GASOLINE

Gasoline, also called *gas* (United States and Canada) or *petrol* (Great Britain), or *benzine* (Europe), is a mixture of volatile, flammable liquid hydrocarbons derived from petroleum and used as fuel for internal-combustion engines.

The hydrocarbons in gasoline boil below 180°C (355°F) or, at most, below 200°C (390°F). The hydrocarbon constituents in this boiling range are those that have 4 to 12 carbon atoms in their molecular structure and are classified into three general types: paraffins (including the cycloparaffins and branched materials), olefins, and aromatics.

Highly branched paraffins, which are particularly valuable constituents of gasolines, are not usually the principal paraffinic constituents of straight-run gasoline. The more predominant paraffinic constituents are usually the normal (straight-chain) isomers, which may dominate the branched isomers by a factor of 2 or more. This is presumed to indicate the tendency to produce long uninterrupted carbon chains during petroleum maturation rather than those in which branching occurs.

Gasoline is manufactured by distillation in which the volatile, more valuable fractions of crude petroleum are separated. Later processes, known as *cracking*, were designed to raise the yield of gasoline from crude oil by converting the higher-molecular-weight constituents of petroleum into lower-molecular-weight products Other methods used to improve the quality of gasoline and increase its supply include *polymerization*, *alkylation*, *isomerization,* and *reforming*.

Polymerization is the conversion of gaseous olefins, such as propylene and butylene, into larger molecules in the gasoline range. A*lkylation* is a process combining an olefin and a paraffin such as *iso*-butane). *Isomerization* is the conversion of straight-chain hydrocarbons to branched-chain hydrocarbons. *Reforming* is the use of either heat or a catalyst to rearrange the molecular structure.

Aviation gasoline, now usually found in use in light aircraft and older civil aircraft, has a narrower boiling range than conventional (automobile) gasoline, that is, 38 to 170°C (100 to 340°F) compared to approximately

–1 to 200°C (30 to 390°F) for automobile gasoline. The narrower boiling range ensures better distribution of the vaporized fuel through the more complicated induction systems of aircraft engines. Aircraft operate at altitudes at which the prevailing pressure is less than the pressure at the surface of the earth (pressure at 17,500 feet is 7.5 psi compared to 14.7 psi at the surface of the earth). Thus, the vapor pressure of aviation gasoline must be limited to reduce boiling in the tanks, fuel lines, and carburetors. Thus, the aviation gasoline does not usually contain the gaseous hydrocarbons (butanes) that give automobile gasoline the higher vapor pressures.

Methanol and a number of other alcohols and ethers are considered high-octane enhancers of gasoline. They can be produced from various hydrocarbon sources other than petroleum and may also offer environmental advantages insofar as the use of oxygenates would presumably suppress the release of vehicle pollutants into the air.

Of all the oxygenates, methyl-*t*-butyl ether (MTBE) is attractive for a variety of technical reasons. It has a low vapor pressure, can be blended with other fuels without phase separation, and has the desirable octane characteristics. If oxygenates achieve recognition as vehicle fuels, the biggest contributor will probably be methanol, the production of which is mostly from synthesis gas derived from methane.

Other additives to gasoline often include detergents to reduce the buildup of engine deposits, anti-icing agents to prevent stalling caused by carburetor icing, and antioxidants (oxidation inhibitors) used to reduce *gum* formation.

GLASS

Glass is a rigid, undercooled liquid having no definite melting point and a sufficiently high viscosity to prevent crystallization that results from the union of the nonvolatile inorganic oxides, sand, and other constituents, and thus is a product with *random* atomic structure.

In order to produce the various glasses, soda ash, salt cake, and limestone or lime are required to flux the silica. In addition, there is a contribution of lead oxide, pearl (as potassium carbonate), saltpeter, borax, boric acid, arsenic trioxide, feldspar, and fluorspar, together with a great variety of metallic oxides, carbonates, and the other salts required for colored glass.

GLUTAMIC ACID

See ***Monosodium Glutamate.***

GLYCEROL

Glycerol (glycerin, melting point: 18°C, boiling point: 290°C, density: 1.2620, flash point: 177°C) is a clear, nearly colorless liquid having a sweet taste but no odor.

Glycerol may be produced by a number of different methods, such as:

1. The saponification of glycerides (oils and fats) to produce soap.

2. The recovery of glycerin from the hydrolysis, or splitting, of fats and oils to produce fatty acids.

3. The chlorination and hydrolysis of propylene and other reactions from petrochemical hydrocarbons.

Natural glycerol is produced as a coproduct of the direct hydrolysis of triglycerides from natural fats and oils in large continuous reactors at elevated temperatures and pressures with a catalyst (Fig. 1). Water flows countercurrent to the fatty acid and extracts glycerol from the fatty phase. The sweet water from the hydrolyzer column contains about 12% glycerol. Evaporation of the sweet water from the hydrolyzer is a much easier operation than with evaporation of spent soap lye glycerin in the kettle process. The high salt content of soap lye glycerin requires frequent soap removal from the evaporators. Hydrolyzer glycerin contains practically no salt and is readily concentrated.

The sweet water is fed to a triple-effect evaporator where the concentration is increased from 12% to 75 to 80% glycerol. After concentration of the sweet water to hydrolyzer crude, the crude is settled for 48 hours at elevated temperatures to reduce fatty impurities that could interfere with subsequent processing. Settled hydrolyzer crude contains approximately 78% glycerol and 22% water. The settled crude is distilled under vacuum at approximately 200°C. A small amount of caustic is usually added to the still feed to saponify fatty impurities and reduce the possibility of codistillation with the glycerol. The distilled glycerin is condensed in three stages at decreasing temperatures. The first stage yields the purest glycerin, usually 99% glycerol and lower-quality grades of glycerin are collected in the

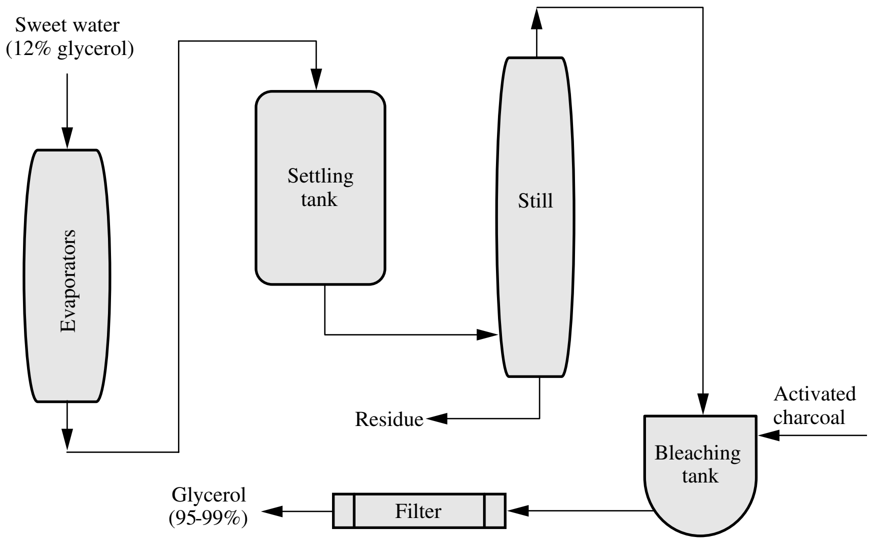

FIGURE 1 Glycerol manufacture using the sweet water process.

second and third condensers. Final purification of glycerin is accomplished by carbon bleaching, followed by filtration or ion exchange.

There are several synthetic methods for the manufacture of glycerol. One process (Fig. 2) involves chlorination of propylene at 510ºC (950ºF) to produce allyl chloride in seconds in amounts greater than 85 percent of theory (based on the propylene). Vinyl chloride, some disubstituted olefins, and some 1,2 and 1,3-dichloropropanes are also formed. Treatment of the allyl chloride with hypochlorous acid at 38ºC (100ºF) produces glycerin dichlorohydrin ($CH_2ClCHClCH_2OH$), which can be hydrolyzed by caustic soda in a 6% Na_2CO_3 solution at 96ºC. The glycerin dichlorohydrin can be hydrolyzed directly to glycerin, but this takes two molecules of caustic soda; hence a more economical procedure is to react with the cheaper calcium hydroxide, taking off the epichlorohydrin as an overhead in a stripping column. The epichlorohydrin is easily hydrated to monochlorohydrin and then hydrated to glycerin with caustic soda.

$$CH_3CH{=}CH_2 + C1_2 \rightarrow CH_2ClCH{=}CH_2 + HCl$$

$$CH_2ClCH{=}CH_2 + HOCl \rightarrow CH_2ClCHClCH_2OH$$

$$CH_2ClCHClCH_2OH + 2NaOH \rightarrow CH_2OHCHOHCH_2OH + 2NaCl$$

The overall yield of glycerin from allyl chloride is above 90 percent.

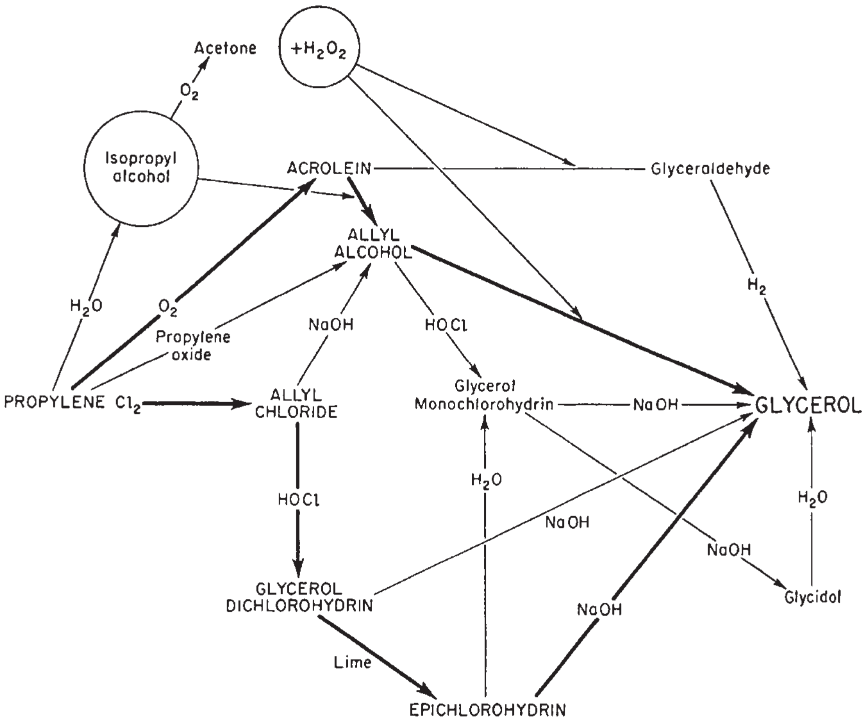

FIGURE 2 Routes for the manufacture of glycerol.

Another process for obtaining glycerol from propylene involves the following reactions, where isopropyl alcohol and propylene furnish acetone and glycerin (through acrolein) in good yield (Fig. 2).

$$CH_3CHOHCH_3 + \text{air} \rightarrow CH_3COCH_3 + H_2O$$

$$CH_3CH{=}CH_2 + \text{air} \rightarrow CH_2{=}CHCHO + H_2O$$

$$CH_2{=}CHCHO + H_2O_2 \rightarrow CHOCHOHCH_2OH$$

$$CHOCHOHCH_2OH \rightarrow CH_2OHCHOHCH_2OH$$

GRAPHITE

See ***Carbon.***

GYPSUM

See ***Calcium Sulfate.***