

PRODUCTION OF KEROSENE

BACKGROUND

Kerosene is an oil distillate commonly used as a fuel or solvent. It is a thin, clear liquid consisting of a mixture of hydrocarbons that boil between 302°F and 527°F (150°C and 275°C). While kerosene can be extracted from coal, oil shale, and wood, it is primarily derived from refined petroleum. Before electric lights became popular, kerosene was widely used in oil lamps and was one of the most important refinery products. Today kerosene is primarily used as a heating oil, as fuel in jet engines, and as a solvent for insecticide sprays.

History

Petroleum byproducts have been used since ancient times as adhesives and water proofing agents. Over 2,000 years ago, Arabian scientists explored ways to distill petroleum into individual components that could be used for specialized purposes. As new uses were discovered, demand for petroleum increased. Kerosene was discovered in 1853 by Abraham Gesner. A British physician, Gesner developed a process to extract the inflammable liquid from asphalt, a waxy petroleum mixture. The term kerosene is, in fact, derived from the Greek word for wax. Sometimes spelled kerosine or kerosiene, it is also called coal oil because of its asphalt origins.

Kerosene was an important commodity in the days before electric lighting and it was the first material to be chemically extracted on a large commercial scale. Mass refinement of kerosene and other petroleum products actually began in 1859 when oil was discovered in the United States. An entire industry evolved to develop oil drilling and purification techniques. Kerosene continued to be the most important refinery product throughout the late 1890s and early 1900s. It was surpassed by gasoline in the 1920s with the increasing popularity of the internal combustion engine. Other uses were found for kerosene after the demise of oil lamps, and today it is primarily used in residential heating and as a fuel additive. In the late 1990s, annual production of kerosene had grown to approximately 1 billion gal (3.8 billion l) in the United States alone.

Raw Materials

Kerosene is extracted from a mixture of petroleum chemicals found deep within the earth. This mixture consists of oil, rocks, water, and other contaminants in subterranean reservoirs made of porous layers of sandstone and carbonate rock. The oil itself is derived from decayed organisms that were buried along with the sediments of early geological eras. Over tens of millions of years, this organic residue was converted to petroleum by a pair of complex chemical processes known as diagenesis and catagenesis. Diagenesis, which occurs below 122°F (50°C), involves both microbial activity and chemical reactions such as dehydration, condensation, cyclization, and polymerization. Catagenesis occurs between 122°F and 392°F (50°C and 200°C) and involves thermocatalytic cracking, decarboxylation, and hydrogen disproportionation.

The combination of these complex reactions creates the hydrocarbon mixture known as petroleum.

The Manufacturing Process

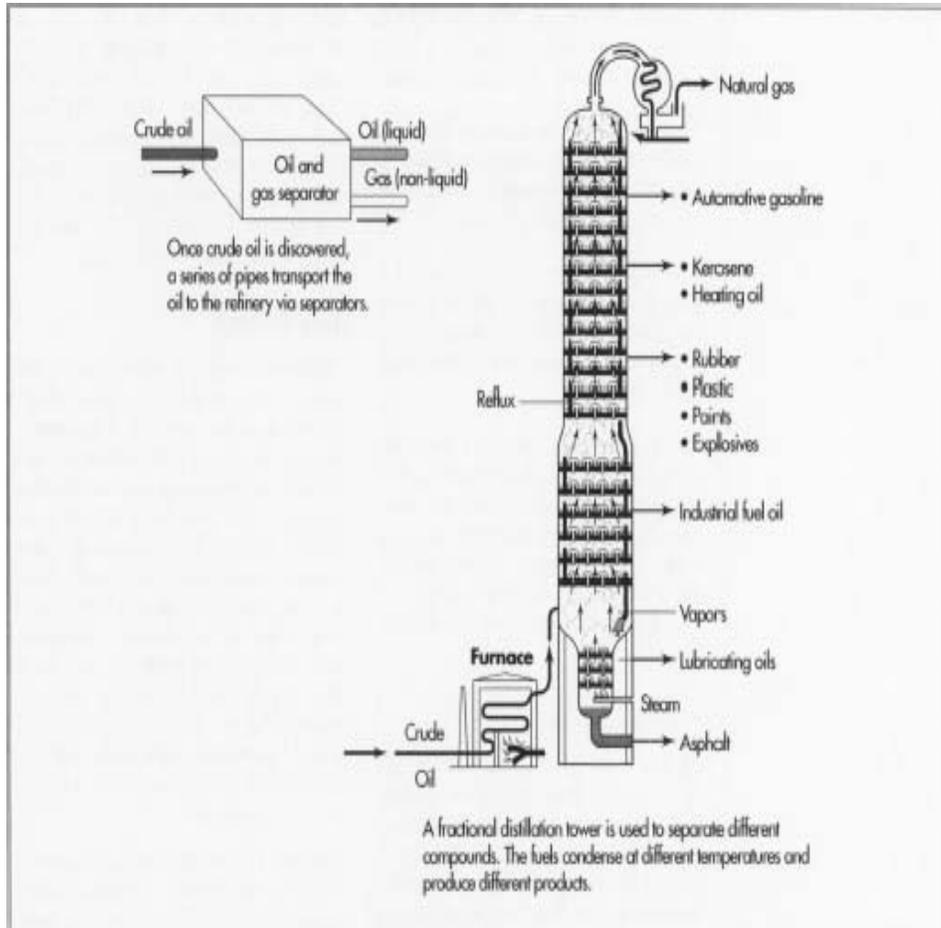
Crude oil recovery

- 1 The first step in the manufacture of kerosene is to collect the crude oil. Most oil supplies are buried deep beneath the earth and there are three primary types of drilling operations used to bring it to the surface. One method, Cable-Tooled Drilling, involves using a jackhammer chisel to dislodge rock and dirt to create a tunnel to reach oil deposits that reside just below the earth's surface. A second process, Rotary Drilling, is used to reach oil reservoirs that are much deeper underground. This process requires sinking a drill pipe with a rotating steel bit into the ground. This rotary drill spins rapidly to pulverize earth and rock. The third drilling process is Off Shore Drilling and it uses a large ocean borne platform to lower a shaft to the ocean floor.
- 2 When any of these drilling processes break into an underground reservoir, a geyser erupts as dissolved hydrocarbon gases push the crude oil to the surface. These gases will force about 20% of the oil out of the well. Water is then pumped into the well to flush more of the oil out. This flushing process will recover about 50% of the buried oil. By adding a surfactant to the water even more oil can be recovered. However, even with the most rigorous flushing it is still impossible to remove 100% of the oil trapped underground. The crude oil recovered is pumped into large storage tanks and transported to a refining site.
- 3 After the oil is collected, gross contaminants such as gases, water, and dirt are removed. Desalting is one cleansing operation that can be performed both in the oilfield and at the refinery site. After the oil has been washed, the water is separated from the oil. The properties of the crude oil are evaluated to determine which petroleum products can best be extracted from it. The key properties of interest include density, sulfur content, and other physical properties of the oil related to its carbon chain distribution. Since crude oil is a combination of many different hydrocarbon materials that are miscible in one another, it must be separated into its components before it can be turned into kerosene.

Separation

- 4 Distillation is one type of separation process involves heating the crude oil to separate its components. In this process the stream of oil is pumped into the bottom of a distillation column where it is heated. The lighter hydrocarbon components in the mixture rise to the top of the column and most of the high boiling-point fractions are left at the bottom. At the top of the column these lighter vapors reach the condenser which cools them and returns them to a liquid state. The columns used to separate lighter oils are proportionally tall and thin (up to 116 ft [35 m] tall) because they only require atmospheric pressure. Tall distillation columns can more efficiently separate hydrocarbon mixtures because

they allow more time for the high boiling compounds to condense before they reach the top of the column.



To separate some of the heavier fractions of oil, distillations columns must be operated at approximately one tenth of atmospheric pressure (75 mm Hg). These vacuum columns are structured to be very wide and short to help control pressure fluctuations. They can be over 40 ft (12 m) in diameter.

- 5 The condensed liquid fractions can be collected separately. The fraction that is collected between 302°F and 482°F (150°C and 250°C) is kerosene. By comparison, gasoline is distilled between 86°F and 410°F (30°C and 210°C). By recycling the distilled kerosene through the column multiple times its purity can be increased. This recycling process is known as refluxing.

Purification

- 6 Once the oil has been distilled into its fractions, further processing in a series of chemical reactors is necessary to create kerosene. Catalytic reforming, akylation,

- catalytic cracking, and hydroprocessing are four of the major processing techniques used in the conversion of kerosene. These reactions are used to control the carbon chain distribution by adding or removing carbon atoms from the hydrocarbon backbone. These reaction processes involve transferring the crude oil fraction into a separate vessel where it is chemically converted to kerosene.
- 7 Once the kerosene has been reacted, additional extraction is required to remove secondary contaminants that can affect the oil's burning properties. Aromatic compounds, which are carbon ring structures such as benzene, are one class of contaminant that must be removed. Most extraction processes are conducted in large towers that maximize the contact time between the kerosene and the extraction solvent. Solvents are chosen based on the solubility of the impurities. In other words, the chemical impurities are more soluble in the solvent than they are the kerosene. Therefore, as the kerosene flows through the tower, the impurities will tend to be drawn into the solvent phase. Once the contaminants have been pulled out of the kerosene, the solvent is removed leaving the kerosene in a more purified state. The following extraction techniques are used to purify kerosene.

The Udex extraction process became popular in the United States during the 1970s. It uses a class of chemicals known as glycols as solvents. Both diethylene glycol and tetraethylene glycol are used because they have a high affinity for aromatic compounds.

The Sulfolane process was created by the Shell company in 1962 and is still used in many extraction units 40 years later. The solvent used in this process is called sulfolane, and it is a strong polar compound that is more efficient than the glycol systems used in the Udex process. It has a greater heat capacity and greater chemical stability. This process uses a piece of equipment known as a rotating disk contractor to help purify the kerosene.

The Lurgi Arosolvan Process uses N-methyl-2-pyrrolidinone mixed with water or glycol which increases the selectivity of the solvent for contaminants. This process involves a multiple stage extracting towers up to 20 ft (6 m) in diameter and 116 ft (35 m) high.

The dimethyl sulfoxide process involves two separate extraction steps that increase the selectivity of the solvent for the aromatic contaminants. This allows extraction of these contaminants at lower temperatures. In addition, chemicals used in this process are non-toxic and relatively inexpensive. It uses a specialized column, known as a Kuhni column, that is up to 10 ft (3 m) in diameter.

The Union Carbide process uses the solvent tetraethylene glycol and adds a second extraction step. It is somewhat more cumbersome than other glycol processes.

The Formex process uses N-formyl morpholine and a small percentage of water as the solvent and is flexible enough to extract aromatics from a variety of hydrocarbon materials.

The Redox process (Recycle Extract Dual Extraction) is used for kerosene destined for use in diesel fuel. It improves the octane number of fuels by selectively removing aromatic contaminants. The low aromatic kerosene produced by these process is in high demand for aviation fuel and other military uses.

Final processing

- 8 After extraction is complete, the refined kerosene is stored in tanks for shipping. It is delivered by tank trucks to facilities where the kerosene is packaged for commercial use. Industrial kerosene is stored in large metal tanks, but it may be packaged in small quantities for commercial use. Metal containers may be used because kerosene is not a gas and does not require pressurized storage vessels. However, its flammability dictates that it must be handled as a hazardous substance.

Quality Control

The distillation and extraction processes are not completely efficient and some processing steps may have to be repeated to maximize the kerosene production. For example, some of the unconverted hydrocarbons may be separated by further distillation and recycled for another pass into the converter. By recycling the petroleum waste through the reaction sequence several times, the quality of kerosene production can be optimized.

By products/Waste

Some portion of the remaining petroleum fractions that can not be converted to kerosene may be used in other applications such as lubricating oil. In addition, some of the contaminants extracted during the purification process can be used commercially. These include certain aromatic compounds such as paraffin. The specifications for kerosene and these other petroleum byproducts are set by the American Society for Testing and Materials (ASTM) and the American Petroleum Institute (API).

The Future

The future of kerosene depends on the discovery of new applications as well as the development of new methods of production. New uses include increasing military demand for high grade kerosene to replace much of its diesel fuel with JP-8, which is a kerosene based jet fuel. The diesel fuel industry is also exploring a new process that involves adding kerosene to low sulfur diesel fuel to prevent it from gelling in cold weather. Commercial aviation may benefit by reducing the risk of jet fuel explosion by

creating a new low-misting kerosene. In the residential sector, new and improved kerosene heaters that provide better protection from fire are anticipated to increase demand.

As demand for kerosene and its byproducts increases, new methods of refining and extracting kerosene will become even more important. One new method, developed by ExxonMobil, is a low-cost way to extract high purity normal paraffin from kerosene. This process uses ammonia that very efficiently absorbs the contaminants. This method uses vapor phase fixed-bed adsorption technology and yields a high level of paraffin that are greater than 90% pure.

Gasoline, mixture of the lighter liquid used chiefly as a fuel for internal-combustion engines. It is produced by the fractional distillation of oil; by condensation or adsorption from natural gas; by thermal or catalytic decomposition of petroleum or its fractions; by the hydrogenation of producer gas or coal; or by the polymerization of hydrocarbons of lower molecular weight

Gasoline produced by the direct distillation of crude petroleum is known as straight-run gasoline. It is usually distilled continuously in a bubble tower which separates the gasoline from the other fractions of the oil having higher boiling points, such as kerosene, fuel oil, lubricating oil, and grease. The range of temperatures in which gasoline boils and is distilled off is roughly between 38° and 205° C (100° and 400° F). The yield of gasoline from this process varies from about 1 percent to about 50 percent, depending on the petroleum. Straight-run gasoline now makes up only a small part of U.S. gasoline production because of the superior merits of the various processes.

In many parts of the country natural gas contains a percentage of natural gasoline that may be recovered by condensation or adsorption. The most common process for the extraction of natural gasoline includes passing the gas as it comes from the well through a series of towers containing a light oil called straw oil. The oil absorbs the gasoline, which is then distilled off. Other processes involve adsorption of the gasoline on activated alumina, activated carbon, or silica gel.

High-grade gasoline can be produced by a process known as hydrofining, that is, the hydrogenation of refined petroleum oils under high pressure in the presence of a catalyst such as molybdenum oxide. Hydrofining not only converts oils of low value into gasoline of higher value but also at the same time purifies the gasoline chemically by removing undesirable elements such as sulfur. Producer gas, coal, and coal-tar distillates can also be hydrogenated to form gasoline.

For use in high-compression engines, it is desirable to produce gasoline that will burn evenly and completely in order to prevent knocking, the sound and damage caused by premature ignition of a part of the fuel and air charge in the combustion chamber of an internal-combustion engine. The antiknock characteristics of a gasoline are directly related to its efficiency and are indicated by its octane number. This is a rating that describes performance of a fuel in comparison with that of a standard fuel containing

given percentages of isooctane and heptane. If the performance of the rated fuel is the same as that of a standard fuel with a certain percentage of isooctane, the octane number given the rated fuel is the same as the percentage of isooctane in the standard fuel. The higher this number, the less likely a fuel is to cause knocking. Cracked gasoline has better antiknock characteristics than straight-run gasoline, and any gasoline can be further improved by the addition of such substances as tetraethyl or tetramethyl lead. Since it was discovered, however, that the emission of lead from gasolines combined with such additives is dangerous to living beings—among other effects, raising blood pressure—research on new ways to reduce the knocking characteristics of gasoline was intensified.

PRODUCTION OF AVIATION FUEL

The requirements for jet fuels

Mixtures of gasoline and diesel oil fractions were used as fuel in 1944, but with increasing requirements efforts were being made to use highest boiling fractions only in order to release all gasoline for other critical uses. Tests were in progress using materials from the sump phase and pre-hydrogenation steps in coal hydrogenation. The tests had shown that only a low aromatic content could be tolerated if clean burning was to be obtained, and it was also concluded that some gasoline was necessary in order to obtain satisfactory ignition.

The status toward the end of the war was that gasoline-rich mixtures were still being used with the higher boiling diluents being any available material such that the blend not the following specifications.

1. Viscosity maximum 12 centistokes at -31 degrees Fahrenheit (or maximum 22 centistokes at -4 degrees Fahrenheit). The viscosity specification was to insure flow through the fuel pump and good distribution in the fuel jets.
2. Pour point maximum -31 degrees Fahrenheit. (It was stated in another instance that in practice the maximum pour point was -40 degrees Fahrenheit and that no crystal appearance could occur above -13 degrees Fahrenheit). In a flight of one (1) to one and one-half (1½) hours, such as is experienced with jet fighters, the contents of the fuel tank can reach a temperature low as -31 degree Fahrenheit. For long distance flights it was believed that the pour point specification would have to be lowered to -56 degrees Fahrenheit.
3. The fuel shall burn without carbon formation. aromatic oils deposit carbon in the combustion chamber and the turbine. Paraffinic oils are clean burning and therefore desired for jet fuels. It was the opinion in Germany that the chemical character (and hence burning quality) of the fuel was of more importance than such properties as boiling range.
4. Heating value minimum 16,000 BTU per pound.
5. Sulfur content maximum 1.0 percent weight.

Two grades of aviation gasoline were produced one with a motor method octane number of 91, and the other of 95. The former contained about 10 percent volume aromatics,

while the latter, known as C-3 contained about 40 percent volume aromatics and would thus allow much higher power output under rich mixture conditions. Both grades contained 4.35 cc. tetra-ethyl lead per gallon. The 50 percent distilled specifications were 221 and 230 degrees Fahrenheit, for B-4 and C-3, respectively.

The B-4 grade was produced directly by the addition of tetra-ethyl lead to the entire liquid product from the large coal and coal tar hydrogenation plants. The volatility was adjusted to about 7 pounds Reid vapor pressure by stabilizing and no further refining or blending was done.

The C-3 grade was a leaded blend of about 15 percent volume of synthetic isoparaffins and 85 percent volume of a base stock containing 45 to 50 percent volume aromatics, produced by further processing of a hydrogenated gasoline almost identical to unleaded B-4. The C-3 grade represented at least two-thirds ($\frac{2}{3}$) of the combined volume of the two grades.

Small amounts of synthetic aromatic compounds such as diethyl benzene, were used as components, but with unimportant exceptions, no additives or components other than those mentioned above were included in the commercial blends. No inhibitors of any kind were normally used.

Synthetic isoparaffins were manufactured primarily by the alkylation of butylenes and isobutene. Some isobutylene polymerization and polymer hydrogenation was being carried out. No propylene or amylene alkylation was being done. No triptane synthesis had been developed, and no isoparaffin synthesis other than those mentioned above were being used.

Isobutylene for polymerization was made by dehydrogenation of isobutyl alcohol which was synthesized directly from carbon monoxide and hydrogen. Normal butylenes for alkylation was produced by catalytic dehydrogenation of normal butane produced by the coal and tar hydrogenation plants. Isobutane for alkylation came in part directly from the hydrogenation plants and in part by catalytic isomerization of some of the normal butane.

To produce the bulk of high aromatic content base stock used in C-3, a process known as DHD was employed. This process produced aromatics both by dehydrogenation of naphthenes and by cyclization of paraffins. Hydroforming was used at one refinery to produce base stock, crude oil fractions.

1. A specific and efficient catalytic process for dealkylating aromatics;
2. A catalytic cracking process for normal paraffins boiling in the kerosene range, producing primarily C₃, C₄ and C₅ olefins;
3. A catalytic process for producing an ultimate weight yield of 70 to 78 percent of toluene from normal heptane, and
4. A process for producing high quality gasoline isoparaffins by combining propane and isobutane via chlorination.

The fuel was a mixture of gasoline and diesel oil fractions. The specifications for jet fuel were lenient; no unusual quality was demanded and no unusual specifications were forthcoming.