PETROLEUM

Crude petroleum from a well is processed in several ways.

1. Removal of water, acids and other inorganics, like powdered rock
2. Distillation to separate the components
3. Catalytic cracking to produce higher concentrations of useful products

About 90% of all the petroleum is burned. The remaining 10% becomes feedstock for the production of petrochemicals, many of which you are familiar with.

Distillation of Petroleum into Broad Temperature Range Fractions

Temperature (^oC)	# Carbons	Fraction and Product
<20	1-4	Gases: butane,propane,ethane,methane
20-100	5-7	Petroleum ether, ligroin
50-180	6-12	Gasoline
175-230	11-17	Kerosene, jet fuel
230-305	13-18	Diesel fuel, home heating "oil"
305-405	18-25	Heavy heating oil
reduced pressure	20-30	lubricating oil, petroleum jelly, paraffin
NON-VOLATILE		ASPHALT

Within each fraction, the boiling range includes a variety of isomers for each carbon count; highly branched compounds have lower boiling points than slightly branched, hence the overlapping carbon counts. The gasoline fraction contains a high concentration of cyclic compounds such as cyclohexanes and the kerosene fraction a high concentration of aromatic compounds.

Cracking and Reforming

The mixture of compounds in a natural oil well does not match the need for petroleum products either in chain length or branching pattern. Thus the carbon chains of much of the petroleum are shortened and isomerized by a process called catalytic cracking. The fractions are heated separately with platinum catalysts similar to those in an automobile catalytic converter; they catalyze the rupture of C-H and C-C bonds, reducing the molecular weight and increasing branching, ring formation and sometimes unsaturation.

Gasoline and Octane Rating

A typical gasoline is a complex mixture from cracking and distillation; some of its components burn more smoothly than others. A "straight" chain hydrocarbon burns too fast in an internal combustion engine, its combustion proceeding by a series of little explosions called pinging. Highly branched hydrocarbons burn more slowly and make better automobile fuels. Branched hydrocarbons are expensive to make because fragmentation into lower molecular weight compounds (like ethylene) competes with the isomerization, reducing the yield of the branched compounds. A way to evaluate fuels and alternatives to branched hydrocarbons were needed.

A scale (octane rating) was developed which compares real gasoline with test mixtures of heptane (rating 0) and "isooctane" (2,2,4-trimethylpentane) (rating 100). Over the years, the experiments done to compare the fuels have changed, but the basic procedure of comparing with heptane / isooctane mixtures has not. Until about 1980, octane rating was increased by the addition of tetraethyllead, a compound which readily produces radical intermediates crucial for burning. Lead salts in the exhaust are all neurotoxins, and thus lead is no longer added to fuel. The most common octane enhancers in now are aromatics (toluene 9%, benzene 1%) and the more expensive ethers (methyl *t*-butyl ether, MTBE).

COAL

Coal is a complex mixture of polynuclear (many rings sharing sides) aromatic hydrocarbons. When coal is heated to about 2700F in the absence of air (a process called destructive distillation), some of the large molecules fall apart to form a gas (coal gas), a volatile liquid (coal oil) and coal tar (used for roofing and road paving). Coal gas was used for lighting and as fuel in Germany during WW2. Coal oil consists of 63% benzene, 14% toluene and 7% xylene, important petrochemicals.

PETROCHEMICALS

Cracking of coal or oil produces benzene, toluene, ethylbenzene and xylenes; they are used to improve octane rating, as solvents, and as starting materials for explosives (toluene for TNT) and polymers, often called plastics (toluenediisocyanate for polyurethanes, ethylbenzene for polystyrene). Cyclohexane (formed in cracking or by hydrogenation of benzene) serves as starting material for both monomers of the nylon polymer. Of the small molecules produced by cracking, the most important is ethylene (ethene), a gas used to make polyethylene, and as a starting material to make more complex polymers such as polystyrene. Ethylene is converted to vinyl chloride (chloroethene) which becomes PVC, used for making pipes and raincoats, and ethylene oxide (a three-membered ring with 2 carbons and an oxygen), the source of ethylene glycol (ethane-1,2-diol) the key ingredient in antifreeze and polyesters.

All the isomers of C_4H_{10} and C_4H_8 are also produced by cracking, as is butadiene C_4H_6. Most of the butadiene ends up in SBR rubber as automobile tires; its isomer 2-methyl-2-propene is converted to methyl *t*-butyl ether, an octane enhancer. In a clever two-for-one process, benzene and propene are reacted to make cumene (isopropylbenzene), which is then oxidized to make acetone, an excellent solvent, and phenol, an important antiseptic (Noxema) and starting material for epoxy resins and polycarbonates (glass substitutes).

FOR FURTHER READING:

1. Donald L. Burdick and William L. Leffler, *Petrochemicals in Nontechnical Language*, PennWell Books, Tulsa, OK 1990.
2. Cynthia M. Friend, "Catalysis on Surfaces", *Scientific American*, **April 1993**, 74 - 79.
3. D. R. Blackmore and A. Thomas, *Fuel Economy of the Gasoline Engine*, Wiley, NY, 1977.