

1.1 ELEMENTARY IDEAS OF GAS AND LIQUID RESERVOIRS.(1)

RESERVES AND RAW MATERIALS: Estimates of the reserves of such essential minerals as petroleum are inexact, but of vital importance in predicting future trends and in planning. To make such statistics more reliable, it is customary to use the term "proved reserves" to refer to minerals known to exist in well-defined fields and which are recoverable by present production methods. Not all the petroleum existing underground is recoverable. Heavy crude recovery seldom exceeds 50 percent. Under favorable circumstances, up to 80 percent of lighter crude may be brought to the surface. Although some is wasted, practically all natural gas can be recovered and utilized. Proved reserves of the world in 1981 were estimated at $1.03 \times 10^{11} \text{ m}^3$ of which the proved reserves in the United States constituted $4.20 \times 10^9 \text{ m}^3$. The actual useful size of reserves is dependent upon the recovery techniques used. Ashburn, in 1887, estimated that wasteful production techniques in Pennsylvania and New York oil fields would ultimately result in the recovery of only 11 to 12 percent of the oil present. If methods now available had been used then, 2 to 2.5 times more oil would have been taken out than was actually recovered by natural flow and pumping. The key to the problem is proper conservation and utilization of reservoir energy. Oil is usually underlain with water under considerable pressure and overlain with gas, as shown in Fig. Withdrawal of oil from the proper place at a sufficiently low rate allows the pressure to be maintained, saving much pumping energy. Natural gas or CO₂ can be returned to repressure wells. In one instance, a slower rate of oil production and recycling natural gas at 9.6 MPa enabled a net recovery of 70 percent of the oil originally present. This is twice the amount recoverable without repressuring. Natural high pressure CO₂ is often piped long distances to use in oil fields. Air is not suitable for repressuring, because it causes deterioration in the quality of the oil produced.

1.3 PETROLEUM REFINING PROCESSES (1)

BASIC REFINERY PROCESS: DESCRIPTION AND HISTORY. Petroleum refining has evolved continuously in response to changing consumer demand for better and different products. The original requirement was to produce kerosene as a cheaper and better source of light than whale oil. The development of the internal combustion engine led to the production of gasoline and diesel fuels. The evolution of the airplane created a need first for high-octane aviation gasoline and then for jet fuel, a sophisticated form of the original product, kerosene. Present-day refineries produce a variety of products including many required as feedstock for the petrochemical industry.

1. Distillation Processes. The first refinery, opened in 1861, produced kerosene by simple atmospheric distillation. Its by-products included tar and naphtha. It was soon discovered that high-quality lubricating oils could be produced by distilling petroleum under vacuum. However, for the next 30 years kerosene was the product consumers wanted. Two significant events changed this situation: (1) invention of the electric light decreased the demand for kerosene, and (2) invention of the internal combustion engine created a demand for diesel fuel and gasoline (naphtha).

2. Thermal Cracking Processes. With the advent of mass production and World War I, the number of gasoline-powered vehicles increased dramatically and the demand for

gasoline grew accordingly. However, distillation processes produced only a certain amount of gasoline from crude oil. In 1913, the thermal cracking process was developed, which subjected heavy fuels to both pressure and intense heat, physically breaking the large molecules into smaller ones to produce additional gasoline and distillate fuels. Visbreaking, another form of thermal cracking, was developed in the late 1930's to produce more desirable and valuable products.

3. Catalytic Processes. Higher-compression gasoline engines required higher-octane gasoline with better antiknock characteristics. The introduction of catalytic cracking and polymerization processes in the mid- to late 1930's met the demand by providing improved gasoline yields and higher octane numbers. Alkylation, another catalytic process developed in the early 1940's, produced more high-octane aviation gasoline and petrochemical feedstock for explosives and synthetic rubber. Subsequently, catalytic isomerization was developed to convert hydrocarbons to produce increased quantities of alkylation feedstock. Improved catalysts and process methods such as hydrocracking and reforming were developed throughout the 1960's to increase gasoline yields and improve antiknock characteristics. These catalytic processes also produced hydrocarbon molecules with a double bond (alkenes) and formed the basis of the modern petrochemical industry.

4. Treatment Processes. Throughout the history of refining, various treatment methods have been used to remove nonhydrocarbons, impurities, and other constituents that adversely affect the properties of finished products or reduce the efficiency of the conversion processes. Treating can involve chemical reaction and/or physical separation. Typical examples of treating are chemical sweetening, acid treating, clay contacting, caustic washing, hydrotreating, drying, solvent extraction, and solvent dewaxing. Sweetening compounds and acids desulfurize crude oil before processing and treat products during and after processing. Following the Second World War, various reforming processes improved gasoline quality and yield and produced higher-quality products. Some of these involved the use of catalysts and/or hydrogen to change molecules and remove sulfur. A number of the more commonly used treating and reforming processes are described in this chapter of the manual.

TABLE HISTORY OF REFINING

Year	Process name	Purpose	By-products, etc.
1862	Atmospheric distillation	Produce kerosene	Naphtha, tar, etc.
1870	Vacuum distillation	Lubricants (original) Cracking feedstocks (1930's)	Asphalt, residual coker feedstocks
1913	Thermal cracking	Increase gasoline	Residual, bunker fuel
1916	Sweetening	reduce sulfur & odor	Sulfur
1930	Thermal reforming	Improve octane number	Residual
1932	Hydrogenation	Remove sulfur	Sulfur

1932	Coking	Produce gasoline basestocks	Coke
1933	Solvent extraction	Improve lubricant viscosity index	Aromatics
1935	Solvent dewaxing	Improve pour point	Waxes
1935	Cat. polymerization	Improve gasoline yield & octane number	Petrochemical feedstocks
1937	Catalytic cracking	Higher octane gasoline	Petrochemical feedstocks
1939	Visbreaking	reduce viscosity	Increased distillate, tar
1940	Alkylation	Increase gasoline octane & yield	High-octane aviation gasoline
1940	Isomerization	Produce alkylation feedstock	Naphtha
1942	Fluid catalytic cracking	Increase gasoline yield & octane	Petrochemical feedstocks
1950	Deasphalting	Increase cracking feedstock	Asphalt
1952	Catalytic reforming	Convert low-quality naphtha	Aromatics
1954	Hydrodesulfurization	Remove sulfur	Sulfur
1956	Inhibitor sweetening	Remove mercaptan	Disulfides
1957	Catalytic isomerization	Convert to molecules with high octane number	Alkylation feedstocks
1960	Hydrocracking	Improve quality and reduce sulfur	Alkylation feedstocks
1974	Catalytic dewaxing	Improve pour point	Wax
1975	Residual hydrocracking	Increase gasoline yield from residual	Heavy residuals