process.** An extraction technique using propane, butanes, and pentanes to isolate asphalt.

**residue.** The bottoms from a crude oil distilling unit, vacuum flasher, thermal cracker, or visbreaker. See also **long residue** and **short residue**.

**ring compounds.** Hydrocarbon molecules in which the carbon atoms form at least one closed ring such as naphthalenes or aromatics. Also called *cyclics*.

**RON.** An abbreviation for Research Octane Number.

**ROSE.** An abbreviation for residual oil supercritical extraction (process).

**RVP.** An abbreviation for Reid vapor pressure.

**salt dome.** A naturally occurring column of salt several hundred feet to thousands of feet below the surface. Many salt domes are suitable for leaching out caverns for use as hydrocarbon storage.

**sats gas plant.** The set of columns and treaters in a refinery that handle separation and treatment of the saturated gases.

**short residue.** Flasher bottoms or residue from the vacuum flasher.

**sieve trays.** A variation of the trays used in fractionating columns, consisting of perforated plates to allow vapor passage.

**slack wax.** The rejected product from dewaxing lube base stocks.

**slurry oil.** Cycle oil from the cat cracker fractionator bottom that has errant catalyst in it. Usually sent to a settling tank. See also **clarified oil**.

**smoke point.** The maximum height of flame in millimeters at which kerosene will burn without creating smoke. Measured in a standard wicked lamp.

**solvent extraction.** A fractionation process based on selective solubility. A liquid solvent is introduced at the top of a column. As it passes the feed, which enters near the bottom as a vapor, it selectively dissolves a target constituent. The solvent is then removed via the bottom of the column and put through an easy solvent/extract fractionation. From the top of the column comes a raffinate stream, the feed stripped out of the extract. Butadienes and aromatics are some products recovered by solvent extraction.

**sour crude.** Crude typically containing 1.5% (by weight) or more sulfur.

**spent catalyst.** Catalyst that has been through a reaction and is no longer as active because of substances or other contaminants deposited on it (in the case of solid) or mixed with it (in the case of liquid).

**sponge oil.** The liquid used in an absorption plant to soak up the constituent to be extracted. See also **absorption** and **solvent extraction**.

**stability.** A measure of the resistance of petroleum products to forming gums while in storage.

**stabilizer.** A fractionator used to remove butanes and lighter components from gasoline range streams to make them less volatile.

**steam cracking.** The same as cat cracking, but specifically referring to the steam injected with the catalyst and feed to give the mixture lift up the riser.

**steam methane reformer.** A primary source of hydrogen in a refinery, this operating unit converts methane and steam to hydrogen, with by-products of carbon monoxide and carbon dioxide.

**straight run.** A product of distillation but no chemical conversion.

**Sulfolane.**  $(\text{CH}_2)_4\text{SO}_2$ . A chemical used as a solvent in extraction and extractive distillation processes.

**surface area.** The total area that a solid catalyst exposes to the feeds in a reaction. Surface area is enhanced in some catalysts like zeolites by extensive microscopic pores.

**sweet crude.** Crude typically containing 0.5% (by weight) or less sulfur.

**sweetening.** The conversion of mercaptans in gasoline into nonsmelly disulfides.

**synthesis gas.** The product of a reforming operation in which a hydrocarbon, usually methane, and water are chemically rearranged to produce carbon monoxide, carbon dioxide, and hydrogen. The composition of the product stream can be varied to fit the needs for hydrogen and carbon monoxide at refineries or chemical plants. Also known as *syn gas*.

**tail ends.** Small amounts of hydrocarbon in a cut that vaporize slightly outside the effective initial boiling point and the effective end point.

**tar.** Complex, large molecules of predominantly carbon with some hydrogen and miscellaneous other elements that generally deteriorate the quality of processes and the apparatus.

**TEL.** An abbreviation for tetraethyl lead.

**tetraethyl lead (TEL).** A nearly extinct additive used to enhance the octane number of gasolines. Use of TEL is outlawed in most countries as a health hazard.

**thermal cracking.** A refinery process of cracking heavy streams such as flasher bottoms or cat-cracked cycle oil into light products using high temperatures.

**toluene.**  $C_6H_5CH_3$ . One of the aromatic compounds used as a chemical feedstock, most notoriously for the manufacture of TNT, trinitrotoluene.

**topped crude.** Crude that has been run through a distilling unit to remove the gas oil and lighter streams. The so-called simple refineries that do this generally sell the long residue as residual fuel.

**unsaturated.** A class of hydrocarbons similar to paraffins and naphthenes but having double bonds or triple bonds replacing the missing hydrogens.

**vacuum distillation.** Distillation under reduced pressure in order to keep the temperature low and prevent cracking. Often used to create cat cracker feed or to distill lubricant feedstocks.

**valve trays.** Fractionator trays that have perforations covered by discs that operate as valves and allow the upward passage of vapor.

**vapor lock.** Atmospheric conditions of high temperature or low pressure can cause gasoline to vaporize in the fuel line, disabling the fuel pump and shutting down the engine due to vapor lack.

**vapor pressure.** See **Reid vapor pressure**.

**visbreaking.** Mild thermal cracking aimed at producing sufficient middle distillates to reduce the viscosity of the heavy feed.

**viscosity.** The measure of a liquid's resistance to flow.

**volatile.** A hydrocarbon is volatile if it has a sufficient amount of butanes and lighter material to noticeably give off vapors at atmospheric conditions.

**volatiles.** Oil patch nomenclature for butane and propane, and sometimes ethane.

**wet gas.** Natural gas that has not had the  $C_4$  and natural gasoline removed. Also the equivalent refinery gas stream.

**white oil.** Sometimes kerosene, sometimes treated kerosene used for pharmaceutical purposes and in the food industry.

**xylene.**  $C_6H_4(CH_3)_2$ . One of the aromatics compounds. Xylene has a benzene ring and two methyl radicals attached and has three isomers, ortho-, para-, and metaxylene. Used as a gasoline blending component or a chemical feedstock for making phthalic acids and resins.

**yield.** Either the percent of a desired product or all the products resulting from a process involving chemical changes to the feed.

**zeolytes.** Compounds used extensively as catalysts, made of silica or aluminum, as well as sodium or calcium and other compounds. Zeolytes come in a variety of forms—porous and sandlike or gelatinous—and provide the platform for numerous catalysts. The solid zeolytes have extensive pores that give them very large surface areas. The precise control during fabrication of the pore sizes enables selected access to different size molecules during reactions.

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