

OIL REFINERY

An oil refinery or petroleum refinery is an industrial process plant where crude oil is processed and refined into more useful petroleum products, such as gasoline, diesel fuel, asphalt base, heating oil, kerosene, and liquefied petroleum gas. Oil refineries are typically large sprawling industrial complexes with extensive piping running throughout, carrying streams of fluids between large chemical processing units. In many ways, oil refineries use much of the technology of, and can be thought of as types of chemical plants. The crude oil feedstock has typically been processed by an oil production plant. There is usually an oil depot (tank farm) at or near an oil refinery for storage of bulk liquid products.

Operation

Crude oil is separated into fractions by fractional distillation. The fractions at the top of the fractionating column have lower boiling points than the fractions at the bottom. The heavy bottom fractions are often cracked into lighter, more useful products. All of the fractions are processed further in other refining units.

Raw or unprocessed crude oil is not generally useful. Although “light, sweet” (low viscosity, low sulfur) crude oil has been used directly as a burner fuel for steam vessel propulsion, the lighter elements form explosive vapors in the fuel tanks and are therefore hazardous, especially in warships. Instead, the hundreds of different hydrocarbon molecules in crude oil are separated in a refinery into components which can be used as fuels, lubricants, and as feedstock in petro processes that manufacture such products as plastics, detergents, solvents, elastomers and fibers such as nylon and polyesters.

Petroleum fossil fuels are burned in internal combustion engines to provide power for ships, automobiles, aircraft engines, lawn mowers, chainsaws, and other machines. Different boiling points allow the hydrocarbons to be separated by distillation. Since the lighter liquid products are in great demand for use in internal combustion engines, a modern refinery will convert heavy hydrocarbons and lighter gaseous elements into these higher value products.

The oil refinery in Nigeria alone is capable of processing about 1.7million tons (3 million barrels) of crude oil a year. Its two cooling towers are landmarks of the city’s skyline.

Oil can be used in a variety of ways because it contains hydrocarbons of varying molecular masses, forms and lengths such as paraffins, aromatics, naphthenes (or cycloalkanes), alkenes, dienes, and alkynes. While the molecules in crude oil include different atoms such as sulfur and nitrogen, the hydrocarbons are the most common form of molecules, which are molecules of varying lengths and complexity made of hydrogen and carbon atoms, and a small number of oxygen

atoms.

The differences in the structure of these molecules account for their varying physical and chemical properties, and it is this variety that makes crude oil useful in a broad range of applications.

Once separated and purified of any contaminants and impurities, the fuel or lubricant can be sold without further processing. Smaller molecules such as isobutane and propylene or butylenes can be recombined to meet specific octane requirements by processes such as alkylation, or less commonly, dimerization.

Octane grade of gasoline can also be improved by catalytic reforming, which involves removing hydrogen from hydrocarbons producing compounds with higher octane ratings such as aromatics. Intermediate products such as gas oils can even be

reprocessed to break a heavy, long-chained oil into a lighter short-chained one, by various forms of cracking such as fluid catalytic cracking, thermal cracking, and hydrocracking. The final step in gasoline production is the blending of fuels with different octane ratings, vapor pressures, and other properties to meet product specifications.

Oil refineries are large scale plants, processing about a hundred thousand to several hundred thousand barrels of crude oil a day. Because of the high capacity, many of the units operate continuously, as opposed to processing in batches, at steady state or nearly steady state for months to years. The high capacity also makes process optimization and advanced process control very desirable.

Major products

Petroleum products are usually grouped into three categories: light distillates (LPG, gasoline, naphtha), middle distillates (kerosene, diesel), heavy distillates and residuum (heavy fuel oil, lubricating oils, wax, asphalt). This classification is based on the way crude oil is distilled and separated into fractions (called distillates and residuum) as in the above drawing.

- Liquid petroleum gas (LPG)
- Gasoline (also known as petrol)
- Naphtha
- Kerosene and related jet aircraft fuels
- Diesel fuel
- Fuel oils
- Lubricating oils
- Paraffin wax
- Asphalt and Tar
- Petroleum coke

Common process units found in a refinery

- Desalter unit washes out salt from the crude oil before it enters the atmospheric distillation unit.
- Atmospheric Distillation unit distills crude oil into fractions. See Continuous distillation.
- Vacuum Distillation unit further distills residual bottoms after atmospheric distillation.
- Naphtha Hydro treater unit uses hydrogen to desulfurize naphtha from atmospheric distillation. Must hydro treat the naphtha before sending to a Catalytic Reformer unit.
- Catalytic Reformer unit is used to convert the naphtha-boiling range molecules into higher octane reformat(reformer product). The reformat has higher content of aromatics and cyclic hydrocarbons). An important byproduct of a reformer is hydrogen released during the catalyst reaction. The hydrogen is used either in the hydro treaters or the hydrocracker.
- Distillate Hydrotreater unit desulfurizes distillates (such as diesel) after atmospheric distillation.
- Fluid Catalytic Cracker (FCC) unit upgrades heavier fractions into lighter, more valuable products.
- Hydrocracker unit uses hydrogen to upgrade heavier fractions into lighter, more valuable products.
- Visbreaking unit upgrades heavy residual oils by thermally cracking them into lighter, more valuable reduced viscosity products.
- Merox unit treats LPG, kerosene or jet fuel by oxidizing mercaptans to organic disulfides.
- Coking units (delayed coking, fluid coker, and flexicoker) process very heavy residual oils into gasoline and diesel fuel, leaving petroleum coke as a residual product.
- Alkylation unit produces high-octane component for gasoline blending.
- Dimerization unit converts olefins into higher-octane gasoline blending components. For example, butenes can be dimerized into isooctene which may subsequently be hydrogenated to form isooctane. There are also other uses for dimerization.
- Isomerization unit converts linear molecules to higher-octane branched molecules for blending into gasoline or feed to alkylation units.
- Steam reforming unit produces hydrogen for the hydrotreaters or hydrocracker.
- Liquified gas storage units for propane and similar gaseous fuels at pressure sufficient to maintain in liquid form. These are usually spherical vessels or bullets (horizontal vessels with rounded ends).
- Storage tanks for crude oil and finished products, usually cylindrical, with some sort of vapor emission control and surrounded by an earthen berm to contain spills.

- Amine gas treater, Claus unit, and tail gas treatment for converting hydrogen sulfide from hydro desulfurization into elemental sulfur.
- Utility units such as cooling towers for circulating cooling water, boiler plants for steam generation, instrument air systems for pneumatically operated control valves and an electrical substation.
- Wastewater collection and treating systems consisting of API separators, dissolved air flotation (DAF) units and some type of further treatment (such as an activated sludge biotreater) to make such water suitable for reuse or for disposal.
- Solvent refining units use solvent such as cresol or furfural to remove unwanted, mainly asphaltenic materials from lubricating oil stock (or diesel stock).
- Solvent dewaxing units remove the heavy waxy constituents petrolatum from vacuum distillation products.

Flow diagram of typical refinery

The image below is a schematic flow diagram of a typical oil refinery that depicts the various unit processes and the flow of intermediate product streams that occurs between the inlet crude oil feedstock and the final end products. The diagram depicts only one of the literally hundreds of different oil refinery configurations. The diagram also does not include any of the usual refinery facilities providing utilities such as steam, cooling water, and electric power as well as storage tanks for crude oil feedstock and for intermediate products and end products.

There are many process configurations other than that depicted above. For example, the vacuum distillation unit may also produce fractions that can be refined into end products such as: spindle oil used in the textile industry, light machinery oil, motor oil, and steam cylinder oil. As another example, the vacuum residue may be processed in a coker unit to produce petroleum coke.

Schematic flow diagram of a typical oil refinery

Specialty end products

These will blend various feedstocks, mix appropriate additives, provide short term storage, and prepare for bulk loading to trucks, barges, product ships, and railcars.

- Gaseous fuels such as propane, stored and shipped in liquid form under pressure in specialized railcars to distributors.
- Liquid fuels blending (producing automotive and aviation grades of gasoline, kerosene, various aviation turbine fuels, and diesel fuels, adding dyes, detergents, antiknock additives, oxygenates, and anti-fungal compounds as required). Shipped by barge, rail, and tanker ship. May be shipped regionally in dedicated pipelines to point consumers, particularly aviation jet fuel to major airports, or piped to distributors in multi-product pipelines using product separators called pipeline inspection gauges ("pigs").

- Lubricants (produces light machine oils, motor oils, and greases, adding viscosity stabilizers as required), usually shipped in bulk to an offsite packaging plant.
- Wax (paraffin), used in the packaging of frozen foods, among others. May be shipped in bulk to a site to prepare as packaged blocks.
- Sulfur (or sulfuric acid), byproducts of sulfur removal from petroleum which may have up to a couple percent sulfur as organic sulfur-containing compounds. Sulfur and sulfuric acid are useful industrial materials.

Sulfuric acid is usually prepared and shipped as the acid precursor oleum.

- Bulk tar shipping for offsite unit packaging for use in tar-and-gravel roofing.
- Asphalt unit. Prepares bulk asphalt for shipment.
- Petroleum coke, used in specialty carbon products or as solid fuel.
- Petrochemicals or petrochemical feedstocks, which are often sent to petrochemical plants for further processing in a variety of ways. The petrochemicals may be olefins or their precursors, or various types of aromatic petrochemicals.

Siting/locating of petroleum refineries

The principles of finding a construction site for refineries are similar to those for other chemical plants:

- The site has to be reasonably far from residential areas.
- Facilities for raw materials access and products delivery to markets should be easily available.
- Processing energy requirements should be easily available.
- Waste product disposal should not cause difficulties.

For refineries which use large amounts of process steam and cooling water, an abundant source of water is important. Because of this, oil refineries are often located (associated to a port) near navigable rivers or even better on a sea shore. Either are of dual purpose, making also available cheap transport by river or by sea. Although the advantages of crude oil transport by pipeline are evident, and the method is also often used by oil companies to deliver large output products such as fuels to their bulk distribution terminals, pipeline delivery is not practical for small output products. For these, rail cars, road tankers or barges may be used.

It is useful to site refineries in areas where there is abundant space to be used by the same company or others, for the construction of petrochemical plants, solvent manufacturing (fine fractionating) plants and/or similar plants to allow these easy access to large output refinery products for further processing, or plants that produce chemical additives that the refinery may need to blend into a product at source rather than at blending terminals.

Safety and environmental concerns

Fire at Union Oil refinery, Wilmington, California, 1951

MiRO refinery at Karlsruhe

The refining process releases numerous different chemicals into the atmosphere; consequently, there are substantial air pollution emissions and a notable odor normally accompanies the presence of a refinery. Aside from air pollution impacts there are also wastewater concerns, risks of industrial accidents such as fire and explosion, and noise health effects due to industrial noise.

The public has demanded that many governments place restrictions on contaminants that refineries release, and most refineries have installed the equipment needed to comply with the requirements of the pertinent environmental protection regulatory agencies. In the United States, there is strong pressure to prevent the development of new refineries, and no major refinery has been built in the country since Marathon's Garyville, Louisiana facility in 1976. However, many existing refineries have been expanded during that time. Environmental restrictions and pressure to prevent construction of new refineries may have also contributed to rising fuel prices in the United States. Additionally, many refineries (over 100 since the 1980s) have closed due to obsolescence and/or merger activity within the industry itself. This activity has been reported to Congress and in specialized studies not widely publicised.

Environmental and safety concerns mean that oil refineries are sometimes located some distance away from major urban areas.

Nevertheless, there are many instances where refinery operations are close to populated areas and pose health risks such as in the Campo de Gibraltar, a CEPSA refinery near the towns of Gibraltar, Algeciras, La Linea, San Roque and Los Barrios with a combined population of over 300,000 residents within a 5-mile (8.0 km) radius and the CEPSA refinery in Santa Cruz on the island of Tenerife, Spain which is sited in a densely-populated city center and next to the only two major evacuation routes in and out of the city. In California's Contra Costa County and Solano County, a shoreline necklace of refineries and associated chemical plants are adjacent to urban areas in Richmond, Martinez, Pacheco, Concord, Pittsburg, Vallejo and Benicia, with occasional accidental events that require "shelter in place" orders to the adjacent populations.

Corrosion problems and prevention

Petroleum refineries run as efficiently as possible to reduce costs. One major factor that decreases efficiency is corrosion of the metal components found throughout the process line of the hydrocarbon refining process. Corrosion causes the failure of parts in addition to dictating the cleaning schedule of the refinery, during which the entire production facility must be shut down and cleaned. The cost of corrosion in the petroleum industry has been estimated at US\$3.7 billion. Corrosion occurs in various forms in the refining process, such as pitting corrosion from water droplets,

embrittlement from hydrogen, and stress corrosion cracking from sulfide attack. From a materials standpoint, carbon steel is used for upwards of 80% of refinery components, which is beneficial due to its low cost. Carbon steel is resistant to the most common forms of corrosion, particularly from hydrocarbon impurities at temperatures below 205°C, but other corrosive chemicals and environments prevent its use everywhere. Common replacement materials are low alloy steels containing chromium and molybdenum, with stainless steels containing more chromium dealing with more corrosive environments. More expensive materials commonly used are nickel, titanium, and copper alloys. These are primarily saved for the most problematic areas where extremely high temperatures or very corrosive chemicals are present.

Corrosion is fought by a complex system of monitoring, preventative repairs and careful use of materials. Monitoring methods include both off-line checks taken during maintenance and on-line monitoring. Off-line checks measure corrosion after it has occurred, telling the engineer when equipment must be replaced based on the historical information he has collected. This is referred to as preventative management.

On-line systems are a more modern development, and are revolutionizing the way corrosion is approached. There are several types of on-line corrosion monitoring technologies such as linear polarization resistance, electrochemical noise and electrical resistance. On-Line monitoring has generally had slow reporting rates in the past (minutes or hours) and been limited by process conditions and sources of error but newer technologies can report rates up to twice per minute with much higher accuracy (referred to as real-time monitoring). This allows process engineers to treat corrosion as another process variable that can be optimized in the system. Immediate responses to process changes allow the control of corrosion mechanisms, so they can be minimized while also maximizing production output. In an ideal situation having on-line corrosion information that is accurate and realtime

will allow conditions that cause high corrosion rates to be identified and reduced. This is known as predictive management.

Materials methods include selecting the proper material for the application. In areas of minimal corrosion, cheap materials are preferable, but when bad corrosion can occur, more expensive but longer lasting materials should be used. Other materials methods come in the form of protective barriers between corrosive substances and the equipment metals. These can be either a lining of refractory material such as standard Portland cement or other special acid-resistant cements that are shot onto the inner surface of the vessel. Also available are thin overlays of more expensive metals that protect cheaper metal against corrosion without requiring lots of material.

