



MAY 2014

**Chemical
Engineering
Progress**

An AIChE Publication

CEP

www.aiche.org/cep



An Oil Refinery Walk-Through

- 6 UPDATE**
- 22 A New Graduate's Lessons Learned**
- 28 3D-Printed Prosthetics**
- 42 Material Selection**
- 52 Institute News: Meeting Highlights**

An Oil Refinery Walk-Through

TIM OLSEN
EMERSON PROCESS MANAGEMENT

Refineries may appear complicated at first glance. Breaking them down into a series of units makes them easier to understand. This article describes the basic building blocks of a fuels refinery, from crude oil inlet to fuels distribution.

Refineries that process crude oil into transportation fuels can be overwhelming to the outside observer — with their multitude of tanks and vessels, numerous pipes of varying sizes, fired heaters, pumps and compressors, instrumentation and control systems, and more. The primary purpose of all of this is to economically convert raw crude oil into more-useful fuels and petrochemicals.

This article gives an overview of each unit within a refinery and explains how intermediates are transformed into transportation fuels. It focuses only on refineries that produce transportation fuels, such as gasoline, diesel, and jet fuel, and does not discuss integrated petrochemical complexes.

The simple flow diagram in Figure 1 shows how crude oil is converted into higher-value fuel products. First, the raw crude is washed in a desalter and heated. Next, it enters the atmospheric crude fractionator, followed by the vacuum fractionator. These first units in a refinery involve no chemical reactions or catalysts; rather, based on each component's boiling point, they separate and distribute the range of components for further downstream processing and conversion. Downstream units include such equipment as pumps and compressors, heat exchangers, reactors, and distillation columns. Some of these downstream units contain a specific catalyst to convert one product to a different product with more desirable qualities. Streams are then separated into intermediate products and off-gases. Finally, certain intermediate products from these units are blended into final products as per required specifications, such as octane and Reid vapor pressure (RVP) for gasoline.

Crude oils vary significantly with respect to their API

gravity (a measure of relative density), component mixture, and levels of metals, sulfur (sweet crudes contain less than 0.42% sulfur, sour crudes more than that), and various salts. Crude assays are descriptions of different crude oils with a distillation range to indicate the quantity of components in each boiling point range. This information is used to determine relative flows out of the atmospheric crude fractionator.

Each refinery has been designed to process crude oil of a particular composition, whether that is the composition of a single crude oil or the composition of a blend of crude oils. If an individual crude oil with the desired feed properties for a refinery is not available for processing, multiple crudes can be blended to obtain a feedstock that better matches the refinery's capabilities.

As the crude oil is separated and distributed to downstream processing units, more scrutiny is given to four main types of components — paraffins, olefins, naphthenes, and aromatics (PONA). The crude's PONA content is important in setting the objectives of the catalysts used in downstream units in terms of functionality and desired reaction conversion.

In the U.S., crude oil is measured on a volumetric basis at a standard temperature of 60°F, typically in units of barrels (1 bbl = 42 gal) per day (bpd). Outside the U.S., crude oil tends to be measured on a mass basis in units of metric tons per day. In general, a small refinery produces 100,000 bpd or less, a mid-size refinery is in the range of 100,000–250,000 bpd, and large refineries (typically integrated with a petrochemical processing facility) produce 250,000 bpd or more.

Crude desalter

After it is received at the refinery, crude oil is stored in large tanks in a tank farm. The first step of the refining process is mixing the crude oil with water in the line upstream of the desalter vessel to dissolve the salts contained in the crude oil. The salts and sediment are captured in the water phase (now referred to as brine), which is then separated from the oil. The desalter typically contains electric grids that assist with the oil-water separation. This allows for a smaller vessel design; without the grids, the required residence time in the vessel would be much higher and a larger vessel would be required. Salts need to be removed from the crude oil to mitigate vessel and piping fouling and corrosion, as well as poisoning of downstream catalysts.

Before the desalted oil enters the atmospheric fractionator, it is preheated by several heat exchangers and a fired heater. Up to 50% of the required heat may come from heat exchange with the side-cut and product draws exiting the atmospheric crude fractionator; the remaining heat comes from the fired heater. This preheating raises the crude oil's temperature to 650–700°F. Above this temperature, thermal cracking would more readily occur, producing carbon or coke deposits on the piping and equipment that would require a shutdown for cleaning.

Atmospheric crude fractionator

The primary objective of the atmospheric crude fractionator (Figure 2) is to separate the desalted, 650–700°F crude oil into fractions, or cuts, based on the boiling point ranges of the components (known as cut points).

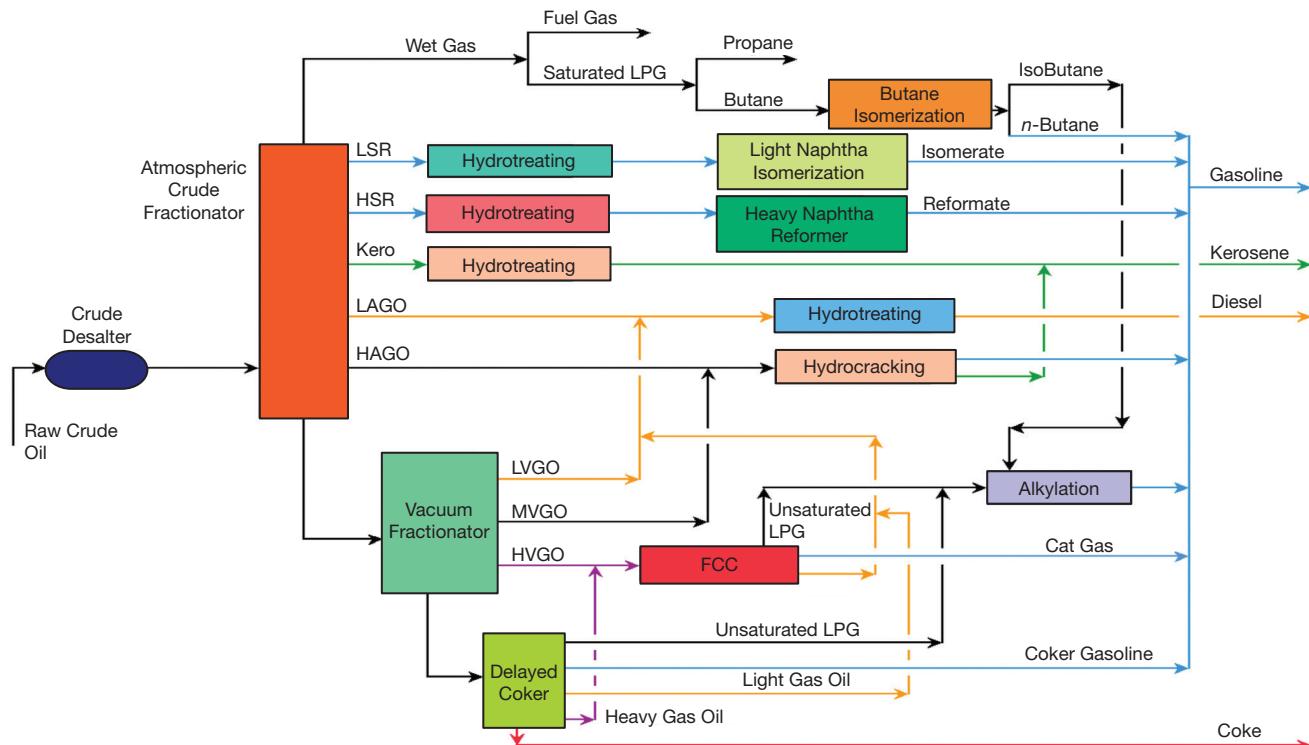
Lighter fractions come off the top of the column and progressively heavier components with higher boiling points are pulled off as side draws further down the tower. Each side-cut draw has a target initial boiling point (IBP) and end boiling point (EBP) to match the capabilities and specifications of downstream units. Typical cut points for the atmospheric fractionator and the vacuum fractionator that follows it are:

- light straight-run (LSR) naphtha, 90–190°F
 - heavy straight-run (HSR) naphtha, 190–330°F
 - kerosene, *i.e.*, jet fuel, 330–480°F
 - light atmospheric gas oil (LAGO), 480–610°F
 - heavy atmospheric gas oil (HAGO), 610–800°F
 - vacuum gas oil (VGO), 800–1,050°F
 - vacuum-reduced crude (VRC), above 1,050°F

The target cut-point ranges typically do not change, but flowrates must change if a different feedstock crude oil is used.

Each side draw feeds a stripping column, which uses

Article continues on next page



▲ **Figure 1.** This refinery flow diagram demonstrates how raw crude oil is converted into fuels.

LSR = light straight-run naphtha, HSR = heavy straight run naphtha, Kero = kerosene, LAGO = light atmospheric gas oil.

HAGO = heavy atmospheric gas oil, LVGO = light vacuum gas oil, MVGO = medium vacuum gas oil, HVGO = heavy vacuum gas oil.

Back to Basics

steam to establish (or control) the IBP of the material leaving the bottom of the side-cut stripper. Steam enters the bottom of the stripper and reduces the hydrocarbon partial pressure. The process fluid partially vaporizes to reestablish vapor-liquid equilibrium. (The heat of vaporization comes from the process fluid itself, not from the stripping steam.) As mentioned earlier, these side draws are used to preheat the incoming crude oil. Typical side-draw cuts include light and heavy naphtha, kerosene or jet fuel, diesel, and light and heavy gas oil. The bottoms draw, referred to as atmospheric residuum, is a heavy, high-boiling-point oil, which is sent to the vacuum column for further separation.

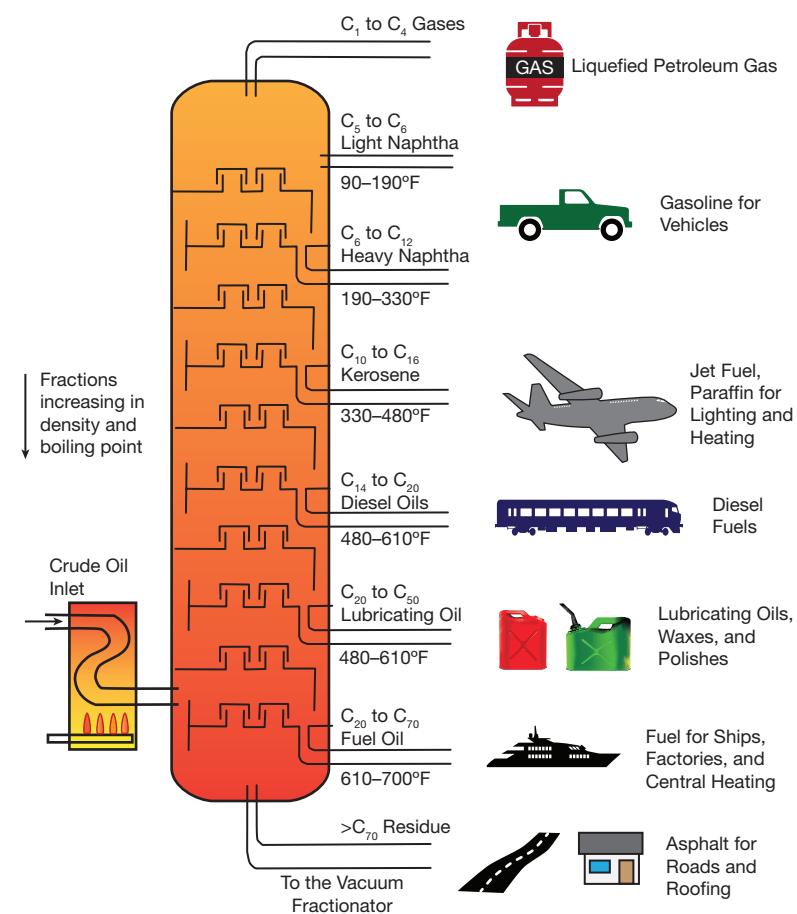
Vacuum fractionator

Downstream of the atmospheric crude fractionator (which operates at temperatures up to 650–700°F), the vacuum fractionator further separates the heavy, higher-boiling-point components under a vacuum to prevent thermal cracking. Because boiling points decrease with lower pres-

sure, these separations can be achieved without initiating thermal cracking. Steam is added to the vacuum column's inlet to prevent fouling and to the vacuum fractionator bottoms to improve vaporization of these heavy components. The vacuum fractionator tends to be much larger in diameter than the atmospheric crude fractionator (a good way to tell the two apart from a distance) because under a vacuum the vaporized crude oil occupies a larger volume.

Gas concentration unit

The light hydrocarbon gases that come off the top of the atmospheric crude unit are concentrated, separated, and distributed to where they are needed in what is often referred to as the saturated-gas concentration unit (not shown on Figure 1). Gases are typically separated into wet gases (propane and butane, or liquefied petroleum gas [LPG]) and dry gases (ethane and methane) through a series of distillation columns. The dry gases are primarily used as fuel throughout the refinery for the fired heaters and boilers. Purchased natural gas is used to supplement this fuel gas based on refinery fuel demands.



▲ Figure 2. One of the first major units in a refinery, the atmospheric crude fractionator typically operates at 90°F up to 700°F. It separates crude oil into components based on their boiling points.

Fluidized catalytic cracker

The fluidized catalytic cracker (FCC), illustrated in Figure 3, was developed collaboratively by refiners during World War II to help meet gasoline demands for the war. Its function is to break — or crack — long-chain hydrocarbons such as heavy gas oil into lighter, shorter, naphtha-boiling-range hydrocarbons. Its unique process dynamics can make the FCC unit one of the most challenging refinery units to operate.

The FCC gets its name because the catalyst is so fine that it flows like a liquid. The mixture of fluidized catalyst and feed is reacted at high temperatures (900–1,000°F). The cracking reaction is endothermic, and is fueled by the exothermic catalyst-regeneration reaction. Because about 5 wt% of the feed ends up as coke on the catalyst, the catalyst must be regenerated by introducing air into the regenerator to burn off the coke. The catalyst flowrate is about 1 ton per thousand barrels of oil feed.

The reactor and regenerator typically sit side by side in a common steel structure, which makes it easy to identify the FCC unit. The catalyst regenerator exit temperatures can range from 1,200°F to 1,500°F.

Downstream of the FCC reactor is the FCC main fractionator column, which is

the first step in the separation and recovery of the cracked hydrocarbon vapors from the reactor. It is similar to an atmospheric fractionator, but with two key differences: the vapors must be cooled before any fractionation can begin, and significant quantities of light gases pass overhead with the gasoline. The reaction products enter the main FCC fractionation column at high temperatures, 900–1,000°F. The products that are withdrawn from the fractionator include heavy cat naphtha (HCN), light cycle oil (LCO), heavy cycle oil (HCO), and slurry oil from the column bottoms.

Large quantities of heavy oil are circulated over a series of bottom fractionator trays to cool the vapors and wash down entrained catalyst. The heat removed by the main column bottoms and the heavy oil is used for feed preheating, steam generation, and reboiler heating in the unsaturated-gas concentration unit, or some combination of the three. Gas compression and cooling are used to separate the light hydrocarbons from the net gas as a liquid. The remaining vapor phase is passed through two absorbers to further recover light hydrocarbons into the liquid phases leaving the absorbers. A series of distillation columns processes the liquids from the overhead receiver of the main fractionator to remove light gases (*e.g.*, butane) from the gasoline cut, and then the remaining gases are separated into alkylation feed (*e.g.*, olefin LPGs), ethane, and fuel gas. This gasoline intermediate product is known as FCC gasoline or sometimes “cat gas.”

Butane isomerization unit and alkylation unit

The alkylation unit combines an isobutene feed with olefins (*e.g.*, propylene or butylene) produced in the FCC unit to form larger molecules known as alkylate, which is used in gasoline blending to raise the fuel’s octane. The alkylate component of gasoline has the highest quality of all refinery products. It has high octane (both research octane number [RON] and motor octane number [MON]), low selectivity (*i.e.*, the difference between RON and MON), low RVP, no aromatics, and no sulfur. These qualities make alkylate a valuable gasoline blending component. Alkylate is a main component added to raise the octane of gasoline and produce a premium grade (*e.g.*, 93-octane, compared to 87- or 89-octane for regular grades).

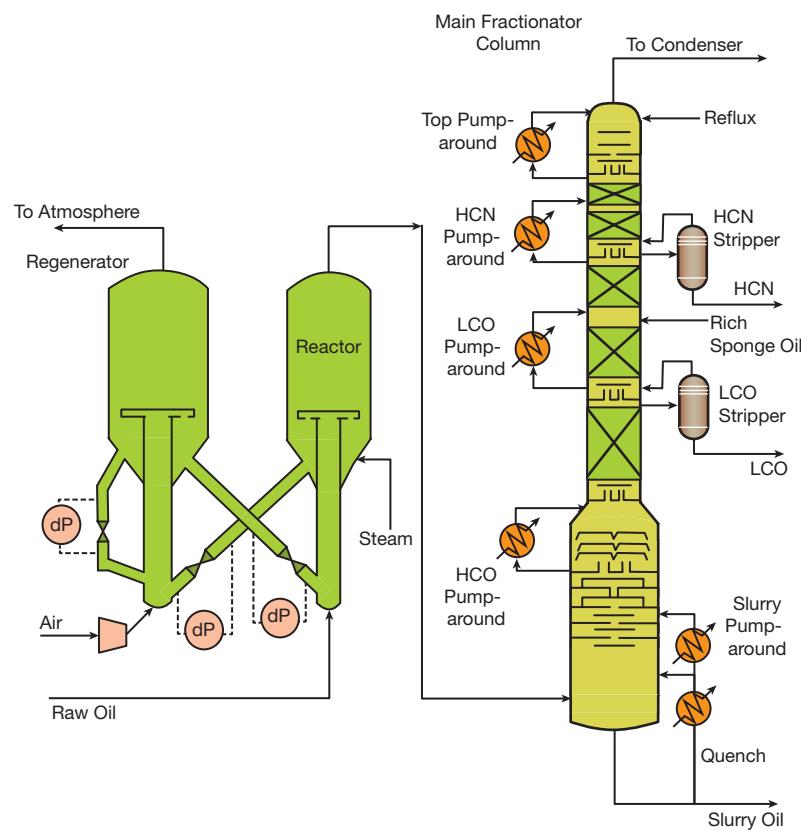
Because isobutane gives the alkylate a much better octane rating than *n*-butane, butane isomerization is required. The butane isomerization unit converts *n*-butane into isobutane with excess hydrogen and catalyst. The hydrogen is added to avoid carbon deposition on

the catalyst and to shift the reaction to generate more of the desired components. Next, a large distillation column known as a de-isobutanizer (DIB) separates *n*-butane from isobutane. The DIB is often the tallest column in the refinery — the large size is a reflection of how difficult it is to separate these butane isomers because of their close boiling points.

The isobutane from the butane isomerization unit, the olefins from the FCC, and sometimes olefins from the coker (discussed later) are the feeds to the alkylation unit. Alkylation units require an acid catalyst, either sulfuric acid or hydrofluoric acid. Both catalysts operate at low temperatures and high isobutane-to-olefin ratios to reduce side reactions and acid (catalyst) consumption. Without this high ratio, the olefins could easily react with each other to combine into much larger (unwanted) molecules, such as C12s, C16s, C20s, etc.

When butane isomerization and olefin alkylation take place in a single unit, the bottom of the column serves as a product separator to capture the alkylate for gasoline blending, *n*-butane is taken as a side draw, and the overhead is isobutane.

Article continues on next page



▲ **Figure 3.** The fluidized catalytic cracking (FCC) unit converts heavy vacuum gas oil (HVGO) from the vacuum fractionator into gasoline intermediates. The FCC is composed of a reactor, a catalyst regenerator, and a downstream main fractionating column, as well as a series of distillation columns.

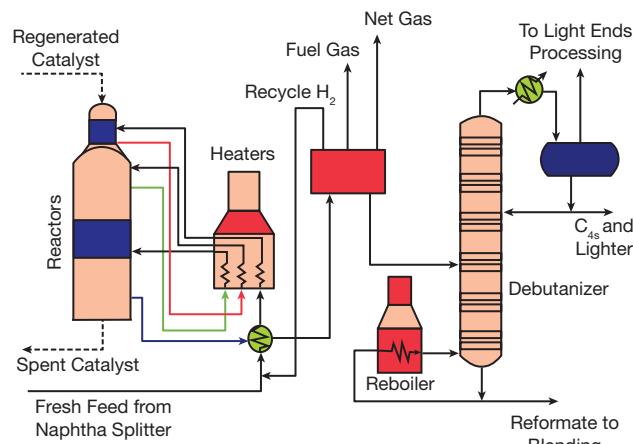
Back to Basics

Light naphtha isomerization unit

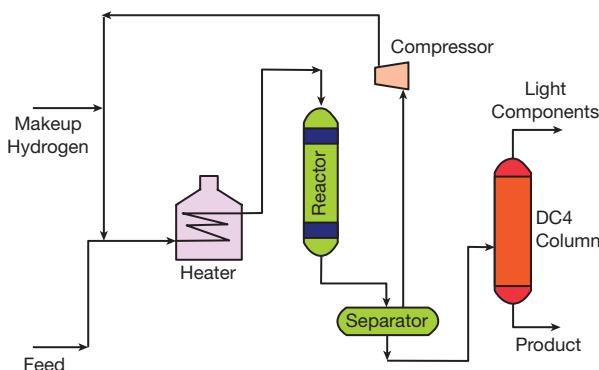
The light naphtha isomerization unit saturates benzene and isomerizes light naphtha normal paraffins (pentanes and hexanes) into branched molecules that are higher-octane gasoline components for blending.

Like the butane isomerization unit, it converts *n*-pentane and *n*-hexane into isopentane and isohexane in the presence of excess hydrogen and catalyst. The light naphtha can be pretreated in a de-isopentanizer or de-isoheptanizer column to separate the isoparaffins from the *n*-paraffins and shift the equilibrium reaction toward the isoparaffins.

After the isomerization reactors, a distillation column removes butane and lighter gases from the gasoline intermediate product, which is referred to as isomerate.



▲ **Figure 4.** The naphtha reformer converts naphthenes into aromatics to increase the gasoline octane rating or to obtain a feedstock for aromatics production. The reformer produces a gasoline intermediate known as the reformate.



▲ **Figure 5.** The naphtha hydrotreater removes impurities from the heavy straight-run (HSR) naphtha prior to it entering the naphtha reformer. The DC4 column is a debutanizer that removes butanes from the naphtha product.

Heavy naphtha reformer and hydrotreater

The heavy naphtha reformer (Figure 4) contributes to increasing the gasoline octane rating by converting naphthenes into aromatics and generating a reformate gasoline component. The reforming process is unusual in that the reaction is endothermic. It is carried out in a series of three or four reactors, each of which is preceded by a fired heater.

The catalyst needs to be regenerated. Two main process designs exist: semi-regeneration, which requires a shutdown to regenerate the catalyst *in situ* in the reactor; and continuous catalyst regeneration (CCR), in which flowing catalyst spheres circulate from the reactor to the regenerator and back. The CCR design is depicted in Figure 4.

The reforming process also generates the hydrogen needed by the refinery's hydrocracking and hydrotreating units, as well as benzene, toluene, and xylene (BTX) feedstocks for downstream petrochemical processing. Hydrotreaters (Figure 5) are located throughout the refinery. Their main purpose is to remove impurities such as sulfur, nitrogen, oxygen, metallic salts, olefins, and to a lesser extent aromatics (although saturating aromatics is usually not desired). They also serve as hydrodesulfurization units to remove sulfur from the FCC naphtha in order to meet regulatory requirements. The hydrotreating reaction is not intended to change the boiling range of the feed (unlike hydrocracking).

Hydrocracking

Older hydrocracking units in the U.S. were designed primarily to maximize the production of gasoline and jet fuel. Newer hydrocracking units are more focused on maximizing ultra-low-sulfur diesel and jet fuel production, with less focus on gasoline (Figure 6).

Not all refiners have a hydrocracker, mainly because of the high capital costs associated with its construction and its high hydrogen consumption. Operating pressures can reach 3,000 psig, and piping, vessels, pumps, compressors, and instruments that can handle this high pressure are expensive. Additionally, a refiner would need to build a hydrogen generation plant or buy hydrogen for hydrocracker use.

Although the cracking reactions are endothermic, the overall process is highly exothermic due to the concurrent hydrotreating reactions, with reactor temperatures that can range from 550°F to 850°F. Cool hydrogen is added to the inlet of each catalyst bed in the reactor to control the reactor's

TIM OLSEN (Email: Tim.Olsen@emerson.com) has been with Emerson Process Management for 16 years. He is a refining consultant within the global refining industry solutions group, where he supports Emerson's technical and business strategy. He is a past chair of AIChE's Fuels and Petrochemicals Div., and was the Meeting Program Chair for the recent 2014 AIChE Spring Meeting in New Orleans, LA. He has a BS in chemical engineering from Iowa State Univ. with an emphasis in industrial engineering and process control, and an MBA from the Univ. of Iowa.

internal temperature. The addition of hydrogen increases the production of isoparaffins (which are desired over normal paraffins because they are higher-quality gasoline-blending components) and limits the production of olefins.

The hydrocracking unit includes a product fractionator to separate light gases, gasoline, and diesel. The bottoms product from that column is typically recycled for a second chance at reacting.

Delayed coking and asphalt production

The delayed coker (Figure 7) thermally cracks heavy feedstocks to produce solid coke and lighter components that are blended into gasoline or fed to other processing units.

Delayed cokers are easy to identify from a distance — they look like a pair of oil derricks on top of a pair of vertical drums. Delayed cokers are always installed in pairs and their operation is cycled every 24 hr — one is online (as indicated by the solid lines in Figure 7) while the other is offline (dashed lines) so that the coke can be cut out of it.

The vacuum fractionator bottoms are sent with steam to a fired heater and then to the online coke drum, where the entrained liquid is thermally cracked to coke and other vapor products. As the coke drum fills, the cracked vapors

leave the top of the drum and are returned to the bottom of the fractionator, where the light intermediate products like gasoline separate as they travel up the column.

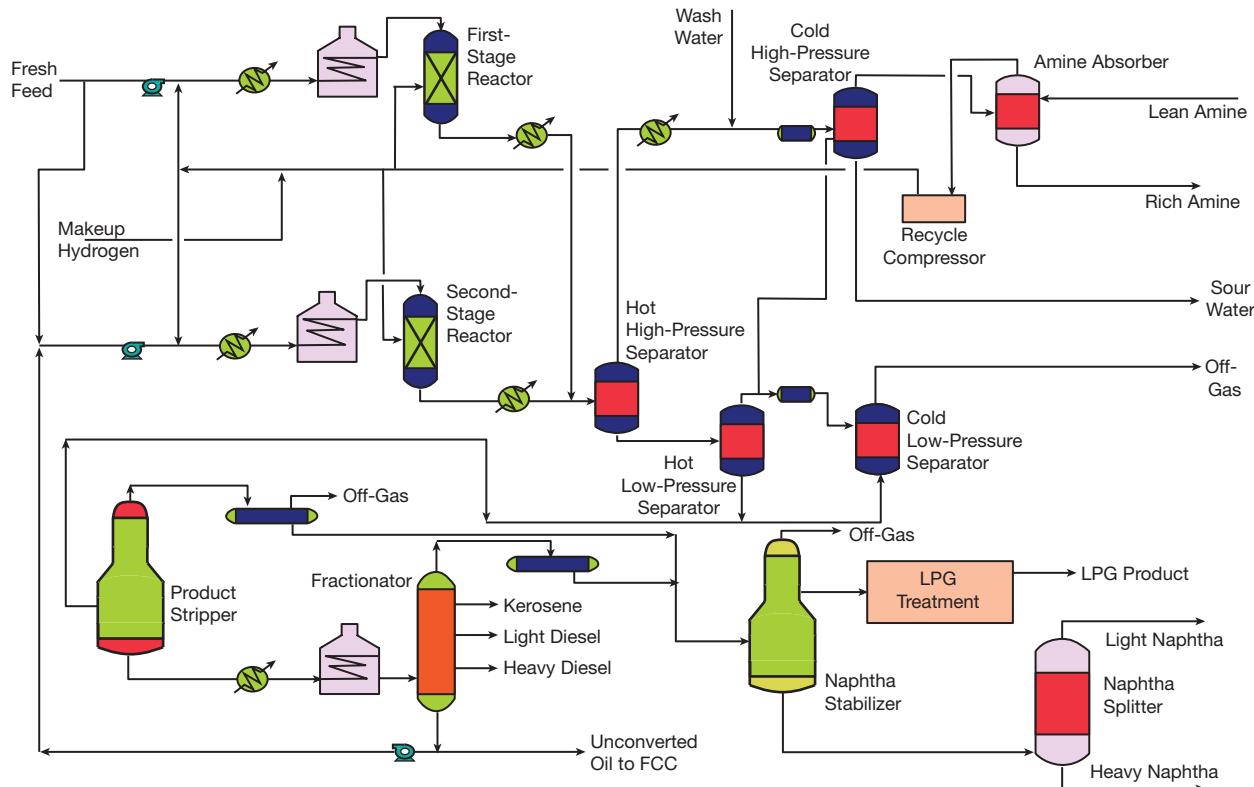
Refineries without thermal cracking units have the option of producing asphalt or selling the vacuum residuum to other refineries that can process it.

Amine treating and sulfur recovery

An amine treating unit (not shown in Figure 1) captures the hydrogen sulfide from the refinery gas streams and concentrates it through absorption into an amine solution. These rich amine streams are routed to an amine regenerator column; the overhead vapor from this column contains the released hydrogen sulfide, which is converted into elemental sulfur in a sulfur recovery unit (also not shown in Figure 1). The bottoms from the amine regenerator is the lean amine, which is circulated back to the various amine absorbers in the refinery.

As regulations over the past few decades have placed stricter limits on sulfur emissions and reduced the amount of sulfur that fuel products may contain, the sulfur recovery units have required revamps for higher capacity and greater onstream availability.

Article continues on next page



▲ **Figure 6.** Hydrocracking units operate at high pressures (up to 3,000 psig) and are big hydrogen consumers. They maximize ultra-low-sulfur diesel and jet fuel production.

Back to Basics

Blending

Various fuel components are blended into final commercial products that meet particular specifications based on the consumer's location. In the U.S., there are many different location-dependent gasoline specifications. For example, large urban areas typically have more-restrictive fuel specifications.

Intermediate products include alkylate, isomerate, reformate, cat gas, hydrocracker gas, and coker gas. Normal butane is also added as needed to meet RVP specifications, which are different in summer and winter, and in winter vary by location.

Diesel is also blended from each of the various units that produce intermediate products, such as the crude unit, FCC, hydrocracker, and delayed coker.

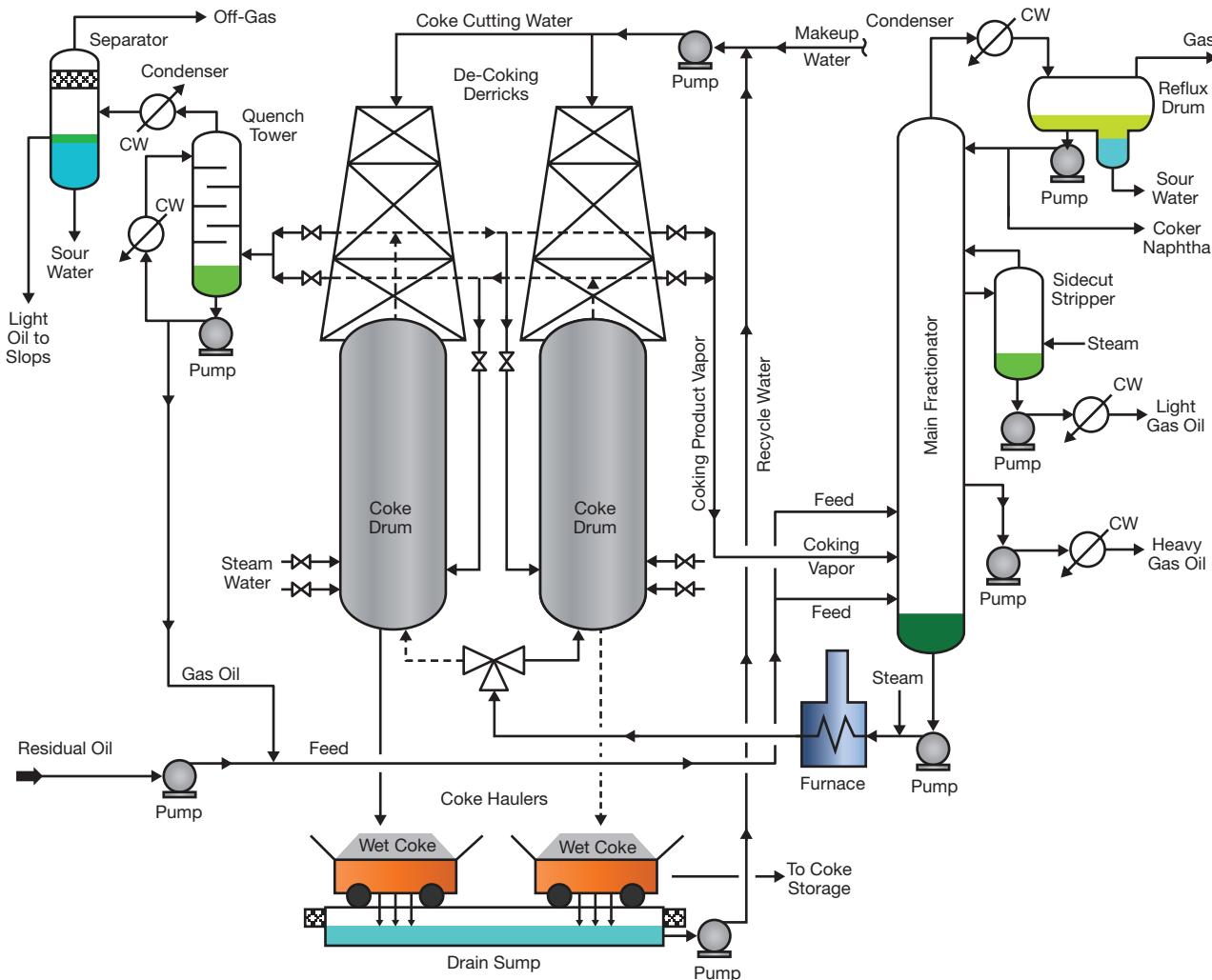
Tank farm and distribution

Finally, transportation fuel products need to be distributed to the consumer. These products are typically transported by pipelines to terminals. At the terminals, ethanol and other biofuels, as well as various additives, are added, and then the gasoline or diesel is trucked to commercial distribution stations. The additives account for the differences among various brands of fuel.

The refinery's tank farm has various sizes of tanks to store crude oil coming into the refinery, intermediate products (e.g., petrochemical feedstocks), liquefied petroleum gases, and fuel products.

The next time you fill up your vehicle, you will have a greater understanding of the path the crude oil had to travel to become a fuel.

CEP



▲ **Figure 7.** The delayed coker thermally cracks heavy feedstocks from the vacuum fractionator to generate solid coke and gasoline intermediates. Delayed cokers are always installed in pairs. Their operation is cycled every 24 hr — one is online (as indicated by the solid lines) while the other is offline (dashed lines). The quench system in the upper left corner is used only when a drum is being steamed prior to de-coking. Image by Milton Beychok (http://en.wikipedia.org/wiki/File:Delayed_Coker.png).