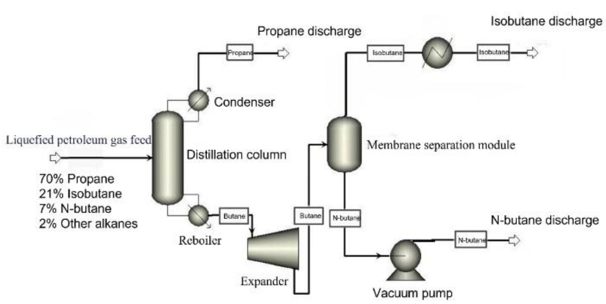
PRODUCTS FROM PETROLEUM AND NATURAL GAS

Liquefied Petroleum Gas (LP-Gas)

This is a mixture of propane and butane, two hydrocarbons which are gaseous at atmospheric pressure but liquid if higher pressure is applied. They are obtained from natural gas at natural gasoline plants and also from refinery gases. A large volume of the gas can be compressed into a small volume of liquid, simplifying handling problems. Liquefied petroleum gas, or "bottled gas" as it is sometimes known, is an important domestic fuel in rural communities and even in small communities which have a central distributing system, where the LP-Gas is supplied to consumers through the gas lines. LP-Gas is also widely used as an intermediate material in petrochemical manufacturing, and it is also being used to a growing extent as motor fuel in trucks and buses.

The propane and butane constituents of liquefied petroleum gas are obtained from natural gas at natural gasoline plants and also from gases produced at refineries when crude oil is processed.

The propane and butane hydrocarbons are separated from the gas stream by distillation. The presence of ethane is avoided because this light hydrocarbon does not liquefy under pressure at atmospheric temperatures.



If the LP-Gas contains pentane, a liquid hydrocarbon heavier than butane, this component may separate in a liquid state in the gas lines. This shows the importance of careful fractionation of the propane-butane mixture to remove undesirable hydrocarbons.

Natural gas and natural gasoline contain no unsaturated hydrocarbons, but these may be present in refinery gas streams. The unsaturated hydrocarbons have a tendency to polymerize and form gummy deposits, making their presence undesirable in liquefied petroleum gas. Care is taken by manufacturers to keep the propane and butane free of hydrogen sulfide, which is corrosive and on burning produces sulfur dioxide, a gas having a pungent odor. However, a minute quantity of ethyl mercaptan, a sulfur compound having an exceptionally strong and disagreeable odor, is added to the odorless propane and butane to warn the customer of gas leaks.

Gasoline

The largest volume of gasoline is used in operating automobiles. Modern high-compression motors require gasoline of high antiknock characteristics, which can be obtained only by specially processing crude oil. The use of these expensive fuels is justified because they will suppress engine knock. Several grades of gasoline are made with varying antiknock values. The boiling range of gasoline is varies with the season of the year and can be adjusted to geographical conditions. Such adjustments are made by varying the composition of the motor gasoline, which is a blend of many refinery streams.

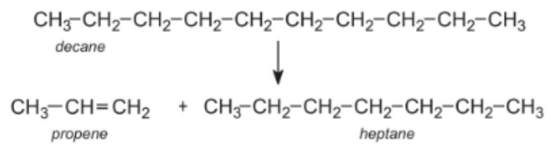
The manufacture of high antiknock gasoline was made possible by the development of cracking, reforming, alkylation, polymerization, isomerization, and other processes, which were briefly mentioned earlier. Most of these processes use catalysts to control the chemical reactions leading toward the formation of the desirable types of hydrocarbons.

Major Manufacturing Processes

Process	Purpose	Key Feature
Cracking	Break heavy fractions into low-boiling gasoline	Thermal or catalytic; improves antiknock
Reforming	Improve antiknock rating	Thermal or catalytic; uses expensive catalysts (e.g., platinum)
Alkylation, Polymerization, Isomerization	Produce desirable hydrocarbon structures	Briefly mentioned as enablers of high-octane gasoline

Cracking

Cracking, *as the name suggests, is a process in which large hydrocarbon molecules are broken down into smaller and more useful ones, for example:*



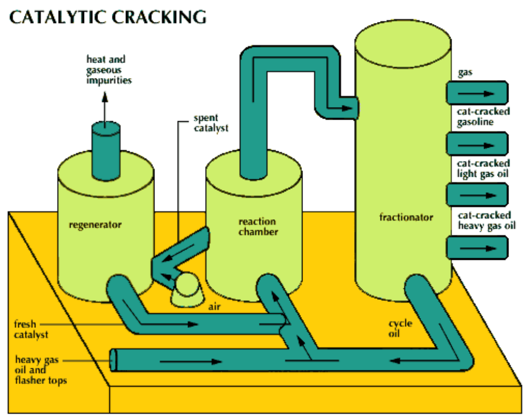
When heavy petroleum fractions are heated to the high temperatures at which they decompose, low-boiling gasoline fractions are formed. These fractions have better antiknock characteristics than the gasoline fractions obtained from the same crude oil by straight distillation. These cracking processes are of two major types: thermal, using heat, and catalytic, using catalysts in addition to heat. Catalytic cracking processes produce gasolines of higher antiknock quality, better stability, and lower sulfur content than the thermal cracking processes.

Thermal cracking processes are divided into two groups depending on the pressure employed. In the "liquid-phase" processes, the pressure ranges from 1,000 to 1,500 psi and the temperature from 850 to 950°F. In the "vapor-phase" processes, pressures vary from 50 to 150 psi, and temperatures from 1050 to 1200°F. High temperatures produce gasolines of excellent antiknock quality because of the large quantities of aromatic hydrocarbons formed, but these gasolines also contain many highly unstable hydrocarbons, which must be removed from the finished product.

Catalytic cracking *is a vital petroleum refining process that breaks down complex, heavy hydrocarbon feedstocks into lighter, high-value products like gasoline, kerosene, and LPG, using catalysts (typically zeolites) at lower temperatures and pressures than thermal cracking. It produces higher-octane, more stable fuels*

In catalytic cracking, petroleum fractions are usually vaporized at pressures close to atmospheric, and the vapors are contacted with a catalyst. The catalyst may be an active, naturally occurring clay or a synthetic alumina-silica compound to which other elements may be added. These catalysts suppress the formation of unstable hydrocarbons and favor the formation of hydrocarbons having excellent antiknock characteristics, such as aromatics and isoparaffins.

In the original **Houdry cracking process**, petroleum vapors were passed through a stationary catalyst bed. When the catalyst lost its activity, it was regenerated by passing air through it and burning off the carbon. In the later Thermoform and Fluid catalytic cracking processes, granular and very finely divided catalysts are used, respectively. The catalyst is recirculated between the cracking chamber and the kiln where it is regenerated by burning.



Cracking – Detailed

A. Thermal Cracking

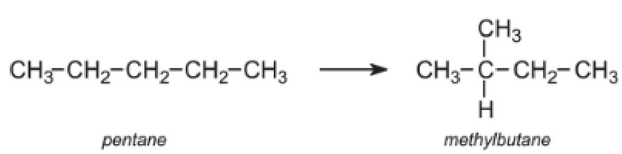
- **Liquid-phase:** 1000–1500 psi, 850–950°F
- **Vapor-phase:** 50–150 psi, 1050–1200°F
- **Product:** High aromatics → excellent antiknock, but also unstable hydrocarbons.

Catalytic Cracking

- **Conditions:** Near atmospheric pressure + catalyst (natural clay or synthetic alumina-silica).
- **Advantages:**
  - Higher antiknock quality.
  - Better stability.
  - Lower sulfur content.
  - Suppresses unstable hydrocarbons; favors aromatics & isoparaffins.
- **Process types:**
  - **Houdry (fixed bed):** Stationary catalyst, regenerated by burning off carbon.
  - **Thermofor (granular catalyst):** Circulated between cracker and regenerator.
  - **Fluid (fine powder):** Circulated continuously.

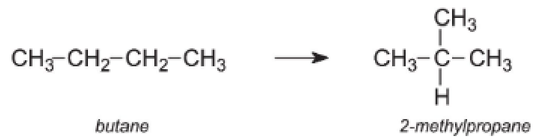
Isomerization

Isomerization *is the process in which hydrocarbon molecules are rearranged into a more useful isomer. For example:*



The process is particularly useful in enhancing the octane rating of petrol, as branched alkanes burn more efficiently in a car engine than straight-chain alkanes.

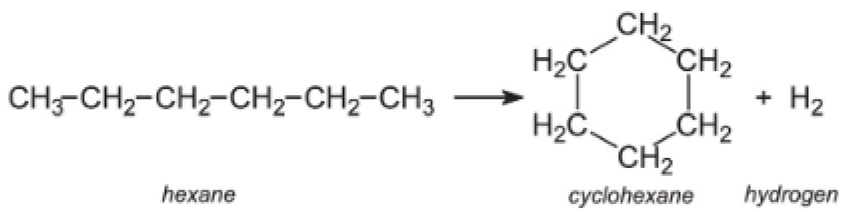
An important example is the isomerisation of butane (from LPG) to 2-methylpropane (isobutane):



Butane vapour is passed over a solid catalyst, aluminium chloride, on an inert solid at ca 300 K. The two alkanes are then separated either by distillation or by passing them through a molecular sieve, an aluminosilicate. The branched chain alkane is trapped and the straight chain passes through and is recirculated into the reactor. The 2-methylpropane is subsequently released and used to make a branched alkane, 2,2,4-trimethylpentane (iso-octane), for petrol.

Reforming processes

Reforming *is another process in which hydrocarbon molecules are rearranged into other molecules, usually with the loss of a small molecule such as hydrogen. An example is the conversion of an alkane molecule into a cycloalkane or an aromatic hydrocarbon for example:*



Reforming processes, which, like cracking, may be thermal or catalytic, are used to further improve the antiknock ratings of the gasoline fractions obtained from cracking or from the distillation of crude oil. The end boiling point of the charge stock to the reforming units is only slightly higher than that of the reformed gasoline and may be considered to remain almost unchanged. The modern reforming processes use very expensive catalysts, like platinum. To reduce mechanical loss, the catalyst beds are usually stationary.

Sulfur compounds, which are undesirable in gasolines, decompose in the presence of cracking and reforming catalysts to produce hydrogen sulfide, a gas having acidic properties. Since hydrogen sulfide can be separated from hydrocarbons much more easily than the original sulfur compounds, the sulfur content of catalytically cracked, reformed, or treated gasolines is lower than that of thermal gasolines.

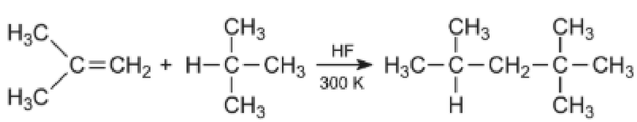
Figure 6 A view of three fixed-bed reactors (Unit 3) which operate in series at an oil refiner. The reforming reaction, which produces aromatic hydrocarbons and hydrogen, takes place in reactor 1, followed by isomerisation reactions in reactor 2 and finally in reactor 3, cracking reactions.

Aromatic hydrocarbons are formed from other ring hydrocarbons and from straight-chain hydrocarbons in catalytic reforming. They can be separated from other hydrocarbons by using a solvent. The unextracted nonaromatic hydrocarbons are returned to the process and recycled to increase the conversion. The aromatic extracts are used in gasoline blends and petroleum solvents. They are also a source of benzene and toluene, formerly obtained only from coal tar.

Alkylation

Alkylation *is the transfer of an alkyl group from one molecule to another. In a refinery, alkylation refers to the alkylation of alkanes,*

For example, 2-methylpropane (isobutane) with alkenes, in the presence of a strong acid catalyst such as hydrofluoric acid or sulfuric acid. The reaction is carried out at mild temperatures (between 273 and 303K). Cooling is needed as the reaction is exothermic.



2,2,4-trimethylpentane

With propene, 2-methylpropane forms a mixture containing a high proportion of 2,3- and 2,4-dimentylpentanes. These mixtures have very good antiknock properties and are added to petrol to increase the octane rating.

If sulfuric acid is used as the catalyst. many refineries will have a dedicated plant which takes in the waste sulfuric acid from the alkylation plant. In the recycling of sulfuric acid, the diluted acid is heated strongly to form sulfur dioxide which is then fed into a contact process plant, regenerating pure acid.

Hydrogenation

Hydrogenation *is a chemical reaction that adds hydrogen atoms (H_2) to unsaturated organic compounds (typically carbon-carbon double or triple bonds) to saturate them, usually requiring a metal catalyst like nickel, palladium, or platinum. This process is widely used in the food industry to convert liquid oils into solid fats and in petrochemicals for refining.*

Hydrogen finds considerable application in the manufacture of gasoline and other petroleum products. Petroleum fractions are cracked, reformed, or treated in the presence of hydrogen and catalysts to produce saturated hydrocarbons and to eliminate sulfur compounds. The hydrogen is obtained as a byproduct of catalytic reforming. However, it can be manufactured by refineries from methane by a relatively cheap process if the installation is large.

Treating

Gasoline is often treated with chemicals before it is a finished refinery product. The purpose is to remove small quantities of the objectionable substances, such as unstable hydrocarbons and some oxygen and sulfur compounds. The selection of the treating agents depends on the composition of the gasoline stream.

Clay and synthetic catalysts can be employed for removing the unsaturated hydrocarbons and sulfur. Sodium hydroxide finds increasingly wide application in gasoline treating, including the removal of mercaptans, which are sulfur compounds of objectionable odor. Some treating processes convert mercaptans into high-boiling and odorless disulfides. A well-known example is "doctor treatment," which employs lead oxide, sodium hydroxide, and elemental sulfur for the conversion.

However, the disulfides have poor stability and are objectionable in other respects.

These "sweetening" processes are now being replaced by processes, such as the Dua layer, Solutizer, and Unisol, which remove the mercaptans instead of converting them into gasoline-soluble disulfides.

The selection of the gasoline manufacturing and treating processes is a local refinery problem of major importance. On this selection depends the ability of the refinery to produce gasolines of various grades. The processes used must also be flexible and adjustable to the fluctuations in the market demand.

Gasoline Additives

Gasoline quality is much improved by the use of additives, that is, small quantities of chemicals which have a disproportionately large effect in enhancing certain desirable properties of the finished product. Additives cannot change the distillation range, vapor pressure, and similar physical characteristics of petroleum fuels. However, they are effective in raising the antiknock value, or octane number, of the fuel, reducing the formation of engine deposits, and improving oxidation stability and other properties. Gasolines with the various types of additives, as well as the straight fuel themselves, are rigorously tested by the oil supplying com panies under prescribed laboratory conditions and in road-test programs under a wide range of driving conditions before they are offered to the public.