**Cracking**

Cracking is a [petroleum refining](http://www.eoearth.org/article/Petroleum_refining" \o "Petroleum refining) process in which heavy-molecular weighthydrocarbons are broken up into light hydrocarbon molecules by the application of[heat](http://www.eoearth.org/article/Heat" \o "Heat) and pressure, with or without the use of catalysts, to derive a variety of fuel products. Cracking is one of the principal ways in which crude oil is converted into useful fuels such as motor gasoline, jet fuel, and home heatng oil.

**Thermal Cracking**

Thermal cracking is a refining process in which [heat](http://www.eoearth.org/article/Heat" \o "Heat) (~800°C) and pressure (~700kPa) are used to break down, rearrange, or combine hydrocarbon molecules. The first thermal cracking process was developed around 1913. Distillate fuels and heavy oils were heated under pressure in large drums until they cracked into smaller molecules with better antiknock characteristics. However, this method produced large amounts of solid, unwanted coke. This early process has evolved into the following applications of thermal cracking: visbreaking, steam cracking, and coking.

**Steam Cracking Process**

Steam cracking is a petrochemical process sometimes used in refineries to produce olefinic raw materials (e.g., ethylene) from various feedstock for petrochemicals manufacture. The feedstock range from ethane to vacuum gas oil, with heavier feeds giving higher yields of by-products such as naphtha. The most common feeds are ethane, butane, and naphtha. Steam cracking is carried out at temperatures of 1,500°-1,600° F, and at pressures slightly above atmospheric. Naphtha produced from steam cracking contains benzene, which is extracted prior to hydrotreating. Residual from steam cracking is sometimes blended into heavy fuels.

Visbreaking, a mild form of thermal cracking, significantly lowers the viscosity of heavy crude-oil residue without affecting the boiling point range. Residual from the atmospheric distillation tower is heated (800°-950° F) at atmospheric pressure and mildly cracked in a heater (Figure 2). It is then quenched with cool gas oil to control overcracking, and flashed in a distillation tower. Visbreaking is used to reduce the pour point of waxy residues and reduce the viscosity of residues used for blending with lighter fuel oils (Figure 1). Middle distillates may also be produced, depending on product demand. The thermally cracked residue tar, which accumulates in the bottom of the fractionation tower, is vacuum flashed in a stripper and the distillate recycled.

Coking is a severe method of thermal cracking used to upgrade heavy residuals into lighter products or distillates (Figure 3). Coking produces straight-run gasoline (coker naphtha) and various middle-distillate fractions used as catalytic cracking feedstock. The process so completely reduces [hydrogen](http://www.eoearth.org/article/Hydrogen" \o "Hydrogen) that the residue is a form of [carbon](http://www.eoearth.org/article/Carbon" \o "Carbon) called "coke." The two most common processes are delayed coking and continuous (contact or fluid) coking. Three typical types of coke are obtained (sponge coke, honeycomb coke, and needle coke) depending upon the reaction mechanism, time, temperature, and the crude feedstock.

**Delayed Coking**

In delayed coking the heated charge (typically residuum from atmospheric distillation towers) is transferred to large coke drums which provide the long residence time needed to allow the cracking reactions to proceed to completion. Initially the heavy feedstock is fed to a furnace which heats the residuum to high temperatures (900°-950° F) at low pressures (25-30 psi) and is designed and controlled to prevent premature coking in the heater tubes (Figure 4). The mixture is passed from the heater to one or more coker drums where the hot material is held approximately 24 hours (delayed) at pressures of 25-75 psi, until it cracks into lighter products. Vapors from the drums are returned to a fractionator where gas, naphtha, and gas oils are separated out. The heavier hydrocarbons produced in the fractionator are recycled through the furnace.

After the coke reaches a predetermined level in one drum, the flow is diverted to another drum to maintain continuous operation. The full drum is steamed to strip out uncracked hydrocarbons, cooled by water injection, and decoked by mechanical or hydraulic methods. The coke is mechanically removed by an auger rising from the bottom of the drum. Hydraulic decoking consists of fracturing the coke bed with high-pressure water ejected from a rotating cutter.

**Continuous Coking**

Continuous (contact or fluid) coking is a moving-bed process that operates at temperatures higher than delayed coking. In continuous coking, thermal cracking occurs by using heat transferred from hot, recycled coke particles to feedstock in a radial mixer, called a reactor, at a pressure of 50 psi. Gases and vapors are taken from the reactor, quenched to stop any further reaction, and fractionated. The reacted coke enters a surge drum and is lifted to a feeder and classifier where the larger coke particles are removed as product. The remaining coke is dropped into the preheater for recycling with feedstock. Coking occurs both in the reactor and in the surge drum. The process is automatic in that there is a continuous flow of coke and feedstock.

**Catalytic Cracking**

Catalytic cracking breaks complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products and decrease the amount of residuals. This process rearranges the molecular structure of hydrocarbon compounds to convert heavy hydrocarbon feedstock into lighter fractions such as kerosene, gasoline, liquified petroleum gas (LPG), heating oil, and petrochemical feedstock (Figure 5).

Catalytic cracking is similar to thermal cracking except that catalysts facilitate the conversion of the heavier molecules into lighter products. Use of a catalyst (a material that assists a chemical reaction but does not take part in it) in the cracking reaction increases the yield of improved-quality products under much less severe operating conditions than in thermal cracking. Typical temperatures are from 850°-950° F at much lower pressures of 10-20 psi. The catalysts used in refinery cracking units are typically solid materials (zeolite, aluminum hydrosilicate, treated bentonite clay, fuller's earth, bauxite, and silica-alumina) that come in the form of powders, beads, pellets or shaped materials called extrudites.

There are three basic functions in the catalytic cracking process:

* **Reaction:** Feedstock reacts with catalyst and cracks into different hydrocarbons;
* **Regeneration:** Catalyst is reactivated by burning off coke; and
* **Fractionation:** Cracked hydrocarbon stream is separated into various products.

The three types of catalytic cracking processes are fluid catalytic cracking (FCC), moving-bed catalytic cracking, and Thermofor catalytic cracking (TCC). The catalytic cracking process is very flexible, and operating parameters can be adjusted to meet changing product demand. In addition to cracking, catalytic activities include dehydrogenation, hydrogenation, and isomerization.

**Fluid Catalytic Cracking (FCC)**

Fluid catalytic cracking or "cat cracking," is the basic gasoline-making process. Using intense[heat](http://www.eoearth.org/article/Heat" \o "Heat) (about 1,000 degrees Fahrenheit), low pressure and a powdered catalyst (a substance that accelerates chemical reactions), the cat cracker can convert most relatively heavy fractions into smaller gasoline molecules. The fluid cracker consists of a catalyst section and a fractionating section that operate together as an integrated processing unit (Figure 6). The catalyst section contains the reactor and regenerator, which, with the standpipe and riser, forms the catalyst circulation unit. The fluid catalyst is continuously circulated between the reactor and the regenerator using air, oil vapors, and steam as the conveying media.

A typical FCC process involves mixing a preheated hydrocarbon charge with hot, regenerated catalyst as it enters the riser leading to the reactor. The charge is combined with a recycle stream within the riser, vaporized, and raised to reactor temperature (900°-1,000° F) by the hot catalyst. As the mixture travels up the riser, the charge is cracked at 10-30 psi. In the more modern FCC units, all cracking takes place in the riser. The "reactor" no longer functions as a reactor; it merely serves as a holding vessel for the cyclones. This cracking continues until the oil vapors are separated from the catalyst in the reactor cyclones. The resultant product stream (cracked product) is then charged to a fractionating column where it is separated into fractions, and some of the heavy oil is recycled to the riser.

Spent catalyst is regenerated to get rid of coke that collects on the catalyst during the process. Spent catalyst flows through the catalyst stripper to the regenerator, where most of the coke deposits burn off at the bottom where preheated air and spent catalyst are mixed. Fresh catalyst is added and worn-out catalyst removed to optimize the cracking process.

**Moving Bed Catalytic Cracking**

The moving-bed catalytic cracking process is similar to the FCC process. The catalyst is in the form of pellets that are moved continuously to the top of the unit by conveyor or pneumatic lift tubes to a storage hopper, then flow downward by gravity through the reactor, and finally to a regenerator. The regenerator and hopper are isolated from the reactor by steam seals. The cracked product is separated into recycle gas, oil, clarified oil, distillate, naphtha, and wet gas.

**Thermofor Catalytic Cracking**

In a typical thermofor catalytic cracking unit, the preheated feedstock flows by gravity through the catalytic reactor bed. The vapors are separated from the catalyst and sent to a fractionating tower. The spent catalyst is regenerated, cooled, and recycled. The flue gas from regeneration is sent to a [carbon monoxide](http://www.eoearth.org/article/Carbon_monoxide" \o "Carbon monoxide) boiler for [heat](http://www.eoearth.org/article/Heat" \o "Heat) recovery.

Hydrocracking

Hydrocracking is a two-stage process combining catalytic cracking and hydrogenation, wherein heavier feedstocks are cracked in the presence of [hydrogen](http://www.eoearth.org/article/Hydrogen" \o "Hydrogen) to produce more desirable products. The process employs high pressure, high temperature, a catalyst, and hydrogen. Hydrocracking is used for feedstocks that are difficult to process by either catalytic cracking or reforming, since these feedstocks are characterized usually by a high polycyclic aromatic content and/or high concentrations of the two principal catalyst poisons, sulfur and [nitrogen](http://www.eoearth.org/article/Nitrogen" \o "Nitrogen) compounds.

The hydrocracking process largely depends on the nature of the feedstock and the relative rates of the two competing reactions, hydrogenation and cracking. Heavy aromatic feedstock is converted into lighter products under a wide range of very high pressures (1,000-2,000 psi) and fairly high temperatures (750°-1,500° F), in the presence of [hydrogen](http://www.eoearth.org/article/Hydrogen" \o "Hydrogen) and special catalysts. When the feedstock has a high paraffinic content, the primary function of hydrogen is to prevent the formation of polycyclic aromatic compounds. Another important role of hydrogen in the hydrocracking process is to reduce tar formation and prevent buildup of coke on the catalyst. Hydrogenation also serves to convert sulfur and [nitrogen](http://www.eoearth.org/article/Nitrogen" \o "Nitrogen) compounds present in the feedstock to hydrogen sulfide andammonia.

Hydrocracking produces relatively large amounts of isobutane for alkylation feedstock. Hydrocracking also performs isomerization for pour-point control and smoke-point control, both of which are important in high-quality jet fuel.

**Hydrocracking Process**

In the first stage, preheated feedstock is mixed with recycled [hydrogen](http://www.eoearth.org/article/Hydrogen" \o "Hydrogen) and sent to the first-stage reactor, where catalysts convert sulfur and [nitrogen](http://www.eoearth.org/article/Nitrogen" \o "Nitrogen) compounds to hydrogen sulfide and ammonia (Figure 8). Limited hydrocracking also occurs.

After the hydrocarbon leaves the first stage, it is cooled and liquefied and run through a hydrocarbon separator. The hydrogen is recycled to the feedstock. The liquid is charged to a fractionator. Depending on the products desired (gasoline components,jet fuel, and gas oil), the fractionator is run to cut out some portion of the first stage reactor out-turn. Kerosene-range material can be taken as a separate side-draw product or included in the fractionator bottoms with the gas oil.

The fractionator bottoms are again mixed with a [hydrogen](http://www.eoearth.org/article/Hydrogen" \o "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 fractionator.

**Catalytic Reforming**

Catalytic reforming is an important process used to convert low-octane naphthas into high-octane gasoline blending components called reformates. Reforming represents the total effect of numerous reactions such as cracking, polymerization, dehydrogenation, and isomerization taking place simultaneously (Figure 9). Depending on the properties of the naphtha feedstock (as measured by the paraffin, olefin, naphthene, and aromatic content) and catalysts used, reformates can be produced with very high concentrations of toluene, benzene, xylene, and other aromatics useful in gasoline blending and petrochemical processing. [Hydrogen](http://www.eoearth.org/article/Hydrogen" \o "Hydrogen), a significant by-product, is separated from the reformate for recycling and use in other processes.

A catalytic reformer comprises a reactor section and a product-recovery section (Figure 10). More or less standard is a feed preparation section in which, by combination of hydrotreatment and distillation, the feedstock is prepared to specification. Most processes use platinum as the active catalyst. Sometimes platinum is combined with a second catalyst (bimetallic catalyst) such as rhenium or another noble metal.

There are many different commercial catalytic reforming processes including platforming, powerforming, ultraforming, and Thermofor catalytic reforming. In the platforming process, the first step is preparation of the naphtha feed to remove impurities from the naphtha and reduce catalyst degradation. The naphtha feedstock is then mixed with [hydrogen](http://www.eoearth.org/article/Hydrogen" \o "Hydrogen), vaporized, and passed through a series of alternating furnace and fixed-bed reactors containing a platinum catalyst. The effluent from the last reactor is cooled and sent to a separator to permit removal of the hydrogen-rich gas stream from the top of the separator for recycling. The liquid product from the bottom of the separator is sent to a fractionator called a stabilizer (butanizer). It makes a bottom product called reformate; butanes and lighter go overhead and are sent to the saturated gas plant.

Some catalytic reformers operate at low pressure (50-200 psi), and others operate at high pressures (up to 1,000 psi). Some catalytic reforming systems continuously regenerate the catalyst in other systems. One reactor at a time is taken off-stream for catalyst regeneration, and some facilities regenerate all of the reactors during turnarounds.

**Catalytic hydrotreating**

Catalytic hydrotreating is a hydrogenation process used to remove about 90% of contaminants such as [nitrogen](http://www.eoearth.org/article/Nitrogen" \o "Nitrogen), sulfur, [oxygen](http://www.eoearth.org/article/Oxygen" \o "Oxygen), and metals from liquid petroleum fractions. These contaminants, if not removed from the petroleum fractions as they travel through the refinery processing units, can have detrimental effects on the equipment, the catalysts, and the quality of the finished product. Typically, hydrotreating is done prior to processes such as catalytic reforming so that the catalyst is not contaminated by untreated feedstock. Hydrotreating is also used prior to catalytic cracking to reduce sulfur and improve product yields, and to upgrade middle-distillate petroleum fractions into finished kerosene, diesel fuel, and heating fuel oils. In addition, hydrotreating converts olefins and aromatics to saturated compounds.

**Catalytic Hydrodesulfurization Process**

Hydrotreating for sulfur removal is called hydrodesulfurization. In a typical catalytic hydrodesulfurization unit, the feedstock is deaerated and mixed with [hydrogen](http://www.eoearth.org/article/Hydrogen" \o "Hydrogen), preheated in a fired heater (600°-800° F) and then charged under pressure (up to 1,000 psi) through a fixed-bed catalytic reactor (Figure 12). In the reactor, the sulfur and [nitrogen](http://www.eoearth.org/article/Nitrogen" \o "Nitrogen) compounds in the feedstock are converted into hydrogen sulfide (H2S) and ammonia (NH3). The reaction products leave the reactor and after cooling to a low temperature enter a liquid/gas separator. The hydrogen-rich gas from the high-pressure separation is recycled to combine with the feedstock, and the low-pressure gas stream rich in H2S is sent to a gas treating unit where H2S is removed. The clean gas is then suitable as fuel for the refinery furnaces. The liquid stream is the product from hydrotreating and is normally sent to a stripping column for removal of H2S and other undesirable components. In cases where steam is used for stripping, the product is sent to a vacuum drier for removal of water. Hydrodesulfurized products are blended or used as catalytic reforming feedstock.

**Other Hydrotreating Processes**

Hydrotreating processes differ depending upon the feedstock available and catalysts used. Hydrotreating can be used to improve the burning characteristics of distillates such as kerosene. Hydrotreatment of a kerosene fraction can convert aromatics into naphthenes, which are cleaner-burning compounds.

Lube-oil hydrotreating uses catalytic treatment of the oil with [hydrogen](http://www.eoearth.org/article/Hydrogen" \o "Hydrogen) to improve product quality. The objectives in mild lube hydrotreating include saturation of olefins and improvements in color, odor, and acid nature of the oil. Mild lube hydrotreating also may be used following solvent processing. Operating temperatures are usually below 600° F and operating pressures below 800 psi. Severe lube hydrotreating, at temperatures in the 600°-750° F range and hydrogen pressures up to 3,000 psi, is capable of saturating aromatic rings, along with sulfur and [nitrogen](http://www.eoearth.org/article/Nitrogen" \o "Nitrogen) removal, to impart specific properties not achieved at mild conditions.

Hydrotreating also can be employed to improve the quality of pyrolysis gasoline (pygas), a by-product from the manufacture ofethylene. Traditionally, the outlet for pygas has been motor gasoline blending, a suitable route in view of its high octane number. However, only small portions can be blended untreated owing to the unacceptable odor, color, and gum-forming tendencies of this material. The quality of pygas, which is high in diolefin content, can be satisfactorily improved by hydrotreating, whereby conversion of diolefins into mono-olefins provides an acceptable product for motor gas blending.