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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 doesn't behave. It is not *a* 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 where it starts to boil and hold it at that temperature, some of it will vaporize and some of it won't.

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.

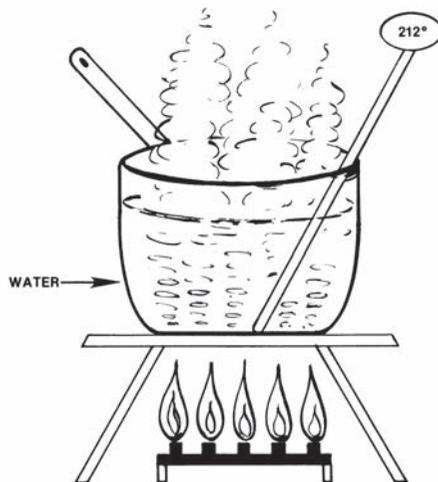


Fig. 3-1. Boiling Water

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's because the chemical compound H_2O boils at 212°F. At atmospheric pressure, it boils at no more, no less.

Crude Oil Composition

Now back to crude oil. Unlike water, crude is not *a single* chemical compound but thousands, sometimes over hundreds of thousands of different compounds. Some are as simple as CH_4 (methane); some are as complex as $C_{35}H_{50}$. CH_4 and $C_{35}H_{50}$ are the chemist's shorthand for individual types of chemical compounds. 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 rub, 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 adjust the flame under the pot to maintain the temperature at 150°F. After a while, the crude stops boiling.

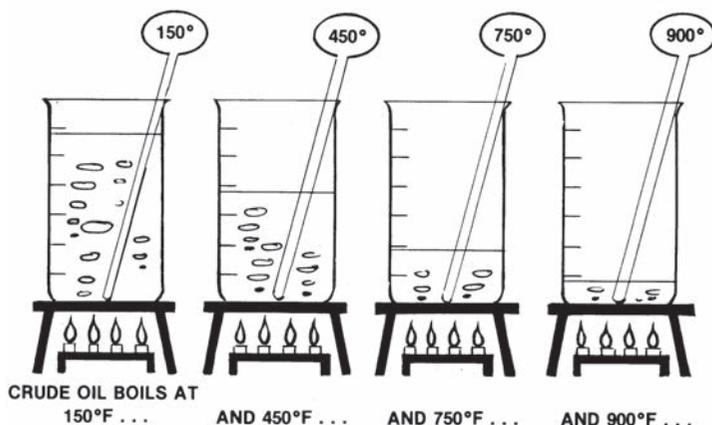


Fig. 3-2. Boiling Crude Oil

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

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

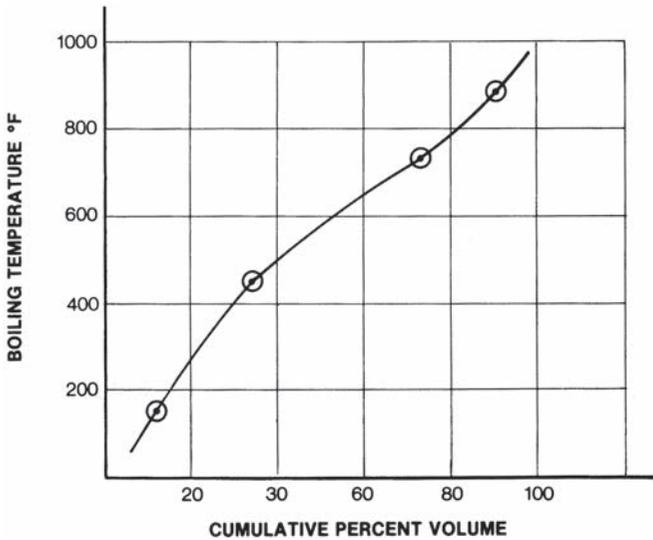


Fig. 3-3. Crude Oil Distillation Curve

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. The crude from each and every oil field has a unique distillation curve that helps characterize what kinds of hydrocarbons are in that crude. Figure 3-4 shows a sampling of worldwide crudes. The light crudes tend to have more gasoline, naphtha, and kerosene; the heavy crudes tend to have more gas oil and residue. Refinery management always want to know how much of each of these components are in the various crudes available to them. They will have their laboratory run an *assay* of the crudes. The first test

Bigger and Heavier

Generally the more carbon atoms in the compound, the higher the boiling temperature, as shown in these examples:

Compound	Formula	Boiling Temperature	Weight Lbs/Gal
Propane	C_3H_8	-44°F	4.2
Butane	C_4H_{10}	31°F	4.9
Decane	$C_{10}H_{22}$	345°F	6.1
Cetane	$C_{16}H_{34}$	549°F	6.5

It is also easy to notice the relationship between the weight of the molecules and the temperature at which they boil.

they run doesn't use a pot with crude oil in it. Rather they use an apparatus like that in Figure 3-5 to separate the components in fractions.

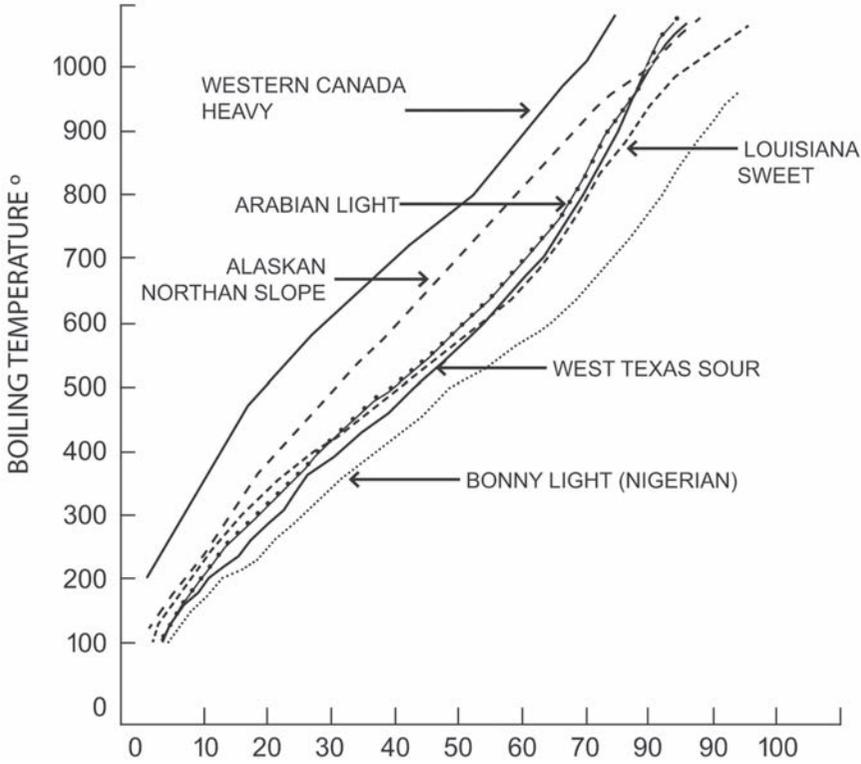


Fig. 3-4. Distillation Curves of Some Crudes

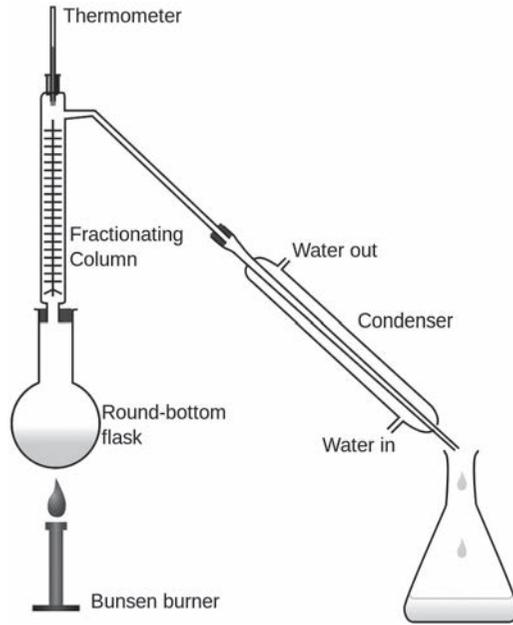


Fig. 3-5. Distillation Apparatus

The crude is heated slowly. As the ever warmer vapors reach the top, the temperatures are recorded. The vapors then pass through a water jacket and condense; the liquid volumes are recorded (alongside the concurrent temperatures) as they accumulate, giving a distillation curve. Courtesy Teresa Knott.

Fractions

To further specify the character of crude oil, 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 cutpoints to describe the fractions in crude oil are:

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 characteristic of each of those fractions, but some are already apparent from their names. Figure 3-6 shows where the various cuts plot on a typical distillation curve.

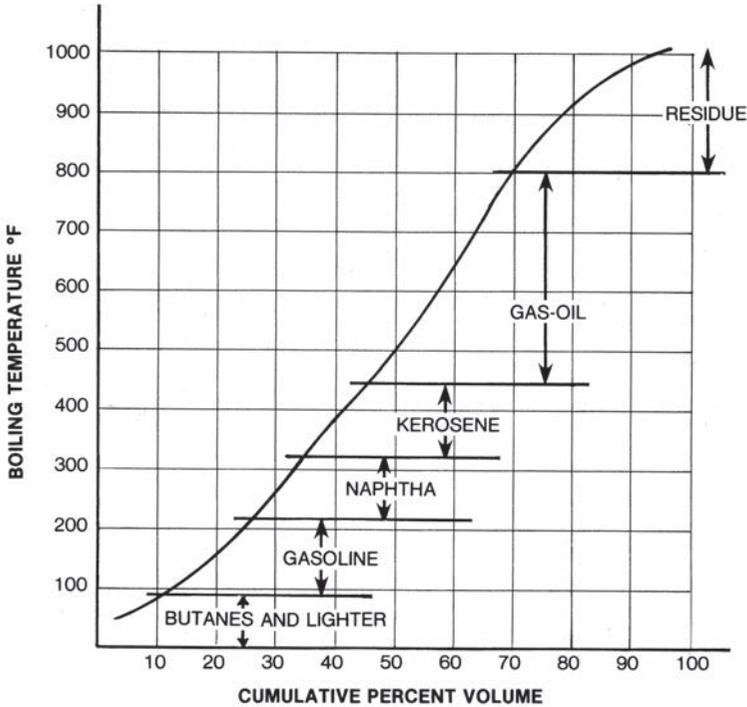


Fig. 3-6. Fractions (or Cuts) from Crude Oil

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 3-7 and run through the steps to determine which crude has higher kerosene content (a bigger kerosene cut.)

Kerosene has a boiling temperature range from about 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 percent on the horizontal axis. That's 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 percent on the horizontal axis. That's the amount that has boiled off when kerosene stops boiling off.

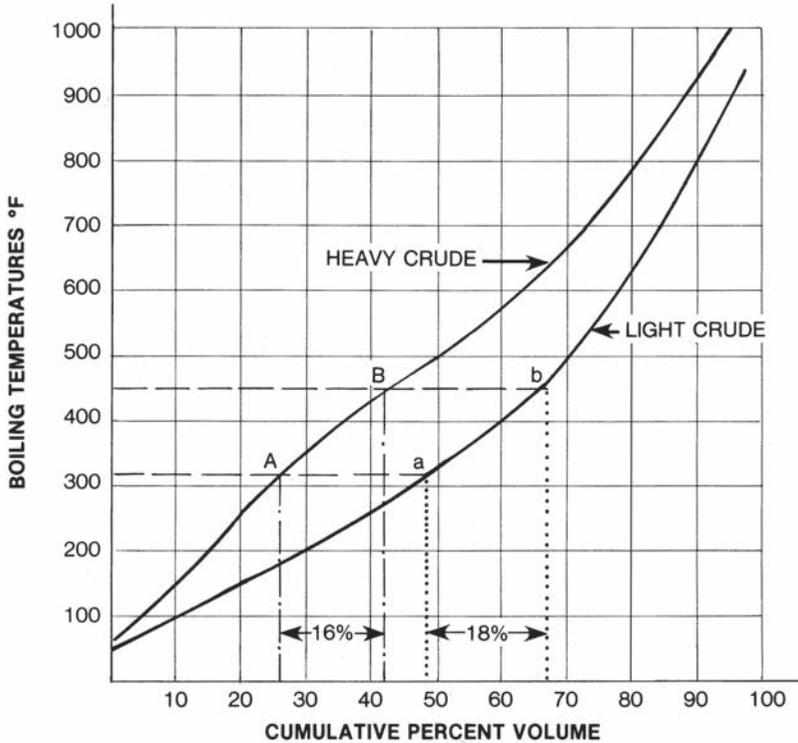


Fig. 3-7. Kerosene Cut from Two Different Crudes

3. Calculate the cumulative percent volume from the *initial boiling point* of the kerosene to the *end point*: $42 - 26 = 16$ percent. The heavy crude contains 16 percent kerosene.
4. Now do the same procedure for the light crude and find that there is $66.5 - 48.5 = 18$ percent.

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, despite a dozen or more other considerations.

Gravities

Gravities measure the relative 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'll 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. Counterintuitively, the higher the API gravity, the lighter the compound, as shown in Figure 3-8
3. The reverse is true for specific gravity

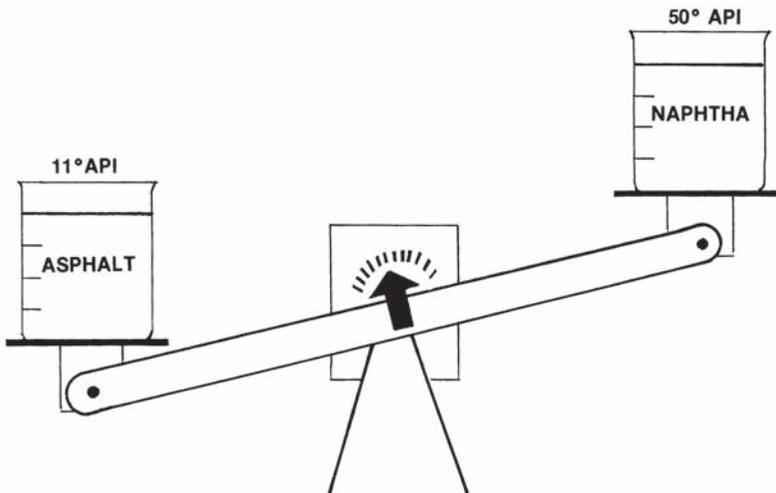


Fig. 3-8. API Gravities of Asphalt and Gasoline

The higher the degree API, the lower the weight.

Typical gravities:

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

Common knowledge says oil floats on water. The sheen you might have seen from a boat motor or a dock gasoline pump results from oil not dissolving in water and being at an API gravity above 10^o. Not all oil weighs that little. Industry lore (as documented by your author) 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^o API material.

Tonnes, Barrels, and Gallons

A volumetric convention grew out of the Pennsylvania oil fields, according to oil patch lore. Oil was initially shipped to market by horse-drawn wagon or flat-car in used 46, 48, and 50 gallon wine, pickle, apple, biscuit, nail, and other types of 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 most of the rest of the world, 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. 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, despite all this, 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.

Displacement

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.

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 little yellow bits of elemental sulfur, a chemical all by itself, but is almost always a sulfur compound. In some cases, the sulfur could be in the form of hydrogen sulfide, H_2S , a toxic gas, or a mercaptan, another smelly sulfur compound. Both these require special treatment for removal. More pervasively, sulfur may be chemically bonded to some of the more complicated oil 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 many words later on in Chapter 16.

The parlance in discussing crude oils of varying sulfur content is to categorize them into *sweet* crudes and *sour* crudes. This quaint, faintly oriental 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. Early on, an unknown soul discovered that kerosene with higher sulfur content had a more sour taste and 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. (The silver tarnishing resulted from burning sulfur-containing oil, forming byproduct sulfur oxides that chemically attacked the silver, creating silver sulfate, another name for tarnish.)

Sulfur or Sulphur?

Americans generally spell sulfur with an *f*, while British use a *ph*. Both are acceptable, but Yanks, eschewing the more phonetic form, are unaccountably more etymologically frugal in this regard.

Sweets and Sours

Typical sweet crudes include West Texas Intermediate, the popular traded crude on the New York Mercantile Exchange, many Louisiana and 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.

Today, sweet crudes typically have 0.5 percent sulfur content or less, sour 1.5 percent 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 all the crude oil tasters are up in the gourmet cloud in the sky.

Metals, Acids, and Wax

Carbon and hydrogen from the organic material buried deep in the earth were not the only elements around. Others snuck into the hydrocarbon molecules as they cooked over time. Like crudes with high sulfur content, crudes with high heavy metals and high acid content are always discounted against their counterpart “clean” crudes.

Metals

Different metals resided in the source rocks where the crude oil formed—vanadium, nickel, copper, lead, iron, magnesium, sodium, molybdenum, zinc, cadmium, titanium, manganese, chromium, cobalt, antimony, uranium, aluminum, tin, barium, gallium, silver, and arsenic. After all, it’s dirt. Many ended up hooking up with the hydrocarbons in miniscule amounts. Some, even small amounts, endanger full exploitation of the oil as it passes through the refining system. Nickel and vanadium, for example, will poison cat cracking catalyst, making frequent replacement necessary.

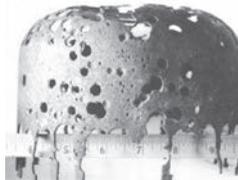


Fig. 3–9. Bubble Cap Pitted by High TAN Crude

Acids

As crudes form, instead of a plain old hydrocarbon, some carbon, hydrogen, and any oxygen atoms can form a carboxylic acid, whose formula is R-COOH. The R stands for a hydrocarbon molecule that the carboxyl group, -COOH has hooked up with. Hydrocarbons with naphthenes in their structure are more susceptible to attracting carboxylic groups, and naphthenic crudes tend to have more (naphthenic) acids in them.

Crude oil assays list the results of a test for acid content—Total Acid Number, or TAN. The test involves measuring the small amount of potassium hydroxide, a base, necessary to neutralize any acid in a same small amount of the crude. Modern refinery laboratories may use spectrometry to determine the TAN. Table 3-1 has the TANs of some international crudes.

Table 3-1. TANs of Various Crudes

TANs of Various Crudes		
Forties	North Sea	0.095
Tapis	Malaysia	0.215
Zafira	Equitorial Guinea	0.768
Pazflor	Sonagol	1.631

The presence of acids can lead to destructive corrosion of pipelines, tankage, and particularly refinery operating units where high temperatures enhance chemical interaction. (See Figure 3-9, a device that will be dealt with in Chapter 4.) Refineries processing high TAN number crudes may have to treat the crude oil or its heavier fractions with hydrogen to reduce the $-\text{COOH}$ group to H_2O and CO_2 . A TAN of 0.017 would not be an issue for a refinery but one with a 3.6 TAN would be worrisome.

Wax

Long chain paraffins, those with thirty or more carbons and especially those with lots of branches, solidify at ambient temperatures. Some crudes are rich in these paraffins and as a result present special problems in transportation; they have to be moved in heated pipelines, trucks, or tank cars to avoid becoming a solid, immovable mass, especially in cold weather.

Review

Figure 3-4 shows the distillation curves for six different crudes, three U.S. and three 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.

Exercises

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

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

How much naphtha (220 – 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.

15

Distillate and Residual Fuels

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 ninety-five percent of the hydrocarbons that boil above 350° F and that are not cracked into gasoline blending components end up as one of these four 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 USA 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 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 USA, *Jet A-1* elsewhere) has a boiling point specification of 205-300° C. (The 205 is actually the ten percent 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. Some air-line passengers flying at 35,000 feet 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 due to the lack of enough hydrogen to form H_2O .

Military jet fuel (JP-5 and JP-8) has a lower ten percent recovery point at the lower end to allow more naphtha to get in. The nominal 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 the dust bins of history. Originally, refiners established six grades of fuel oils, which were 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 be vaporized easily for use as lighting and cooking fuel.
- 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. In the past it was rebranded extensively to road oil, poured directly on dirt roads for a semi-permanent hard surface that helped keep down dirt and dust.
- Number 6 oil is 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. Residual fuel comes in varying grades reflecting the sulfur content.

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 box below, "Liquids don't burn.") Numerous recorded tragedies have come from situations where gasoline inadvertently got mixed with home 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).

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



Fig. 15-1. Flash Point Danger

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.

As 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. On the upstroke, 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.

In most places outside the USA, automotive diesel fuel is known as *gas oil*. The name comes from the fact that the fuel has been boiled out of the crude oil and then condensed back to liquid oil, as opposed to residual fuel which 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.

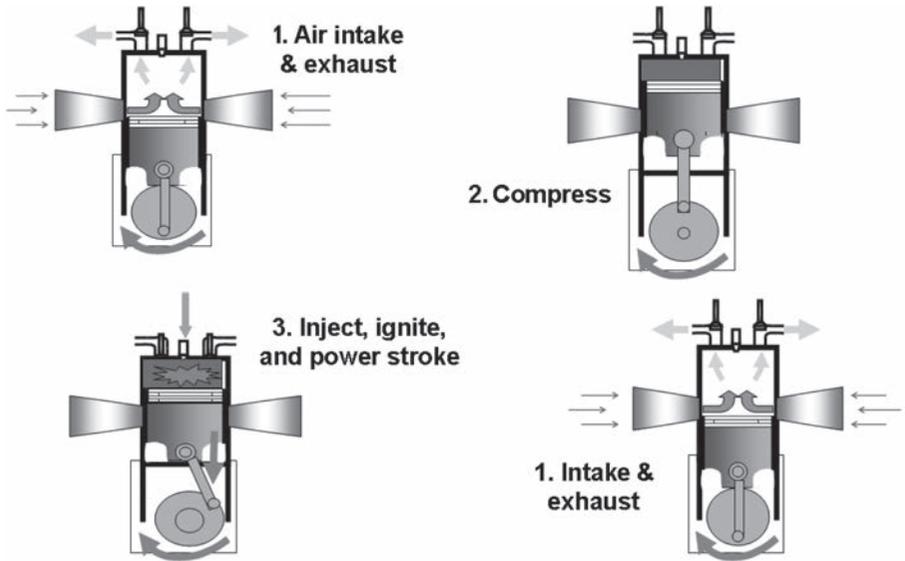


Fig. 15-2. Two Stroke Diesel Engine

Cetane number.

For gasoline engines, pre-ignition 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-methyl-naphthalene ($C_{11}H_{12}$). 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 multi-lined chart) or a formula involving the gravity and the fifty percent 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—just the opposite of octane num-

bers. The cracked light gas oils tend to have higher aromatic content (and cetane number of thirty-two to thirty-five) 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 fifty to fifty-five. 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 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 fees. If the market doesn't allow that, sometimes a refiner will use an *ignition accelerator* additive to boost the cetane number by as much as ten. In cold weather, kerosene is often added to lower the pour point and at the same time raise the cetane number. (Kerosene is about fifty-five cetane.)

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

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: because of more severe hydrotreating, more aromatics are converted to naphthenes and paraffins. Unfortunately, the more severe the treatment to remove sulfur, the more by-product gases get formed.

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 build-up for flow improvement
- anti-oxidants 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 is resid (residual fuel), when a refiner runs out of coker or other residue reduction capacity or doesn't have an asphalt operation. This last resort generally returns less money per barrel than the cost of the crude oil. It's 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, to sell the flasher bottoms a refiner will dilute them 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 and Heating Values, residual fuels contain a lot of energy to be captured at the burner tip.

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 other 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 doesn't go out the stack (people used to say *smoke* stack, but no one uses that term any more) and get 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 eight to twelve pistons and cylinders two to three feet in

diameter, with strokes five to eight 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 100-135 rpm, compared to the thousands that register on the dash of a diesel car.

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:

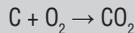


Burning more complex molecules such as a residual fuel, $\text{C}_{20}\text{H}_{24}$, gives corresponding amounts of carbon dioxide and water. In each case, to get a complete reaction, the hydrocarbon has to be in intimate contact with oxygen. For that reason,

Liquids don't burn. Vapors burn.

That explains the mechanics of flash points. A low flash point, 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 sufficient carbon/oxygen contact and the chemical reaction.



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—it leaves the firebox, cylinder, or turbine as a dark colored 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.

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 shed may require a maximum 0.1-0.5 percent sulfur; a ship at sea may be able to burn five percent sulfur resid, but new restrictions under United Nations agency, the International Maritime Organization, limit sulfur content to 0.5 percent around the world but 0.1 percent in or near ports.

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 hydro-

treater, 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.

Exercises

1. How do 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's the difference between furnace oil and diesel?
3. What two options can a shipbuilder use to power a ship with residual fuel?