Oil Refinery Engineering & Synthetic Fuel Technologies

Royal Randall

Devyn Snodgrass

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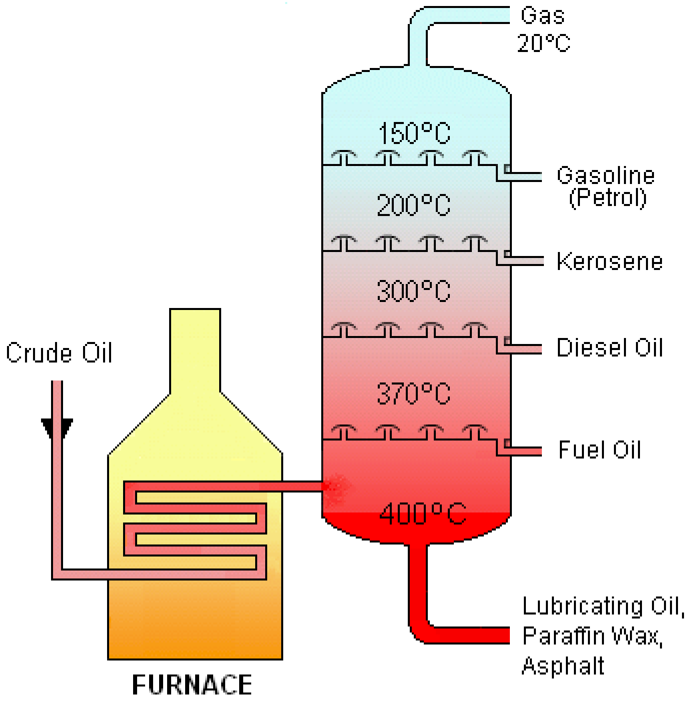
Oil Refinery

Anacortes Refinery (Tesoro), on the north end of March Point southeast of Anacortes, Washington

An **oil refinery** or **petroleum refinery** is an industrial process plant where crude oil is processed and refined into more useful petroleum products, such as gasoline, diesel fuel, asphalt base, heating oil, kerosene, and liquefied petroleum gas. Oil refineries are typically large sprawling industrial complexes with extensive piping running throughout, carrying streams of fluids between large chemical processing units. In many ways, oil refineries use much of the technology of, and can be thought of as types of chemical plants. The crude oil feedstock has typically been processed by an oil production plant. There is usually an oil depot (tank farm) at or near an oil refinery for storage of bulk liquid products.

An oil refinery is considered an essential part of the downstream side of the petroleum industry.

Operation



Crude oil is separated into fractions by fractional distillation. The fractions at the top of the fractionating column have lower boiling points than the fractions at the bottom. The heavy bottom fractions are often cracked into lighter, more useful products. All of the fractions are processed further in other refining units.

Raw or unprocessed crude oil is not generally useful. Although "light, sweet" (low viscosity, low sulfur) crude oil has been used directly as a burner fuel for steam vessel propulsion, the lighter elements form explosive vapors in the fuel tanks and are therefore hazardous, especially in warships. Instead, the hundreds of different hydrocarbon molecules in crude oil are separated in a refinery into components which can be used as fuels, lubricants, and as feedstock in petrochemical processes that manufacture such products as plastics, detergents, solvents, elastomers and fibers such as nylon and polyesters.

Petroleum fossil fuels are burned in internal combustion engines to provide power for ships, automobiles, aircraft engines, lawn mowers, chainsaws, and other machines. Different boiling points allow the hydrocarbons to be separated by distillation. Since the lighter liquid products are in great demand for use in internal combustion engines, a modern refinery will convert heavy hydrocarbons and lighter gaseous elements into these higher value products.

The oil refinery in Haifa, Israel is capable of processing about 9 million tons (66 million barrels) of crude oil a year. Its two cooling towers are landmarks of the city's skyline.

Oil can be used in a variety of ways because it contains hydrocarbons of varying molecular masses, forms and lengths such as paraffins, aromatics, naphthenes (or cycloalkanes), alkenes, dienes, and alkynes. While the molecules in crude oil include different atoms such as sulfur and nitrogen, the hydrocarbons are the most common form of molecules, which are molecules of varying lengths and complexity made of hydrogen and carbon atoms, and a small number of oxygen atoms. The differences in the structure of these molecules account for their varying physical and chemical properties, and it is this variety that makes crude oil useful in a broad range of applications.

Once separated and purified of any contaminants and impurities, the fuel or lubricant can be sold without further processing. Smaller molecules such as isobutane and propylene or butylenes can be recombined to meet specific octane requirements by processes such as alkylation, or less commonly, dimerization. Octane grade of gasoline can also be improved by catalytic reforming, which involves removing hydrogen from hydrocarbons producing compounds with higher octane ratings such as aromatics. Intermediate products such as gasoils can even be reprocessed to break a heavy, long-chained oil into a lighter short-chained one, by various forms of cracking such as fluid catalytic cracking, thermal cracking, and hydrocracking. The final step in gasoline production is the blending of fuels with different octane ratings, vapor pressures, and other properties to meet product specifications.

Oil refineries are large scale plants, processing about a hundred thousand to several hundred thousand barrels of crude oil a day. Because of the high capacity, many of the units operate continuously, as opposed to processing in batches, at steady state or nearly steady state for months to years. The high capacity also makes process optimization and advanced process control very desirable.

Major products

Petroleum products are usually grouped into three categories: light distillates (LPG, gasoline, naphtha), middle distillates (kerosene, diesel), heavy distillates and residuum (heavy fuel oil, lubricating oils, wax, asphalt). This classification is based on the way crude oil is distilled and separated into fractions (called distillates and residuum) as in the above drawing.

- Liquified petroleum gas (LPG)
- Gasoline (also known as petrol)
- Naphtha
- Kerosene and related jet aircraft fuels
- Diesel fuel
- Fuel oils
- Lubricating oils
- Paraffin wax
- Asphalt and tar
- Petroleum coke

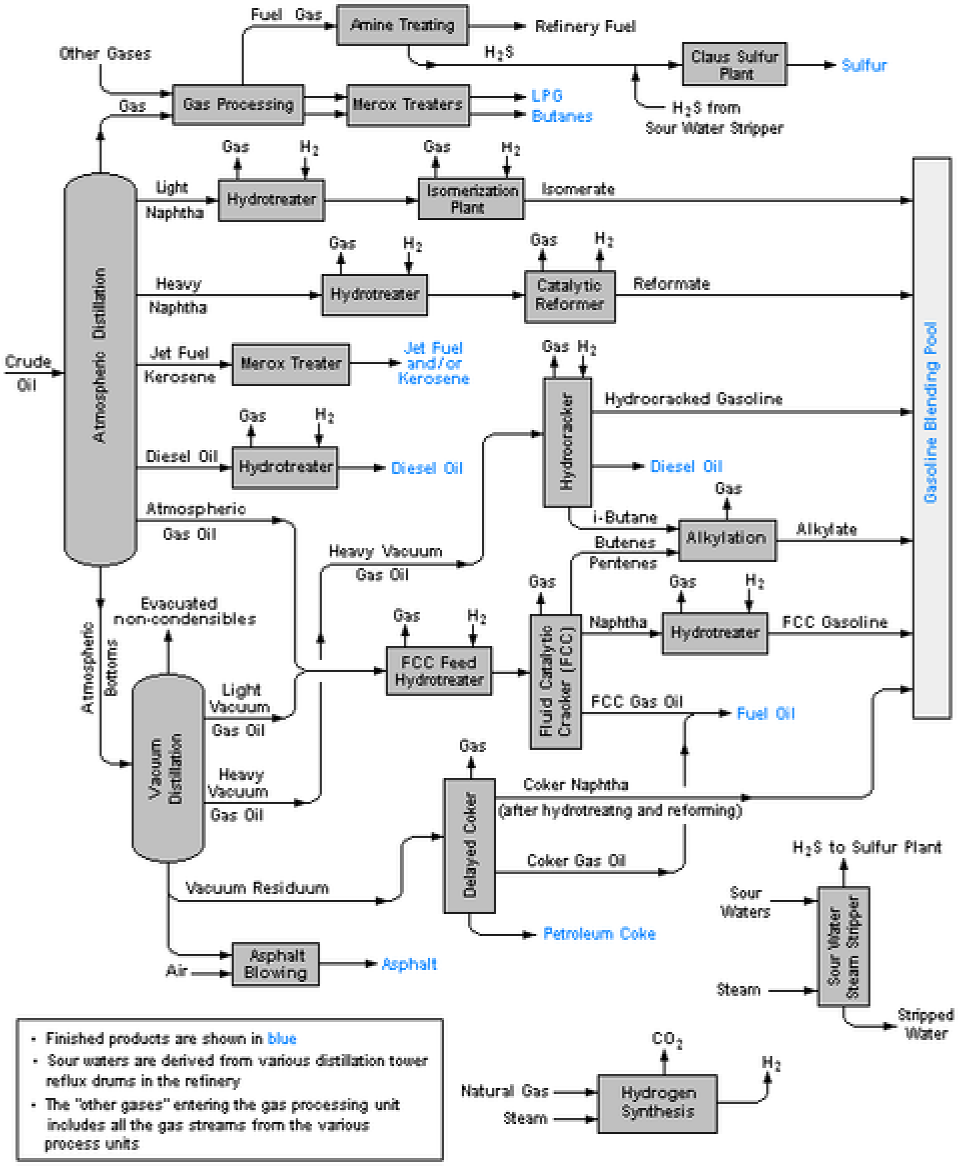
Common process units found in a refinery

- Desalter unit washes out salt from the crude oil before it enters the atmospheric distillation unit.
- Atmospheric distillation unit distills crude oil into fractions.
- Vacuum distillation unit further distills residual bottoms after atmospheric distillation.
- Naphtha hydrotreater unit uses hydrogen to desulfurize naphtha from atmospheric distillation. Must hydrotreat the naphtha before sending to a Catalytic Reformer unit.
- Catalytic reformer unit is used to convert the naphtha-boiling range molecules into higher octane reformate (reformer product). The reformate has higher content of aromatics and cyclic hydrocarbons). An important byproduct of a reformer is hydrogen released during the catalyst reaction. The hydrogen is used either in the hydrotreaters or the hydrocracker.

- Distillate hydrotreater unit desulfurizes distillates (such as diesel) after atmospheric distillation.
- Fluid catalytic cracker (FCC) unit upgrades heavier fractions into lighter, more valuable products.
- Hydrocracker unit uses hydrogen to upgrade heavier fractions into lighter, more valuable products.
- Visbreaking unit upgrades heavy residual oils by thermally cracking them into lighter, more valuable reduced viscosity products.
- Merox unit treats LPG, kerosene or jet fuel by oxidizing mercaptans to organic disulfides.
- Coking units (delayed coking, fluid coker, and flexicoker) process very heavy residual oils into gasoline and diesel fuel, leaving petroleum coke as a residual product.
- Alkylation unit produces high-octane component for gasoline blending.
- Dimerization unit converts olefins into higher-octane gasoline blending components. For example, butenes can be dimerized into isooctene which may subsequently be hydrogenated to form isooctane. There are also other uses for dimerization.
- Isomerization unit converts linear molecules to higher-octane branched molecules for blending into gasoline or feed to alkylation units.
- Steam reforming unit produces hydrogen for the hydrotreaters or hydrocracker.
- Liquified gas storage units store propane and similar gaseous fuels at pressure sufficient to maintain them in liquid form. These are usually spherical vessels or bullets (horizontal vessels with rounded ends.
- Storage tanks store crude oil and finished products, usually cylindrical, with some sort of vapor emission control and surrounded by an earthen berm to contain spills.
- Slug catcher used when product (crude oil and gas) that comes from a pipeline with two-phase flow, has to be buffered at the entry of the units.
- Amine gas treater, Claus unit, and tail gas treatment convert hydrogen sulfide from hydrodesulfurization into elemental sulfur.
- Utility units such as cooling towers circulate cooling water, boiler plants generates steam, and instrument air systems include pneumatically operated control valves and an electrical substation.
- Wastewater collection and treating systems consist of API separators, dissolved air flotation (DAF) units and further treatment units such as an activated sludge biotreater to make water suitable for reuse or for disposal.
- Solvent refining units use solvent such as cresol or furfural to remove unwanted, mainly asphaltenic materials from lubricating oil stock or diesel stock.
- Solvent dewaxing units remove the heavy waxy constituents petrolatum from vacuum distillation products.

Flow diagram of typical refinery

The image below is a schematic flow diagram of a typical oil refinery that depicts the various unit processes and the flow of intermediate product streams that occurs between the inlet crude oil feedstock and the final end products. The diagram depicts only one of the literally hundreds of different oil refinery configurations. The diagram also does not include any of the usual refinery facilities providing utilities such as steam, cooling water, and electric power as well as storage tanks for crude oil feedstock and for intermediate products and end products.

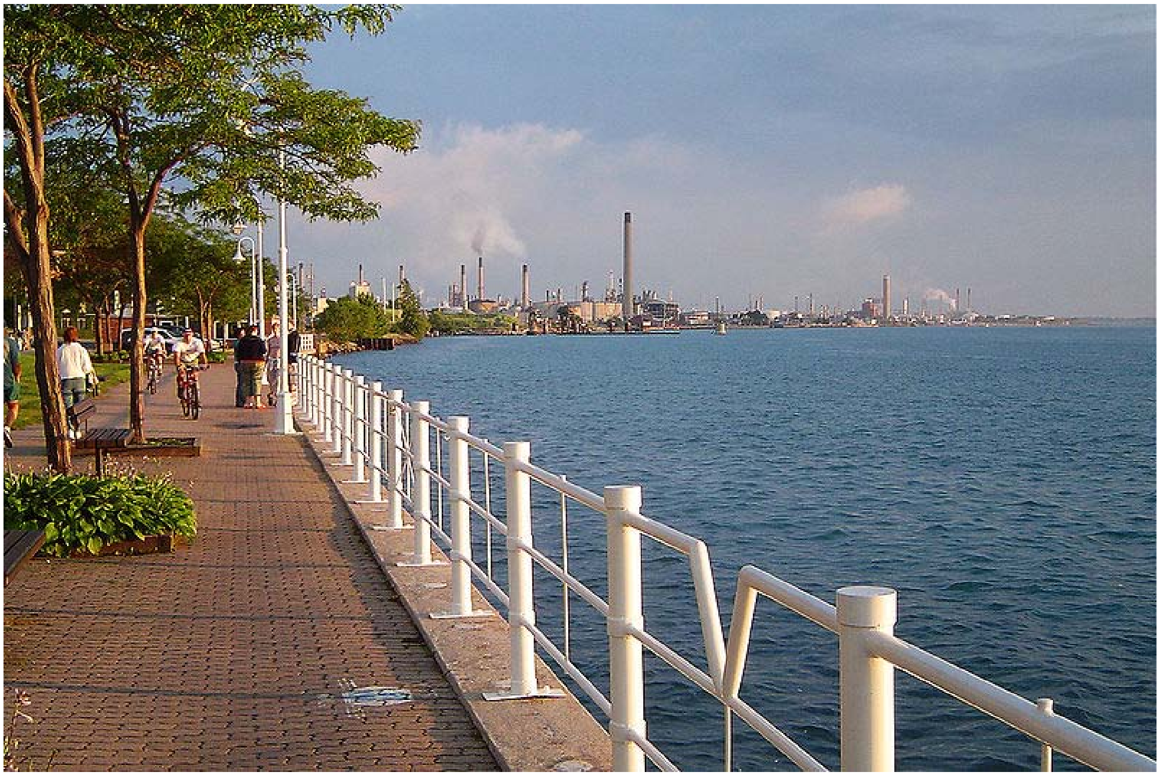


- Finished products are shown in blue
- Sour waters are derived from various distillation tower reflux drums in the refinery
- The "other gases" entering the gas processing unit includes all the gas streams from the various process units

Schematic flow diagram of a typical oil refinery

There are many process configurations other than that depicted above. For example, the vacuum distillation unit may also produce fractions that can be refined into endproducts such as: spindle oil used in the textile industry, light machinery oil, motor oil, and steam cylinder oil. As another example, the vacuum residue may be processed in a coker unit to produce petroleum coke.

Specialty end products



Sarnia, Ontario is a major Great Lakes refining area for Shell, Imperial Oil, ExxonMobil, Suncor Energy, Dow Chemicals, Bayer, and others.

These will blend various feedstocks, mix appropriate additives, provide short term storage, and prepare for bulk loading to trucks, barges, product ships, and railcars.

- Gaseous fuels such as propane, stored and shipped in liquid form under pressure in specialized railcars to distributors.
- Liquid fuels blending (producing automotive and aviation grades of gasoline, kerosene, various aviation turbine fuels, and diesel fuels, adding dyes, detergents, antiknock additives, oxygenates, and anti-fungal compounds as required). Shipped by barge, rail, and tanker ship. May be shipped regionally in dedicated pipelines to point consumers, particularly aviation jet fuel to major airports, or piped to distributors in multi-product pipelines using product separators called pipeline inspection gauges ("pigs").
- Lubricants (produces light machine oils, motor oils, and greases, adding viscosity stabilizers as required), usually shipped in bulk to an offsite packaging plant.
- Wax (paraffin), used in the packaging of frozen foods, among others. May be shipped in bulk to a site to prepare as packaged blocks.
- Sulfur (or sulfuric acid), byproducts of sulfur removal from petroleum which may have up to a couple percent sulfur as organic sulfur-containing compounds. Sulfur and sulfuric acid are useful industrial materials. Sulfuric acid is usually prepared and shipped as the acid precursor oleum.

- Bulk tar shipping for offsite unit packaging for use in tar-and-gravel roofing.
- Asphalt unit. Prepares bulk asphalt for shipment.
- Petroleum coke, used in specialty carbon products or as solid fuel.
- Petrochemicals or petrochemical feedstocks, which are often sent to petrochemical plants for further processing in a variety of ways. The petrochemicals may be olefins or their precursors, or various types of aromatic petrochemicals.

Siting/locating of petroleum refineries

A party searching for a site to construct a refinery or a chemical plant needs to consider the following issues:

- The site has to be reasonably far from residential areas.

- Infrastructure should be available for supply of raw materials and shipment of products to markets.

- Energy to operate the plant should be available.

- Facilities should be available for waste disposal.

Refineries which use a large amount of steam and cooling water need to have an abundant source of water. Oil refineries therefore are often located nearby navigable rivers or on a sea shore, nearby a port. Such location also gives access to transportation by river or by sea. The advantages of transporting crude oil by pipeline are evident, and oil companies often transport a large volume of fuel to distribution terminals by pipeline. Pipeline may not be practical for products with small output, and rail cars, road tankers, and barges are used.

Petrochemical plants and solvent manufacturing (fine fractionating) plants need spaces for further processing of a large volume of refinery products for further processing, or to mix chemical additives with a product at source rather than at blending terminals.

Safety and environmental concerns

Fire at Union Oil refinery, Wilmington, California, 1951

MiRO refinery at Karlsruhe

The refining process releases numerous different chemicals into the atmosphere; consequently, there are substantial air pollution emissions and a notable odor normally accompanies the presence of a refinery. Aside from air pollution impacts there are also wastewater concerns, risks of industrial accidents such as fire and explosion, and noise health effects due to industrial noise.

The public has demanded that many governments place restrictions on contaminants that refineries release, and most refineries have installed the equipment needed to comply with the requirements of the pertinent environmental protection regulatory agencies. In the United States, there is strong pressure to prevent the development of new refineries, and no major refinery has been built in the country since Marathon's Garyville, Louisiana facility in 1976. However, many existing refineries have been expanded during that time. Environmental restrictions and pressure to prevent construction of new refineries may have also contributed to rising fuel prices in the United States. Additionally, many refineries (over 100 since the 1980s) have closed due to obsolescence and/or merger activity within the industry itself. This activity has been reported to Congress and in specialized studies not widely publicised.

Environmental and safety concerns mean that oil refineries are sometimes located some distance away from major urban areas. Nevertheless, there are many instances where refinery operations are close to populated areas and pose health risks such as in the Campo de Gibraltar, a CEPSA refinery near the towns of Gibraltar, Algeciras, La Linea, San Roque and Los Barrios with a combined population of over 300,000 residents within a 5-mile (8.0 km) radius and the CEPSA refinery in Santa Cruz on the island of Tenerife, Spain which is sited in a densely populated city center and next to the only two major evacuation routes in and out of the city. In California's Contra Costa County and Solano County, a shoreline necklace of refineries, built in the early 20th century before this area was populated, and associated chemical plants are adjacent to urban areas in Richmond, Martinez, Pacheco, Concord, Pittsburg, Vallejo and Benicia, with occasional accidental events that require "shelter in place" orders to the adjacent populations.

Corrosion problems and prevention

Petroleum refineries run as efficiently as possible to reduce costs. One major factor that decreases efficiency is corrosion of the metal components found throughout the process line of the hydrocarbon refining process. Corrosion causes the failure of parts in addition to dictating the cleaning schedule of the refinery, during which the entire production facility must be shut down and cleaned. The cost of corrosion in the petroleum industry has been estimated at US$3.7 billion.

Corrosion occurs in various forms in the refining process, such as pitting corrosion from water droplets, embrittlement from hydrogen, and stress corrosion cracking from sulfide attack. From a materials standpoint, carbon steel is used for upwards of 80% of refinery components, which is beneficial due to its low cost. Carbon steel is resistant to the most common forms of corrosion, particularly from hydrocarbon impurities at temperatures below 205 °C, but other corrosive chemicals and environments prevent its use everywhere. Common replacement materials are low alloy steels containing chromium and molybdenum, with stainless steels containing more chromium dealing with more corrosive environments. More expensive materials commonly used are nickel, titanium, and copper alloys. These are primarily saved for the most problematic areas where extremely high temperatures or very corrosive chemicals are present.

Corrosion is fought by a complex system of monitoring, preventative repairs and careful use of materials. Monitoring methods include both off-line checks taken during maintenance and on-line monitoring. Off-line checks measure corrosion after it has occurred, telling the engineer when equipment must be replaced based on the historical information he has collected. This is referred to as preventative management.

On-line systems are a more modern development, and are revolutionizing the way corrosion is approached. There are several types of on-line corrosion monitoring technologies such as linear polarization resistance, electrochemical noise and electrical resistance. On-Line monitoring has generally had slow reporting rates in the past (minutes or hours) and been limited by process conditions and sources of error but newer technologies can report rates up to twice per minute with much higher accuracy (referred to as real-time monitoring). This allows process engineers to treat corrosion as another process variable that can be optimized in the system. Immediate responses to process changes allow the control of corrosion mechanisms, so they can be minimized while also maximizing production output. In an ideal situation having on-line corrosion information that is accurate and real-time will allow conditions that cause high corrosion rates to be identified and reduced. This is known as predictive management.

Materials methods include selecting the proper material for the application. In areas of minimal corrosion, cheap materials are preferable, but when bad corrosion can occur, more expensive but longer lasting materials should be used. Other materials methods come in the form of protective barriers between corrosive substances and the equipment metals. These can be either a lining of refractory material such as standard Portland cement or other special acid-resistant cements that are shot onto the inner surface of the vessel. Also available are thin overlays of more expensive metals that protect cheaper metal against corrosion without requiring lots of material.

History

The first oil refineries in the world were built by Ignacy Łukasiewicz near Jasło, Austrian Empire (now in Poland) from 1854 to 1856, but they were initially small as there was no real demand for refined fuel. As Łukasiewicz's kerosene lamp gained popularity, the refining industry grew in the area.

World's first large refinery opened at Ploieşti, Romania, in 1856-1857, with United States investment. After being taken over by Nazi Germany, the Ploieşti refineries were bombed in Operation Tidal Wave by the Allies during the Oil Campaign of World War II. Another early large refinery is Oljeön, Sweden (1875), now preserved as a museum at Engelsberg Ironworks, a UNESCO World Heritage Site, and part of the Ekomuseum Bergslagen.

At one point, the refinery in Ras Tanura, Saudi Arabia owned by Saudi Aramco was claimed to be the largest oil refinery in the world. For most of the 20th century, the largest refinery was the Abadan Refinery in Iran. This refinery suffered extensive damage during the Iran-Iraq war. The world's largest refinery complex is the Jamnagar Refinery Complex, consisting of two refineries side by side operated by Reliance Industries Limited in Jamnagar, India with a combined production capacity of 1,240,000 barrels per day (197,000 m^3/d) (J-1 660,000 bbl/d (105,000 m^3/d), J-2 580,000 bbl/d (92,000 m^3/d). PDVSA's Paraguana refinery complex in Venezuela with a capacity of 956,000 bbl/d (152,000 m^3/d) and SK Energy's Ulsan in South Korea with 840,000 bbl/d (134,000 m^3/d) are the second and third largest, respectively.

Oil refining in the United States

In the 19th century, refineries in the U.S. processed crude oil primarily to recover the kerosene. There was no market for the more volatile fraction, including gasoline, which was considered waste and was often dumped directly into the nearest river. The invention of the automobile shifted the demand to gasoline and diesel, which remain the primary refined products today. Today, national and state legislation requires refineries to meet stringent air and water cleanliness standards. In fact, oil companies in the U.S. perceive obtaining a permit to build a modern refinery to be so difficult and costly that no new refineries have been built (though many have been expanded) in the U.S. since 1976. More than half the refineries that existed in 1981 are now closed due to low utilization rates and accelerating mergers. As a result of these closures total US refinery capacity fell between 1981 to 1995, though the operating capacity stayed fairly constant in that time period at around 15,000,000 barrels per day (2,400,000 m^3/d). Increases in facility size and improvements in efficiencies have offset much of the lost physical capacity of the industry. In 1982 (the earliest data provided), the United States operate 301 refineries with a combined capacity of 17.9 million barrels of crude oil each calendar day. In 2010, there were 149 operable U.S. refineries with a combined capacity of 17.6 million barrels per calendar day.

In 2009 through 2010, as revenue streams in the oil business dried up and profitability of oil refineries fell due to lower demand for product and high reserves of supply preceding the economic recession, oil companies began to close or sell refineries. Due to EPA regulations, the costs associated with closing a refinery are very high, meaning that many former refineries are re-purposed.

Chapter 2

Catalytic Reforming

Catalytic reforming is a chemical process used to convert petroleum refinery naphthas, typically having low octane ratings, into high-octane liquid products called **reformates** which are components of high-octane gasoline (also known as petrol). Basically, the process re-arranges or re-structures the hydrocarbon molecules in the naphtha feedstocks as well as breaking some of the molecules into smaller molecules. The overall effect is that the product reformate contains hydrocarbons with more complex molecular shapes having higher octane values than the hydrocarbons in the naphtha feedstock. In so doing, the process separates hydrogen atoms from the hydrocarbon molecules and produces very significant amounts of byproduct hydrogen gas for use in a number of the other processes involved in a modern petroleum refinery. Other byproducts are small amounts of methane, ethane, propane and butanes.

This process is quite different from and not to be confused with the catalytic steam reforming process used industrially to produce various products such as hydrogen, ammonia and methanol from natural gas, naphtha or other petroleum-derived feedstocks. Nor is this process to be confused with various other catalytic reforming processes that use methanol or biomass-derived feedstocks to produce hydrogen for fuel cells or other uses.

History

In the 1940s, Vladimir Haensel, a research chemist working for Universal Oil Products (UOP), developed a catalytic reforming process using a catalyst containing platinum. Haensel's process was subsequently commercialized by UOP in 1949 for producing a high octane gasoline from low octane naphthas and the UOP process become known as the Platforming process. The first Platforming unit was built in 1949 at the refinery of the Old Dutch Refining Company in Muskegon, Michigan.

In the years since then, many other versions of the process have been developed by some of the major oil companies and other organizations. Today, the large majority of gasoline produced worldwide is derived from the catalytic reforming process.

To name a few of the other catalytic reforming versions that were developed, all of which utilized a platinum and/or a rhenium catalyst:

- Rheniforming: Developed by Chevron Oil Company.
- Powerforming: Developed by Esso Oil Company, now known as ExxonMobil.
- Magnaforming: Developed by Englehard Catalyst Company and Atlantic Richfield Oil Company.
- Ultraforming: Developed by Standard Oil of Indiana, now a part of the British Petroleum Company.
- Houdriforming: Developed by the Houdry Process Corporation.
- CCR Platforming: A Platforming version, designed for continuous catalyst regeneration, developed by UOP.
- Octanizing: A catalytic reforming version developed by Axens, a subsidiary of Institut francais du petrole (IFP), designed for continuous catalyst regeneration.

Chemistry

Before describing the reaction chemistry of the catalytic reforming process as used in petroleum refineries, the typical naphthas used as catalytic reforming feedstocks will be discussed.

Typical naphtha feedstocks

A petroleum refinery includes many unit operations and unit processes. The first unit operation in a refinery is the continuous distillation of the petroleum crude oil being refined. The overhead liquid distillate is called naphtha and will become a major component of the refinery's gasoline (petrol) product after it is further processed through a catalytic hydrodesulfurizer to remove sulfur-containing hydrocarbons and a catalytic reformer to reform its hydrocarbon molecules into more complex molecules with a higher octane rating value. The naphtha is a mixture of very many different hydrocarbon compounds. It has an initial boiling point of about 35 °C and a final boiling point of about 200 °C, and it contains paraffin, naphthene (cyclic paraffins) and aromatic hydrocarbons ranging from those containing 4 carbon atoms to those containing about 10 or 11 carbon atoms.

The naphtha from the crude oil distillation is often further distilled to produce a "light" naphtha containing most (but not all) of the hydrocarbons with 6 or less carbon atoms and a "heavy" naphtha containing most (but not all) of the hydrocarbons with more than 6 carbon atoms. The heavy naphtha has an initial boiling point of about 140 to 150 °C and a final boiling point of about 190 to 205 °C. The naphthas derived from the distillation of crude oils are referred to as "straight-run" naphthas.

It is the straight-run heavy naphtha that is usually processed in a catalytic reformer because the light naphtha has molecules with 6 or less carbon atoms which, when reformed, tend to crack into butane and lower molecular weight hydrocarbons which are not useful as high-octane gasoline blending components. Also, the molecules with 6 carbon atoms tend to form aromatics which is undesirable because governmental environmental regulations in a number of countries limit the amount of aromatics (most particularly benzene) that gasoline may contain.

It should be noted that there are a great many petroleum crude oil sources worldwide and each crude oil has its own unique composition or "assay". Also, not all refineries process the same crude oils and each refinery produces its own straight-run naphthas with their own unique initial and final boiling points. In other words, naphtha is a generic term rather than a specific term.

The table just below lists some fairly typical straight-run heavy naphtha feedstocks, available for catalytic reforming, derived from various crude oils. It can be seen that they differ significantly in their content of paraffins, naphthenes and aromatics:

Typical Heavy Naphtha Feedstocks

Crude oil name ⇒	**Barrow Island**	**Mutineer-Exeter**	**CPC Blend**	**Draugen**
Location ⇒	**Australia**	**Australia**	**Kazakhstan**	**North Sea**
Initial boiling point, °C	149	140	149	150
Final boiling point, °C	204	190	204	180
Paraffins, liquid volume %	46	62	57	38
Naphthenes, liquid volume %	42	32	27	45
Aromatics, liquid volume %	12	6	16	17

Some refinery naphthas include olefinic hydrocarbons, such as naphthas derived from the fluid catalytic cracking and coking processes used in many refineries. Some refineries may also desulfurize and catalytically reform those naphthas. However, for the most part, catalytic reforming is mainly used on the straight-run heavy naphthas, such as those in the above table, derived from the distillation of crude oils.

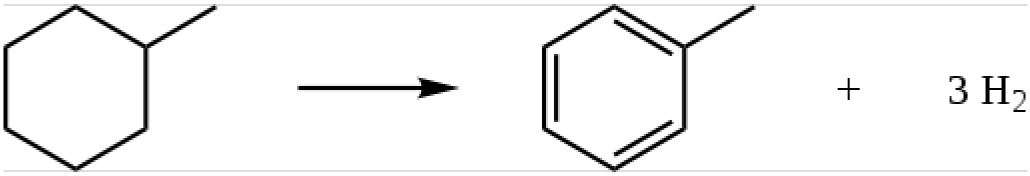
The reaction chemistry

There are a good many chemical reactions that occur in the catalytic reforming process, all of which occur in the presence of a catalyst and a high partial pressure of hydrogen. Depending upon the type or version of catalytic reforming used as well as the desired reaction severity, the reaction conditions range from temperatures of about 495 to 525 °C and from pressures of about 5 to 45 atm.

The commonly used catalytic reforming catalysts contain noble metals such as platinum and/or rhenium, which are very susceptible to poisoning by sulfur and nitrogen compounds. Therefore, the naphtha feedstock to a catalytic reformer is always pre-processed in a hydrodesulfurization unit which removes both the sulfur and the nitrogen compounds.

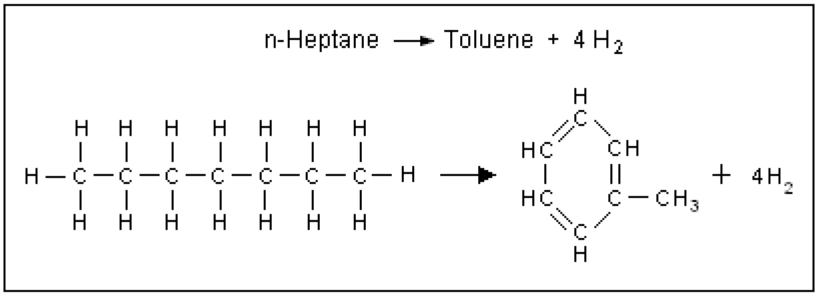
The four major catalytic reforming reactions are:

1: The dehydrogenation of naphthenes to convert them into aromatics as exemplified in the conversion methylcyclohexane (a naphthene) to toluene (an aromatic), as shown below:

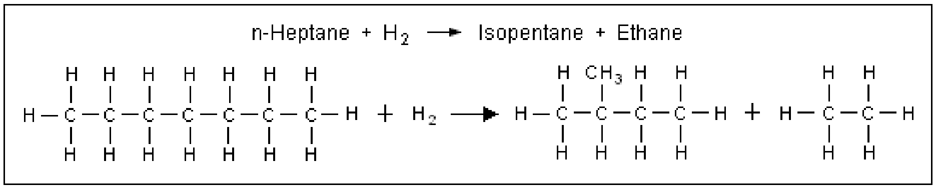


2: The isomerization of normal paraffins to isoparaffins as exemplified in the conversion of normal octane to 2,5-Dimethylhexane (an isoparaffin), as shown below:

3: The dehydrogenation and aromatization of paraffins to aromatics (commonly called dehydrocyclization) as exemplified in the conversion of normal heptane to toluene, as shown below:



4: The hydrocracking of paraffins into smaller molecules as exemplified by the cracking of normal heptane into isopentane and ethane, as shown below:



The hydrocracking of paraffins is the only one of the above four major reforming reactions that consumes hydrogen. The isomerization of normal paraffins does not consume or produce hydrogen. However, both the dehydrogenation of naphthenes and the dehydrocyclization of paraffins produce hydrogen. The overall net production of hydrogen in the catalytic reforming of petroleum naphthas ranges from about 50 to 200 cubic meters of hydrogen gas (at 0 °C and 1 atm) per cubic meter of liquid naphtha feedstock. In the United States customary units, that is equivalent to 300 to 1200 cubic feet of hydrogen gas (at 60 °F and 1 atm) per barrel of liquid naphtha feedstock. In many petroleum refineries, the net hydrogen produced in catalytic reforming supplies a significant part of the hydrogen used elsewhere in the refinery (for example, in hydrodesulfurization processes). The hydrogen is also necessary in order to hydrogenolyze any polymers that form on the catalyst.

Process description

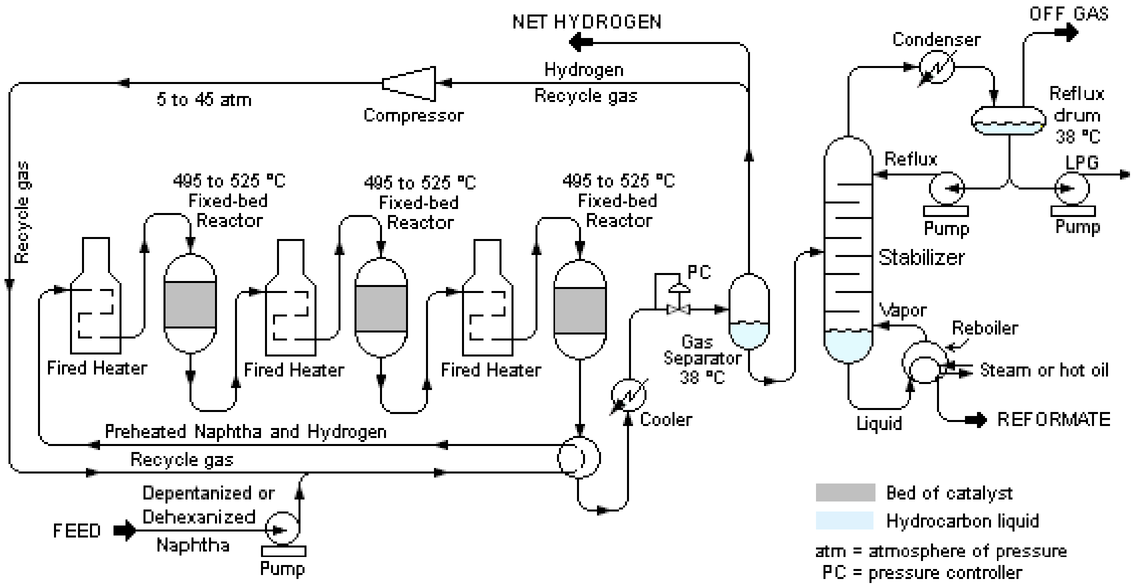
The most commonly used type of catalytic reforming unit has three reactors, each with a fixed bed of catalyst, and all of the catalyst is regenerated *in situ* during routine catalyst regeneration shutdowns which occur approximately once each 6 to 24 months. Such a unit is referred to as a semi-regenerative catalytic reformer (SRR).

Some catalytic reforming units have an extra *spare* or *swing* reactor and each reactor can be individually isolated so that any one reactor can be undergoing in situ regeneration while the other reactors are in operation. When that reactor is regenerated, it replaces another reactor which, in turn, is isolated so that it can then be regenerated. Such units, referred to as *cyclic* catalytic reformers, are not very common. Cyclic catalytic reformers serve to extend the period between required shutdowns.

The latest and most modern type of catalytic reformers are called continuous catalyst regeneration reformers (CCR). Such units are characterized by continuous in-situ regeneration of part of the catalyst in a special regenerator, and by continuous addition of the regenerated catalyst to the operating reactors. As of 2006, two CCR versions available: UOP's CCR Platformer process and Axen's Octanizing process. The installation and use of CCR units is rapidly increasing.

Many of the earliest catalytic reforming units (in the 1950s and 1960's) were non-regenerative in that they did not perform in situ catalyst regeneration. Instead, when needed, the aged catalyst was replaced by fresh catalyst and the aged catalyst was shipped to catalyst manufacturer's to be either regenerated or to recover the platinum content of the aged catalyst. Very few, if any, catalytic reformers currently in operation are non-regenerative.

The process flow diagram below depicts a typical semi-regenerative catalytic reforming unit.



Schematic diagram of a typical semi-regenerative catalytic reformer unit in a petroleum refinery

The liquid feed (at the bottom left in the diagram) is pumped up to the reaction pressure (5 to 45 atm) and is joined by a stream of hydrogen-rich recycle gas. The resulting liquid-gas mixture is preheated by flowing through a heat exchanger. The preheated feed mixture is then totally vaporized and heated to the reaction temperature (495 to 520 °C) before the vaporized reactants enter the first reactor. As the vaporized reactants flow through the fixed bed of catalyst in the reactor, the major reaction is the dehydrogenation of naphthenes to aromatics (as described earlier herein) which is highly endothermic and results in a large temperature decrease between the inlet and outlet of the reactor. To maintain the required reaction temperature and the rate of reaction, the vaporized stream is reheated in the second fired heater before it flows through the second reactor. The temperature again decreases across the second reactor and the vaporized stream must again be reheated in the third fired heater before it flows through the third reactor. As the vaporized stream proceeds through the three reactors, the reaction rates decrease and the reactors therefore become larger. At the same time, the amount of reheat required between the reactors becomes smaller. Usually, three reactors are all that is required to provide the desired performance of the catalytic reforming unit.

Some installations use three separate fired heaters as shown in the schematic diagram and some installations use a single fired heater with three separate heating coils.

The hot reaction products from the third reactor are partially cooled by flowing through the heat exchanger where the feed to the first reactor is preheated and then flow through a water-cooled heat exchanger before flowing through the pressure controller (PC) into the gas separator.

Most of the hydrogen-rich gas from the gas separator vessel returns to the suction of the recycle hydrogen gas compressor and the net production of hydrogen-rich gas from the reforming reactions is exported for use in the other refinery processes that consume hydrogen (such as hydrodesulfurization units and/or a hydrocracker unit).

The liquid from the gas separator vessel is routed into a fractionating column commonly called a *stabilizer*. The overhead offgas product from the stabilizer contains the byproduct methane, ethane, propane and butane gases produced by the hydrocracking reactions as explained in the above discussion of the reaction chemistry of a catalytic reformer, and it may also contain some small amount of hydrogen. That offgas is routed to the refinery's central gas processing plant for removal and recovery of propane and butane. The residual gas after such processing becomes part of the refinery's fuel gas system.

The bottoms product from the stabilizer is the high-octane liquid reformate that will become a component of the refinery's product gasoline.

Catalysts and mechanisms

Most catalytic reforming catalysts contain platinum or rhenium on a silica or silica-alumina support base, and some contain both platinum and rhenium. Fresh catalyst is chlorided (chlorinated) prior to use.

The noble metals (platinum and rhenium) are considered to be catalytic sites for the dehydrogenation reactions and the chlorinated alumina provides the acid sites needed for isomerization, cyclization and hydrocracking reactions.

The activity (i.e., effectiveness) of the catalyst in a semi-regenerative catalytic reformer is reduced over time during operation by carbonaceous coke deposition and chloride loss. The activity of the catalyst can be periodically regenerated or restored by in situ high temperature oxidation of the coke followed by chlorination. As stated earlier herein, semi-regenerative catalytic reformers are regenerated about once per 6 to 24 months.

Normally, the catalyst can be regenerated perhaps 3 or 4 times before it must be returned to the manufacturer for reclamation of the valuable platinum and/or rhenium content.

Chapter 3

Fluid Catalytic Cracking

Fluid catalytic cracking (FCC) is the most important conversion process used in petroleum refineries. It is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils to more valuable gasoline, olefinic gases and other products. Cracking of petroleum hydrocarbons was originally done by thermal cracking which has been almost completely replaced by catalytic cracking because it produces more gasoline with a higher octane rating. It also produces byproduct gases that are more olefinic, and hence more valuable, than those produced by thermal cracking.

The feedstock to an FCC is usually that portion of the crude oil that has an initial boiling point of 340 °C or higher at atmospheric pressure and an average molecular weight ranging from about 200 to 600 or higher. This portion of crude oil is often referred to as heavy gas oil. The FCC process vaporizes and breaks the long-chain molecules of the high-boiling hydrocarbon liquids into much shorter molecules by contacting the feedstock, at high temperature and moderate pressure, with a fluidized powdered catalyst.

In effect, refineries use fluid catalytic cracking to correct the imbalance between the market demand for gasoline and the excess of heavy, high boiling range products resulting from the distillation of crude oil.

As of 2006, FCC units were in operation at 400 petroleum refineries worldwide and about one-third of the crude oil refined in those refineries is processed in an FCC to produce high-octane gasoline and fuel oils. During 2007, the FCC units in the United States processed a total of 5,300,000 barrels (834,300,000 litres) per day of feedstock and FCC units worldwide processed about twice that amount.

Flow diagram and process description

The modern FCC units are all continuous processes which operate 24 hours a day for as much as 2 to 3 years between shutdowns for routine maintenance.

There are a number of different proprietary designs that have been developed for modern FCC units. Each design is available under a license that must be purchased from the design developer by any petroleum refining company desiring to construct and operate an FCC of a given design.

Basically, there are two different configurations for an FCC unit: the "stacked" type where the reactor and the catalyst regenerator are contained in a single vessel with the reactor above the catalyst regenerator and the "side-by-side" type where the reactor and catalyst regenerator are in two separate vessels. These are the major FCC designers and licensors:

Side-by-side configuration:

- CB&I Lummus
- ExxonMobil Research and Engineering (EMRE)
- Shell Global Solutions International
- Stone & Webster Engineering Corporation (The Shaw Group) / Institut Francais Petrole (IFP)
- Universal Oil Products (UOP) - currently fully owned subsidiary of Honeywell

Stacked configuration:

- Kellogg Brown & Root (KBR)

Each of the proprietary design licensors claims to have unique features and advantages.

Reactor and Regenerator

The schematic flow diagram of a typical modern FCC unit in Figure 1 below is based upon the "side-by-side" configuration. The preheated high-boiling petroleum feedstock (at about 315 to 430 °C) consisting of long-chain hydrocarbon molecules is combined with recycle slurry oil from the bottom of the distillation column and injected into the *catalyst riser* where it is vaporized and cracked into smaller molecules of vapor by contact and mixing with the very hot powdered catalyst from the regenerator. All of the cracking reactions take place in the catalyst riser. The hydrocarbon vapors "fluidize" the powdered catalyst and the mixture of hydrocarbon vapors and catalyst flows upward to enter the *reactor* at a temperature of about 535 °C and a pressure of about 1.72 bar.

The reactor is in fact merely a vessel in which the cracked product vapors are: (a) separated from the so-called *spent catalyst* by flowing through a set of two-stage cyclones within the reactor and (b) the *spent catalyst* flows downward through a steam stripping section to remove any hydrocarbon vapors before the spent catalyst returns to the *catalyst regenerator*. The flow of spent catalyst to the regenerator is regulated by a *slide valve* in the spent catalyst line.

Since the cracking reactions produce some carbonaceous material (referred to as *coke*) that deposits on the catalyst and very quickly reduces the catalyst reactivity, the catalyst is regenerated by burning off the deposited coke with air blown into the regenerator. The regenerator operates at a temperature of about 715 °C and a pressure of about 2.41 barg. The combustion of the coke is exothermic and it produces a large amount of heat that is partially absorbed by the regenerated catalyst and provides the heat required for the vaporization of the feedstock and the endothermic cracking reactions that take place in the catalyst riser. For that reason, FCC units are often referred to as being *heat balanced*.

The hot catalyst (at about 715 °C) leaving the regenerator flows into a *catalyst withdrawal well* where any entrained combustion flue gases are allowed to escape and flow back into the upper part to the regenerator. The flow of regenerated catalyst to the feedstock injection point below the catalyst riser is regulated by a slide valve in the regenerated catalyst line. The hot flue gas exits the regenerator after passing through multiple sets of two-stage cylones that remove entrained catalyst from the flue gas,

The amount of catalyst circulating between the regenerator and the reactor amounts to about 5 kg per kg of feedstock which is equivalent to about 4.66 kg per litre of feedstock. Thus, an FCC unit processing 75,000 barrels/day (12,000,000 litres/day) will circulate about 55,900 metric tons per day of catalyst.

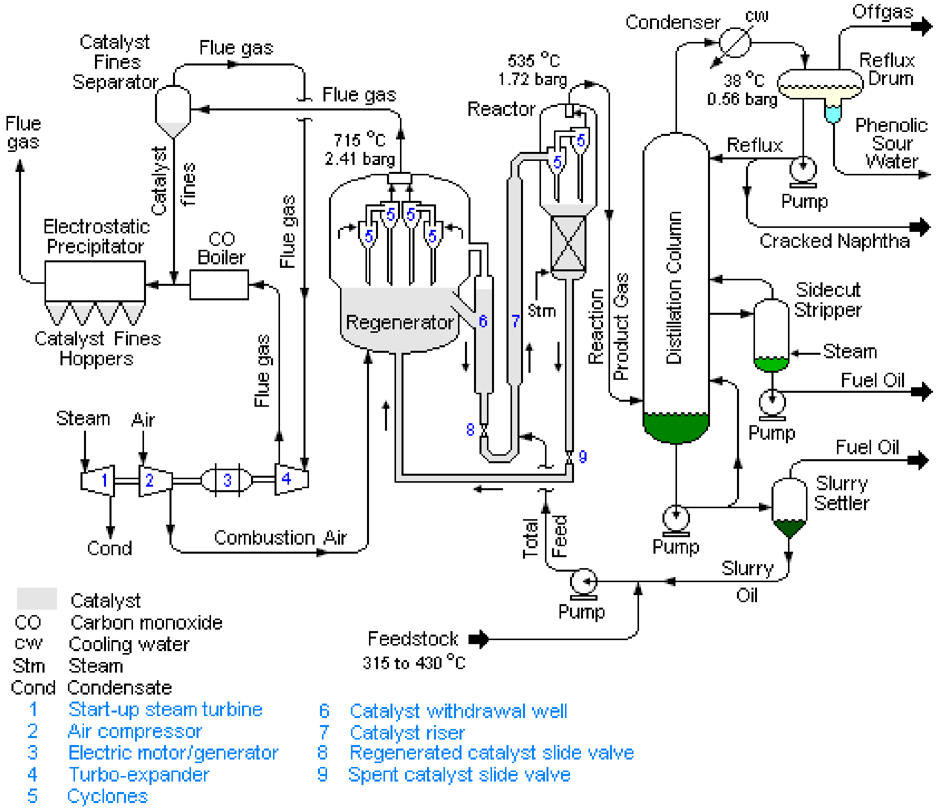


Figure 1: A schematic flow diagram of a Fluid Catalytic Cracking unit as used in petroleum refineries

Distillation column

The reaction product vapors (at 535 °C and a pressure of 1.72 barg) flow from the top of the reactor to the bottom section of the distillation column (commonly referred to as the *main fractionator*) where they are distilled into the FCC end products of cracked naphtha, fuel oil and offgas. After further processing for removal of sulfur compounds, the cracked naphtha becomes a high-octane component of the refinery's blended gasolines.

The main fractionator offgas is sent to what is called a *gas recovery unit* where it is separated into butanes and butylenes, propane and propylene, and lower molecular weight gases (hydrogen, methane, ethylene and ethane). Some FCC gas recovery units may also separate out some of the ethane and ethylene.

Although the schematic flow diagram above depicts the main fractionator as having only one sidecut stripper and one fuel oil product, many FCC main fractionators have two sidecut strippers and produce a light fuel oil and a heavy fuel oil. Likewise, many FCC main fractionators produce a light cracked naphtha and a heavy cracked naphtha. The terminology *light* and *heavy* in this context refers to the product boiling ranges, with light products having a lower boiling range than heavy products.

The bottom product oil from the main fractionator contains residual catalyst particles which were not completely removed by the cyclones in the top of the reactor. For that reason, the bottom product oil is referred to as a *slurry oil*. Part of that slurry oil is recycled back into the main fractionator above the entry point of the hot reaction product vapors so as to cool and partially condense the reaction product vapors as they enter the main fractionator. The remainder of the slurry oil is pumped through a slurry settler. The bottom oil from the slurry settler contains most of the slurry oil catalyst particles and is recycled back into the catalyst riser by combining it with the FCC feedstock oil. The so-called *clarified slurry oil* or decant oil is withdrawn from the top of slurry settler for use elsewhere in the refinery, as a heavy fuel oil blending component, or as carbon black feedstock.

Regenerator flue gas

Depending on the choice of FCC design, the combustion in the regenerator of the coke on the spent catalyst may or may not be complete combustion to carbon dioxide (CO_2). The combustion air flow is controlled so as to provide the desired ratio of carbon monoxide (CO) to carbon dioxide for each specific FCC design.

In the design shown in Figure 1, the coke has only been partially combusted to CO_2. The combustion flue gas (containing CO and CO_2) at 715 °C and at a pressure of 2.41 barg is routed through a secondary catalyst separator containing *swirl tubes* designed to remove 70 to 90 percent of the particulates in the flue gas leaving the regenerator. This is required to prevent erosion damage to the blades in the turbo-expander that the flue gas is next routed through.

The expansion of flue gas through a turbo-expander provides sufficient power to drive the regenerator's combustion air compressor. The electrical motor-generator can consume or produce electrical power. If the expansion of the flue gas does not provide enough power to drive the air compressor, the electric motor/generator provides the needed additional power. If the flue gas expansion provides more power than needed to drive the air compressor, than the electric motor/generator converts the excess power into electric power and exports it to the refinery's electrical system.

The expanded flue gas is then routed through a steam-generating boiler (referred to as a *CO boiler*) where the carbon monoxide in the flue gas is burned as fuel to provide steam for use in the refinery as well as to comply with any applicable environmental regulatory limits on carbon monoxide emissions.

The flue gas is finally processed through an electrostatic precipitator (ESP) to remove residual particulate matter to comply with any applicable environmental regulations regarding particulate emissions. The ESP removes particulates in the size range of 2 to 20 microns from the flue gas.

The steam turbine in the flue gas processing system (shown in the above diagram) is used to drive the regenerator's combustion air compressor during start-ups of the FCC unit until there is sufficient combustion flue gas to take over that task.

Chemistry

Before delving into the chemistry involved in catalytic cracking, it will be helpful to briefly discuss the composition of petroleum crude oil.

Petroleum crude oil consists primarily of a mixture of hydrocarbons with small amounts of other organic compounds containing sulfur, nitrogen and oxygen. The crude oil also contains small amounts of metals such as copper, iron, nickel and vanadium.

Table 1

Carbon	83-87%
Hydrogen	10-14%
Nitrogen	0.1-2%
Oxygen	0.1-1.5%
Sulfur	0.5-6%
Metals	< 0.1%

The elemental composition ranges of crude oil are summarized in Table 1 and the hydrocarbons in the crude oil can be classified into three types:

- Paraffins or alkanes: saturated straight-chain or branched hydrocarbons, without any ring structures

- Naphthenes or cycloalkanes: saturated hydrocarbons having one or more ring structures with one or more side-chain paraffins
- Aromatics: hydrocarbons having one or more unsaturated ring structures such as benzene or unsaturated polycyclic ring structures such as naphthalene or phenanthrene, any of which may also have one or more side-chain paraffins.

Olefins or alkenes, which are unsaturated straight-chain or branched hydrocarbons, do not occur naturally in crude oil.

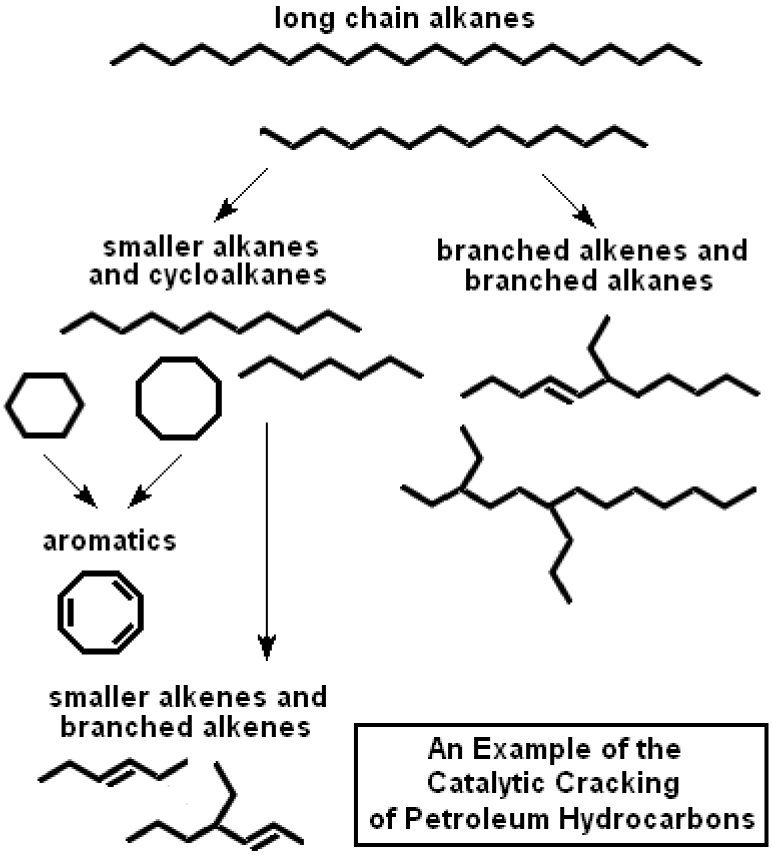


Figure 2: Diagrammatic example of the catalytic cracking of petroleum hydrocarbons

In plain language, the fluid catalytic cracking process breaks large hydrocarbon molecules into smaller molecules by contacting them with powdered catalyst at a high temperature and moderate pressure which first vaporizes the hydrocarbons and then breaks them. The cracking reactions occur in the vapor phase and start immediately when the feedstock is vaporized in the catalyst riser.

Figure 2 is a very simplified schematic diagram that exemplifies how the process breaks high boiling, straight-chain alkane (paraffin) hydrocarbons into smaller straight-chain alkanes as well as branched-chain alkanes, branched alkenes (olefins) and cycloalkanes (naphthenes). The breaking of the large hydrocarbon molecules into smaller molecules is more technically referred to by organic chemists as *scission* of the carbon-to-carbon bonds.

As depicted in Figure 2, some of the smaller alkanes are then broken and converted into even smaller alkenes and branched alkenes such as the gases ethylene, propylene, butylenes and isobutylenes. Those olefinic gases are valuable for use as petrochemical feedstocks. The propylene, butylene and isobutylene are also valuable feedstocks for certain petroleum refining processes that convert them into high-octane gasoline blending components.

As also depicted in Figure 2, the cycloalkanes (naphthenes) formed by the initial breakup of the large molecules are further converted to aromatics such as benzene, toluene and xylenes which boil in the gasoline boiling range and have much higher octane ratings than alkanes.

By no means does Figure 2 include all the chemistry of the primary and secondary reactions taking place in the fluid catalytic process. There are a great many other reactions involved.

Catalysts

Modern FCC catalysts are fine powders with a bulk density of 0.80 to 0.96 g/cc and having a particle size distribution ranging from 10 to 150 μm and an average particle size of 60 to 100 μm. The design and operation of an FCC unit is largely dependent upon the chemical and physical properties of the catalyst. The desirable properties of an FCC catalyst are:

- Good stability to high temperature and to steam
- High activity
- Large pore sizes
- Good resistance to attrition
- Low coke production

A modern FCC catalyst has four major components: crystalline zeolite, matrix, binder and filler. Zeolite is the primary active component and can range from about 15 to 50 weight percent of the catalyst. The zeolite used in FCC catalysts is referred to as *faujasite* or as *Type Y* and is composed of silica and alumina tetrahedra with each tetrahedron having either an aluminum or a silicon atom at the center and four oxygen atoms at the corners. It is a molecular sieve with a distinctive lattice structure that allows only a certain size range of hydrocarbon molecules to enter the lattice. In general, the zeolite does not allow molecules larger than 8 to 10 nm (i.e., 80 to 90 angstroms) to enter the lattice.

The catalytic sites in the zeolite are strong acids (equivalent to 90% sulfuric acid) and provide most of the catalytic activity. The acidic sites are provided by the alumina tetrahedra. The aluminum atom at the center of each alumina tetrahedra is at a +3 oxidation state surrounded by four oxygen atoms at the corners which are shared by the neighboring tetrahedra. Thus, the net charge of the alumina tetrahedra is -1 which is balanced by a sodium ion during the production of the catalyst. The sodium ion is later replaced by an ammonium ion which is vaporized when the catalyst is subsequently dried, resulting in the formation of Lewis and Brønsted acidic sites. In some FCC catalysts, the Brønsted sites may be later replaced by rare earth metals such as cerium and lanthanum to provide alternative activity and stability levels.

The matrix component of an FCC catalyst contains amorphous alumina which also provides catalytic activity sites and in larger pores that allows entry for larger molecules than does the zeolite. That enables the cracking of higher-boiling, larger feedstock molecules than are cracked by the zeolite.

The binder and filler components provide the physical strength and integrity of the catalyst. The binder is usually silica sol and the filler is usually a clay (kaolin).

Nickel, vanadium, iron, copper and other metal contaminants, present in FCC feedstocks in the parts per million range, all have detrimental effects on the catalyst activity and performance. Nickel and vanadium are particularly troublesome. There are a number of methods for mitigating the effects of the contaminant metals:

- Avoid feedstocks with high metals content: This seriously hampers a refinery's flexibility to process various crude oils or purchased FCC feedstocks.
- Feedstock feed pretreatment: Hydrodesulfurization of the FCC feedstock removes some of the metals and also reduces the sulfur content of the FCC products. However, this is quite a costly option.
- Increasing fresh catalyst addition: All FCC units withdraw some of the circulating *equilibrium catalyst* as spent catalyst and replaces it with fresh catalyst in order to maintain a desired level of activity. Increasing the rate of such exchange lowers the level of metals in the circulating *equilibrium catalyst*, but this is also quite a costly option.
- Demetallization: The commercial proprietary *Demet Process* removes nickel and vanadium from the withdrawn spent catalyst. The nickel and vanadium are converted to chlorides which are then washed out of the catalyst. After drying, the demetallized catalyst is recycled into the circulating catalyst. Removals of about 95 percent nickel removal and 67 to 85 percent vanadium have been reported. Despite that, the use of the Demet process has not become widespread, perhaps because of the high capital expenditure required.
- Metals passivation: Certain materials can be used as additives which can be impregnated into the catalyst or added to the FCC feedstock in the form of metal-organic compounds. Such materials react with the metal contaminants and passivate the contaminants by forming less harmful compounds that remain on the catalyst. For example, antimony and bismuth are effective in passivating nickel and tin is effective in passivating vanadium. A number of proprietary passivation processes are available and fairly widely used.

The major suppliers of FCC catalysts worldwide include Albemarle Corporation, W.R. Grace Company and BASF Catalysts (formerly Engelhard).

History

The first commercial use of catalytic cracking occurred in 1915 when Almer M. McAfee of the Gulf Refining Company developed a batch process using aluminum chloride (a Friedel Crafts catalyst known since 1877) to catalytically crack heavy petroleum oils. However, the prohibitive cost of the catalyst prevented the widespread use of McAfee's process at that time.

In 1922, a French mechanical engineer named Eugene Jules Houdry and a French pharmacist named E.A. Prudhomme set up a laboratory near Paris to develop a catalytic process for converting lignite coal to gasoline. Supported by the French government, they built a small demonstration plant in 1929 that processed about 60 tons per day of lignite coal. The results indicated that the process was not economically viable and it was subsequently shutdown.

Houdry had found that Fuller's Earth, a clay mineral containing aluminosilicate (Al_2SiO_6), could convert oil derived from the lignite to gasoline. He then began to study the catalysis of petroleum oils and had some success in converting vaporized petroleum oil to gasoline. In 1930, the Vacuum Oil Company invited him to come to the United States and he moved his laboratory to Paulsboro, New Jersey.

In 1931, the Vacuum Oil Company merged with Standard Oil of New York (Socony) to form the Socony-Vacuum Oil Company. In 1933, a small Houdry process unit processing 200 barrels per day (32,000 litres per day) of petroleum oil. Because of the economic depression of the early 1930s, Socony-Vacuum was no longer able to support Houdry's work and gave him permission to seek help elsewhere.

In 1933, Houdry and Socony-Vacuum joined with Sun Oil Company in developing the Houdry process. Three years later, in 1936, Socony-Vacuum converted an older thermal cracking unit in their Paulsboro refinery in New Jersey to a small demonstration unit using the Houdry process to catalytically crack 2,000 barrels per day (318,000 litres per day) of petroleum oil.

In 1937, Sun Oil began operation of a new Houdry unit processing 12,000 barrels per day (2,390,000 litres per day) in their Marcus Hook refinery in Pennsylvania. The Houdry process at that time used reactors with a fixed bed of catalyst and was a semi-batch operation involving multiple reactors with some of the reactors in operation while other reactors were in various stages of regenerating the catalyst. Motor-driven valves were used to switch the reactors between online operation and offline regeneration and a cycle timer managed the switching. Almost 50 percent of the cracked product was gasoline as compared with about 25 percent from the thermal cracking processes.

By 1938, when the Houdry process was publicly announced, Socony-Vacuum had eight additional units under construction. Licensing the process to other companies also began and by 1940 there were 14 Houdry units in operation processing 140,000 barrels per day (22,300,000 litres per day).

The next major step was to develop a continuous process rather than the semi-batch Houdry process. That step was implemented by advent of the moving-bed process known as the Thermafor Catalytic Cracking (TCC) process which used a bucket conveyor-elevator to move the catalyst from the regeneration kiln to the separate reactor section. A small demonstration TCC unit was built in Socony-Vacuum's Paulsboro refinery in 1941 and operated successfully. Then a full-scale commercial TCC unit processing 10,000 barrels per day (1,590,000 litres per day) began operation in 1943 at the Beaumont, Texas refinery of Magnolia Oil Company, an affiliate of Socony-Vacuum. By the end of World War II in 1945, the processing capacity of the TCC units in operation was about 300,000 barrels per day (47,700,000 litres per day).

It is said that the Houdry and TCC units were a major factor in the winning of World War II by supplying the high-octane gasoline needed by the air forces of Great Britain and the United States.

In the years immediately after World War II, the Houdriflow process and the air-lift TCC process were developed as improved variations on the moving-bed theme. Just like Houdry's fixed-bed reactors, the moving-bed designs were prime examples of good engineering by developing a method of continuously moving the catalyst between the reactor and regeneration sections.

This fluid catalytic cracking process had first been investigated in the 1920s by Standard Oil of New Jersey, but research on it was abandoned during the economic depression years of 1929 to 1939. In 1938, when the success of Houdry’s process had become apparent, Standard Oil of New Jersey resumed the project as part of a consortium of that include five oil companies (Standard Oil of New Jersey, Standard Oil of Indiana, Anglo-Iranian Oil, Texas Oil and Dutch Shell), two engineering-construction companies (M.W. Kellogg and Universal Oil Products) and a German chemical company (I.G. Farben). The consortium was called Catalytic Research Associates (CRA) and its purpose was to develop a catalytic cracking process which would not impinge on Houdry's patents.

Chemical engineering professors Warren K. Lewis and Edwin R. Gilliland of the Massachusetts Institute of Technology (MIT) suggested to the CRA researchers that a low velocity gas flow through a powder might "lift" it enough to cause it to flow in a manner similar to a liquid. Focused on that idea of a fluidized catalyst, researchers Donald Campbell, Homer Martin, Eger Murphree and Charles Tyson of the Standard Oil of New Jersey (now Exxon-Mobil Company) developed the first fluidized catalytic cracking unit. Their U.S. Patent No. 2,451,804, *A Method of and Apparatus for Contacting Solids and Gases*, describes their milestone invention. Based on their work, M. W. Kellogg Company constructed a large pilot plant in the Baton Rouge, Louisiana refinery of the Standard Oil of New Jersey. The pilot plant began operation in May 1940.

Based on the success of the pilot plant, the first commercial fluid catalytic cracking plant (known as the Model I FCC) began processing 13,000 barrels per day (2,070,000 litres per day) of petroleum oil in the Baton Rouge refinery on May 25, 1942, just four years after the CRA consortium was formed and in the midst of World War II. A little more than a month later, in July 1942, it was processing 17,000 barrels per day (2,700,000 litres per day). In 1963, that first Model I FCC unit was shut down after 21 years of operation and subsequently dismantled.

In the many decades since the Model I FCC unit began operation, the fixed bed Houdry units have all been shut down as have most of the moving bed units (such as the TCC units) while hundreds of FCC units have been built. During those decades, many improved FCC designs have evolved and cracking catalysts have been greatly improved, but the modern FCC units are essentially the same as that first Model I FCC unit.

Note: All of the refinery and company names in this history section (with the exception of Universal Oil Products) have changed over time by mergers and buyouts. Some have changed a number of times.

Chapter 4

Cracking (Chemistry)

In petroleum geology and chemistry, *cracking* is the process whereby complex organic molecules such as kerogens or heavy hydrocarbons are broken down into simpler molecules such as light hydrocarbons, by the breaking of carbon-carbon bonds in the precursors. The rate of cracking and the end products are strongly dependent on the temperature and presence of catalysts. Cracking is the breakdown of a large alkane into smaller, more useful alkanes and an alkene. Simply put, hydrocarbon cracking is the process of breaking long-chain hydrocarbons into short ones.

Factory of Shukhov cracking process, Baku, USSR, 1934.

History and patents

The thermal cracking method (also known as "Shukhov cracking process") was invented by Russian engineer Vladimir Shukhov and patented in 1891 in the Russian empire, patent no. 12926, November 27, 1891. This process was modified by the American engineer William Merriam Burton and patented as U.S. patent 1,049,667 on June 8, 1908.

In 1924, the delegation of the American "Sinckler Oil" paid a visit to Shukhov. The "Sinckler Oil" firm protested the personal right appropriated by the Rockefeller "Standard Oil" concern on the discovery of oil cracking. It indicated that Burton's patent used by the "Standard Oil" concern was the modified patent of Shukhov. Shukhov proved to the Americans that the Burton's method was just the slightly changed modification of his 1891 patents. However, an agreement between the American companies finally was made not to buy the patent from Soviet Russia.

Applications

Oil refinery cracking processes allow the production of "light" products such as liquified petroleum gas (LPG) and gasoline from heavier crude oil distillation fractions such as gas oils and residues. Fluid catalytic cracking produces a high yield of gasoline and LPG, while hydrocracking is a major source of jet fuel, diesel, naphtha, and LPG.

Thermal cracking is currently used to "upgrade" very heavy fractions ("upgrading", "visbreaking"), or to produce light fractions or distillates, burner fuel and/or petroleum coke. Two extremes of the thermal cracking in terms of product range are represented by the high-temperature process called "steam cracking" or pyrolysis (ca. 750 °C to 900 °C or more) which produces valuable ethylene and other feedstocks for the petrochemical industry, and the milder-temperature delayed coking (ca. 500 °C) which can produce, under the right conditions, valuable needle coke, a highly crystalline petroleum coke used in the production of electrodes for the steel and aluminium industries.

Fluid catalytic cracking

Fluid catalytic cracking is a commonly used process, and a modern oil refinery will typically include a *cat cracker*, particularly at refineries in the U.S., due to the high demand for gasoline. The process was first used in around 1942 and employs a powdered catalyst. During the Second World War, in contrast to the Axis Forces which suffered severe shortages of gasoline and artificial rubber, the Allied Forces were supplied with plentiful supplies of the materials. Initial process implementations were based on low activity alumina catalyst and a reactor where the catalyst particles were suspended in a rising flow of feed hydrocarbons in a fluidized bed.

Aluminum-catalyzed cracking systems are still in use in high school and university laboratories in experiments concerning alkanes and alkenes. The catalyst is usually obtained by crushing pumice stones, which contain mainly aluminium oxide and silica into small, porous pieces. In the laboratory, aluminium oxide (or porous pot) must be heated.

In newer designs, cracking takes place using a very active zeolite-based catalyst in a short-contact time vertical or upward sloped pipe called the "riser". Pre-heated feed is sprayed into the base of the riser via feed nozzles where it contacts extremely hot fluidized catalyst at 1230 °F to 1400 °F (665 °C to 760 °C). The hot catalyst vaporizes the feed and catalyzes the cracking reactions that break down the high molecular weight oil into lighter components including LPG, gasoline, and diesel. The catalyst-hydrocarbon mixture flows upward through the riser for just a few seconds and then the mixture is separated via cyclones. The catalyst-free hydrocarbons are routed to a main fractionator for separation into fuel gas, LPG, gasoline, naphtha, light cycle oils used in diesel and jet fuel, and heavy fuel oil.

During the trip up the riser, the cracking catalyst is "spent" by reactions which deposit coke on the catalyst and greatly reduce activity and selectivity. The "spent" catalyst is disengaged from the cracked hydrocarbon vapors and sent to a stripper where it is contacted with steam to remove hydrocarbons remaining in the catalyst pores. The "spent" catalyst then flows into a fluidized-bed regenerator where air (or in some cases air plus oxygen) is used to burn off the coke to restore catalyst activity and also provide the necessary heat for the next reaction cycle, cracking being an endothermic reaction. The "regenerated" catalyst then flows to the base of the riser, repeating the cycle.

The gasoline produced in the FCC unit has an elevated octane rating but is less chemically stable compared to other gasoline components due to its olefinic profile. Olefins in gasoline are responsible for the formation of polymeric deposits in storage tanks, fuel ducts and injectors. The FCC LPG is an important source of C_3-C_4 olefins and isobutane that are essential feeds for the alkylation process and the production of polymers such as polypropylene.

Hydrocracking

In 1920, a plant for the commercial hydrogenation of brown coal was commissioned at Leuna in Germany.

Hydrocracking is a catalytic cracking process assisted by the presence of an elevated partial pressure of hydrogen gas. Similar to the hydrotreater, the function of hydrogen is the purification of the hydrocarbon stream from sulfur and nitrogen hetero-atoms.

The products of this process are saturated hydrocarbons; depending on the reaction conditions (temperature, pressure, catalyst activity) these products range from ethane, LPG to heavier hydrocarbons consisting mostly of isoparaffins. Hydrocracking is normally facilitated by a bifunctional catalyst that is capable of rearranging and breaking hydrocarbon chains as well as adding hydrogen to aromatics and olefins to produce naphthenes and alkanes.

Major products from hydrocracking are jet fuel and diesel, while also high octane rating gasoline fractions and LPG are produced. All these products have a very low content of sulfur and other contaminants.

It is very common in India, Europe and Asia because those regions have high demand for diesel and kerosene. In the US, Fluid Catalytic Cracking is more common because the demand for gasoline is higher.

Steam cracking

Steam cracking is a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons. It is the principal industrial method for producing the lighter alkenes (or commonly olefins), including ethene (or ethylene) and propene (or propylene).

In steam cracking, a gaseous or liquid hydrocarbon feed like naphtha, LPG or ethane is diluted with steam and briefly heated in a furnace without the presence of oxygen. Typically, the reaction temperature is very high, at around 850°C, but the reaction is only allowed to take place very briefly. In modern cracking furnaces, the residence time is reduced to milliseconds to improve yield, resulting in gas velocities faster than the speed of sound. After the cracking temperature has been reached, the gas is quickly quenched to stop the reaction in a transfer line heat exchanger or inside a quenching header using quench oil.

The products produced in the reaction depend on the composition of the feed, the hydrocarbon to steam ratio and on the cracking temperature and furnace residence time.

Light hydrocarbon feeds such as ethane, LPGs or light naphtha give product streams rich in the lighter alkenes, including ethylene, propylene, and butadiene. Heavier hydrocarbon (full range and heavy naphthas as well as other refinery products) feeds give some of these, but also give products rich in aromatic hydrocarbons and hydrocarbons suitable for inclusion in gasoline or fuel oil. The higher cracking temperature (also referred to as severity) favours the production of ethene and benzene, whereas lower severity produces higher amounts of propene, C4-hydrocarbons and liquid products. The process also results in the slow deposition of coke, a form of carbon, on the reactor walls. This degrades the efficiency of the reactor, so reaction conditions are designed to minimize this. Nonetheless, a steam cracking furnace can usually only run for a few months at a time between de-cokings. Decokes require the furnace to be isolated from the process and then a flow of steam or a steam/air mixture is passed through the furnace coils. This converts the hard solid carbon layer to carbon monoxide and carbon dioxide. Once this reaction is complete, the furnace can be returned to service.

Chemistry

"Cracking" breaks larger molecules into smaller ones, through thermic or catalytic method.

The thermal cracking process follows a homolytic mechanism, that is, bonds break symmetrically and thus pairs of free radicals are formed.

The catalytic cracking process involves the presence of acid catalysts (usually solid acids such as silica-alumina and zeolites) which promote a heterolytic (asymmetric) breakage of bonds yielding pairs of ions of opposite charges, usually a carbocation and the very unstable hydride anion. Carbon-localized free radicals and cations are both highly unstable and undergo processes of chain rearrangement, C-C scission in position beta as in cracking, and intra- and intermolecular hydrogen transfer or hydride transfer. In both types of processes, the corresponding reactive intermediates (radicals, ions) are permanently regenerated, and thus they proceed by a self-propagating chain mechanism. The chain of reactions is eventually terminated by radical or ion recombination.

Thermal cracking

The first thermal cracking method, the Shukhov cracking process, was invented by Russian engineer Vladimir Shukhov, in the Russian empire, Patent No. 12926, November 27, 1891.

William Merriam Burton developed one of the earliest thermal cracking processes in 1912 which operated at 700 - 750 °F (370 - 400 °C) and an absolute pressure of 90 psi (620 kPa) and was known as the *Burton process*. Shortly thereafter, in 1921, C.P. Dubbs, an employee of the Universal Oil Products Company, developed a somewhat more advanced thermal cracking process which operated at 750°F -860 °F (400°C - 460 °C) and was known as the *Dubbs process*. The Dubbs process was used extensively by many refineries until the early 1940s when catalytic cracking came into use.

Modern high-pressure thermal cracking operates at absolute pressures of about 7,000 kPa. An overall process of disproportionation can be observed, where "light", hydrogen-rich products are formed at the expense of heavier molecules which condense and are depleted of hydrogen. The actual reaction is known as homolytic fission and produces alkenes, which are the basis for the economically important production of polymers.

A large number of chemical reactions take place during steam cracking, most of them based on free radicals. Computer simulations aimed at modeling what takes place during steam cracking have included hundreds or even thousands of reactions in their models. The main reactions that take place include:

Initiation reactions, where a single molecule breaks apart into two free radicals. Only a small fraction of the feed molecules actually undergo initiation, but these reactions are necessary to produce the free radicals that drive the rest of the reactions. In steam cracking, initiation usually involves breaking a chemical bond between two carbon atoms, rather than the bond between a carbon and a hydrogen atom..

$$CH_3CH_3 \rightarrow 2\ CH_3\bullet$$

Hydrogen abstraction occurs where a free radical removes a hydrogen atom from another molecule, turning the second molecule into a free radical.

$$CH_3\bullet + CH_3CH_3 \rightarrow CH_4 + CH_3CH_2\bullet$$

Radical decomposition occurs where a free radical breaks apart into two molecules, one an alkene, the other a free radical. This is the process that results in the alkene products of steam cracking.

$CH_3CH_2\bullet \rightarrow CH_2{=}CH_2 + H\bullet$

Radical addition, the reverse of radical decomposition, occurs where a radical reacts with an alkene to form a single, larger free radical. These processes are involved in forming the aromatic products that result when heavier feedstocks are used.

$CH_3CH_2\bullet + CH_2{=}CH_2 \rightarrow CH_3CH_2CH_2CH_2\bullet$

Termination reactions occur when two free radicals react with each other to produce products that are not free radicals. Two common forms of termination are *recombination*, where the two radicals combine to form one larger molecule, and *disproportionation*, where one radical transfers a hydrogen atom to the other, giving an alkene and an alkane.

$CH_3\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2CH_3$
$CH_3CH_2\bullet + CH_3CH_2\bullet \rightarrow CH_2{=}CH_2 + CH_3CH_3$

Thermal cracking is an example of a reaction whose energetics are dominated by entropy ($\Delta S°$) rather than by enthalpy ($\Delta H°$) in the Gibbs Free Energy equation $\Delta G°=\Delta H°-T\Delta S°$. Although the bond dissociation energy D for a carbon-carbon single bond is relatively high (about 375 kJ/mol) and cracking is highly endothermic, the large positive entropy change resulting from the fragmentation of one large molecule into several smaller pieces, together with the extremely high temperature, makes $T\Delta S°$ term larger than the $\Delta H°$ term, thereby favoring the cracking reaction.

Here is an example of cracking of butane CH_3-CH_2-CH_2-CH_3

- 1st possibility (48%): breaking is done on the CH_3-CH_2 bond.

CH_3* / *CH_2-CH_2-CH_3

After a certain number of steps, we will obtain an alkane and an alkene: CH_4 + CH_2=CH-CH_3

- 2nd possibility (38%): breaking is done on the CH_2-CH_2 bond.

CH_3-CH_2* / *CH_2-CH_3

After a certain number of steps, we will obtain an alkane and an alkene from different types: CH_3-CH_3 + CH_2=CH_2

- 3rd possibility (14%): breaking of a C-H bond

After a certain number of steps, we will obtain an alkene and hydrogen gas: CH_2=CH-CH_2-CH_3 + H_2 this is very useful since the catalyst can be recycled.

Chapter 5

Visbreaker

A **visbreaker** is a processing unit in oil refinery whose purpose is to reduce the quantity of residual oil produced in the distillation of crude oil and to increase the yield of more valuable middle distillates (heating oil and diesel) by the refinery. A visbreaker thermally cracks large hydrocarbon molecules in the oil by heating in a furnace to reduce its viscosity and to produce small quantities of light hydrocarbons (LPG and gasoline). The process name of "visbreaker" refers to the fact that the process reduces (i.e., breaks) the viscosity of the residual oil. The process is non-catalytic.

Process objectives

The objectives of visbreaking are:

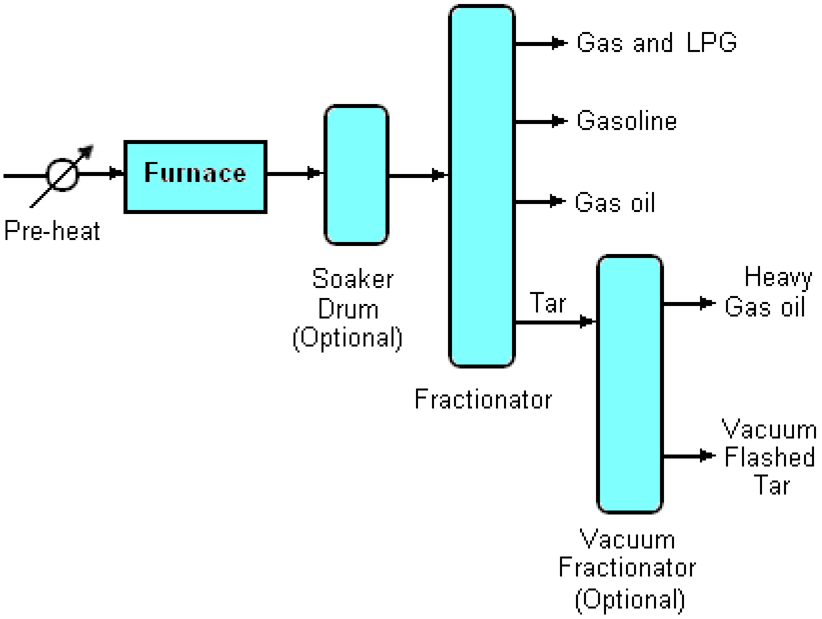
- Reduce the viscosity of the feed stream: Typically this is the residue from vacuum distillation of crude oil but can also be the residue from hydroskimming operations, natural bitumen from seeps in the ground or tar sands, and even certain high viscosity crude oils.

- Reduce the amount of residual fuel oil produced by a refinery: Residual fuel oil is generally regarded as a low value product. Demand for residual fuel continues to decrease as it is replaced in its traditional markets, such as fuel needed to generate steam in power stations, by cleaner burning alternative fuels such as natural gas.

- Increase the proportion of middle distillates in the refinery output: Middle distillate is used as a diluent with residual oils to bring their viscosity down to a marketable level. By reducing the viscosity of the residual stream in a visbreaker, a fuel oil can be made using less diluent and the middle distillate saved can be diverted to higher value diesel or heating oil manufacture.

Technology

Coil visbreaking



A schematic diagram of a Visbreaker unit

The term coil (or furnace) visbreaking is applied to units where the cracking process occurs in the furnace tubes (or "coils"). Material exiting the furnace is quenched to halt the cracking reactions: frequently this is achieved by heat exchange with the virgin material being fed to the furnace, which in turn is a good energy efficiency step, but sometimes a stream of cold oil (usually gas oil) is used to the same effect. The gas oil is recovered and re-used. The extent of the cracking reaction is controlled by regulation of the speed of flow of the oil through the furnace tubes. The quenched oil then passes to a fractionator where the products of the cracking (gas, LPG, gasoline, gas oil and tar) are separated and recovered.

Soaker visbreaking

In soaker visbreaking, the bulk of the cracking reaction occurs not in the furnace but in a drum located after the furnace called the soaker. Here the oil is held at an elevated temperature for a pre-determined period of time to allow cracking to occur before being quenched. The oil then passes to a fractionator. In soaker visbreaking, lower temperatures are used than in coil visbreaking. The comparatively long duration of the cracking reaction is used instead.

Process options

Visbreaker tar can be further refined by feeding it to a vacuum fractionator. Here additional heavy gas oil may be recovered and routed either to catalytic cracking, hydrocracking or thermal cracking units on the refinery. The vacuum-flashed tar (sometimes referred to as pitch) is then routed to fuel oil blending. In a few refinery locations, visbreaker tar is routed to a delayed coker for the production of certain specialist cokes such as anode coke or needle coke.

Soaker visbreaking versus coil visbreaking

From the standpoint of yield, there is little or nothing to choose between the two approaches. However, each offers significant advantages in particular situations:

- **De-coking**: The cracking reaction forms petroleum coke as a byproduct. In coil visbreaking, this lays down in the tubes of the furnace and will eventually lead to fouling or blocking of the tubes. The same will occur in the drum of a soaker visbreaker, though the lower temperatures used in the soaker drum lead to fouling at a much slower rate. Coil visbreakers therefore require frequent de-coking. This is quite labour intensive, but can be developed into a routine where tubes are de-coked sequentially without the need to shutdown the visbreaking operation. Soaker drums require far less frequent attention but their being taken out of service normally requires a complete halt to the operation. Which is the more disruptive activity will vary from refinery to refinery.

- **Fuel Economy**: The lower temperatures used in the soaker approach mean that these units use less fuel. In cases where a refinery buys fuel to support process operations, any savings in fuel consumption could be extremely valuable. In such cases, soaker visbreaking may be advantageous.

Quality and yields

Feed quality and product quality

The quality of the feed going into a visbreaker will vary considerably with the type of crude oil that the refinery is processing. The following is a typical quality for the vacuum distillation residue of Arabian light (a crude oil from Saudi Arabia and widely refined around the world):

Density (kg/l)	**Viscosity at 100 °C (centistokes)**	**Sulphur Content (wt%)**
1.020	930	4.0

Once this material has been run through a visbreaker (and, again, there will be considerable variation from visbreaker to visbreaker as no two will operate under exactly the same conditions) the reduction in viscosity is dramatic:

Density (kg/l)	Viscosity at 100 °C (centistokes)	Sulphur Content (wt%)
1.048	115	4.7

Yields

The yields of the various hydrocarbon products will depend on the "severity" of the cracking operation as determined by the temperature the oil is heated to in the visbreaker furnace. At the low end of the scale, a furnace heating to 425 °C would crack only mildly, while operations at 500 °C would be considered as very severe. Arabian light crude residue when visbroken at 450 °C would yield around 76% (by weight) of tar, 15% middle distillates, 6% gasolines and 3% gas and LPG.

Fuel oil stability

The severity of visbreaker operation is normally limited by the need to produce a visbreaker tar that can be blended to make a stable fuel oil.

Stability in this case is taken to mean the tendency of a fuel oil to produce sediments when stored. These sediments are undesirable as they can quickly foul the filters of pumps used to move the oil necessitating time-consuming maintenance.

Vacuum residue fed to a visbreaker can be considered to be composed of the following:

- **Asphaltenes**: large polycyclic molecules that are suspended in the oil in a coloidal form
- **Resins**: also polycyclic but of a lower molecular weight than asphaltenes
- **Aromatic hydrocarbons**: derivatives of benzene, toluene and xylenes
- **Parafinic hydrocarbons**: alkanes

Visbreaking preferentially cracks aliphatic compounds which have relatively low sulphur contents, low density and high viscosity and the effect of their removal can be clearly seen in the change in quality between feed and product. A too severe cracking in a visbreaker will lead to the asphaltene colloid becoming metastable. Subsequent addition of a diluent to manufacture a finished fuel oil can cause the colloid to break down, preciptating asphaltenes as a sludge. It has been observed that a paraffinic diluent is more likely to cause precipitation than an aromatic one. Stability of fuel oil is assessed using a number of proprietary tests (for example "P" value and SHF tests).

Economics

Viscosity blending

The viscosity blending of two or more liquids having different viscosities is a three-step procedure. The first step is to calculate the Viscosity Blending Index (VBI) of each component of the blend using the following equation (known as a Refutas equation):

$$(1)\quad \mathbf{VBN = 14.534 \times ln[ln(}\boldsymbol{v}\mathbf{ + 0.8)] + 10.975}$$

where **v** is the viscosity in square millimeters per second (mm²/s) or centistokes (cSt) and **ln** is the natural logarithm ($\log_e$). It is important that the viscosity of each component of the blend be obtained at the same temperature.

The next step is to calculate the VBN of the blend, using this equation:

$$(2)\quad \mathbf{VBN_{Blend} = [}\boldsymbol{w}_\mathbf{A} \times \mathbf{VBN_A] + [}\boldsymbol{w}_\mathbf{B} \times \mathbf{VBN_B] + ... + [}\boldsymbol{w}_\mathbf{X} \times \mathbf{VBN_X]}$$

where **w** is the weight fraction (i.e., % ÷ 100) of each component of the blend.

Once the viscosity blending number of a blend has been calculated using equation (2), the final step is to determine the viscosity of the blend by using the invert of equation (1):

$$(3)\quad \mathbf{v = e^{e^{(VBN - 10.975) \div 14.534}} - 0.8}$$

where **VBN** is the viscosity blending number of the blend and **e** is the transcendental number 2.71828, also known as Euler's number.

Example economics for a two-component blend

A marketable fuel oil, such as for fueling a power station, might be required to have a viscosity of 40 centistokes at 100 °C. It might be prepared using either the virgin or visbroken residue described above combined with a distillate diluent ("cutter stock"). Such a cutter stock could typically have a viscosity at 100 °C of 1.3 centistokes. Rearranging equation (2) above for a simple two component blend shows that the percentage of cutterstock required in the blend is found by:

$$(4)\quad \mathbf{\%cutter\ stock = [VBN_{40} - VBN_{residue}] \div [VBN_{cutter\ stock} - VBN_{residue}]}$$

Using the viscosities quoted in the tables above for the residues from Arab Light crude oil and calculating VBNs according to equation (1) gives:

For **virgin** residue (i.e., the unconverted feed to the visbreaker): 27.5% cutter stock in the blend

For **visbroken** residue: 13.3% cutter stock in the blend.

As middle distillates have a far higher value in the market place than fuel oils, it can be seen that the use of a visbreaker will considerably improve the economics of fuel oil manufacture. For example, if the cutter stock is taken to have a value of $300 per tonne and fuel oil $150 per ton (oil prices naturally change quickly, but these prices, and more importantly the differences between them, are not unrealistic), it is a simple matter to calculate the value of the different residues in this example as being:

Virgin residue: $93.1 per tonne

Visbroken residue: $127.0 per tonne

Chapter 6

Merox

Merox is an acronym for mercaptan oxidation. It is a proprietary catalytic chemical process developed by UOP used in oil refineries and natural gas processing plants to remove mercaptans from LPG, propane, butanes, light naphthas, kerosene and jet fuel by converting them to liquid hydrocarbon disulfides.

The Merox process requires an alkaline environment which, in some of the process versions, is provided by an aqueous solution of sodium hydroxide (NaOH), a strong base, commonly referred to as *caustic*. In other versions of the process, the alkalinity is provided by ammonia, which is a weak base.

The catalyst in some versions of the process is a water-soluble liquid. In other versions, the catalyst is impregnated onto charcoal granules.

Processes within oil refineries or natural gas processing plants that remove mercaptans and/or hydrogen sulfide (H_2S) are commonly referred to as *sweetening* processes because they results in products which no longer have the sour, foul odors of mercaptans and hydrogen sulfide. The liquid hydrocarbon disulfides may remain in the sweetened products, they may be used as part of the refinery or natural gas processing plant fuel, or they may be processed further.

The Merox process is usually more economical than using a catalytic hydrodesulfurization process for much the same purpose.

Types of Merox process units

UOP has developed many versions of the Merox process for various different applications:

- Conventional Merox for extraction of mercaptans from LPG, propane, butanes or light naphthas.
- Conventional Merox for sweetening jet fuels and kerosenes.

- Merox for extraction of mercaptans from refinery and natural gases.

- Minalk Merox for sweetening of naphthas. This process continuously injects just a few ppm of caustic into the feed naphtha.

- Caustic-free Merox for sweetening jet fuels and kerosenes. This process injects small amounts of ammonia and water (rather than caustic) into the feed naphtha to provide the required alkalinity.

- Caustic-free Merox for sweetening of naphthas. This process also injects small amounts of ammonia and water (rather than caustic) into the feed naphtha to provide the required alkalinity.

In all of the above Merox versions, the overall oxidation reaction that takes place in converting mercaptans to disulfides is:

$$4\ RSH + O_2 \rightarrow 2RSSR + 2H_2O$$

The most common mercaptans removed are:

- Methanethiol - CH_3SH [m-mercaptan]
- Ethanethiol - C_2H_5SH [e- mercaptan]
- 1-Propanethiol - C_3H_7SH [n-P mercaptan]
- 2-Propanethiol - $CH_3CH(SH)CH_3$ [2C3 mercaptan]
- Butanethiol - C_4H_9SH [n-butyl mercaptan]
- *tert*-Butyl mercaptan - $C(CH_3)_3SH$ [t-butyl mercaptan]
- Pentanethiol - $C_5H_{11}SH$ [pentyl mercaptan]

In some of the above Merox process versions, the catalyst is a liquid. In others, the catalyst is in the form of impregnated charcoal granules.

Process flow diagrams and descriptions of the two conventional versions of the Merox process are presented in the following sections.

Conventional Merox for extracting mercaptans from LPG

The conventional Merox process for extraction and removal of mercaptans from liquefied petroleum gases (LPG), such as propane, butanes and mixtures of propane and butanes, can also be used to extract and remove mercaptans from light naphthas. It is a two-step process. In the first step, the feedstock LPG or light naphtha is contacted in the trayed extractor vessel with an aqueous caustic solution containing UOP's proprietary liquid catalyst. The caustic solution reacts with mercaptans and extracts them. The reaction that takes place in the extractor is:

$$2RSH + 2\ NaOH \rightarrow 2NaSR + 2\ H_2O$$

In the above reaction, RSH is a mercaptan and R signifies an organic group such as a methyl, ethyl, propyl or other group. For example, the ethyl mercaptan (ethanethiol) has the formula C_2H_5SH.

The second step is referred to as regeneration and it involves heating and oxidizing of the caustic solution leaving the extractor. The oxidations results in converting the extracted mercaptans to organic disulfides (RSSR) which are liquids that are water-insoluble and are then separated and decanted from the aqueous caustic solution. The reaction that takes place in the regeneration step is:

$$4NaSR + O_2 + 2H_2O \rightarrow 2RSSR + 4NaOH$$

After decantation of the disulfides, the regenerated "lean" caustic solution is recirculated back to the top of the extractor to continue extracting mercaptans.

The net overall Merox reaction covering the extraction and the regeneration step may be expressed as:

$$4\ RSH + O_2 \rightarrow 2RSSR + 2H_2O$$

The feedstock entering the extractor must be free of any H_2S. Otherwise, any H_2S entering the extractor would react with the circulating caustic solution and interfere with the Merox reactions. Therefore, the feedstock is first "prewashed" by flowing through a batch of aqueous caustic to remove any H_2S. The reaction that takes place in the prewash vessel is:

$$H_2S + NaOH \rightarrow NaSH + H_2O$$

The batch of caustic solution in the prewash vessel is periodically discarded as "spent_caustic" and replaced by fresh caustic as needed.

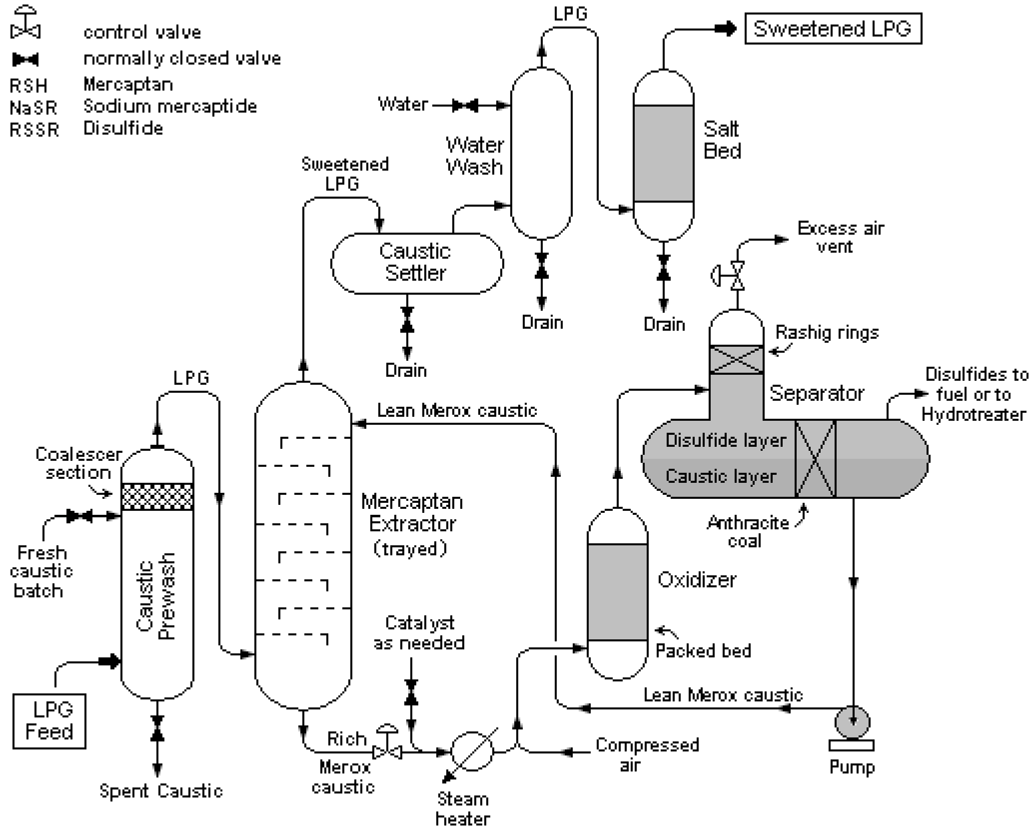
Flow diagram

The flow diagram below depicts the equipment and the flow paths involved in the process. The LPG (or light naphtha) feedstock enters the prewash vessel and flows upward through a batch of caustic which removes any H_2S that may be present in the feedstock. The coalescer at the top of the prewash vessel prevents caustic from being entrained and carried out of the vessel.

The feedstock then enters the mercaptan extractor and flows upward through the contact trays where the LPG intimately contacts the downflowing Merox caustic that extracts the mercaptans from the LPG. The sweetened LPG exits the tower and flows through: a caustic settler vessel to remove any entrained caustic, a water wash vessel to further remove any residual entrained caustic and a vessel containing a bed of rock salt to remove any entrained water. The dry sweetened LPG exits the Merox unit.

The caustic solution leaving the bottom of the mercaptan extractor ("rich" Merox caustic) flows through a control valve which maintains the extractor pressure needed to keep the LPG liquified. It is then injected with UOP's proprietary liquid catalyst (on an as needed basis), flows through a steam-heated heat exchanger and is injected with compressed air before entering the oxidiser vessel where the extracted mercaptans are converted to disulfides. The oxidizer vessel has a packed bed to keep the aqueous caustic and the water-insoluble disulfide well contacted and well mixed.

The caustic-disulfide mixture then flows into the separator vessel where it is allowed to form a lower layer of "lean" Merox caustic and an upper layer of disulfides. The vertical section of the separator is for the disengagement and venting of excess air and includes a Raschig ring section to prevent entrainment of any disulfides in the vented air. The disulfides are withdrawn from the separator and routed to fuel storage or to a hydrotreater unit. The regenerated lean Merox caustic is then pumped back to the top of the extractor for reuse.



CHEMICAL REACTIONS IN LPG MEROX TREATING

Caustic Prewash:
$NaOH + H_2S \rightarrow NaSH + H_2O$

Extraction:
$2RSH + 2NaOH \rightarrow 2NaSR + 2H_2O$

Overall Mercaptan Conversion:
$4RSH + O_2 \rightarrow 2RSSR + 2H_2O$

Regeneration:
$4NaSR + O_2 + 2H_2O \rightarrow 2RSSR + 4NaOH$

Conventional Merox process unit for extracting mercaptans from LPG

Conventional Merox for sweetening jet fuel or kerosene

The conventional Merox process for the removal of mercaptans (i.e., sweetening) of jet fuel or kerosene is a one-step process. The mercaptan oxidation reaction takes place in an alkaline environment as the feedstock jet fuel or kerosene, mixed with compressed air, flows through a fixed bed of catalyst in a reactor vessel. The catalyst consists of charcoal granules that have been impregnated with UOP's proprietary catalyst. The oxidation reaction that takes place is:

$$4\ RSH + O_2 \rightarrow 2RSSR + 2H_2O$$

As is the case with the conventional Merox process for treating LPG, the jet fuel or kerosene sweetening process also requires that the feedstock be prewashed to remove any H_2S that would interfere with the sweetening. The reaction that takes place in the batch caustic prewash vessel is:

$$H_2S + NaOH \rightarrow NaSH + H_2O$$

Flow diagram

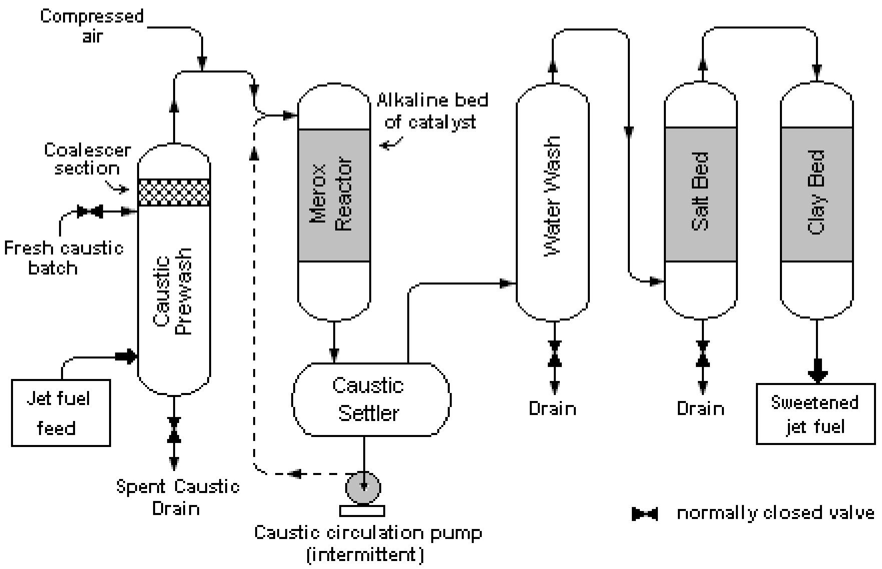
The Merox reactor is a vertical vessel containing a bed of charcoal granules that have been impregnated with the UOP catalyst. The charcoal granules may be impregnated with the catalyst in situ#chemistry and chemical engineering or they may be purchased from UOP as pre-impregnated with the catalyst. An alkaline environment is provided by caustic being pumped into reactor on an intermittent, as needed basis.

The jet fuel or kerosene feedstock from the top of the caustic prewash vessel is injected with compressed air and enters the top of the Merox reactor vessel along with any injected caustic. The mercaptan oxidation reaction takes place as the feedstock percolates downward over the catalyst. The reactor effluent flows through a caustic settler vessel where it forms a bottom layer of aqueous caustic solution and an upper layer of water-insoluble sweetened product.

The caustic solution remains in the caustic settler so that the vessel contains a reservoir for the supply of caustic that is intermittently pumped into the reactor to maintain the alkaline environment.

The sweetened product from the caustic settler vessel flows through a water wash vessel to remove any entrained caustic as well as any other unwanted water-soluble substances, followed by flowing through a salt bed vessel to remove any entrained water and finally through a clay filter vessel. The clay filter removes any oil-soluble substances, organometallic compounds (especially copper) and particulate matter, which might prevent meeting jet fuel product specifications.

The pressure maintained in the reactor is chosen so that the injected air will completely dissolve in the feedstock at the operating temperature.



CHEMICAL REACTIONS IN JET FUEL MEROX TREATING

Caustic Prewash:
$NaOH + H_2S \rightarrow NaSH + H_2O$

Merox Reaction:
$4RSH + O_2 \rightarrow 2RSSR + 2H_2O$

Conventional Merox process unit for sweetening jet fuel or kerosene

Chapter 7

Amine Gas Treating and Slugcatcher

Amine gas treating

Amine gas treating, also known as **gas sweetening** and **acid gas removal**, refers to a group of processes that use aqueous solutions of various alkylamines (commonly referred to simply as amines) to remove hydrogen sulfide (H_2S) and carbon dioxide (CO_2) from gases. It is a common unit process used in refineries, and is also used in petrochemical plants, natural gas processing plants and other industries.

Processes within oil refineries or chemical processing plants that remove hydrogen sulfide and/or mercaptans are commonly referred to as ***sweetening*** processes because they result in products which no longer have the sour, foul odors of mercaptans and hydrogen sulfide.

There are many different amines used in gas treating:

- Monoethanolamine (MEA)
- Diethanolamine (DEA)
- Methyldiethanolamine (MDEA)
- Diisopropylamine (DIPA)
- Aminoethoxyethanol (diglycolamine) (DGA)

The most commonly used amines in industrial plants are the alkanolamines MEA, DEA, and MDEA.

Amines are also used in many oil refineries to remove sour gases from liquid hydrocarbons such as liquified petroleum gas (LPG).

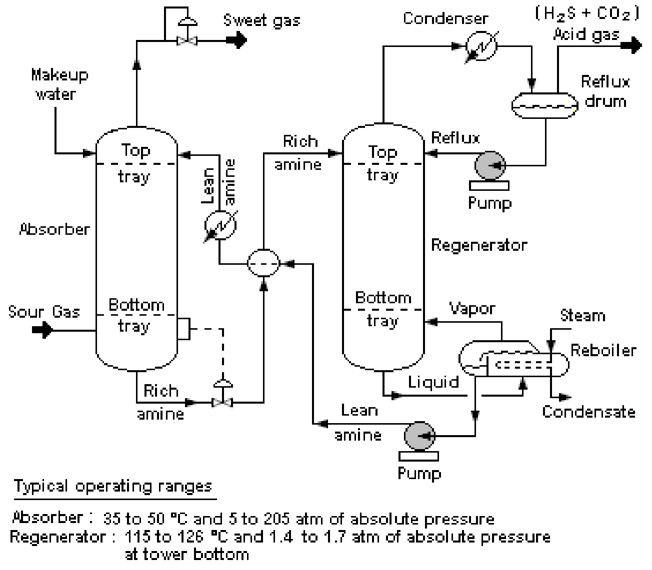
Description of a typical amine treater

Gases containing H_2S or both H_2S and CO_2 are commonly referred to as *sour gases* or *acid gases* in the hydrocarbon processing industries.

The chemistry involved in the amine treating of such gases varies somewhat with the particular amine being used. For one of the more common amines, methanolamine (MEA) denoted as *RNH_2*, the chemistry may be simply expressed as:

$$RNH_2 + H_2S \iff RNH_3HS$$

A typical amine gas treating process (as shown in the flow diagram below) includes an **absorber** unit and a **regenerator** unit as well as accessory equipment. In the absorber, the downflowing amine solution absorbs H_2S and CO_2 from the upflowing sour gas to produce a sweetened gas stream (i.e., an H_2S-free gas) as a product and an amine solution rich in the absorbed acid gases. The resultant "rich" amine is then routed into the regenerator (a stripper with a reboiler) to produce regenerated or "lean" amine that is recycled for reuse in the absorber. The stripped overhead gas from the regenerator is concentrated H_2S and CO_2. In oil refineries, that stripped gas is mostly H_2S, much of which often comes from a sulfur-removing process called hydrodesulfurization. This H_2S-rich stripped gas stream is then usually routed into a Claus process to convert it into elemental sulfur. In fact, the vast majority of the 64,000,000 metric tons of sulfur produced worldwide in 2005 was byproduct sulfur from refineries and other hydrocarbon processing plants. Another sulfur-removing process is the WSA Process which recovers sulfur in any form as concentrated sulfuric acid. In some plants, more than one amine absorber unit may share a common regenerator unit.



Process flow diagram of a typical amine treating process used in industrial plants

The amine concentration in the absorbent aqueous solution is an important parameter in the design and operation of an amine gas treating process. Depending on which one of the following four amines the unit was designed to use and what gases it was designed to remove, these are some typical amine concentrations, expressed as weight percent of pure amine in the aqueous solution:

- Monoethanolamine: About 20 % for removing H_2S and CO_2, and about 32 % for removing only CO_2.
- Diethanolamine: About 20 to 25 % for removing H_2S and CO_2
- Methyldiethanolamine: About 30 to 55% % for removing H_2S and CO_2
- Diglycolamine: About 50 % for removing H_2S and CO_2

The choice of amine concentration in the circulating aqueous solution depends upon a number of factors and may be quite arbitrary. It is usually made simply on the basis of experience. The factors involved include whether the amine unit is treating raw natural gas or petroleum refinery by-product gases that contain relatively low concentrations of both H_2S and CO_2 or whether the unit is treating gases with a very high percentage of CO_2 such as the offgas from the steam reforming process used in ammonia production or the flue gases from power plants. Both H_2S and CO_2 are acid gases and hence corrosive to carbon steel. However, in an amine treating unit, CO_2 is the stronger acid of the two. H_2S forms a film of iron sulfide on the surface of the steel that acts to protect the steel. When treating gases with a very high percentage of CO_2, corrosion inhibitors are often used and that permits the use of higher concentrations of amine in the circulating solution. Another factor involved in choosing an amine concentration is the relative solubility of H_2S and CO_2 in the selected amine. For more information about selecting the amine concentration, the reader is referred to Kohl and Nielsen's book.

The choice of the type of amine will affect the required circulation rate of amine solution, the energy consumption for the regeneration and the ability to selectively remove either H_2S alone or CO_2 alone if desired.

The current emphasis on removing CO_2 from the flue gases emitted by fossil fuel power plants has led to much interest in using amines for that purpose.

In the specific case of the industrial synthesis of ammonia, for the steam reforming process of hydrocarbons to produce gaseous hydrogen, amine treating is one of the commonly used processes for removing excess carbon dioxide in the final purification of the gaseous hydrogen.

Slugcatcher

Slugcatcher is the name of a unit in the gas refinery or petroleum industry in which slugs at the outlet of pipelines are collected or caught. A slug is a large quantity of gas or liquid that exits the pipeline.

Slugs

Pipelines that transport both gas and liquids together, known as two-phase flow, can operate in a flow regime known as slugging flow or slug flow. Under the influence of gravity liquids will tend to settle on the bottom of the pipeline, while the gases occupy the top section of the pipeline. Under certain operating conditions gas and liquid are not evenly distributed throughout the pipeline, but travel as large plugs with mostly liquids or mostly gases through the pipeline. These large plugs are called slugs.

Slugs exiting the pipeline can overload the gas/liquid handling capacity of the plant at the pipeline outlet, as they are often produced at a much larger rate than the equipment is designed for.

Slugs can be generated by different mechanisms in a pipeline:

- **Terrain slugging** is caused by the elevations in the pipeline, which follows the ground elevation or the sea bed. Liquid can accumulate at a low point of the pipeline until sufficient pressure builds up behind it. Once the liquid is pushed out of the low point, it can form a slug.
- **Hydrodynamic slugging** is caused by gas flowing at a fast rate over a slower flowing liquid phase. The gas will form waves on the liquid surface, which may grow to bridge the whole cross-section of the line. This creates a blockage on the gas flow, which travels as a slug through the line.
- **Riser-based slugging**, also known as **severe slugging**, is associated with the pipeline risers often found in offshore oil production facilities. Liquids accumulate at the bottom of the riser until sufficient pressure is generated behind it to push the liquids over the top of the riser, overcoming the static head. Behind this slug of liquid follows a slug of gas, until sufficient liquids have accumulated at the bottom to form a new liquid slug.
- **Pigging slugs** are caused by pigging operations in the pipeline. The pig is designed to push all or most of the liquids contents of the pipeline to the outlet. This intentionally creates a liquid slug.

Slugs formed by terrain slugging, hydrodynamic slugging or riser-based slugging are periodical in nature. Whether a slug is able to reach the outlet of the pipeline depends on the rate at which liquids are added to the slug at the front (i.e. in the direction of flow) and the rate at which liquids leave the slug at the back. Some slugs will grow as they travel the pipeline, while others are dampened and disappear before reaching the outlet of the pipeline.

Purpose of the slugcatcher

A slugcatcher is a vessel with sufficient buffer volume to store the largest slugs expected from the upstream system. The slugcatcher is located between the outlet of the pipeline and the processing equipment. The buffered liquids can be drained to the processing equipment at a much slower rate to prevent overloading the system. As slugs are a periodical phenomenon, the slugcatcher should be emptied before the next slug arrives.

Slugcatchers can be used continuously or on-demand. A slugcatcher permanently connected to the pipeline will buffer all production, including the slugs, before it is sent to the gas and liquid handling facilities. This is used for difficult to predict slugging behaviour found in terrain slugging, hydrodynamic slugging or riser-based slugging.

Alternatively, the slug catcher can be bypassed in normal operation and be brought online when a slug is expected, usually during pigging operations. An advantage of this set-up is that inspection and maintenance on the slugcatcher can be done without interrupting the normal operation.

Slugcatcher design

Slugcatchers are designed in different forms:

- A **vessel type** slugcatcher is essentially a conventional vessel. This type is simple in design and maintenance.
- A **finger type** slugcatcher consists of several long pieces of pipe ('fingers'), which together form the buffer volume. The advantage of this type of slugcatcher is that pipe segments are simpler to design for high pressures, which are often encountered in pipeline systems, than a large vessel. A disadvantage is that its footprint can become excessively large. An example of a large finger-type slugcatcher can be seen in Den Helder, The Netherlands, using Google Maps.
- A **Parking Loop** slugcatcher combines features of the vessel and finger types. The Gas/Liquid Separation occurs in the Vessel, while the Liquid is stored in the parking loop shaped fingers.

A basic slug catcher design contains the buffer volume for gas and liquid. A control system is used for controlled outflow of gas and liquid to the downstream processing facilities. The inlet section is designed to promote the separation of gas and liquid.

Chapter 8

Vacuum Distillation

Under atmospheric pressure, Dimethyl sulfoxide boils at 189°C. Under a vacuum, it distills off into the connected receiver at only 70°C.

Vacuum distillation is a method of distillation whereby the pressure above the liquid mixture to be distilled is reduced to less than its vapor pressure (usually less than atmospheric pressure) causing evaporation of the most volatile liquid(s) (those with the lowest boiling points). This distillation method works on the principle that boiling occurs when the vapor pressure of a liquid exceeds the ambient pressure. Vacuum distillation is used with or without heating the solution.

Laboratory-scale applications

Laboratory-scale vacuum distillation is used when liquids to be distilled have high atmospheric boiling points or chemically change at temperatures near their atmospheric boiling points. Temperature sensitive materials (such as beta carotene) also require vacuum distillation to remove solvents from the mixture without damaging the product. Another reason vacuum distillation is used is that compared to steam distillation there is a lower level of residue build up. This is important in commercial applications where temperature transfer is produced using heat exchangers.

Vacuum distillation is sometimes referred to as low temperature distillation.

There many laboratory applications for vacuum distillation as well as many types of distillation set-ups and apparatuses.

Safety is an important consideration when using glassware as part of the set-up. All of the glass components should be carefully examined for scratches and cracks which could result in implosions when the vacuum is applied. Wrapping as much of the glassware with tape as is practical helps to prevent dangerous scattering of glass shards in the event of an implosion.

Rotary evaporation

Rotary evaporation is a type of vacuum distillation apparatus used to remove bulk solvents from the liquid being distilled. It is also used by environmental regulatory agencies for determining the amount of solvents in paint, coatings and inks.

Rotary evaporation set-ups include an apparatus referred to as a *Rotovap* which rotates the distillation flask (sometimes called the *still pot*) to enhance the distillation. Rotating the flask throws up liquid on the walls of the flask and thus increases the surface area for evaporation.

Heat is often applied to the rotating distillation flask by partially immersing it in a heated bath of water or oil. Typically, the vacuum in such systems is generated by a water aspirator or a vacuum pump of some type.

Distillation of high-boiling and/or air sensitive materials

Some compounds have high boiling point temperatures as well as being air sensitive. A simple laboratory vacuum distillation glassware set-up can be used, in which the vacuum can be replaced with an inert gas after the distillation is complete.

However, this is not a completely satisfactory system if it is desired to collect fractions under a reduced pressure.

For better results or for very air sensitive compounds, either a Perkin triangle distillation set-up or a short-path distillation set-up can be used.

Perkin triangle distillation set-up

The Perkin triangle set-up (Image 5) uses a series of Teflon valves to allow the distilled fractions to be isolated from the distillation flask without the main body of the distillation set-up being removed from either the vacuum or the heat source, and thus can remain in a state of reflux.

To do this, the distillate receiver vessel is first isolated from the vacuum by means of the Teflon valves.

The vacuum over the sample is then replaced with an inert gas (such as nitrogen or argon) and the distillate receiver can then be stoppered and removed from the system.

Vacuum distillation set-up using a short-path head

Vacuum distillation of moderately air/water-sensitive liquid can be done using standard Schlenk-line techniques (Image 6).

When assembling the set-up apparatus, all of the connecting lines are clamped so that they cannot pop off.

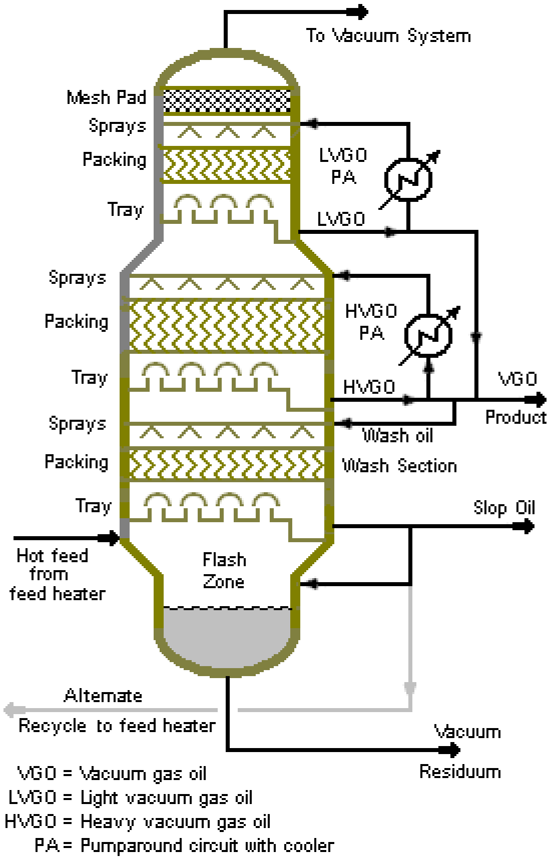
Once the apparatus is assembled, and the liquid to be distilled is in the still pot, the desired vacuum is established in the system by using the vacuum connection on the short-path distillation head. Care is taken to prevent potential "bumping" as the liquid in the still pot degases.

While establishing the vacuum, the flow of coolant is started through the short-path distillation head. Once the desired vacuum is established, heat is applied to the still pot.

If needed, the first portion of distillate can be discarded by purging with inert gas and changing out the distillate receiver.

When the distillation is complete: the heat is removed, the vacuum connection is closed, and inert gas is purged through the distillation head and the distillate receiver. While under the inert gas purge, remove the distillate receiver and cap it with an air-tight cap. The distillate receiver can be stored under vacuum or under inert gas by using the side-arm on the distillation flask.

Industrial-scale applications



Simplified drawing of a typical dry vacuum distillation column as used in oil refineries

Large-scale vacuum distillation tower at Fawley oil refinery

Typical industrial applications utilize the heat pump cycle to maximize efficiency. This type of distillation is in use in the oil industry where common ASTM standards are D1160, D2892, D5236. These standards describe typical applications of vacuum distillation at pressures of about 1-100 mbar. Pilot plants up to 60 L can be built in accordance with these standards.

Industrial-scale vacuum distillation has several advantages. Close boiling mixtures may require many equilibrium stages to separate the key components. One tool to reduce the number of stages needed is to utilize vacuum distillation. Vacuum distillation columns (as depicted in the drawing to the right) typically used in oil refineries have diameters ranging up to about 14 metres (46 feet), heights ranging up to about 50 metres (164 feet), and feed rates ranging up to about 25,400 cubic metres per day (160,000 barrels per day).

Vacuum distillation increases the relative volatility of the key components in many applications. The higher the relative volatility, the more separable are the two components; this connotes fewer stages in a distillation column in order to effect the same separation between the overhead and bottoms products. Lower pressures increase relative volatilities in most systems.

A second advantage of vacuum distillation is the reduced temperature requirement at lower pressures. For many systems, the products degrade or polymerize at elevated temperatures.

Vacuum distillation can improve a separation by:

- Prevention of product degradation or polymer formation because of reduced pressure leading to lower tower bottoms temperatures,
- Reduction of product degradation or polymer formation because of reduced mean residence time especially in columns using packing rather than trays.
- Increasing capacity, yield, and purity.

Another advantage of vacuum distillation is the reduced capital cost, at the expense of slightly more operating cost. Utilizing vacuum distillation can reduce the height and diameter, and thus the capital cost of a distillation column.

Vacuum distillation in petroleum refining

Petroleum crude oil is a complex mixture of hundreds of different hydrocarbon compounds generally having from 3 to 60 carbon atoms per molecule, although there may be small amounts of hydrocarbons outside that range. The refining of crude oil begins with distilling the incoming crude oil in a so-called *atmospheric distillation column* operating at pressures slightly above atmospheric pressure.

In distilling the crude oil, it is important not to subject the crude oil to temperatures above 370 to 380 °C because the high molecular weight components in the crude oil will undergo thermal cracking and form petroleum coke at temperatures above that. Formation of coke would result in plugging the tubes in the furnace that heats the feed stream to the crude oil distillation column. Plugging would also occur in the piping from the furnace to the distillation column as well as in the column itself.

The constraint imposed by limiting the column inlet crude oil to a temperature of more than 370 to 380 °C yields a residual oil from the bottom of the atmospheric distillation column consisting entirely of hydrocarbons that boil above 370 to 380 °C.

To further distill the residual oil from the atmospheric distillation column, the distillation must be performed at absolute pressures as low as 10 to 40 mmHg (also referred to as Torr) so as to limit the operating temperature to less than 370 to 380 °C.

Image 1 is a photograph of a large vacuum distillation column in a petroleum refinery and Image 2 is a process diagram of a petroleum refinery vacuum distillation column that depicts the internals of the column.

The 10 to 40 mmHg absolute pressure in a vacuum distillation column increases the volume of vapor formed per volume of liquid distilled. The result is that such columns have very large diameters.

Distillation columns such those in Images 1 and 2, may have diameters of 15 meters or more, heights ranging up to about 50 meters, and feed rates ranging up to about 25,400 cubic meters per day (160,000 barrels per day).

The vacuum distillation column internals must provide good vapor-liquid contacting while, at the same time, maintaining a very low pressure increase from the top of the column top to the bottom. Therefore, the vacuum column uses distillation trays only where withdrawing products from the side of the column (referred to as *side draws*). Most of the column uses packing material for the vapor-liquid contacting because such packing has a lower pressure drop than distillation trays. This packing material can be either structured sheet metal or randomly dumped packing such as Raschig rings.

The absolute pressure of 10 to 40 mmHg in the vacuum column is most often achieved by using multiple stages of steam jet ejectors.

Chapter 9

Floating Production Storage and Offloading

FPSO *Mystras* at work off the shore of Nigeria

FPSO *Crystal Ocean* moored at the Port of Melbourne

A **floating production, storage and offloading (FPSO)** unit is a floating vessel used by the offshore industry for the processing of hydrocarbons and for storage of oil. A FPSO vessel is designed to receive hydrocarbons produced from nearby platforms or subsea template, process them, and store oil until it can be offloaded onto a tanker or transported through a pipeline. FPSOs are preferred in frontier offshore regions as they are easy to install, and do not require a local pipeline infrastructure to export oil. FPSOs can be a conversion of an oil tanker or can be a vessel built specially for the application. A vessel used only to store oil (without processing it) is referred to as a **floating storage and offloading vessel (FSO)**.

History

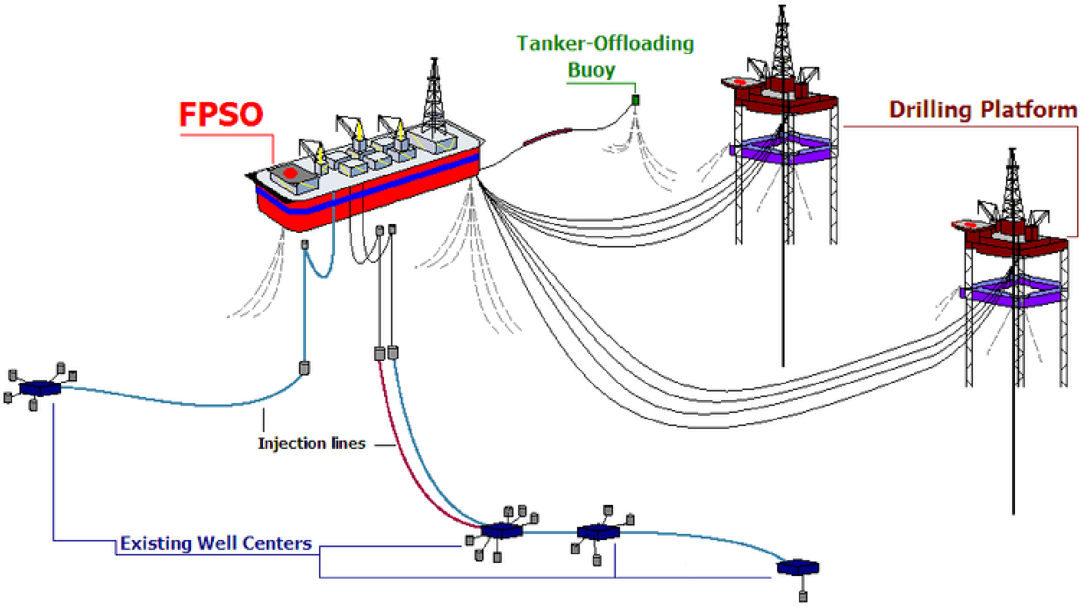
Oil has been produced from offshore locations since the late 1940s. Originally, all oil platforms sat on the seabed, but as exploration moved to deeper waters and more distant locations in the 1970s, floating production systems came to be used.

The first oil FPSO was the *Shell Castellon*, built in Spain in 1977.

The *Sanha* LPG FPSO operates offshore Angola, and is the first such vessel with complete onboard liquefied petroleum gas processing and export facilities. It can store up to 135,000 cubic meters of LPG while awaiting export tankers for offloading.

There are so far no LNG FPSOs. In the opposite (discharge and regasification) end of the LNG chain, the first ever conversion of a LNG carrier (Golar LNG owned Moss type LNG carrier) into an LNG floating storage and regasification unit was carried out in 2007 by Keppel shipyard in Singapore. An LNG FPSO works under the same principles an oil FPSO works under, taking the well stream and separating out the natural gas (primarily methane and ethane) and producing LNG, which is stored and offloaded. On July 29, 2009, Shell and Samsung announced an agreement to build up to 10 LNG FPSOs: Likely size and capacity: 456 meters in length and 74 meters in width, with a capacity of 450,000 cubic meters Estimated cost $5b. Already Flex LNG has four contracts for smaller units at the same yard.

Mechanisms



FPSO diagram

Oil produced from offshore production platforms can be transported to the mainland either by pipeline or by tanker. When a tanker is chosen to transport the oil, it is necessary to accumulate oil in some form of storage tank such that the oil tanker is not continuously occupied during oil production, and is only needed once sufficient oil has been produced to fill the tanker. At this point the transport tanker connects to the stern of the storage unit and offloads oil.

In the early days, the storage units consisted of decommissioned oil tankers, which were stripped down and equipped with process/production facilities (becoming therefore FPSOs), and were connected to a permanent mooring point. Today, there are two main types of FPSOs, those built converting an existing oil tanker, and those that are purpose-built. The FPSO design will depend on the area of operation. In benign waters the FPSO may have a simple box shape or it may be a converted tanker. Generally (but not always) the production lines (risers) are connected to a major component of the vessel, called a Turret, which allows the vessel to rotate in order to head into the wind and reduce environmental forces on the moorings. In relatively calm waters, such as in West Africa, turrets can be located externally to the ship structure, hanging off the bow of the FPSO. For harsher environments like the North Sea, the turret is generally located internally. The turrets and the mooring systems can be designed to be disconnectable or to remain permanently moored. Most ship-shaped FPSOs in the North Sea are purpose-built and are permanently moored.

While most FPSOs are ship-shaped, FPSOs may also be semi-submersible type platforms with storage or may have a cylindrical shape. These are moored in fixed orientation.

An FPSO has the capability to carry out some form of separation process. If the unit does not have such facilities, it is generally referred to as a Floating Storage and Offloading unit (see below), and would be operated in conjunction with a production platform.

Advantages

Floating production, storage and offloading vessels are particularly effective in remote or deepwater locations where seabed pipelines are not cost effective. FPSOs eliminate the need to lay expensive long-distance pipelines from the oil well to an onshore terminal. They can also be used economically in smaller oil fields which can be exhausted in a few years and do not justify the expense of installing a pipeline. Once the field is depleted, the FPSO can be moved to a new location. In areas of the world subject to cyclones (northwestern Australia) or icebergs (Canada), some FPSOs are able to release their mooring/riser turret and steam away to safety in an emergency. The turret sinks beneath the waves and can be reconnected later.

Specific types

A **floating storage and offloading unit** (FSO) is a floating storage device, which is a simplified FPSO without the capability for oil or gas processing. Most FSOs are old single hull supertankers that have been converted. An example is *Knock Nevis, ex Seawise Giant*, the world's largest ship, which had been converted to an FSO to be used offshore Qatar.

At the other end of the LNG logistics chain, where the natural gas is brought back to ambient temperature and pressure, ships may also be used as FSRUs. A **LNG floating storage and regasification unit** (FSRU) is a floating storage and regasification system, which receives liquefied natural gas (LNG) from offloading LNG carriers, and the onboard regasification system provides natural gas send-out through flexible risers and pipeline to shore.

Vessels

Records

FPSO Firenze moored at Hellenic Shipyards, 2007

The FPSO operating in the deepest water depth is the Espirito Santo FPSO from Shell America operated by Brazilian Deepwater Production Ltd (a joint venture between MISC Bhd and SBM Offshore). The FPSO is moored at a depth of 1,800 m in the Campos Basin, Brazil and is rated for 100,000 bpd. The EPCI contract was awarded in November 2006 and first oil was achieved in July 2009. The FPSO conversions and internal turret were done at Keppel Shipyard Tuas in Singapore and the topsides were fabricated in modules at Dynamac and BTE in Singapore.

The world's largest FPSO is the *Kizomba A*, with a storage capacity of 2.2 million barrels (350,000 m^3). Built at a cost of over US$800 million by Hyundai Heavy Industries in Ulsan, Korea, it is operated by Esso Exploration Angola (ExxonMobil). Located in 1200 meters (3,940 ft) of water at Deepwater block 200 statute miles (320 km) offshore in the Atlantic Ocean from Angola, Central Africa, it weighs 81,000 tonnes and is 285 meters long, 63 meters wide, and 32 meters high (935 ft by 207 ft (63 m) by 105 ft).

The world's smallest FPSO is the Crystal Ocean, operating in 137 m of water in the Bass Strait between Australia and Tasmania on the Basker Manta Field. It is leased by Roc Oil

(Sydney-based international petroleum exploration and production company) from Rubicon Offshore and is operated on their behalf by AGR Asia Pacific; it is currently producing 5,000 bpd.

The FPSO in the shallowest water depth of just 13 m is the Armada Perkasa in the Okoro field in Nigeria, West Africa, for Afren Energy. This spread moored (fixed orientation) vessel uses 100 mm, 150 mm and 200 mm bore DeepFlex non-steel flexible risers in a double lazy wave formation (with weights and distributed buoyancy) to accommodate the large motion offsets in an environment of extreme waves and currents.

The **Skarv FPSO**, developed and engineered by Aker Solutions for BP Norge, will be the most advanced and largest FPSO deployed in the Norwegian Sea, offshore Mid Norway. Skarv is a gas condensate and oil field development. The development will tie in five sub-sea templates, and the FPSO has capacity to include several smaller wells nearby in the future. The process plant on the vessel can handle about 19 MSm3/d (670 MScf/d) of gas and 13,500 Sm3/d of oil (85,000 bbl/d). An 80 km gas export pipe will tie in to Åsgard transport system. Aker Solutions (formerly Aker Kvaerner) developed the front-end design for the new floating production facility as well as the overall system design for the field and preparation for procurement and project management of the total field development. The hull is an Aker Solutions proprietary "Tentech^{tm}975" design. BP also selected Aker Solutions to perform the detail engineering, procurement and construction management assistance (EPcma) for the Skarv field development. The EPcma contract covers detail engineering and procurement work for the FPSO topsides as well as construction management assistance to BP including hull and topside facilities. The production start for the field is scheduled for August 2011. BP awarded the contract for fabrication of the Skarv FPSO hull to Samsung Heavy Industries in South Korea and the Turret contract to SBM. The FPSO has a length of 292m, breadth of 50.6m and is 29m deep and accommodate 100 people in single cabins. The hull will be delivered in January 2010.

Current FPSOs

Data on operating FPSOs is reported each year in an annual survey.

FPSO Vessel Name	Oilfield	Current Location	Field Operator	Newbuild or Conversion	Startup year	Vessel Designer /Operator
Abo FPSO	Abo	Gulf of Guinea, Nigeria	Agip	Conversion	2003	Prosafe
Agbami FPSO	Nigeria		Star Deep Water Petroleum	Newbuild	2008	Chevron
Akpo FPSO	Akpo	Gulf of Guinea, Nigeria	Total	Newbuild	2009	Total

Al Zaafarana FPSO	Warda	Gulf of Suez, Egypt	Aker Solutions	Conversion	1994	Gemsa Petroleum Co
Anasuria FPSO	Teal, Teal South, Guillemot A	North Sea, UK	Shell	Newbuild	1996	
Anoa Natuna	Anoa Field, Natuna Sea	Indonesia	STAR Energy		1990	STAR Energy,KN, Natuna Sea BV
Aoka Mizu	Ettrick	North Sea, UK	Nexen		2009	Bluewater Energy Services
Arco Ardjuna FSO	Ardjuna Oil Field	West Java Sea, Indonesia	Pertamina Hulu Energy		1973	Pertamina
Armada Perkasa	Okoro Setu	Nigeria	Afren/AMNI	Conversion	2009	Bumi Armada Berhad
Armada Perdana	Oyo	Nigeria	Allied Energy/Agip	Conversion	2010	Bumi Armada Berhad
Åsgard A	Åsgard	North Sea, Norway	Statoil	Newbuild	1999	
Azurite FDPSO	Azurite	Atlantic, Republic of the Congo	Murphy Oil	Conversion	2009	Prosafe Production
Baobab Ivoirien MV10 FPSO	Baobab Field	Côte d'Ivoire	CNR International S.A.R.L.	Conversion	2005	MODEC Inc.
Belanak	Belanak Field	South Natuna Sea, Indonesia	ConocoPhillips	Newbuild	2004	KBR / J. Ray McDermott
Berge Helene(OIM Adarsh Shukla)	Chinguetti	North Atlantic Ocean, Mauretania	Woodside Petroleum	Conversion	2006	
Bleo Holm	Ross, Blake, Parry	North Sea, UK	Talisman Energy	Conversion	1999	Bluewater Energy Services
Bohai Ming Zhu FPSO	Penglai19-3, China	Bohai, China	ConocoPhillips		2003	CNOOC
Bonga FPSO	Bonga	Gulf of Guinea, Nigeria	Shell	Newbuild	2005	Samsung Heavy Industries
Brasil FPSO	Roncador	Campos Basin, Brazil	Petrobras	Conversion	2002	SBM Offshore
Bunga Kertas FPSO	North Lukut & Penara	South China Sea, Peninsula Malaysia	Petronas Carigali	Conversion	2004	DPS/FPSO Ventures
Capixaba FPSO	Golfinho	Espírito Santo Basin, Brazil	Petrobras	Conversion	2006	SBM Offshore
Captain FPSO	Captain	North Sea, UK	Chevron	Newbuild	1996	
Cidade de Niteroi	Jabuti, Brazil	Santos Basin, Brazil	MODEC (for Petrobras)	Conversion	2009	MODEC Inc.
Cidade do Rio de Janeiro MV14 FPSO	Espadarte Sul Field	Campos Basin, Brazil	Petrobras	Conversion	2007	MODEC Inc.
Cidade de Vitoria	Golfinho II	Espírito Santo Basin, Brazil	Petrobras	Conversion	2007	Saipem

FPSO						
Cossack Pioneer	Cossack, Wanaea	Indian Ocean, Australia	Woodside Petroleum	Conversion	1995	
Cuulong MV9 FPSO	Su Tu Den Field	Vietnam	Cuulong Joint Operating Company (CLJOC)	Newbuild	2003	MODEC Inc.
Dalia FPSO	Dalia	South Atlantic Ocean, Angola	Total	Newbuild	2006	
Dhirubhai 1	MA-D6	Bay of Bengal, India	Reliance Industries Limited	Conversion	2008	AFP
Erha	OPL 209	Gulf of Benin, Nigeria	ExxonMobil	Newbuild	2006	
Espadarte FPSO	Espadarte	Campos Basin, Brazil	Petrobras	Conversion	2000	SBM Offshore
Espirito Santo BC-10 FPSO	Espirito Santo (BC10)	Campos Basin, Brazil	Shell Americas	Conversion	2009	SBM Offshore MISC Bhd
Espoir Ivorien	Espoir	Gulf of Guinea, Côte d'Ivoire	CNR	Conversion	2002	Prosafe
Falcon FPSO	Currently none	Johor River, Malaysia	ExxonMobil	Conversion		SBM Offshore
Farwah	Al-Jurf	Mediterranean, Libya	Total		2003	
Four Vanguard	Woollybutt	Indian Ocean, Australia	ENI	Conversion	2003	Premuda
Gimboa FPSO	Gimboa	South Atlantic Ocean, Angola	Sonangol	Conversion	2009	Saipem
Girassol FPSO	Girassol	South Atlantic Ocean, Angola	Total	Newbuild	2001	
Glas Dowr	Sable	Indian Ocean, South Africa	PetroSA	Newbuild	2003	Bluewater Energy Services
Global Producer III	Dumbarton	North Sea, UK	Maersk	Newbuild	2006	Maersk
Greater Plutonio FPSO	Block 18 Greater Plutonio	South Atlantic Ocean, Angola	BP	Newbuild	2007	BP
Griffin Venture FPSO	Griffin, Chinook, Scindian	Indian Ocean, Australia	BHP Billiton	Newbuild	1994	
Gryphon FPSO	Gryphon	North Sea, UK	Maersk		1993	
Hæwene Brim FPSO	Pierce	North Sea, UK	Shell	Newbuild	1999	Bluewater Energy Services
Jasmine Venture MV7 FPSO	Jasmine Field	Thailand	PEARL Energy Pte Ltd.	Conversion	2004	MODEC Inc.
Jotun A	Jotun	North Sea, Norway	ExxonMobil	Newbuild	1999	Bluewater Energy Services
Kakap Natuna FPSO	Kakap KH field	Indonesia	ConocoPhillips(Kakap) Ltd.	Conversion	1986	MODEC Inc.
Kikeh	Kikeh	Sabah, Malaysia	Murphy Oil	Conversion	2007	SBM Offshore MISC Bhd

Kizomba A	Hungo, Chocalho	South Atlantic Ocean, Angola	ExxonMobil	Newbuild	2004	SBM Offshore
Kizomba B	Kissanje, Dikanza	South Atlantic Ocean, Angola	ExxonMobil	Newbuild	2005	SBM Offshore
Kuito FPSO	Kuito	Cabinda, Angola	Chevron	Conversion	1999	SBM Offshore
"Kwame Nkrumah" FPSO	Jubilee Fields	Gulf of Guinea, Ghana	Tullow Oil & Others	Conversion	2010	MODEC Inc
North Sea Producer	MacCulloch	North Sea, UK	ConocoPhillips	Conversion	1997	Maersk
Maersk Curlew	Curlew	North Sea, UK	Shell	Conversion	2002	Maersk
Marlim Sul FPSO	Marlim Sul	Campos Basin, Brazil	Petrobras	Conversion	2004	SBM Offshore
MODEC Venture 11 FPSO	Mutineer-Exeter Field	Australia	Santos Ltd.	Conversion	2005	MODEC Inc.
Mondo FPSO	Luanda, Angola	Block 15, Angola	ExxonMobil	Conversion	2008	SBM Offshore
Munin	Lufeng, Xijiang	South China Sea, China	CNOOC	Newbuild	1997	Bluewater Energy Services
MV8 Langsa Venture FPSO	Langsa field	Malacca Strait, Indonesia	MEDCO MOECO Langsa Ltd.	Conversion	2001	MODEC Inc.
Mystras FPSO	Okono, Okpoho	Gulf of Guinea, Nigeria	Agip	Conversion	2004	Saipem
Nganhurra FPSO	Enfield	Exmouth Sub-basin, Australia	Woodside Petroleum	Newbuild	2006	
Maersk Ngujima-Yin FPSO	Vincent	Exmouth Sub-basin, Australia	Woodside Petroleum	Conversion	2008	Maersk
Norne FPSO	Norne	North Sea, Norway	Statoil	Newbuild	1997	
Northern Endeavour	Laminaria, Corallina	Timor Sea, Indonesia	Woodside Petroleum	Newbuild		
Perintis	MASA field	South China Sea, Peninsular Malaysia	Petronas Carigali	Conversion	1999	Aker Kvaerner/M3Nergy;
Petrojarl Banff	Banff	North Sea, UK	CNR	Newbuild	1999	Teekay Petrojarl;
Petrojarl Foinaven	Foinaven	North Atlantic, UK	BP	Conversion	1997	Teekay Petrojarl
Petrojarl I	Glitne oilfield	North Sea, Norway	Statoil	Newbuild	2001	Teekay Petrojarl
Petrojarl Varg	Varg	North Sea, Norway	Talisman Energy	Newbuild	1999	Teekay Petrojarl
Pertroleo Nautipa FPSO	Etame	South Atlantic Ocean, Gabon	Vaalco Energy	Conversion	2002	Fred Olsen Production, Prosafe
Polvo FPSO	Polvo	South Atlantic Ocean, Brazil	Devon Energy	Conversion	2007	Prosafe

Rang Dong 1	Rang Dong	South China Sea, Vietnam	JVPC, Nippon Oil	Conversion	1998	Mitsubishi Heavy Industries
Raroa II	Maari	Tasman Sea, New Zealand	OMV	Conversion	2008	
Ruby Princess FPSO	Ruby	South China Sea, Vietnam	Petrovietnam	Conversion	1998	Prosafe
Ruby II FPSO	Ruby	South China Sea, Vietnam	Petronas Carigali Vietnam Ltd	Conversion	2010	MISC Bhd
Sanha LPG FPSO	Angola		Chevron	Newbuild	2005	Chevron
Saxi-Batuque FPSO	Luanda, Angola	Block 15, Angola	ExxonMobil	Conversion	2008	SBM Offshore
Schiehallion FPSO	Schiehallion	North Atlantic, UK	BP	Newbuild	1998	Harland & Wolff
Sea Eagle FPSO	EA	Gulf of Guinea, Nigeria	Shell	Newbuild	2003	
SeaRose FPSO	White Rose	Grand Banks of Newfoundland, Canada	Husky Energy	Newbuild	2005	
Seillean FPSO	Cachalote	Esprito Santo Basin, Brazil	Petrobras but built for BP	Newbuild	1986	Noble Corporation
Serpentina FPSO	Zafiro	Gulf of Guinea, Equatorial Guinea	Exxonmobil	Conversion	2003	SBM Offshore
Skarv FPSO	Skarv and Idun	North Sea, Norway	BP	Newbuild	2011	BP
Song Doc MV19 FPSO	Song Doc Field	Vietnam	Truong Son Joint Operating Company (TSJOC)	Conversion	2008	MODEC Inc.
Stybarrow MV16 FPSO	Stybarrow Field	Exmouth Sub-basin, Australia	BHP Billiton Petroleum	Newbuild	2007	MODEC Inc.
Terra Nova	Terra Nova	Grand Banks of Newfoundland, Canada	Suncor	Newbuild	2002	
Triton	Bittern, Guillemot West, Guillemot Northwest	North Sea, UK	Amerada Hess	Newbuild	2000	
Uisge Gorm FPSO	Fife, Fergus, Flora, Angus	North Sea, UK	Amerada Hess	Conversion	1995	Bluewater Energy Services
Umuroa FPSO	Tui	Tasman Sea, New Zealand	Australian Worldwide Exploration	Conversion	2007	APS/Prosafe Production
Xikomba FPSO	Xikomba	Block 15, Angola	ExxonMobil	Conversion	2003	SBM Offshore
Yunus FSO	BDR3	Mediterranean	Syriah & N.T.J. Group	Conversion	1998	Syriah & NTJ Group

Yúum K'ak'náab FPSO	Ku-Maloob-Zaap field	Gulf of Mexico	PEMEX	Newbuild	1998	BW Offshore AS, Norway

Chapter 10

Coal Gasification

Coal gasification is the process of producing coal gas, a type of syngas–a mixture of carbon monoxide (CO) and hydrogen (H_2) gas–from coal. Carbon monoxide, which is a combustible gas, was traditionally used as a source of energy for municipal lighting and heat before the advent of industrial-scale production of natural gas, while the hydrogen obtained from gasification can be used for various purposes such as making ammonia, powering a hydrogen economy, or upgrading fossil fuels. Alternatively, the coal gas (also known as "town gas") can be converted into transportation fuels such as gasoline and diesel through additional treatment via the Fischer-Tropsch process.

History

In the past, coal was converted to make coal gas, which was piped to customers to burn for illumination, heating, and cooking. High prices of oil and natural gas are leading to increased interest in "BTU Conversion" technologies such as gasification, methanation and liquefaction. The Synthetic Fuels Corporation was a U.S. government-funded corporation established in 1980 to create a market for alternatives to imported fossil fuels (such as coal gasification). The corporation was discontinued in 1985.

Early history of gas production by carbonization

Gas lighting in historical center of Wrocław, Poland

The Flemish scientist Jan Baptista van Helmont (1577–1644) discovered that a 'wild spirit' escaped from heated wood and coal, and, thinking that it 'differed little from the chaos of the ancients', he named it *gas* in his *Origins of Medicine* (*c*. 1609). Among several others who carried out similar experiments, were Johann Becker of Munich (*c* 1681) and about three years later John Clayton of Wigan, England, the latter amusing his friends by lighting, what he called, "Spirit of the Coal". William Murdoch (later known as Murdock) (1754–1839) (partner of James Watt) is reputed to have heated coal in his mother's teapot to produce gas. From this beginning, he discovered new ways of making, purifying and storing gas; illuminating his house at Redruth (or his cottage at Soho) in 1792, the entrance to the Manchester Police Commissioners premises in 1797, the exterior of the factory of Boulton and Watt in Birmingham, England, and a large cotton mill in Salford, Lancashire in 1805.

Professor Jan Pieter Minckeleers lit his lecture room at the University of Louvain in 1783 and Lord Dundonald lit his house at Culross, Scotland, in 1787, the gas being carried in sealed vessels from the local tar works. In France, Philippe le Bon patented a gas fire in 1799 and demonstrated street lighting in 1801. Other demonstrations followed in France and in the United States, but, it is generally recognized that the first commercial gas works was built by the London and Westminster Gas Light and Coke Company in Great Peter Street in 1812 laying wooden pipes to illuminate Westminster Bridge with gas lights on New Year's Eve in 1813. In 1816, Rembrandt Peale and four others established the Gas Light Company of Baltimore, the first manufactured gas company in America. In 1821, natural gas was being used commercially in Fredonia, New York. The first German gas works was built in Hannover in 1825 and by 1870 there were 340 gas works in Germany making town gas from coal, wood, peat and other materials.

Working conditions in the Gas Light and Coke Company's Horseferry Road Works, London, in the 1830s were described by a French visitor, Flora Tristan, in her *Promenades Dans Londres*:

Two rows of furnaces on each side were fired up; the effect was not unlike the description of Vulcan's forge, except that the Cyclops were animated with a divine spark, whereas the dusky servants of the English furnaces were joyless, silent and benumbed. ... The foreman told me that stokers were selected from among the strongest, but that nevertheless they all became consumptive after seven or eight years of toil and died of pulmonary consumption. That explained the sadness and apathy in the faces and every movement of the hapless men.

The first public piped gas supply was to 13 gas lamps, each with three glass globes along the length of Pall Mall, London in 1807. The credit for this goes to the inventor and entrepreneur Fredrick Winsor and the plumber Thomas Sugg who made and laid the pipes. Digging up streets to lay pipes required legislation and this delayed the development of street lighting and gas for domestic use. Meanwhile William Murdoch and his pupil Samuel Clegg were installing gas lighting in factories and work places, encountering no such impediments.

Early history of gas production by gasification

In the 1850s every small to medium sized town and city had a gas plant to provide for street lighting. Subscribing customers could also have piped lines to their houses. By this era, gas lighting became accepted. Gaslight trickled down to the middle class and later came gas cookers and stoves.

The 1860s were the golden age of coal gas development. Scientists like Kekulé and Perkin cracked the secrets of organic chemistry to reveal how gas is made and its composition. From this came better gas plants and Perkin's purple dyes, such as

Mauveine. In the 1850s, processes for making Producer gas and Water gas from coke were developed. Unenriched water gas may be described as Blue water gas (BWG).

Mond gas, developed in the 1850s by Ludwig Mond, was producer gas made from coal instead of coke. It contained ammonia and coal tar and was processed to recover these valuable compounds.

Blue water gas (BWG) burns with a non-luminous flame which makes it unsuitable for lighting purposes. Carburetted Water Gas (CWG), developed in the 1860s, is BWG enriched with gases obtained by spraying oil into a hot retort. It has a higher calorific value and burns with a luminous flame.

The carburetted water gas process was improved by Thaddeus S. C. Lowe in 1875. The gas oil was fixed into the BWG via thermocracking in the carburettor and superheater of the CWG generating set. CWG was the dominant technology in the USA from the 1880s until the 1950s, replacing coal gasification. CWG has a CV of 20 MJ/m^3 i.e. slightly more than half that of natural gas.

Development of the gas industry in the UK

The advent of incandescent gas lighting in factories, homes and in the streets, replacing oil lamps and candles with steady clear light, almost matching daylight in its colour, turned night into day for many—making night shift work possible in industries where light was all important—in spinning, weaving and making up garments etc. The social significance of this change is difficult for generations brought up with lighting after dark available at the touch of a switch to appreciate. Not only was industrial production accelerated, but streets were made safe, social intercourse facilitated and reading and writing made more widespread. Gas works were built in almost every town, main streets were brightly illuminated and gas was piped in the streets to the majority of urban households. The invention of the gas meter and the pre-payment meter in the late 1880s played an important role in selling town gas to domestic and commercial customers.

1934 gas cooker in England

The education and training of the large workforce, the attempts to standardise manufacturing and commercial practices and the moderating of commercial rivalry between supply companies prompted the founding of associations of gas managers, first in Scotland in 1861. A British Association of Gas Managers was formed in 1863 in Manchester and this, after a turbulent history, became the foundation of the Institute of Gas Engineers (IGE). In 1903, the reconstructed Institution of Civil Engineers (ICE) initiated courses for students of gas manufacture in the City and Guilds of London Institute. The IGE was granted the Royal Charter in 1929. Universities were slow to respond to the needs of the industry and it was not until 1908 that the first Professorship of Coal Gas and Fuel Industries was founded at the University of Leeds. In 1926, the Gas Light and Coke Company opened *Watson House* adjacent to Nine Elms Gas Works. At first, this was a scientific laboratory. Later it included a centre for training apprentices but its major contribution to the industry was its gas appliance testing facilities, which were made available to the whole industry, including gas appliance manufacturers. Using this facility, the industry established not only safety but also performance standards for both the manufacture of gas appliances and their servicing in customers' homes and commercial premises.

During World War I, the gas industry's by-products, phenol, toluene and ammonia and sulphurous compounds were valuable ingredients for explosives. Much coal for the gas works was shipped by sea and was vulnerable to enemy attack. The gas industry was a large employer of clerks, mainly male before the war. But the advent of the typewriter and the female typist made another important social change that was, unlike the employment of women in war-time industry, to have long-lasting effects.

The inter-war years were marked by the development of the continuous vertical retort which replaced many of the batch fed horizontal retorts. There were improvements in storage, especially the waterless gas holder, and distribution with the advent of 2–4 inch steel pipes to convey gas at up to 50 psi (340 kPa) as feeder mains to the traditional cast iron pipes working at an average of 2–3 inches water gauge (500–750 Pa). Benzole as a vehicle fuel and coal tar as the main feedstock for the emerging organic chemical industry provided the gas industry with substantial revenues. Petroleum supplanted coal tar as the primary feedstock of the organic chemical industry after World War II and the loss of this market contributed to the economic problems of the gas industry after the war.

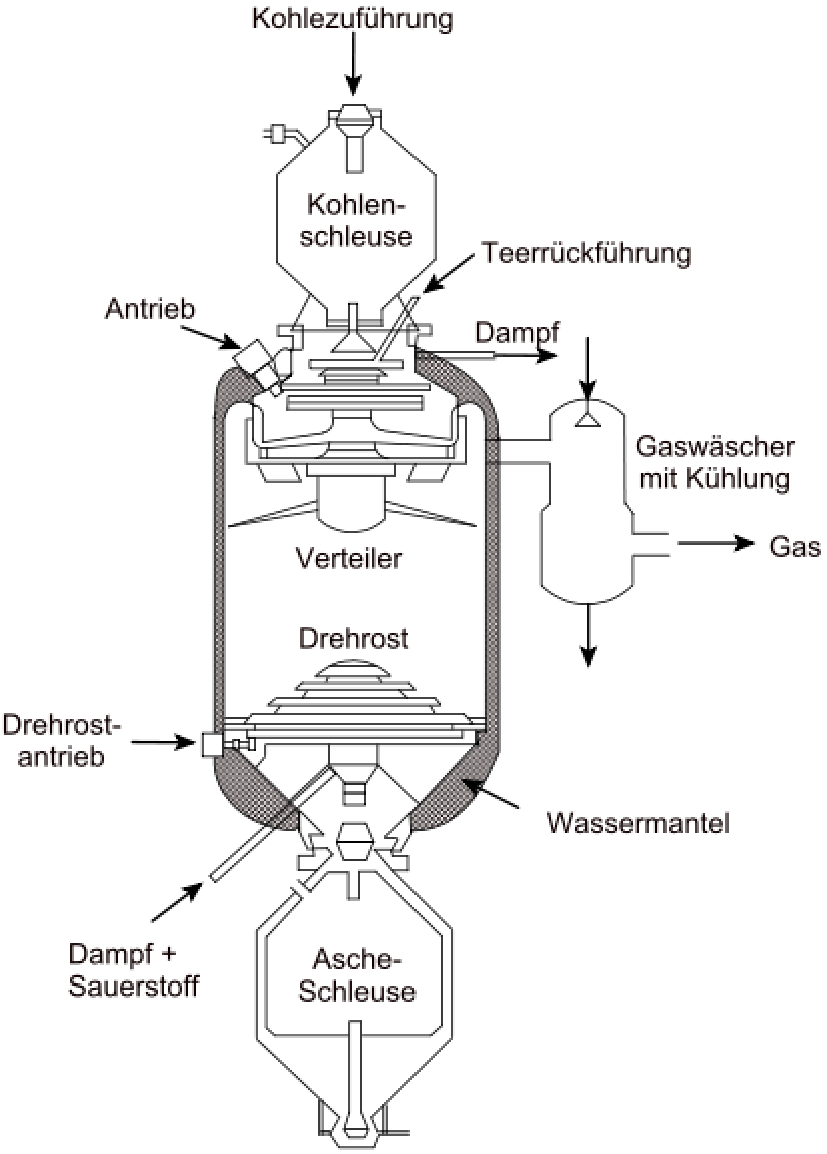
A wide variety of appliances and uses for gas developed over the years. Gas fires, gas cookers, refrigerators, washing machines, hand irons, pokers for fire lighting, gas-heated baths, remotely controlled clusters of gas lights, gas engines of various types and, in later years, gas warm air and hot water central heating and air conditioning, all of which made immense contributions to the improvement of the quality of life in cities and towns world wide. The evolution of electric lighting made available from public supply extinguished the gas light, except where colour matching was practised as in haberdashery shops.

Modern coal gasification

The Great Plains Synfuels Plant has been operating in Beulah, North Dakota since 1984. It produces synthetic natural gas from lignite.

During the 2011 session of the Illinois legislature proposals to provide financial support for state-of-the-art coal gasification plants in Chicago and Southern Illinois were considered. The bills require Illinois utilities to purchase gas at fixed rates from the plants for 30 years. The Chicago plant to be built by Chicago Clean Energy, a subsidiary of Leucadia National Corporation, is budgeted to cost $3 billion. It would be located in an existing industrial area on the Southeast Side on Burley Avenue near 116th Street. In addition to coal the plant would use coke, an oil refinery byproduct, as feed stock. Carbon dioxide produced during the project would be sequestered.The bill to build the Chicago plant was passed by the legislature but vetoed by the Illinois governor Pat Quinn who cited cost issues. Due to uncertainty about natural gas supplies and prices alternative financing is doubtful. Another plant, Indiana Gasification, LLC also a Leucadia National Corporation subsidiary and with a similar business plan, is proposed for Rockport, Indiana where the state has agreed to purchase gas for 30 years at a fixed price.

Process



Scheme of a Lurgi gasifier

During gasification, the coal is blown through with oxygen and steam (water vapor) while also being heated (and in some cases pressurized). If the coal is heated by external heat sources the process is called "allothermal", while "autothermal" process assumes heating of the coal via exothermal chemical reactions occurring inside the gasifier itself.

It is essential that the oxidizer supplied is insufficient for complete oxidizing (combustion) of the fuel. During the reactions mentioned, oxygen and water molecules oxidize the coal and produce a gaseous mixture of carbon dioxide (CO_2), carbon monoxide (CO), water vapour (H_2O), and molecular hydrogen (H_2). (Some by-products like tar, phenols, etc. are also possible end products, depending on the specific gasification technology utilized.) This process has been conducted in-situ within natural coal seams (referred to as underground coal gasification) and in coal refineries. The desired end product is usually syngas (i.e., a combination of $H_2 + CO$), but the produced coal gas may also be further refined to produce additional quantities of H_2:

$$3C \text{ (i.e., coal)} + O_2 + H_2O \rightarrow H_2 + 3CO$$

If the refiner wants to produce alkanes (i.e., hydrocarbons present in natural gas, gasoline, and diesel fuel), the coal gas is collected at this state and routed to a Fischer-Tropsch reactor. If, however, hydrogen is the desired end-product, the coal gas (primarily the CO product) undergoes the water gas shift reaction where more hydrogen is produced by additional reaction with water vapor:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Although other technologies for coal gasification currently exist, all employ, in general, the same chemical processes. For low-grade coals (i.e., "brown coals") which contain significant amounts of water, there are technologies in which no steam is required during the reaction, with coal (carbon) and oxygen being the only reactants. As well, some coal gasification technologies do not require high pressures. Some utilize pulverized coal as fuel while others work with relatively large fractions of coal. Gasification technologies also vary in the way the blowing is supplied.

"Direct blowing" assumes the coal and the oxidizer being supplied towards each other from the opposite sides of the reactor channel. In this case the oxidizer passes through coke and (more likely) ashes to the reaction zone where it interacts with coal. The hot gas produced then passes fresh fuel and heats it while absorbing some products of thermal destruction of the fuel, such as tars and phenols. Thus, the gas requires significant refining before being used in the Fischer-Tropsch reaction. Products of the refinement are highly toxic and require special facilities for their utilization. As a result, the plant utilizing the described technologies has to be very large to be economically efficient. One of such plants called SASOL is situated in the Republic of South Africa (RSA). It was built due to embargo applied to the country preventing it from importing oil and natural gas. RSA is rich in its own brown coal and was able to arrange the use of the well known high pressure "Lurgi" gasification process developed in Germany in the first half of 20-th century.

"Reversed blowing" (as compared to the previous type described which was invented first) assumes the coal and the oxidizer being supplied from the same side of the reactor. In this case there is no chemical interaction between coal and oxidizer before the reaction zone. The gas produced in the reaction zone passes solid products of gasification (coke and ashes), and CO_2 and H_2O contained in the gas are additionally chemically restored to CO and H_2. As compared to the "direct blowing" technology, no toxic by-products are present in the gas: those are disabled in the reaction zone. This type of gasification has been developed in the first half of 20-th century, along with the "direct blowing", but the rate of gas production in it is significantly lower than that in "direct blowing" and there were no further efforts of developing the "reversed blowing" processes until 1980-s when a Soviet research facility KATEKNIIUgol' (R&D Institute for developing Kansk-Achinsk coal field) began R&D activities to produce the technology now known as "TERMOKOKS-S" process. The reason for reviving the interest to this type of gasification process is that it is ecologically clean and able to produce two types of useful products (simultaneously or separately): gas (either combustible or syngas) and middle-temperature coke. The former may be used as a fuel for gas boilers and diesel-generators or as syngas for producing gasoline, etc., the latter - as a technological fuel in metallurgy, as a chemical absorbent or as raw material for household fuel briquettes. Combustion of the product gas in gas boilers is ecologically cleaner than combustion of initial coal. Thus, a plant utilizing gasification technology with the "reversed blowing" is able to produce two valuable products of which one has relatively zero production cost since the latter is covered by competitive market price of the other. As the Soviet Union and its KATEKNIIUgol' ceased to exist, the technology was adopted by the individual scientists who originally developed it and is now being further researched in Russia and commercially distributed worldwide. Industrial plants utilizing it are now known to function in Ulaan-Baatar (Mongolia) and Krasnoyarsk (Russia).

Underground coal gasification

Underground coal gasification is an industrial *in-situ* gasification process, which is carried out in non-mined coal seams using injection of oxidants, and bringing the product gas to surface through production wells drilled from the surface. The product gas could to be used as a chemical feedstock or as fuel for power generation. The technique can be applied to resources that are otherwise not economical to extract and also offers an alternative to conventional coal mining methods for some resources. Compare to the traditional coal mining and gasification, the UCG has less environmental and social impact.

By-products

The by-products of coal gas manufacture included coke, coal tar, sulfur and ammonia; all useful products. Dyes, medicines, including sulfa drugs, saccharin and many organic compounds are therefore derived from coal gas.

Coke is used as a smokeless fuel and for the manufacture of water gas and producer gas. Coal tar was subjected to fractional distillation to recover various products, including

- tar, for roads
- benzole, a motor fuel
- creosote, a wood preservative

- phenol, used in the manufacture of plastics
- cresols, disinfectants

Sulfur is used in the manufacture of sulfuric acid and ammonia is used in the manufacture of fertilisers.

Environmental effects

Gasometer at West Ham

From its original development until the wide-scale adoption of natural gas, more than 50,000 manufactured gas plants were in existence in the United States alone. The process of manufacturing gas usually produced a number of by-products that contaminated the soil and groundwater in and around the manufacturing plant, so many former town gas plants are a serious environmental concern, and cleanup and remediation costs are often high. Manufactured gas plants (MGPs) were typically sited near or adjacent to waterways that were used to transport in coal and for the discharge of wastewater contaminated with tar, ammonia and/or drip oils, as well as outright waste tars and tar-water emulsions.

In the earliest days of MGP operations, coal tar was considered a waste and often disposed into the environment in and around the plant locations. While uses for coal tar developed by the late-19th century, the market for tar varied and plants that could not sell tar at a given time could store tar for future use, attempt to burn it as fuel for the boilers, or dump the tar as waste. Commonly, waste tars were disposed of in old gas holders, adits or even mine shafts (if present). Over time, the waste tars degrade with phenols, benzene (and other mono-aromatics – BTEX) and polycyclic aromatic hydrocarbons released as pollutant plumes that can escape into the surrounding environment. Other wastes included "blue billy", which is a ferroferricyanide compound—the blue colour is from Prussian blue, which was commercially used as a dye. Blue billy is typically a granular material and was sometimes sold locally with the strap line "guaranteed weed free drives". The presence of blue billy can give gas works waste a characteristic musty/bitter almonds or marzipan smell which is associated with cyanide gas.

The shift to the CWG process initially resulted in a reduced output of water gas tar as compared to the volume of coal tars. The advent of automobiles reduced the availability of naphtha for carburetion oil, as that fraction was desirable as motor fuel. MGPs that shifted to heavier grades of oil often experienced problems with the production of tar-water emulsions, which were difficult, time consuming, and costly to break. (The cause of tar-water emulsions is complex and was related to several factors, including free carbon in the carburetion oil and the substitution of bituminous coal as a feedstock instead of coke.) The production of large volumes of tar-water emulsions quickly filled up available storage capacity at MGPs and plant management often dumped the emulsions in pits, from which they may or may not have been later reclaimed. Even if the emulsions were reclaimed, the environmental damage from placing tars in unlined pits remained. The dumping of emulsions (and other tarry residues such as tar sludges, tank bottoms, and off-spec tars) into the soil and waters around MGPs is a significant factor in the pollution found at FMGPs today.

Commonly associated with former manufactured gas plants (known as "FMGPs" in environmental remediation) are contaminants including:

- BTEX
    - Diffused out from deposits of coal/gas tars
    - Leaks of carburetting oil/light oil
    - Leaks from drip pots, that collected condensible hydrocarbons from the gas
- Coal tar waste/sludge
    - Typically found in sumps of gas holders/decanting ponds.
    - Coal tar sludge has no resale value and so was always dumped.
- Volatile organic compounds
- Polycyclic aromatic hydrocarbons (PAHs)
    - Present in coal tar, gas tar, and pitch at significant concentrations.
- Heavy metals
    - Leaded solder for gas mains, lead piping, coal ashes.
- Cyanide
    - Purifier waste has large amounts of complex ferrocyanides in it.
- Lampblack
    - Only found where crude oil was used as gasification feedstock.
- Tar emulsions

Coal tar and coal tar sludges are frequently denser than water and are present in the environment as a dense non-aqueous phase liquid.

In the UK, former gasworks have commonly been developed over for residential and other uses (including the Millennium Dome), being seen as prime developable land in the confines of city boundaries. Situations such as these are now lead to problems associated with planning and the Contaminated Land Regime and have recently been debated in the House of Commons.

The more modern coal gasification processes (circa 1970 to 2006) also have environmental problems requiring various available technologies for mitigation.

Chapter 11

Shale Oil Extraction

Shale oil extraction

Shell's experimental *in situ* shale oil facility, Piceance Basin, Colorado, United States

Process type	Chemical
Industrial sector(s)	Chemical industry, oil industry
Main technologies or sub-processes	Kiviter, Galoter, Petrosix, Fushun, Shell ICP
Feedstock	Oil shale
Product(s)	Shale oil
Leading companies	Royal Dutch Shell, Eesti Energia, Viru Keemia Grupp, Petrobras, Fushun Mining Group

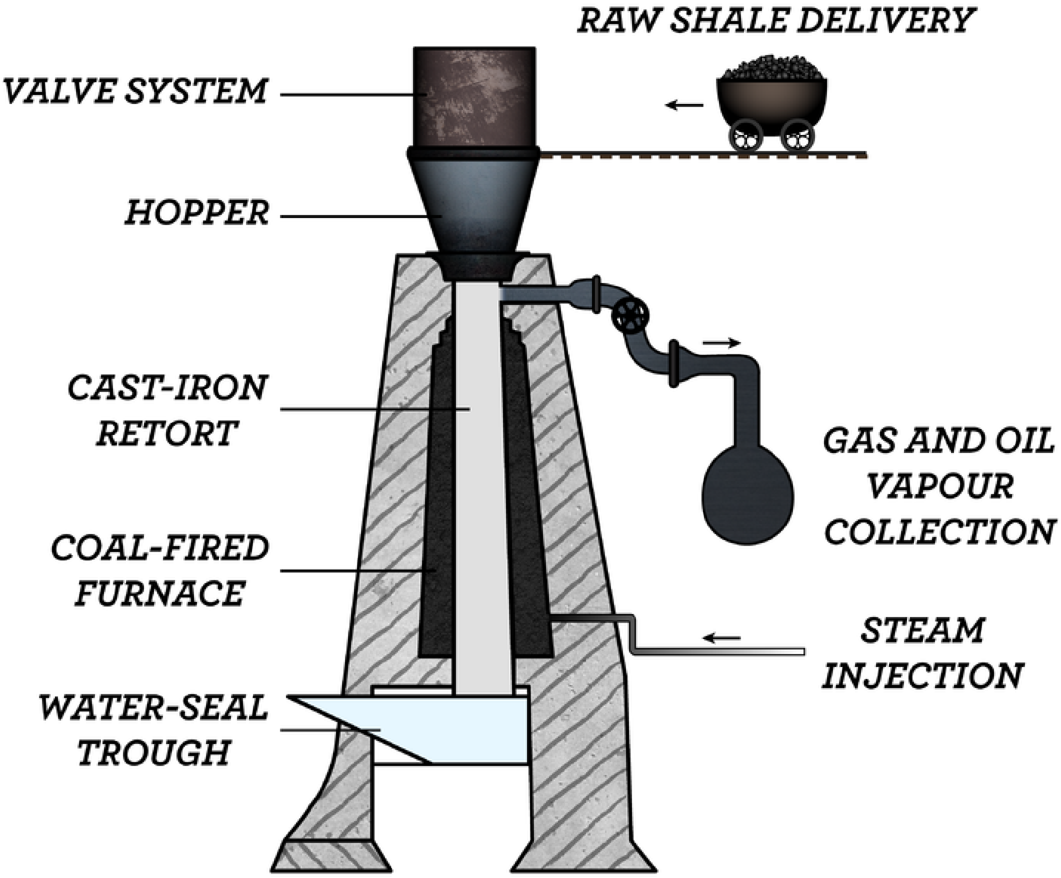
Shale oil extraction is an industrial process for unconventional oil production. This process converts kerogen in oil shale into shale oil by pyrolysis, hydrogenation, or thermal dissolution. The resultant shale oil is used as fuel oil or upgraded to meet refinery feedstock specifications by adding hydrogen and removing sulfur and nitrogen impurities.

Shale oil extraction is usually performed above ground (*ex situ* processing) by mining the oil shale and then treating it in processing facilities. Other modern technologies perform the processing underground (on-site or *in situ* processing) by applying heat and extracting the oil via oil wells.

The earliest description of the process dates to the 10th century. In 1684, Great Britain granted the first formal extraction process patent. Extraction industries and innovations became widespread during the 19th century. The industry shrank in the mid-20th century following the discovery of large reserves of conventional oil, but high petroleum prices at the beginning of the 21st century have led to renewed interest, accompanied by the development and testing of newer technologies.

As of 2010, major long-standing extraction industries are operating in Estonia, Brazil, and China. Its economic viability usually requires a lack of locally available crude oil. National energy security issues have also played a role in its development. Critics of shale oil extraction pose questions about environmental management issues, such as waste disposal, extensive water use, waste water management, and air pollution.

History



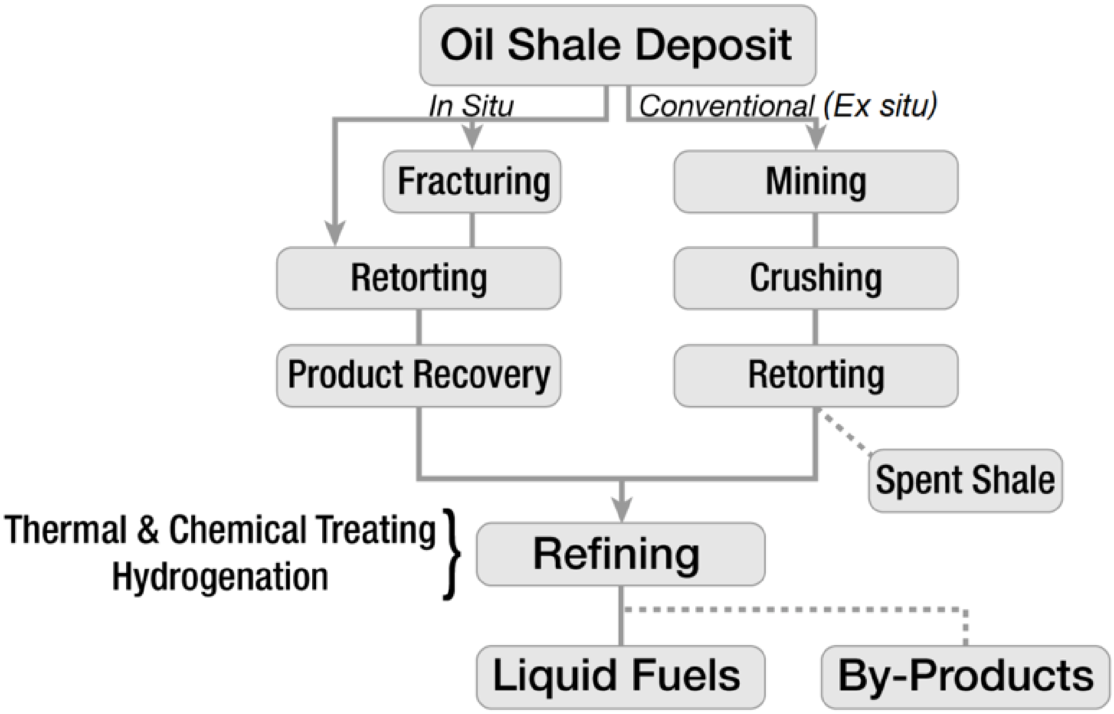
A.C. Kirk's retort, used in the mid-to-late 19th century, was one of the first vertical oil shale retorts. Its design is typical of retorts used in the end of 19th and beginning of 20th century.

In the 10th century, the Arabian physician Masawaih al-Mardini (Mesue the Younger) wrote of his experiments in extracting oil from "some kind of bituminous shale". The first shale oil extraction patent was granted by the British Crown in 1684 to three people who had "found a way to extract and make great quantities of pitch, tarr, and oyle out of a sort of stone". Modern industrial extraction of shale oil originated in France with the implementation of a process invented by Alexander Selligue in 1838, improved upon a decade later in Scotland using a process invented by James Young. During the late 19th century, plants were built in Australia, Brazil, Canada, and the United States. The 1894 invention of the Pumpherston retort, which was much less reliant on coal heat than its predecessors, marked the separation of the oil shale industry from the coal industry.

China (Manchuria), Estonia, New Zealand, South Africa, Spain, Sweden, and Switzerland began extracting shale oil in the early 20th century. However, crude oil discoveries in Texas during the 1920s and in the Middle East in the mid 20th century brought most oil shale industries to a halt. In 1944, the US recommenced shale oil extraction as part of its Synthetic Liquid Fuels Program. These industries continued until oil prices fell sharply in the 1980s. The last oil shale retort in the US, operated by Unocal Corporation, closed in 1991. The US program was restarted in 2003, followed by a commercial leasing program in 2005 permitting the extraction of oil shale and oil sands on federal lands in accordance with the Energy Policy Act of 2005.

As of 2010, shale oil extraction is in operation in Estonia, Brazil, and China. Their industries produced about 1,165 million liters (7.33 million barrels) of shale oil during 2008. Australia, the US, and Canada have tested shale oil extraction techniques via demonstration projects and are planning commercial implementation; Morocco and Jordan have announced their intent to do the same. Only four processes are in commercial use: Kiviter, Galoter, Fushun, and Petrosix.

Process principle



Overview of shale oil extraction

Shale oil extraction process decomposes oil shale and converts its kerogen into shale oil—a petroleum-like synthetic crude oil. The process is conducted by pyrolysis, hydrogenation, or thermal dissolution. The efficiencies of extraction processes are often evaluated by comparing their yields to the results of a Fischer Assay performed on a sample of the shale.

The oldest and the most common extraction method involves pyrolysis (also known as *retorting* or destructive distillation). In this process, oil shale is heated in the absence of oxygen until its kerogen decomposes into condensable shale oil vapors and non-condensable combustible oil shale gas. Oil vapors and oil shale gas are then collected and cooled, causing the shale oil to condense. In addition, oil shale processing produces spent oil shale, which is a solid residue. Spent shale consists of inorganic compounds (minerals) and char (some authors use the terms *coke residue* or *semi-coke* instead of *char*)—a carbonaceous residue formed from kerogen. Burning the char off the spent shale produces oil shale ash. Spent shale and shale ash can be used as ingredients in cement or brick manufacture. The composition of the oil shale may lend added value to the extraction process through the recovery of by-products, including ammonia, sulfur, aromatic compounds, pitch, asphalt, and waxes.

Heating the oil shale to pyrolysis temperature and completing the endothermic kerogen decomposition reactions require a source of energy. Some technologies use other fossil fuels such as natural gas, oil, or coal to generate this heat and experimental methods have used electricity, radio waves, microwaves, or reactive fluids for this purpose. Two strategies are used to reduce, and even eliminate, external heat energy requirements: the oil shale gas and char by-products generated by pyrolysis may be burned as a source of energy, and the heat contained in hot spent oil shale and oil shale ash may be used to pre-heat the raw oil shale.

For *ex situ* processing, oil shale is crushed into smaller pieces, increasing surface area for better extraction. The temperature at which decomposition of oil shale occurs depends on the time-scale of the process. In *ex situ* retorting processes, it begins at 300 °C (570 °F) and proceeds more rapidly and completely at higher temperatures. The amount of oil produced is the highest when the temperature ranges between 480 and 520 °C (900 and 970 °F). The ratio of oil shale gas to shale oil generally increases along with retorting temperatures. For a modern *in situ* process, which might take several months of heating, decomposition may be conducted at temperatures as low as 250 °C (480 °F). Temperatures below 600 °C (1,110 °F) are preferable, as this prevents the decomposition of lime stone and dolomite in the rock and thereby limits carbon dioxide emissions and energy consumption.

Hydrogenation and thermal dissolution (reactive fluid processes) extract the oil using hydrogen donors, solvents, or a combination of these. Thermal dissolution involves the application of solvents at elevated temperatures and pressures, increasing oil output by cracking the dissolved organic matter. Different methods produce shale oil with different properties.

Classification of extraction technologies

Industry analysts have created several classifications of the technologies used to extract shale oil from oil shale.

By process principles: Based on the treatment of raw oil shale by heat and solvents the methods are classified as pyrolysis, hydrogenation, or thermal dissolution.

By location: A frequently used distinction considers whether processing is done above or below ground, and classifies the technologies broadly as *ex situ* (displaced) or *in situ* (in place). In *ex situ* processing, also known as above-ground retorting, the oil shale is mined either underground or at the surface and then transported to a processing facility. In contrast, *in situ* processing converts the kerogen while it is still in the form of an oil shale deposit, following which it is then extracted via oil wells, where it rises in the same way as conventional crude oil. Unlike *ex situ* processing, it does not involve mining or spent oil shale disposal aboveground as spent oil shale stays underground.

By heating method: The method of transfering heat from combustion products to the oil shale may be classified as direct or indirect. While methods that allow combustion products to contact the oil shale within the retort are classified as *direct*, methods that burn materials external to the retort to heat another material that contacts the oil shale are described as *indirect*

By heat carrier: Based on the material used to deliver heat energy to the oil shale, processing technologies have been classified into gas heat carrier, solid heat carrier, wall conduction, reactive fluid, and volumetric heating methods. Heat carrier methods can be sub-classified as direct or indirect.

The following table shows extraction technologies classified by heating method, heat carrier and location (*in situ* or *ex situ*).

Classification of processing technologies by heating method and location (according to Alan Burnham)

Heating Method	Above ground (*ex situ*)	Underground (*in situ*)
Internal combustion	Gas combustion, NTU, Kiviter, Fushun, Union A, Paraho Direct, Superior Direct	Occidental Petroleum MIS, LLNL RISE, Geokinetics Horizontal, Rio Blanco
Hot recycled solids (inert or burned shale)	Alberta Taciuk, Galoter, Enefit, Lurgi-Ruhrgas, TOSCO II, Chevron STB, LLNL HRS, Shell Spher, KENTORT II	–
Conduction through a wall (various fuels)	Pumpherston, Hom Tov, Fischer Assay, Oil-Tech, EcoShale In-Capsule, Combustion Resources	Shell ICP (primary method), American Shale Oil CCR, IEP Geothermic Fuel Cell
Externally generated hot gas	PetroSIX, Union B, Paraho Indirect, Superior Indirect, Syntec (Smith process)	Chevron CRUSH, Omnishale, MWE IGE
Reactive fluids	IGT Hytort (high-pressure H_2), donor solvent processes, Chattanooga fluidized bed reactor	Shell ICP (some embodiments)
Volumetric heating	–	Radio wave, microwave, and electric current processes

By raw oil shale particle size: The various *ex situ* processing technologies may be differentiated by the size of the oil shale particles that are fed into the retorts. As a rule, gas heat carrier technologies process oil shale lumps varying in diameter from 10 to 100 millimeters (0.4 to 3.9 in), while solid heat carrier and wall conduction technologies process fines which are particles less than 10 millimeters (0.4 in) in diameter.

By retort orientation: "Ex-situ" technologies are sometimes classified as vertical or horizontal. Vertical retorts are usually shaft kilns where a bed of shale moves from top to bottom by gravity. Horizontal retorts are usually horizontal rotating drums or screws where shale moves from one end to the other. As a general rule, vertical retorts process lumps using a gas heat carrier, while horizontal retorts process fines using solid heat carrier.

By complexity of technology: *In situ* technologies are usually classified either as *true in situ* processes or *modified in situ* processes. *True in situ* processes do not involve mining or crushing the oil shale. *Modified in situ* processes involve drilling and fracturing the target oil shale deposit to create voids in the deposit. The voids enable a better flow of gases and fluids through the deposit, thereby increasing the volume and quality of the shale oil produced.

Ex situ *technologies*

Internal combustion

Internal combustion technologies burn materials (typically char and oil shale gas) within a vertical shaft retort to supply heat for pyrolysis. Typically raw oil shale particles between 12 millimetres (0.5 in) and 75 millimetres (3.0 in) in size are fed into the top of the retort and are heated by the rising hot gases, which pass through the descending oil shale, thereby causing decomposition of the kerogen at about 500 °C (932 °F) . Shale oil mist, evolved gases and cooled combustion gases are removed from the top of the retort then moved to separation equipment. Condensed shale oil is collected, while non-condensable gas is recycled and used to carry heat up the retort. In the lower part of the retort, air is injected for the combustion which heats the spent oil shale and gases to between 700 °C (1,292 °F) and 900 °C (1,650 °F). Cold recycled gas may enter the bottom of the retort to cool the shale ash. The Union A and Superior Direct processes depart from this pattern. In the Union A process, oil shale is fed through the bottom of the retort and a pump moves it upward. In the Superior Direct process, oil shale is processed in a horizontal, segmented, doughnut-shaped traveling-grate retort.

Internal combustion technologies such as the Paraho Direct are thermally efficient, since combustion of char on the spent shale and heat recovered from the shale ash and evolved gases can provide all the heat requirements of the retort. These technologies can achieve 80-90% of Fischer assay yield. Two well-established shale oil industries use internal combustion technologies: Kiviter process facilities have been operated continuously in Estonia since the 1920s, and a number of Chinese companies operate Fushun process facilities.

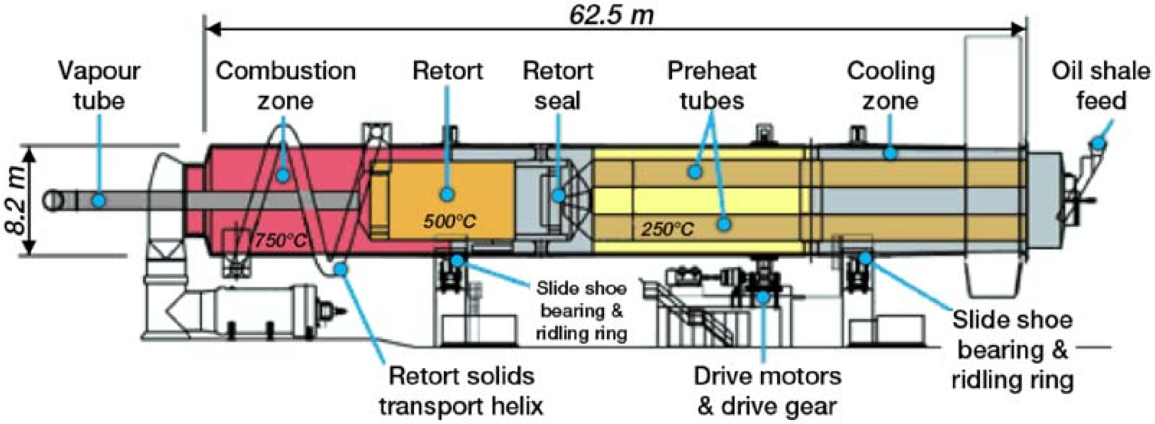
Common drawbacks of internal combustion technologies are that the shale oil gas is diluted by combustion gases and particles smaller than 10 millimeters (0.4 in) can not be processed. Uneven distribution of gas across the retort can result in blockages when hot spots cause particles to fuse or disintegrate.

Hot recycled solids

Hot recycled solids technologies deliver heat to the oil shale by recycling hot solid particles—typically oil shale ash. These technologies usually employ rotating kiln retorts, fed by fine oil shale particles generally having a diameter of less than 10 millimeters (0.4 in); some technologies use particles even smaller than 2.5 millimeters (0.10 in). The recycled particles are heated in a separate chamber or vessel to about 800 °C (1,470 °F) and then mixed with the raw oil shale to cause the shale to decompose at about 500 °C (932 °F). Oil vapour and shale oil gas are separated from the solids and cooled to condense and collect the oil. Heat recovered from the combustion gases and shale ash may be used to dry and preheat the raw oil shale before it is mixed with the hot recycle solids.

In the Galoter and Enefit processes, the spent oil shale is burnt in a separate furnace and the resulting hot ash is separated from the combustion gas and mixed with oil shale particles in a rotating kiln. Combustion gases from the furnace are used to dry the oil shale in a dryer before mixing with hot ash. The TOSCO II process uses ceramic balls instead of shale ash as the hot recycled solids. The distinguishing feature of the Alberta Taciuk Process (ATP) is that the entire process occurs in a single rotating multi–chamber horizontal vessel.

Because the hot recycle solids are heated in a separate furnace, the oil shale gas from these technologies is not diluted with combustion exhaust gas. Another advantage is that there is no limit on the smallest particles that the retort can process, thus allowing all the crushed feed to be used. One disadvantge is that more water is used to handle the resulting finer shale ash.



Alberta Taciuk Processor retort

Conduction through a wall

These technologies transfer heat to the oil shale by conducting it through the retort wall. The shale feed usually consists of fine particles. Their advantage lies in the fact that retort vapors are not combined with combustion exhaust. The Combustion Resources process uses a hydrogen–fired rotating kiln, where hot gas is circulated through an outer annulus. The Oil-Tech staged electrically heated retort consists of individual inter-connected heating chambers, stacked atop each other. Its principal advantage lies in its modular design, which enhances its portability and adaptability. The Red Leaf Resources EcoShale In-Capsule Process combines surface mining with a lower-temperature heating method similar to *in situ* processes by operating within the confines of an earthen structure. A hot gas circulated through parallel pipes heats the oil shale rubble. An installation within the empty space created by mining would permit rapid reclamation of the topography. A general drawback of combustion through a wall technologies is that the retorts are more costly when scaled-up due to the large amount of wall surface area of high-temperature alloys required.

Externally generated hot gas

In general, externally generated hot gas technologies are similar to internal combustion technologies in that they also process oil shale lumps in vertical shaft kilns. Significantly, though, the heat in these technologies is delivered by gases heated outside the retort vessel, and therefore the retort vapors are not diluted with combustion exhaust. The Petrosix and Paraho Indirect employ this technology. In addition to not accepting fine particles as feed, these technologies do not utilize the potential heat of combusting the char on the spent shale and thus must burn more valuable fuels. However, due to the lack of combustion of the spent shale, the oil shale does not exceed 500 °C (932 °F) and significant carbonate mineral decomposition and subsequent CO_2 generation can be avoided for some oil shales. Also, these technologies tend to be the more stable and easier to control than internal combustion or hot solid recyle technologies.

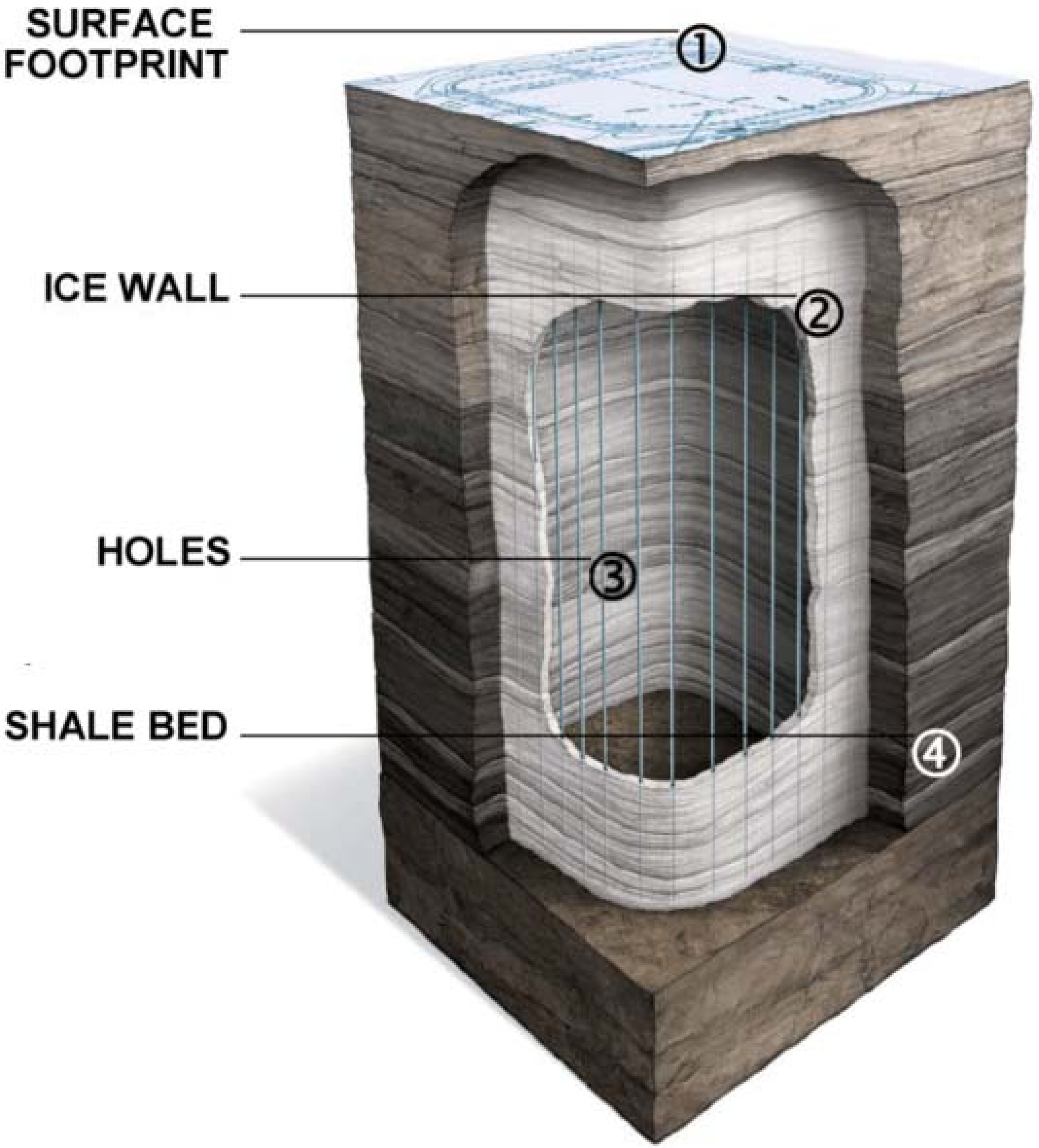
Reactive fluids

Kerogen is tightly bound to the shale and resists dissolution by most solvents. Despite this constraint, extraction using especially reactive fluids has been tested, including those in a supercritical state. Reactive fluid technologies are suitable for processing oil shales with a low hydrogen content. In these technologies, hydrogen gas (H_2) or hydrogen donors (chemicals that donate hydrogen during chemical reactions) react with coke precursors (chemical structures in the oil shale that are prone to form char during retorting but have not yet done so). Reactive fluid technologies include the IGT Hytort (high-pressure H_2) process, donor solvent processes, and the Chattanooga fluidized bed reactor. In the IGT Hytort oil shale is processed in a high-pressure hydrogen environment. The Chattanooga process uses a fluidized bed reactor and an associated hydrogen-fired heater for oil shale thermal cracking and hydrogenation.

In situ *technologies*

In situ technologies heat oil shale underground by injecting hot fluids into the rock formation, or by using linear or planar heating sources followed by thermal conduction and convection to distribute heat through the target area. Shale oil is then recovered through vertical wells drilled into the formation. These technologies are potentially able to extract more shale oil from a given area of land than conventional *ex situ* processing technologies, as the wells can reach greater depths than surface mines. They present an opportunity to recover shale oil from low-grade deposits that traditional mining techniques could not extract.

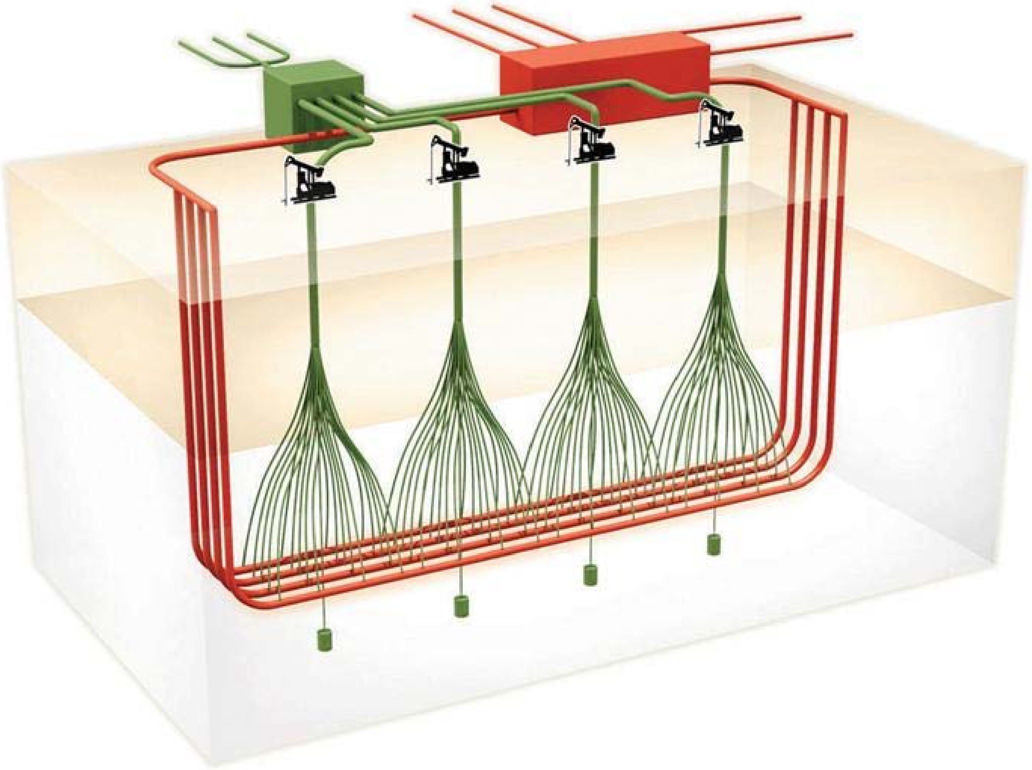
During World War II a modified *in situ* extraction process was implemented without significant success in Germany. One of the earliest successful *in situ* processes was underground gasification by electrical energy (Ljungström method)—a process exploited between 1940 and 1966 for shale oil extraction at Kvarntorp in Sweden. Prior to the 1980s, many variations of the *in situ* process were explored in the United States. The first modified *in situ* oil shale experiment in the United States was conducted by Occidental Petroleum in 1972 at Logan Wash, Colorado. The newest technologies explore a variety of heat sources and heat delivery systems.



Shell's freeze wall for *in situ* shale oil production was designed to separate the process from its surroundings

Wall conduction

Wall conduction *in situ* technologies use heating elements or heating pipes placed within the oil shale formation. The Shell in situ conversion process (Shell ICP) uses electrical heating elements for heating the oil shale layer to between 650 and 700 °F (340 and 370 °C) over a period of approximately four years. The processing area is isolated from surrounding groundwater by a freeze wall consisting of wells filled with a circulating super-chilled fluid. Disadvantages of this process are large electrical power consumption, extensive water use, and the risk of groundwater pollution. The process, under development since the early 1980s, is tested at the Mahogany test site in the Piceance Basin. 1,700 barrels (270 m^3) of oil were extracted in 2004 at a 30-by-40-foot (9.1 by 12 m) testing area.

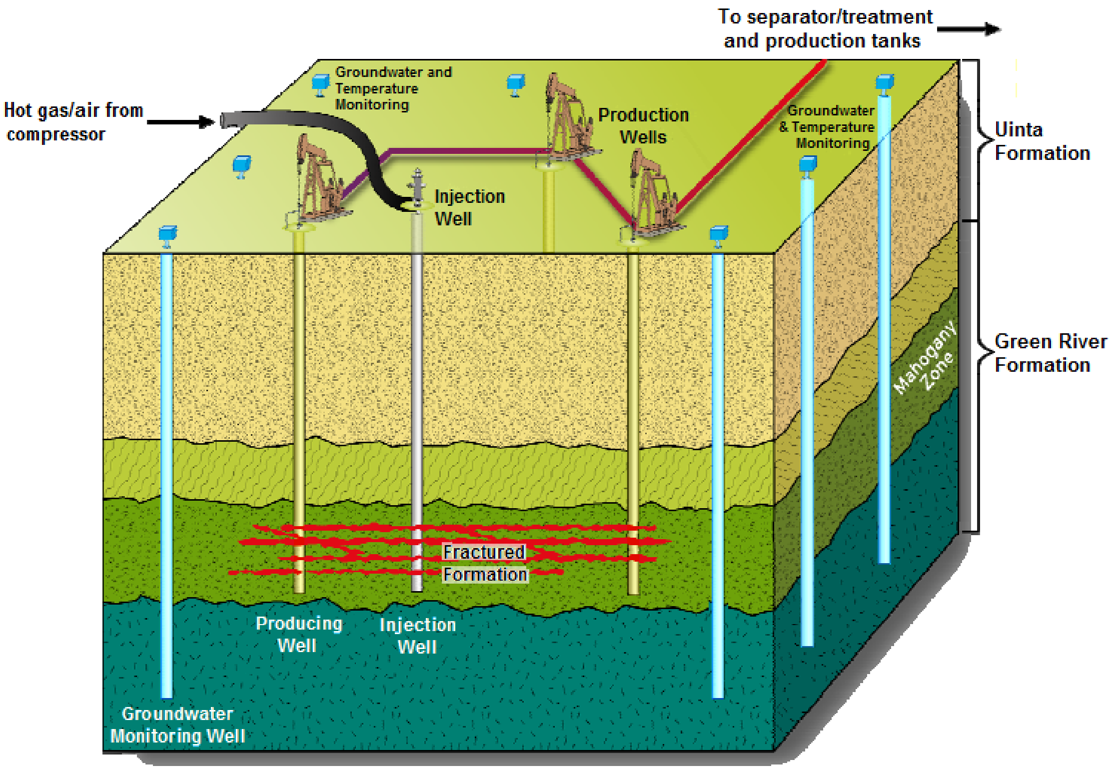


American Shale Oil CCR Process

In the American Shale Oil CCR Process, superheated steam or another heat transfer medium is circulated through a series of pipes placed below the oil shale layer to be extracted. The system combines horizontal wells, through which steam is passed, and vertical wells, which provide both vertical heat transfer through refluxing of converted shale oil and a means to collect the produced hydrocarbons. Heat is supplied by combustion of natural gas or propane in the initial phase and by oil shale gas at a later stage.

The Independent Energy Partners' Geothermic Fuels Cells Process (IEP GFC) extracts shale oil by exploiting a high-temperature stack of fuel cells. The cells, placed in the oil shale formation, are fueled by natural gas during a warm-up period and afterward by oil shale gas generated by its own waste heat.

Externally generated hot gas



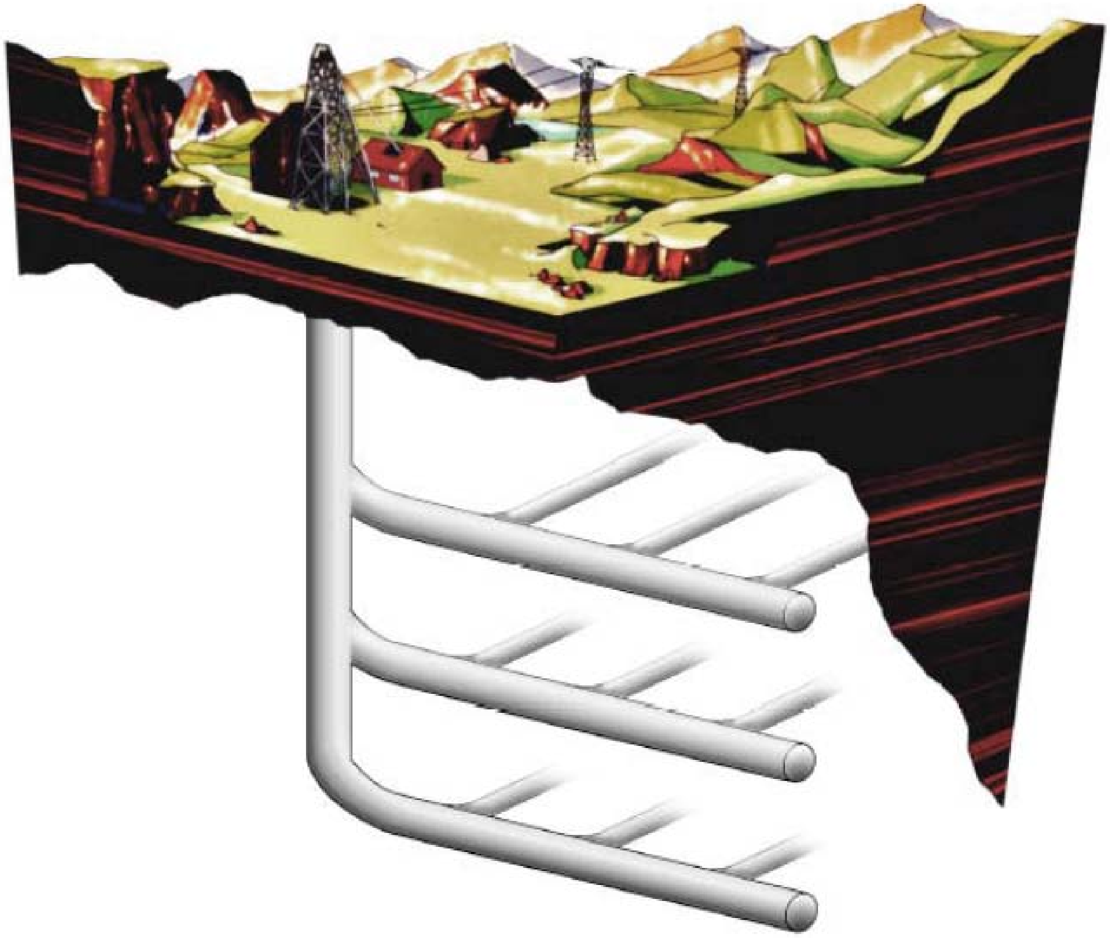
Chevron CRUSH process

Externally generated hot gas *in situ* technologies use hot gases that are heated above-ground and then injected into the oil shale formation. The Chevron CRUSH process, developed by Chevron Corporation in partnership with Los Alamos National Laboratory, injects heated carbon dioxide into the formation via drilled wells and heats the formation through a series of horizontal fractures in which the gas circulates. General Synfuels International has proposed the Omnishale process which involves injecting super-heated air into the oil shale formation. Mountain West Energy's In Situ Vapor Extraction process uses similar principles of injection of high-temperature gas.

ExxonMobil Electrofrac

ExxonMobil's *in situ* technology (ExxonMobil Electrofrac) uses electrical heating with elements of both wall conduction and volumetric heating methods. It injects an electrically conductive material such as calcined petroleum coke into the hydraulic fractures created in the oil shale formation which then forms a heating element. Heating wells are placed in a parallel row with a second horizontal well intersecting them at their toe. This allows opposing electrical charges to be applied at either end.

Volumetric heating

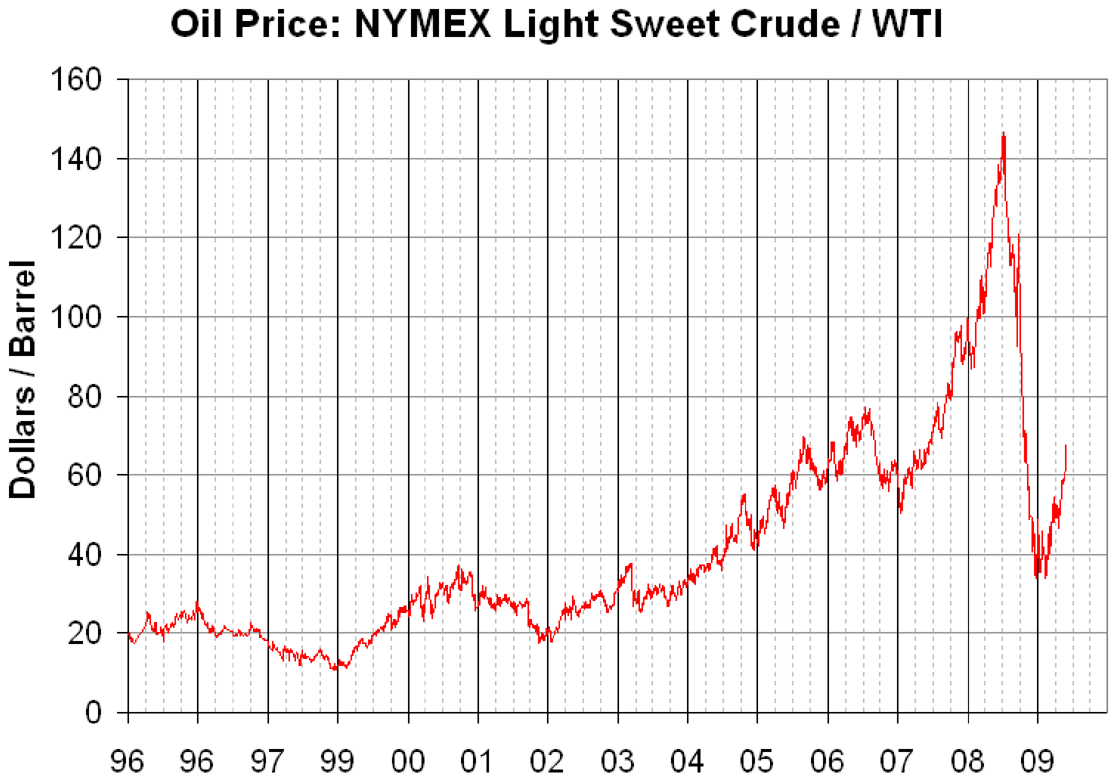


Artist's rendition of a radio wave-based extraction facility

The Illinois Institute of Technology developed the concept of oil shale volumetric heating using radio waves (radio frequency processing) during the late 1970s. This technology was further developed by Lawrence Livermore National Laboratory. The oil shale would be heated by vertical electrode arrays. Deeper volumes could be processed at slower heating rates by installations spaced at tens of meters. The concept presumes a radio frequency at which the skin depth is many tens of meters, thereby overcoming the thermal diffusion times needed for conductive heating. Its drawbacks include intensive electrical demand and the possibility that groundwater or char would absorb undue amounts of the energy. Radio frequency processing in conjunction with critical fluids is being developed by Raytheon together with CF Technologies and tested by Schlumberger.

Microwave heating technologies are based on the same principles as radio wave heating, although it is believed that radio wave heating is an improvement over microwave heating because its energy can penetrate farther into the oil shale formation. The microwave heating process is being tested by Global Resource Corporation. Electro-Petroleum proposes electrically enhanced oil recovery by the passage of direct current between cathodes in producing wells and anodes located either at the surface or at depth in other wells. The passage of the current through the oil shale formation results in resistive Joule heating.

Economics



NYMEX light-sweet crude oil prices 1996–2009 (not adjusted for inflation)

The dominant question for shale oil production is under what conditions shale oil is economically viable. The various attempts to develop oil shale deposits have succeeded only when the shale-oil production cost in a given region is lower than the price of petroleum or its other substitutes. According to a survey conducted by the RAND Corporation, the cost of producing shale oil at a hypothetical surface retorting complex in the United States (comprising a mine, retorting plant, upgrading plant, supporting utilities, and spent oil shale reclamation), would be in a range of US\$70–95 per barrel (\$440–600/m^3), adjusted to 2005 values. Assuming a gradual increase in output after the start of commercial production, the analysis projects a gradual reduction in processing costs to \$30–40 per barrel (\$190–250/m^3) after achieving the milestone of 1 billion barrels ($160×10^6$ m^3). Royal Dutch Shell has announced that its Shell ICP technology would realize a profit when crude oil prices are higher than $30 per barrel ($190/m^3), while some technologies at full-scale production assert profitability at oil prices even lower than $20 per barrel ($130/m^3).

To increase the efficiency of oil shale retorting and by this the viability of the shale oil production, researchers have proposed and tested several co-pyrolysis processes, in which other materials such as biomass, peat, waste bitumen, or rubber and plastic wastes are retorted along with the oil shale. Some modified technologies propose combining a fluidized bed retort with a circulated fluidized bed furnace for burning the by-products of pyrolysis (char and oil shale gas) and thereby improving oil yield, increasing throughput, and decreasing retorting time.

Other ways of improving the economics of shale oil extraction are to increase the size of the operation to achieve economies of scale, use oil shale that is a by-product of coal mining such as at Fushun China, produce specialty chemicals as by Viru Keemia Grupp in Estonia, co-generate electricity from the waste heat and process high grade oil shale that yields more oil per shale processed.

A possible measure of the viability of oil shale as an energy source lies in the ratio of the energy in the extracted oil to the energy used in its mining and processing (Energy Returned on Energy Invested, or EROEI). A 1984 study estimated the EROEI of the various known oil shale deposits as varying between 0.7–13.3; Some companies and newer technologies assert an EROEI between 3 and 10. To increase the EROEI, several combined technologies were proposed. These include the usage of process waste heat, e.g. gasification or combustion of the residual carbon (char), and the usage of waste heat from other industrial processes, such as coal gasification and nuclear power generation.

The water requirements of extraction processes are an additional economic consideration in regions where water is a scarce resource.

Environmental considerations

Objections to its potential environmental impact have stalled governmental support for extraction of shale oil in some countries, such as Australia. Shale oil extraction may involve a number of different environmental impacts that vary with process technologies. Depending on the geological conditions and mining techniques, mining impacts may include acid drainage induced by the sudden rapid exposure and subsequent oxidation of formerly buried materials, the introduction of metals into surface water and groundwater, increased erosion, sulfur gas emissions, and air pollution caused by the production of particulates during processing, transport, and support activities. Surface mining for *ex situ* processing, as with *in situ* processing, requires extensive land use and *ex situ* thermal processing generates wastes that require disposal. Mining, processing, spent oil shale disposal, and waste treatment require land to be withdrawn from traditional uses. Depending on the processing technology, the waste material may contain pollutants including sulfates, heavy metals, and polycyclic aromatic hydrocarbons, some of which are toxic and carcinogenic. Experimental *in situ* conversion processes may reduce some of these impacts, but may instead cause other problems, such as groundwater pollution.

Spent shale often presents a disposal problem

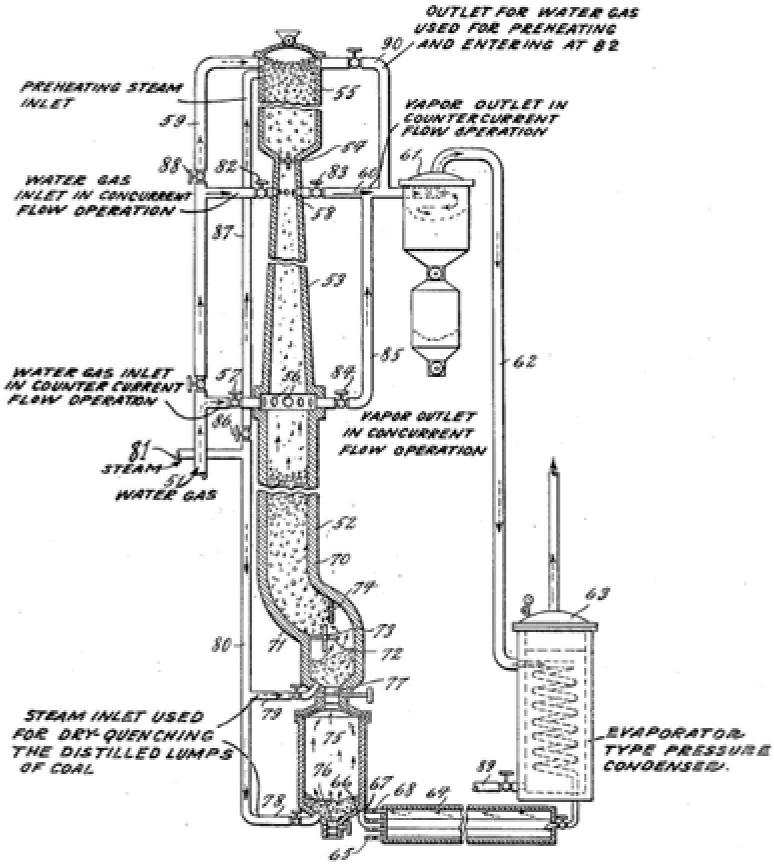
The production and usage of oil shale usually generates more greenhouse gas emissions, including carbon dioxide, than conventional fossil fuels. Depending on the technology and the oil shale composition, shale oil extraction processes may also emit sulfur dioxide, hydrogen sulfide, carbonyl sulfide, and nitrogen oxides. Developing carbon capture and storage technologies may reduce the processes' carbon footprint.

Concerns have been raised over the oil shale industry's use of water, particularly in arid regions where water consumption is a sensitive issue. Above-ground retorting typically consumes between one and five barrels of water per barrel of produced shale oil, depending on technology. Water is usually used for spent oil shale cooling and oil shale ash disposal. *In situ* processing, according to one estimate, uses about one-tenth as much water. In other areas, water must be pumped out of oil shale mines. The resulting fall in the water table may have negative effects on nearby arable land and forests.

A 2008 programmatic environmental impact statement issued by the United States Bureau of Land Management stated that surface mining and retort operations produce 2 to 10 U.S. gallons (7.6 to 38 l; 1.7 to 8.3 imp gal) of waste water per 1 short ton (0.91 t) of processed oil shale.

Chapter 12

Karrick Process



Karrick Process, from U.S. Patent #1,958,918.

The **Karrick process** is a low-temperature carbonization (LTC) and pyrolysis process of carbonaceous materials. Although primarily meant for coal carbonization, it also could be used for processing of oil shale, lignite or any carbonaceous materials. These are heated at 450 °C (800 °F) to 700 °C (1,300 °F) in the absence of air to distill out synthetic fuels–unconventional oil and syngas. It could be used for a coal liquefaction as also for a semi-coke production. The process was the work of oil shale technologist Lewis Cass Karrick at the United States Bureau of Mines in the 1920s.

History

The Karrick process was invented by Lewis Cass Karrick in the 1920s. Although Karrick did not invent coal LTC as such, he perfected the existing technologies resulting the Karrick process. The retort used for the Karrick process based on the Nevada–Texas–Utah Retort, used for the shale oil extraction.

In 1935, a Karrick LTC pilot plant was constructed in the coal research laboratory at the University of Utah. Commercial-size processing plants were operated during 1930s in Colorado, Utah and Ohio. During World War II, similar processing plant was operated by the United States Navy. In Australia, during World War II the Karrick process plants were used for shale oil extraction in New South Wales. In 1950s–1970s, the technology was used by the Rexco Company in thr Snibston plant at Coalville in Leicestershire, England.

Process

The Karrick process is a low-temperature carbonization process, which uses a hermetic retort. For commercial scale production, a retort about 3 feet (0.91 m) in diameter and 20 feet (6.1 m) high would be used. The process of carbonization would last about 3 hours.

Superheated steam is injected continuously into the top of retort filled by coal. At first, in contact with cool coal, the steam condenses to water acting as a cleaning agent. While temperature of coal rises, the destructive distillation starts. Coal is heated at 450 °C (800 °F) to 700 °C (1,300 °F) in the absence of air. The carbonization temperature is lower compared with 800 °C (1,500 °F) to 1,000 °C (1,800 °F) for producing metallurgic coke. The lower temperature optimizes the production of coal tars richer in lighter hydrocarbons than normal coal tar, and therefore it is suitable for processing into fuels. Resulting water, oil and coal tar, and syngas moves out from retort through outlet valves at the bottom of the retort. The residue (char or semi-coke) remains in the retort. While the produced liquids are mostly a by-product, the semi-coke is the main product, a solid and smokeless fuel.

Products

In the Karrick process, 1 short ton of coal yields up to 1 barrel of oils and coal tars (12% by weight), and produces 3,000 cubic feet (85 m^3) of rich coal gas and 1,500 pounds (680 kg) of solid smokeless char or semi-coke (for one metric ton, 0.175 m^3 of oils and coal tars, 95 m^3 of gas, and 750 kg of semi-coke). Yields by volume of approximately 25% gasoline, 10% kerosene and 20% good quality fuel oil are obtainable from coal.

Gasoline obtained from coal by the Karrick process combined with cracking and refining is equal in quality to tetraethyl lead gasolines. More power is developed in internal combustion engines and an increase in fuel economy of approximately 20% is obtainable under identical operating conditions.

Semi-coke can be used for utility boilers and cooking coal in steel smelters, yields more heat than raw coal and can be converted to water gas. Water gas can be converted to oil by the Fischer-Tropsch process. Coal gas from Karrick LTC yields greater energy content than natural gas. Phenolic wastes are used by the chemical industry as feedstock for plastics, etc. Electrical power can be cogenerated at nominal equipment cost.

Economic viability

Oils, including petroleum, have long been extracted from coal. Production plants were merely shut down in the 1880s because crude oil became cheaper than coal liquefaction. The capability itself, however, has never disappeared. Eight years of pilot plant tests by Karrick attest that states, cities or even smaller towns, could make their own gas and generate their own electricity.

A 30 ton plant and oil refinery will show a profit over and above all operating and capital costs and the products will sell at attractive prices for equivalent products. The private sector should require no subsidies, but not in competition with those who skim off the oil from coal and sell the residual smokeless fuel to power plants.}

The cheapest liquid fuel from coal will come when processed by LTC for both liquid fuels and electric power. As a tertiary product of the coal distilling process, electrical energy can be generated at a minimum equipment cost. A Karrick LTC plant with 1 kiloton of daily coal capacity produces sufficient steam to generate 100,000 kilowatt hours of electrical power at no extra cost excepting capital investment for electrical equipment and loss of steam temperature passing through turbines. The process steam cost could be low since this steam could be derived from off-peak boiler capacity or from turbines in central electric stations. Fuel for steam and superheating would subsequently be reduced in cost.

Although no difficulties whatsoever were encountered during the successful operation of the pilot plant in 1935, the commercial Karrick LTC process plant would fail due to mechanical problems, a postulation based on previous failures of other plants using different processes under different conditions. Markets for the described coal products are limited, which makes such a venture economically unsound.

Advantages and disadvantages

Compared to the Bergius process, the Karrick process is cheaper, requires less water and destroys less the thermal value (one-half that of the Bergius process). The smokeless semi-coke fuel, when burned in an open grate or in boilers, delivers 20% to 25% more heat than raw coal. The coal gas should deliver more heat than natural gas per heat unit contained due to the greater quantity of combined carbon and lower dilution of the combustion gases with water vapor.

Chapter 13

Synthetic Fuel

Side-by-side comparison of FT synthetic fuel and conventional fuel. The synthetic fuel is clear as water because of a near-absence of sulfur and aromatics.

Synthetic fuel or **synfuel** is a liquid fuel obtained from coal, natural gas, oil shale, or biomass. It may also refer to fuels derived from other solids such as plastics or rubber waste. It may also (less often) refer to gaseous fuels produced in a similar way. Common use of the term "synthetic fuel" is to describe fuels manufactured via Fischer Tropsch conversion, methanol to gasoline conversion, or direct coal liquefaction.

July 2009 worldwide commercial synthetic fuels production capacity is over 240,000 barrels per day (38,000 m^3/d), with numerous new projects in construction or development.

Classification and principles

The term 'synthetic fuel' has several different meanings and it may include different types of fuels. More traditional definitions, e.g. definition given by the International Energy Agency, define 'synthetic fuel' as any liquid fuel obtained from coal or natural gas. The Energy Information Administration defines synthetic fuels in its Annual Energy Outlook

2006, as fuels produced from coal, natural gas, or biomass feedstocks through chemical conversion into synthetic crude and/or synthetic liquid products. A number of synthetic fuel's definitions include also fuels produced from biomass, and industrial and municipal waste. The definition of synthetic fuel may also consist of oil sands and oil shale as synthetic fuel's sources and in addition to liquid fuels also gaseous fuels are covered. On his 'Synthetic fuels handbook' a petrochemist James G. Speight included liquid and gaseous fuels as well as clean solid fuels produced by conversion of coal, oil shale or tar sands, and various forms of biomass, although he admits that in the context of substitutes for petroleum-based fuels it has even wider meaning. Depending the context, also methanol, ethanol and hydrogen may be included.

Synthetic fuels are produced by the chemical process of conversion. Conversion methods could be direct conversion into liquid transportation fuels, or indirect conversion, in which the source substance is converted initially into syngas which then goes through additional conversion process to become liquid fuels. Basic conversion methods include carbonization and pyrolysis, hydrogenation, and thermal dissolution.

History

Ruins of the German synthetic petrol plant (Hydrierwerke Pölitz – Aktiengesellschaft) in Police, Poland

Direct conversion of coal to synthetic fuel was originally developed in Germany. The Bergius process was developed by Friedrich Bergius, yielding a patent on the Bergius process in 1913. Karl Goldschmidt invited him to build an industrial plant at his factory the Th. Goldschmidt AG (now known as Evonik Industries) in 1914. The production began only in 1919.

Also indirect coal conversion (where coal is gasified and then converted to synthetic fuels) was developed in Germany by Franz Fischer and Hans Tropsch in 1923. During World War II, Germany used synthetic oil manufacturing (German: *Kohleverflüssigung*) to produce substitute (*Ersatz*) oil products by using the Bergius process (from coal), the Fischer–Tropsch process (water gas), and other methods (Zeitz used the TTH and MTH processes). Before World War Two in 1931, the British Department of Scientific and Industrial Research located in Greenwich, England set up a small facility where hydrogen gas at extreme high pressure was combined with coal to make a synthetic fuel.

The Bergius process plants were the primary source of Nazi Germany's high-grade aviation gasoline and the source of most of its synthetic oil, 99% of its synthetic rubber and nearly all of its synthetic methanol, synthetic ammonia, and nitric acid. Nearly 1/3 of the Bergius production was produced by plants in Pölitz (Polish: *Police*) and Leuna, with more than 1/3 more in five other plants (Ludwigshafen had a much smaller Bergius plant which improved "gasoline quality by dehydrogenation" using the DHD process).

Synthetic fuel grades included "T.L. [jet] fuel ", "first quality aviation gasoline", "aviation base gasoline", and "gasoline - middle oil"; and "producer gas" and diesel were synthesized for fuel as well (e.g., converted armored tanks used producer gas).[:4,s2] By early 1944, German synthetic fuel production had reached more than 124,000 barrels per day (19,700 m^3/d) from 25 plants, including 10 in the Ruhr Area.[:239] In 1937, the four central Germany lignite coal plants at Böhlen, Leuna, Magdeburg/Rothensee, and Zeitz, along with the Ruhr Area bituminous coal plant at Scholven/Buer, had produced 4.8 million barrels (760×10^3 m^3) of fuel. Four new hydrogenation plants (German: *Hydrierwerke*) were subsequently erected at Bottrop-Welheim (which used "Bituminous coal tar pitch"), Gelsenkirchen (Nordstern), Pölitz, and, at 200,000 tons/yr Wesseling. Nordstern and Pölitz/Stettin used bituminous coal, as did the new Blechhammer plants. Heydebreck synthesized food oil, which was tested on concentration camp prisoners. The Geilenberg Special Staff was using 350,000 mostly foreign forced laborers to reconstruct the bombed synthetic oil plants, and, in an emergency decentralization program, to build 7 underground hydrogenation plants for bombing protection (none were completed). (Planners had rejected an earlier such proposal because the war was to be won before the bunkers would be completed.) In July 1944, the 'Cuckoo' project underground synthetic oil plant (800,000 m^2) was being "carved out of the Himmelsburg" North of the Mittelwerk, but the plant was unfinished at the end of WWII.

Indirect Fischer-Tropsch ("FT") technologies were brought to the US after World War 2, and a 7,000 barrels per day (1,100 m^3/d) plant was designed by HRI, and built in Brownsville Texas. The plant represented the first commercial use of high-temperature Fischer Tropsch conversion. It operated from 1950 to 1955, when it was shut down when the price of oil dropped due to enhanced production and huge discoveries in the Middle East.

After World War Two, in 1949 a demonstration plant for converting coal to gasoline was built and operated by the U.S. Bureau of Mines in Louisiana, Missouri. Direct coal conversion plants were also developed in the US after WW2, including a 3 TPD plant in Lawrenceville, NJ, and a 250-600 TPD Plant in Catlettsburg, KY.

Processes

There are numerous processes that can be used to produce synthetic fuels.

These broadly fall into three categories: Indirect, Direct, and Biofuel processes.

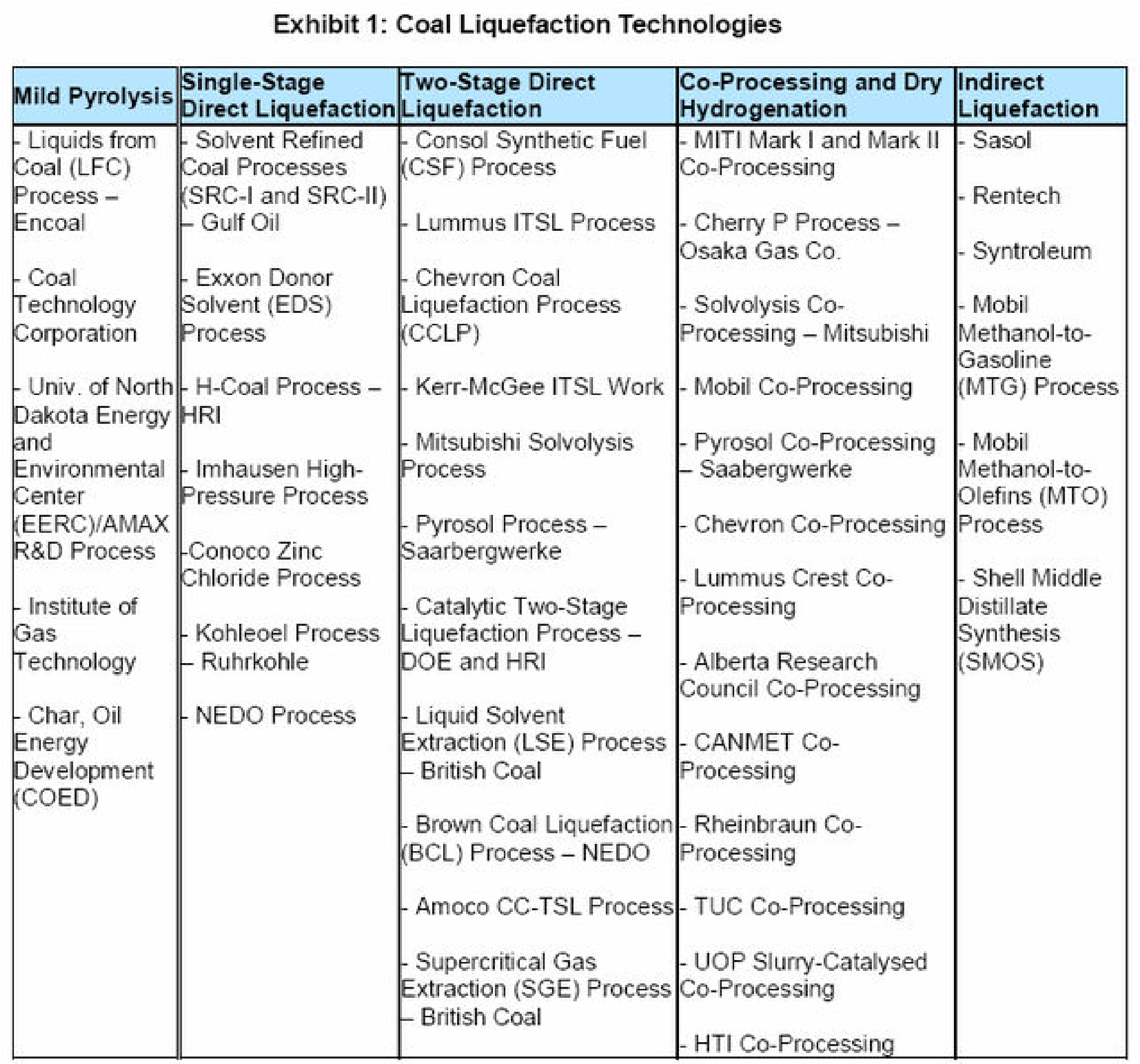


Exhibit 1: Coal Liquefaction Technologies

Mild Pyrolysis	Single-Stage Direct Liquefaction	Two-Stage Direct Liquefaction	Co-Processing and Dry Hydrogenation	Indirect Liquefaction
- Liquids from Coal (LFC) Process – Encoal - Coal Technology Corporation - Univ. of North Dakota Energy and Environmental Center (EERC)/AMAX R&D Process - Institute of Gas Technology - Char, Oil Energy Development (COED)	- Solvent Refined Coal Processes (SRC-I and SRC-II) – Gulf Oil - Exxon Donor Solvent (EDS) Process - H-Coal Process – HRI - Imhausen High-Pressure Process -Conoco Zinc Chloride Process - Kohleoel Process – Ruhrkohle - NEDO Process	- Consol Synthetic Fuel (CSF) Process - Lummus ITSL Process - Chevron Coal Liquefaction Process (CCLP) - Kerr-McGee ITSL Work - Mitsubishi Solvolysis Process - Pyrosol Process – Saarbergwerke - Catalytic Two-Stage Liquefaction Process – DOE and HRI - Liquid Solvent Extraction (LSE) Process – British Coal - Brown Coal Liquefaction (BCL) Process – NEDO - Amoco CC-TSL Process - Supercritical Gas Extraction (SGE) Process – British Coal	- MITI Mark I and Mark II Co-Processing - Cherry P Process – Osaka Gas Co. - Solvolysis Co-Processing – Mitsubishi - Mobil Co-Processing - Pyrosol Co-Processing – Saabergwerke - Chevron Co-Processing - Lummus Crest Co-Processing - Alberta Research Council Co-Processing - CANMET Co-Processing - Rheinbraun Co-Processing - TUC Co-Processing - UOP Slurry-Catalysed Co-Processing - HTI Co-Processing	- Sasol - Rentech - Syntroleum - Mobil Methanol-to-Gasoline (MTG) Process - Mobil Methanol-to-Olefins (MTO) Process - Shell Middle Distillate Synthesis (SMOS)

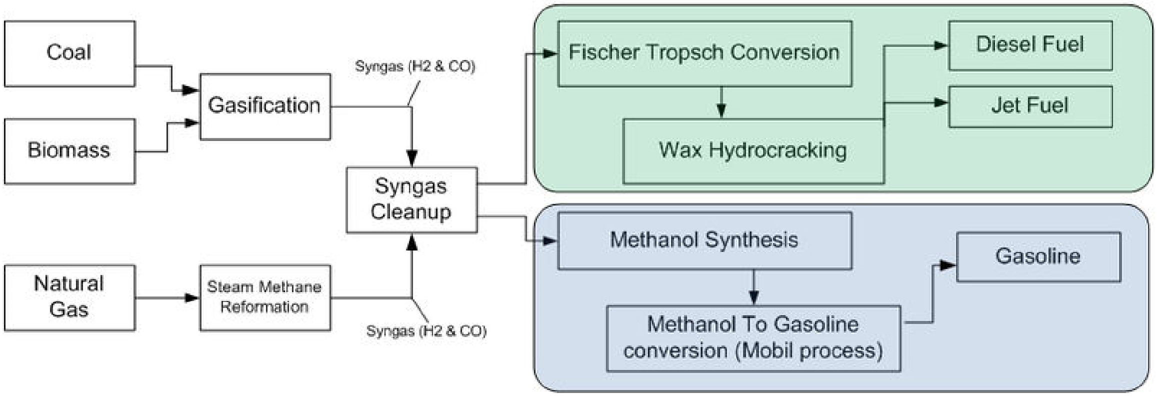
This is a listing of many of the different technologies used for synthetic fuel production. Please note that although this list was compiled for coal to liquids technologies, many of the same processes can also be used with biomass or natural gas feedstocks.

Indirect conversion

Indirect conversion has the widest deployment worldwide, with global production totaling around 260,000 barrels per day (41,000 m^3/d), and many additional projects under active development.

Indirect conversion broadly refers to a process in which biomass, coal, or natural gas is converted to a mix of hydrogen and carbon monoxide known as syngas either through gasification or steam methane reforming, and that syngas is processed into a liquid transportation fuel using one of a number of different conversion techniques depending on the desired end product.

Indirect Conversion Synthetic Fuels Manufacturing Processes



The primary technologies that produce synthetic fuel from syngas are Fischer-Tropsch synthesis and the Mobil process (also known as Methanol To Gasoline, or MTG). There are some technologies under development to produce ethanol from syngas, though these have not yet been demonstrated at commercial scale.

The Fischer-Tropsch process reacts syngas with typically a cobalt or iron-based catalyst, and transforms the gas into liquid products (primarily diesel fuel and jet fuel) and potentially waxes (depending on the FT process employed).

The process of producing synfuels through indirect conversion is often referred to as coal-to-liquids (CTL), gas-to-liquids (GTL) or biomass-to-liquids (BTL), depending on the initial feedstock. At least three projects (Ohio River Clean Fuels, Illinois Clean Fuels, and Rentech Natchez) are combining coal and biomass feedstocks, creating hybrid-feedstock synthetic fuels known as Coal and Biomass To Liquids (CBTL).

Indirect conversion process technologies can also be used to produce hydrogen, potentially for use in fuel cell vehicles, either as slipstream co-product, or as a primary output.

Direct conversion

Direct conversion refers to processes in which coal or biomass feedstocks are converted directly into intermediate or final products, without going through the intermediate step of conversion to syngas via gasification.

Direct conversion processes can be broadly broken up into two different methods: Pyrolysis and carbonization, and hydrogenation.

Hydrogenation processes

One of the main methods of direct conversion of coal to liquids by hydrogenation process is the Bergius process. In this process, coal is liquefied by mixing it with hydrogen gas and heating the system (hydrogenation). Dry coal is mixed with heavy oil recycled from the process. Catalyst is typically added to the mixture. The reaction occurs at between 400 °C (752 °F) to 5,000 °C (9,030 °F) and 20 to 70 MPa hydrogen pressure. The reaction can be summarized as follows:

$$nC + (n+1)H_2 \rightarrow C_nH_{2n+2}$$

After World War I several plants were built in Germany; these plants were extensively used during World War II to supply Germany with fuel and lubricants.

The Kohleoel Process, developed in Germany by Ruhrkohle and VEBA, was used in the demonstration plant with the capacity of 200 ton of lignite per day, built in Bottrop, Germany. This plant operated from 1981 to 1987. In this process, coal is mixed with a recycle solvent and iron catalyst. After preheating and pressurizing, H_2 is added. The process takes place in tubular reactor at the pressure of 300 bar and at the temperature of 470 °C (880 °F). This process was also explored by SASOL in South Africa.

In 1970-1980s, Japanese companies Nippon Kokan, Sumitomo Metal Industries and Mitsubishi Heavy Industries developed the NEDOL process. In this process, coal is mixed with a recycled solvent and a synthetic iron-based catalyst; after preheating H_2 is added. The reaction takes place in tubular reactor at temperature between 430 °C (810 °F) and 465 °C (870 °F) at the pressure 150-200 bar. The produced oil has low quality and requires intensive upgrading. H-Coal process, developed by Hydrocarbon Research, Inc., in 1963, mixes pulverized coal with recycled liquids, hydrogen and catalyst in the ebullated bed reactor. Advantages of this process are that dissolution and oil upgrading are taking place in the single reactor, products have high H/C ration, and a fast ration time, while the main disadvantages are high gas yield, high hydrogen consumption, and limitation of oil usage only as a boiler oil because of impurities.

The SRC-I and SRC-II (Solvent Refined Coal) processes developed by Gulf Oil and implemented as pilot plants in the United States in the 1960s and 1970s. The Nuclear Utility Services Corporation developed hydrogenation process which was patented by Wilburn C. Schroeder in 1976. The process involved dried, pulverized coal mixed with roughly 1wt% molybdenum catalysts. Hydrogenation occurred by use of high temperature and pressure syngas produced in a separate gasifier. The process ultimately yielded a synthetic crude product, Naphtha, a limited amount of C_3/C_4 gas, light-medium weight liquids (C_5-C_{10}) suitable for use as fuels, small amounts of NH_3 and significant amounts of CO_2. Other single-stage hydrogenation processes are the Exxon Donor Solvent Process, the Imhausen High-pressure Process, and the Conoco Zinc Chloride Process.

There is also a number of two-stage direct liquefaction processes; however, after 1980s only the Catalytic Two-stage Liquefaction Process, modified from the H-Coal Process; the Liquid Solvent Extraction Process by British Coal; and the Brown Coal Liquefaction Process of Japan have been developed.

Pyrolysis and carbonization processes

There are a number of different carbonization processes. The carbonization conversion occurs through pyrolysis or destructive distillation, and it produces condensable coal tar, oil and water vapor, non-condesable synthetic gas, and a solid residue-char. The condensed coal tar and oil are then further processed by hydrogenation to remove sulfur and nitrogen species, after which they are processed into fuels.

The typical example of carbonization is the Karrick process. The process was invented by Lewis Cass Karrick in the 1920s. The Karrick process is a low-temperature carbonization process, where coal is heated at 680 °F (360 °C) to 1,380 °F (750 °C) in the absence of air. These temperatures optimize the production of coal tars richer in lighter hydrocarbons than normal coal tar. However, the produced liquids are mostly a by-product and the main product is semi-coke, a solid and smokeless fuel.

The COED Process, developed by FMC Corporation, uses a fluidized bed for processing, in combination with increasing temperature, through four stages of pyrolysis. Heat is transferred by hot gases produced by combustion of part of the produced char. A modification of this process, the COGAS Process, involves the addition of gasification of char. The TOSCOAL Process, an analogue to the TOSCO II oil shale retorting process and Lurgi-Ruhrgas process, which is also used for the shale oil extraction, uses hot recycled solids for the heat transfer.

Liquid yields of pyrolysis and Karrick processes are generally low for practical use for synthetic liquid fuel production. Furthermore, the resulting liquids are of low quality and require further treatment before they can be used as motor fuels. In summary, there is little possibility that this process will yield economically viable volumes of liquid fuel.

Biofuels processes

One example of a Biofuel based synthetic fuel process is Hydrotreated Renewable Jet (HRJ) fuel. There are a number of variants of these processes under development, and the testing and certification process for HRJ aviation fuels is beginning.

There are two such process under development by UOP. One using solid biomass feedstocks, and one using bio-oil and fats. The process using solid second-generation biomass sources such as switchgrass or woody biomass uses pyrolysis to produce a bio-oil, which is then catalytically stabilized and deoxygenated to produce a jet-range fuel. The process using natural oils and fats goes through a deoxygenation process, followed by hydrocracking and isomerization to produce a renewable Synthetic Paraffinic Kerosene jet fuel.

Oil sand and oil shale processes

Synthetic crude may also be created by upgrading bitumen (a tar like substance found in oil sands), or synthesizing liquid hydrocarbons from oil shale. There are number of processes extracting shale oil (synthetic crude oil) from oil shale by pyrolysis, hydrogenation, or thermal dissolution.

Commercialization

The leading company in the commercialization of synthetic fuel is Sasol, a company based in South Africa.

Worldwide commercial synthetic fuels plant capacity is over 240,000 barrels per day (38,000 m^3/d), including indirect conversion Fischer Tropsch plants in South Africa (Mossgas, Secunda CTL), Qatar {Oryx GTL}, and Malaysia (Shell Bintulu), and a Mobil process (Methanol to Gasoline) plant in New Zealand.

Numerous large projects are under construction in China and Qatar. Some analysts believe that Chinese CTL production will exceed that of South Africa by 2015, and new and existing GTL capacity in Qatar should also exceed the July 2009 South African production level some time in 2011.

Existing producers

The leading company in the commercialization of synthetic fuel is Sasol, a company based in South Africa. Sasol operates the world's only commercial Fischer Tropsch coal-to-liquids facility at Secunda, with a capacity of 150,000 barrels per day (24,000 m^3/d).

Sasol's Oryx Fischer Tropsch gas-to-liquids plant in Ras Laffan Industrial City, Qatar is running at 29,000 barrels per day (4,600 m^3/d) capacity, near its anticipated 34,000 barrels per day (5,400 m^3/d) nameplate capacity.

Royal Dutch Shell operates a 14,700 barrels per day (2,340 m^3/d) Fischer Tropsch gas-to-liquids plant in Bintulu, Malaysia.

The Mossgas gas to liquids plant in South Africa produces 45,000 barrels per day (7,200 m^3/d) of Fischer Tropsch synthetic fuels.

Other companies that have developed coal- or gas-to-liquids processes (at the pilot plant or commercial stage) include ExxonMobil, StatoilHydro, Rentech, and Syntroleum .

Projects under construction

The Pearl GTL project, a joint venture of Shell and Qatar Petroleum, is under construction in Ras Laffan, Qatar, and will produce 140,000 barrels per day (22,000 m^3/d) of Fischer Tropsch petroleum liquids starting in 2010 (first train) and 2011 (second train).

The Escravos GTL project in Nigeria is expected to produce 34,000 barrels per day (5,400 m^3/d) of Fischer Tropsch synthetic fuel in 2011.

Shenhua completed a trial run in January 2009, and expects to begin operation in July 2009 of their 1.08 million ton per year (roughly 22,200 barrels per day (3,530 m^3/d)) direct coal liquefaction plant (Erdos CTL) in Ejin Horo Banner in north China's Inner Mongolia autonomous region. Shenhua eventually intends to expand the facility to 5 million tons per year (roughly 102,000 barrels per day (16,200 m^3/d)). The Shenhua Group also expects to complete a 6 Million ton per year (3 Million TPY first phase) coal-to-fuel project using its own Fischer Tropsch indirect conversion technology next to the Inner Mongolia plant in the third quarter of 2009.

Yankuang expects to break ground shortly on a 22,000 barrels per day (3,500 m^3/d) (1 million ton per year) indirect synthetic fuels project. Final products will include 780,800 tons of diesel, 258,400 of naphtha, 56,480 of LPG.

Proposed projects

United States

In the United States, a number of different synthetic fuels projects are moving forward, with the first expected to enter commercial operation starting in 2013.

American Clean Coal Fuels, in their Illinois Clean Fuels project, is developing a 30,000 barrels per day (4,800 m^3/d) Fischer Tropsch biomass and coal to liquids project with carbon capture and sequestration in Oakland Illinois. The project is expected to come online in 2013.

Baard Energy, in their Ohio River Clean Fuels project, are developing a 53,000 barrels per day (8,400 m^3/d) Fischer Tropsch coal and biomass to liquids project with the carbon capture and sequestration. Pending close of a financing package, Baard hopes to begin on site preparation work before the end of 2009, with plant construction starting in 2010. Initial project startup is anticipated in 2013, with full production capacity targeted in 2015.

Rentech is developing a 29,600 barrels per day (4,710 m^3/d) Fischer Tropsch coal and biomass to liquids plant with carbon capture and sequestration in Natchez Mississippi. The project is in the permitting phase, with receipt of permits anticipated by Rentech in 2010.

DKRW is developing a 15,000 to 20,000 barrels per day (2,400 to 3,200 m^3/d) Fischer Tropsch coal to liquids plant with carbon capture and sequestration in Medicine Bow Wyoming. The project is expected to begin operation in 2013.

Aviation fuel

A significant effort is under way to certify FT synthetic fuels for use in US and international aviation fleets. In this effort is being led by an industry coalition known as the Commercial Aviation Alternative Fuels Initiative(CAAFI), also supported by a parallel initiative under way in the US Air Force , to certify FT fuel for use in all aviation platforms. The US Air Force has a stated goal of certifying its entire fleet for use with FT Synthetic Fuel blends by 2011. The CAAFI initiative aims to certify the civilian aviation fleet for FT synthetic fuels blends by 2010, and has programs under way to certify HRJ hydrogenated biofuels as early as 2013.

Presently, certification efforts appear to be ahead of schedule. On June 24, 2009 the ASTM International Aviation Fuels subcommittee voted to approve the creation of a new fuels specification allowing 50/50 blends of FT jet fuel to be used in commercial aviation. Assuming that this action is approved by the Petroleum Products and Lubricants committee of ASTM International, then CAAFI anticipates that the specification will be issued with its official ASTM designation by the fall. Ongoing research is continuing into HRJ fuels for incorporation in the standard, with HRJ fuels inclusion in the standard anticipated by the end of 2010, pending favorable evaluation of the research report.

Sasol has also announced that they have achieved the first approval for 100% synthetic jet fuel use sanctioned by global aviation fuel specification authorities.

On 12 October 2009, a Qatar Airways Airbus A340-600 conducted a the world's first commercial passenger flight using a mixture of kerosene and synthetic Gas-to-Liquid fuel in its flight from London's Gatwick Airport to Doha.

JBUFF (Joint Battlespace Use Fuel of the Future) fuel

Future blends and fuel formulations may result in a JBUFF (Joint Battlespace Use Fuel of the Future) or a single battlespace fuel that can be used in both diesel and jet fuel application. A JBUFF fuel will allow for rapid deployment and logistic enhancement for military and emergency aid environments where various types of equipment can be operated with one fuel in place of several types of fuel.

Initial consumers

In addition to their certification efforts, the United States Air Force has publicly stated their intention to fuel half of their domestic US flights with synthetic fuel by 2016. The commercial aviation industry, working with potential suppliers via CAAFI, is also pushing hard to secure sources of fuel.

The United States Department of Energy projects that domestic consumption of synthetic fuel made from coal and natural gas will rise to 3.7 million barrels per day (590×10^3 m^3/d) in 2030 based on a price of $57 per barrel of high sulfur crude.

Non-transportation "synfuel"

Numerous American companies (TECO, Progress Energy, DTE Energy, Marriott) have also taken advantage of coal-based synfuel tax credits established in the 1970s, although many of the products qualifying for the subsidy are not true synthetic fuels.

The coal industry uses the credit to increase profits on coal-burning powerplants by introducing a "pre-treatment" process that satisfies the technical requirements, then burns the result the same as it would burn coal. Sometimes the amount gained in the tax credit is a major factor in the economic operation of the plant. The synfuel tax credit has been used primarily in this manner since the cheap gas prices of the 1980s stopped any major efforts to create a transportation fuel with the credit, and its continuation is seen as a major "pork project" win for coal industry lobbyists, costing $9 billion per annum. The total production of such synfuels in the United States was an estimated 73 million tons in 2002.

The synthetic fuel tax credit, Section 45K, under which these activities occurred, expired 31 December 2007.

Economics

The economics of synthetic fuel manufacture vary greatly depending the feedstock used, the precise process employed, site characteristics such as feedstock and transportation costs, and the cost of additional equipment required to control emissions. The examples described below indicate a wide range of production costs between $20/BBL for large-scale gas-to-liquids, to as much as $240/BBL for small-scale biomass-to-liquids + Carbon Capture and Sequestration.

In order to be economically viable, projects must do much better than just being competitive head-to-head with oil. They must also generate a sufficient return on investment to justify the capital investment in the project.

GTL economics

A synthetic fuel manufactured from natural gas (GTL), without CCS, in a large scale plant in the Middle East (where gas is relatively inexpensive), is expected to be competitive with oil down to approximately $20 per barrel.

Recent advances by the oil company Shell have seen synthetic fuels start to become profitable. The company is building a GTL (gas-to-liquid) plant in Qatar, due to come online in 2011. It will be capable of producing 300,000 barrels per day (48,000 m^3/d) of synthetic fuels and other products, using natural gas as a feedstock. Their spokesman claims the process will remain competitive with traditional diesel unless the price of crude falls below $20 per barrel.

CTL/CBTL/BTL economics

According to a December 2007 study, a medium scale (30,000 BPD) coal-to-liquids plant (CTL) sited in the US using bituminous coal, is expected to be competitive with oil down to roughly $52–56/bbl crude-oil equivalent. Adding carbon capture and sequestration to the project was expected to add an additional $10/BBL to the required selling price, though this may be offset by revenues from enhanced oil recovery, or by tax credits, or the eventual sale of carbon credits.

A recent NETL study examined the relative economics of a number of different process configurations for the production of indirect FT fuels using biomass, coal, and CCS. This study determined a price at which the plant would not only be profitable, abut also make a sufficient return to yield a 20% return on the equity investment required to build the plant.

This chapter details an analysis which derives the Required Selling Price (RSP) of the FT diesel fuels produced in order to determine the economic feasibility and relative competitiveness of the different plant options. A sensitivity analysis was performed to determine how carbon control regulations such as an emissions trading scheme for transportation fuels would affect the price of both petroleum-derived diesel and FT diesel from the different plants. The key findings of these analyses were: (1) CTL plants equipped with CCS are competitive at crude oil prices as low as $86 per barrel and have less life cycle GHG emissions than petroleum-derived diesel. These plants become more economically competitive as carbon prices increase. (2) The incremental cost of adding simple CCS is very low (7 cents per gallon) because CO_2 capture is an inherent part of the FT process. This becomes the economically preferred option at carbon prices above \$5/mtCO_2eq.27 (3) BTL systems are hindered by limited biomass availability which affects the maximum plant size, thereby limiting potential economies of scale. This, combined with relatively high biomass costs results in FT diesel prices which are double that of other configurations: $6.45 to $6.96/gal compared to $2.56 to $2.82/gal for CTL and 15wt% CBTL systems equipped with CCS. The conclusion reached based on these findings was that both the CTL with CCS and the 8wt% to 15wt% CBTL with CCS configurations may offer the most pragmatic solutions to the nation's energy strategy dilemma: GHG emission reductions which are significant (5% to 33% below the petroleum baseline) at diesel RSPs that are only half as much as the BTL options ($2.56 to $2.82 per gallon compared to $6.45 to $6.96 per gallon for BTL). These options are economically feasible when crude oil prices are $86 to $95 per barrel.

These economics can change in the event that plentiful low-cost biomass sources can be found, lowing the cost of biomass inputs, and improving economies of scale.

Economics for solid feedstock indirect FT process plants are further confused by carbon regulation. Generally, since permitting a CTL plant without CCS will likely be impossible, and CTL+CCS plants have a lower carbon footprint than conventional fuels, carbon regulation is expected to be balance-positive for synthetic fuel production. But it impacts the economics of different process configurations in different ways. The NETL study picked a blended CBTL process using 5-15% biomass alongside coal as the most economical in a range of carbon price and probable future regulation scenarios. Unfortunately, because of scale and cost constraints, pure BTL processes did not score well until very high carbon prices were assumed, though again this may improve with better feedstocks and more efficient larger scale projects.

Chinese direct coal liquefaction economics

News reports have indicated an anticipated cost of production of less than $30 per barrel, based on a direct coal liquefaction process, and a coal mining cost of under $10/ton.

Security considerations

A central consideration for the development of synthetic fuel is the security factor of securing domestic fuel supply from domestic biomass and coal. Nations that are rich in biomass and coal can use synthetic fuel to off-set their use of petroleum derived fuels and foreign oil.

Environmental considerations

The environmental footprint of a given synthetic fuel varies greatly depending on which process is employed, what feedstock is used, what pollution controls are employed, and what the transportation distance and method are for both feedstock procurement and end-product distribution.

In many locations, project development will not be possible due to permitting restrictions if a process design is chosen that does not meet local requirements for clean air, water, and increasingly, lifecycle carbon emissions.

Lifecycle green house gas emissions

Among different indirect FT synthetic fuels production technologies, potential emissions of greenhouse gasses vary greatly. Coal to liquids ("CTL") without carbon capture and sequestration ("CCS") is expected to result in a significantly higher carbon footprint than conventional petroleum-derived fuels (+147%). On the other hand, biomass-to-liquids with CCS could deliver a 358% reduction in lifecycle greenhouse gas emissions. Both of these plants fundamentally use gasification and FT conversion synthetic fuels technology, but they deliver wildly divergent environmental footprints.

File:Coal and biomass co conversion to transportation fuels, Michael E Reed, DOE NETL Office of Fossil Energy, oct 17 2007.jpg
Lifecycle carbon emissions profiles of various fuels, including many synthetic fuels. Coal and biomass co-conversion to transportation fuels, Michael E. Reed, DOE NETL Office of Fossil Energy, Oct 17 2007

Generally, CTL without CCS has a higher greenhouse gas footprint. CTL with CCS has a 9-15% reduction in lifecycle greenhouse gas emissions compared to that of petroleum derived diesel.

CBTL+CCS plants that blend biomass alongside coal while sequestering carbon do progressively better the more biomass is added. Depending on the type of biomass, the assumptions about root storage, and the transportation logistics, at conservatively 40% biomass alongside coal, CBTL+CCS plants achieve a neutral lifecycle greenhouse gas footprint. At more than 40% biomass, they begin to go lifecycle negative, and effectively store carbon in the ground for every gallon of fuels that they produce.

Ultimately BTL plants employing CCS could store massive amounts of carbon while producing transportation fuels from sustainably produced biomass feedstocks, although there are a number of significant economic hurdles, and a few technical hurdles that would have to be overcome to enable the development of such facilities.

Serious consideration must also be given to the type and method of feedstock procurement for either the coal or biomass used in such facilities, as reckless development could exacerbate environmental problems caused by mountaintop removal mining, land use change, fertilizer runoff, food vs. fuels concerns, or many other potential factors. Or they could not. Depending entirely on project-specific factors on a plant-by-plant basis.

Hybrid hydrogen-carbon processes have also been proposed recently as another closed-carbon cycle alternative, combining 'clean' electricity, recycled CO, H_2 and captured CO_2 with biomass as inputs as a way of reducing the biomass needed.

Fuels emissions

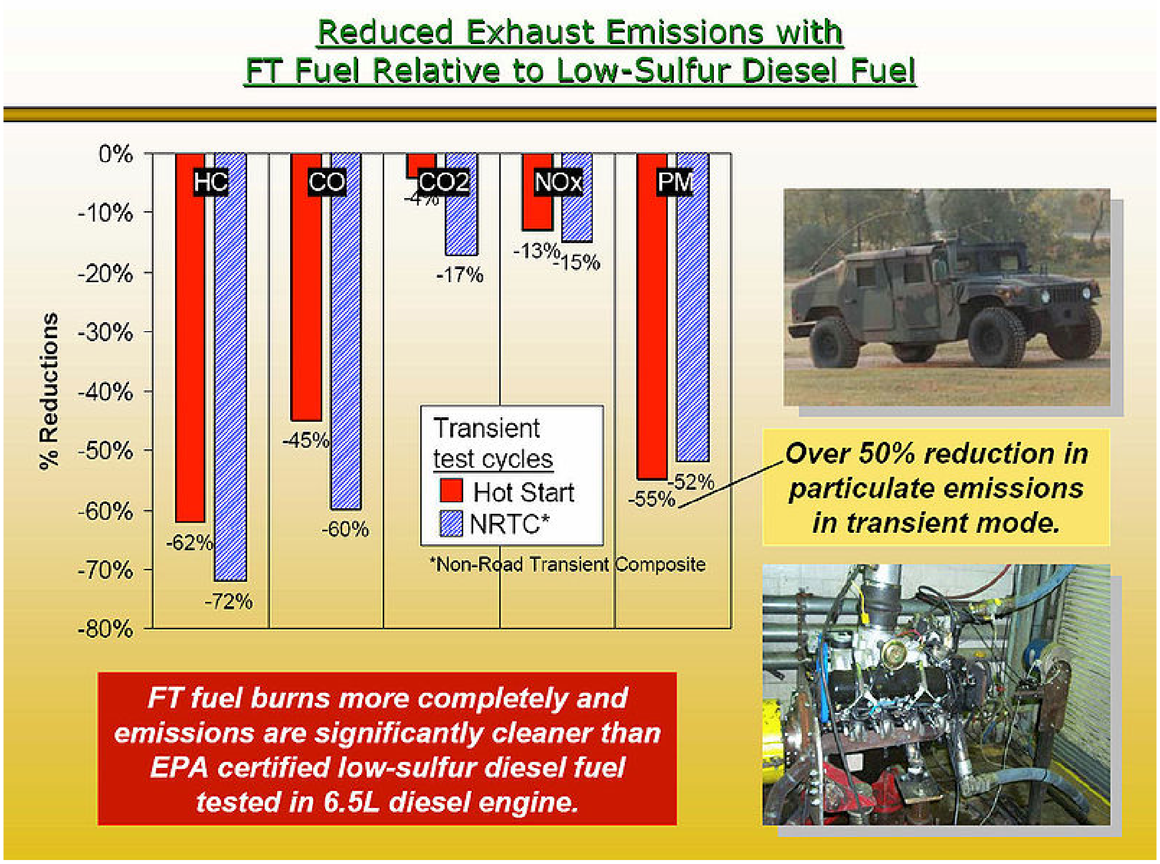
The fuels produced by the various synthetic fuels process also have a wide range of potential environmental performance, though they tend to be very uniform based on the type of synthetic fuels process used (i.e. the tailpipe emissions characteristics of Fischer Tropsch diesel tend to be the same, though their lifecycle greenhouse gas footprint can vary substantially based on which plant produced the fuel, depending on feedstock and plant level sequestration considerations.)

In particular, Fischer tropsch diesel and jet fuels deliver dramatic across-the-board reductions in all major criteria pollutants such as SOx, NOx, Particulate Matter, and Hydrocarbon emissions. These fuels, because of their high level of purity and lack of contaminants, further enable the use of advanced emissions control equipment that has been shown to virtually eliminate HC, CO, and PM emissions from diesel vehicles.

In testimony before the Subcommittee on Energy and Environment of the U.S. House of Representatives the following statement was made by a senior scientist from Rentech:

F-T fuels offer numerous benefits to aviation users. The first is an immediate reduction in particulate emissions. F-T jet fuel has been shown in laboratory combusters and engines to reduce PM emissions by 96% at idle and 78% under cruise operation. Validation of the reduction in other turbine engine emissions is still under way. Concurrent to the PM reductions is an immediate reduction in CO_2 emissions from F-T fuel. F-T fuels inherently reduce CO_2 emissions because they have higher energy content per carbon content of the fuel, and the fuel is less dense than conventional jet fuel allowing aircraft to fly further on the same load of fuel.

The cleanliness of these FT synthetic fuels is further demonstrated by the fact that they are sufficiently non-toxic and environmentally benign as to be considered biodegradable. This owes primarily to the near-absence of sulfur and extremely low level of aromatics present in the fuel.



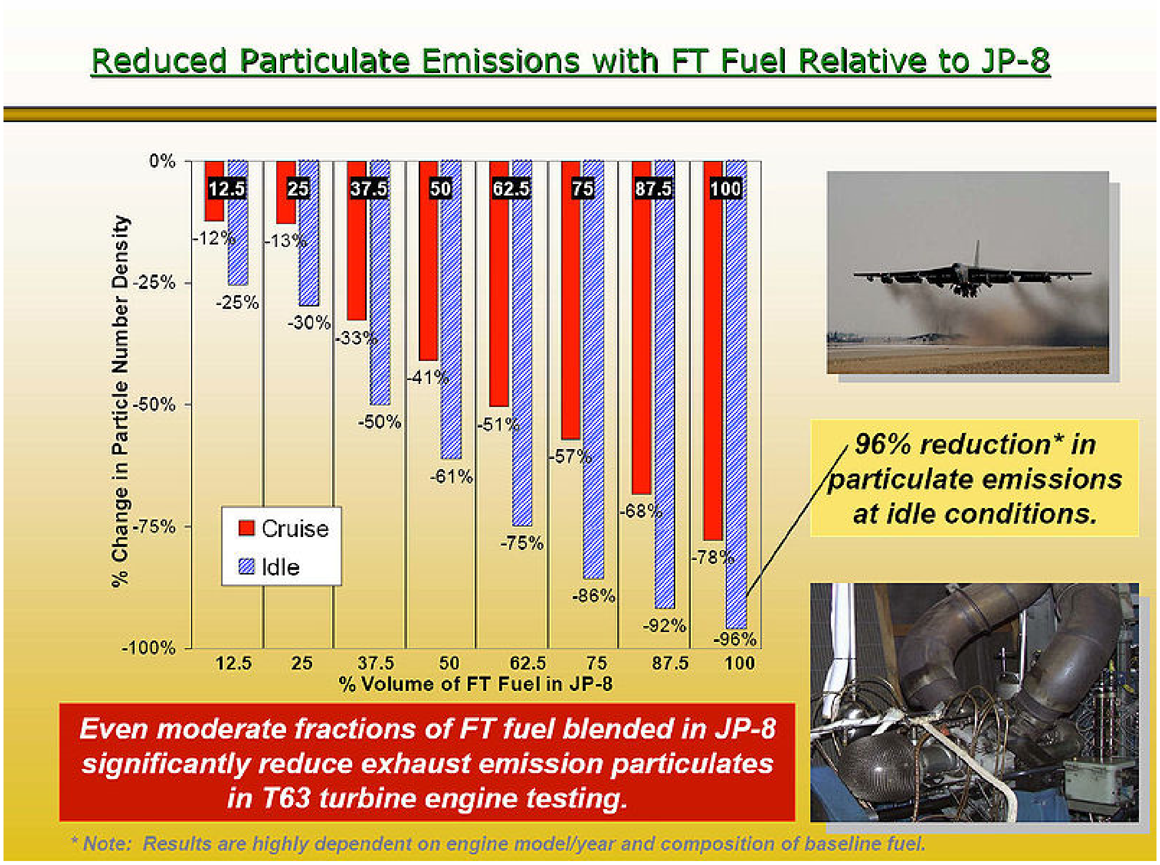
Reduced Exhaust Emissions with FT Fuel Relative to Low-Sulfur Diesel Fuel

*Non-Road Transient Composite

Over 50% reduction in particulate emissions in transient mode.

FT fuel burns more completely and emissions are significantly cleaner than EPA certified low-sulfur diesel fuel tested in 6.5L diesel engine.

Using Fischer Tropsch diesel results in dramatic across the board tailpipe emissions reductions relative to conventional fuels



Reduced Particulate Emissions with FT Fuel Relative to JP-8

96% reduction in particulate emissions at idle conditions.*

Even moderate fractions of FT fuel blended in JP-8 significantly reduce exhaust emission particulates in T63 turbine engine testing.

** Note: Results are highly dependent on engine model/year and composition of baseline fuel.*

Using Fischer Tropsch jet fuels have been proven to dramatically reduce particulate and other aircraft emissions

Sustainability

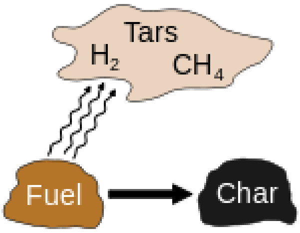
One concern commonly raised about the development of synthetic fuels plants is sustainability. Fundamentally, transitioning from oil to coal or natural gas for transportation fuels production is a transition from one inherently depeleteable geologically limited resource to another.

One of the positive defining characteristics of synthetic fuels production is the ability to use multiple feedstocks (coal, gas, or biomass) to produce the same product from the same plant. In the case of hybrid BCTL plants, some facilities are already planning to use a significant biomass component alongside coal. Ultimately, given the right location with good biomass availability, and sufficiently high oil prices, synthetic fuels plants can be transitioned from coal or gas, over to a 100% sustainable biomass feedstock. This provides a path forwards to true sustainable fuel production, even if the plant originally produced fuels solely from coal, making the infrastructure forwards-compatible even if the original fossil feedstock runs out.

Some synthetic fuels processes can be converted to sustainable production practices more easily than others, depending on the process equipment selected. This is an important design consideration as these facilities are planned and implemented, as additional room must be left in the plant layout to accommodate whatever future materials handling and gasification plant change requirements might be necessary to accommodate a future change in production profile.

Chapter 14

Pyrolysis



Simplified depiction of pyrolysis chemistry.

Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen. Pyrolysis typically occurs under pressure and at operating temperatures above 430 °C (800 °F). The word is coined from the Greek-derived elements *pyr* "fire" and *lysis* "separating".

Pyrolysis is a special case of thermolysis, and is most commonly used for organic materials, being, therefore, one of the processes involved in charring. The pyrolysis of wood, which starts at 200–300 °C (390–570 °F), occurs for example in fires or when vegetation comes into contact with lava in volcanic eruptions. In general, pyrolysis of organic substances produces gas and liquid products and leaves a solid residue richer in carbon content. Extreme pyrolysis, which leaves mostly carbon as the residue, is called carbonization.

The process is used heavily in the chemical industry, for example, to produce charcoal, activated carbon, methanol, and other chemicals from wood, to convert ethylene dichloride into vinyl chloride to make PVC, to produce coke from coal, to convert biomass into syngas, to turn waste into safely disposable substances, and for transforming medium-weight hydrocarbons from oil into lighter ones like gasoline. These specialized uses of pyrolysis may be called various names, such as dry distillation, destructive distillation, or cracking.

Pyrolysis also plays an important role in several cooking procedures, such as baking, frying, grilling, and caramelizing. And it is a tool of chemical analysis, for example, in mass spectrometry and in carbon-14 dating. Indeed, many important chemical substances, such as phosphorus and sulfuric acid, were first obtained by this process. Pyrolysis has been assumed to take place during catagenesis, the conversion of buried organic matter to fossil fuels. It is also the basis of pyrography. In their embalming process, the ancient Egyptians used a mixture of substances, including methanol, which they obtained from the pyrolysis of wood.

Pyrolysis differs from other high-temperature processes like combustion and hydrolysis in that it does not involve reactions with oxygen, water, or any other reagents. In practice, it is not possible to achieve a completely oxygen-free atmosphere. Because some oxygen is present in any pyrolysis system, a small amount of oxidation occurs.

The term has also been applied to the decomposition of organic material in the presence of superheated water or steam (hydrous pyrolysis), for example, in the steam cracking of oil.

Occurrence and uses

Fire

Pyrolysis is usually the first chemical reaction that occurs in the burning of many solid organic fuels, like wood, cloth, and paper, and also of some kinds of plastic. In a wood fire, the visible flames are not due to combustion of the wood itself, but rather of the gases released by its pyrolysis, whereas the flame-less burning of embers is the combustion of the solid residue (charcoal) left behind by it. Thus, the pyrolysis of common materials like wood, plastic, and clothing is extremely important for fire safety and fire-fighting.

Cooking

Pyrolysis occurs whenever food is exposed to high enough temperatures in a dry environment, such as roasting, baking, toasting, grilling, etc.. It is the chemical process responsible for the formation of the golden-brown crust in foods prepared by those methods.

In normal cooking, the main food components that undergo pyrolysis are carbohydrates (including sugars, starch, and fibre) and proteins. Pyrolysis of fats requires a much higher temperature, and, since it produces toxic and flammable products (such as acrolein), it is, in general, avoided in normal cooking. It may occur, however, when grilling fatty meats over hot coals.

Even though cooking is normally carried out in air, the temperatures and environmental conditions are such that there is little or no combustion of the original substances or their decomposition products. In particular, the pyrolysis of proteins and carbohydrates begins at temperatures much lower than the ignition temperature of the solid residue, and the volatile subproducts are too diluted in air to ignite. (In flambé dishes, the flame is due mostly to combustion of the alcohol, while the crust is formed by pyrolysis as in baking.)

Pyrolysis of carbohydrates and proteins requires temperatures substantially higher than 100 °C (212 °F), so pyrolysis does not occur as long as free water is present, e.g., in boiling food — not even in a pressure cooker. When heated in the presence of water, carbohydrates and proteins suffer gradual hydrolysis rather than pyrolysis. Indeed, for most foods, pyrolysis is usually confined to the outer layers of food, and begins only after those layers have dried out.

Food pyrolysis temperatures are, however, lower than the boiling point of lipids, so pyrolysis occurs when frying in vegetable oil or suet, or basting meat in its own fat.

Pyrolysis also plays an essential role in the production of barley tea, coffee, and roasted nuts such as peanuts and almonds. As these consist mostly of dry materials, the process of pyrolysis is not limited to the outermost layers but extends throughout the materials. In all these cases, pyrolysis creates or releases many of the substances that contribute to the flavor, color, and biological properties of the final product. It may also destroy some substances that are toxic, unpleasant in taste, or those that may contribute to spoilage.

Controlled pyrolysis of sugars starting at 170 °C (338 °F) produces caramel, a beige to brown water-soluble product widely used in confectionery and (in the form of caramel coloring) as a coloring agent for soft drinks and other industrialized food products.

Solid residue from the pyrolysis of spilled and splattered food creates the brown-black encrustation often seen on cooking vessels, stove tops, and the interior surfaces of ovens.

Charcoal

Pyrolysis has been used since ancient times for turning wood into charcoal on an industrial scale. Besides wood, the process can also use sawdust and other wood waste products.

Charcoal is obtained by heating wood until its complete pyrolysis (carbonization) occurs, leaving only carbon and inorganic ash. In many parts of the world, charcoal is still produced semi-industrially, by burning a pile of wood that has been mostly covered with mud or bricks. The heat generated by burning part of the wood and the volatile byproducts pyrolyzes the rest of the pile. The limited supply of oxygen prevents the charcoal from burning. A more modern alternative is to heat the wood in an airtight metal vessel, which is much less polluting and allows the volatile products to be condensed.

The original vascular structure of the wood and the pores created by escaping gases combine to produce a light and porous material. By starting with a dense wood-like material, such as nutshells or peach stones, one obtains a form of charcoal with particularly fine pores (and hence a much larger pore surface area), called activated carbon, which is used as an adsorbent for a wide range of chemical substances.

Biochar

Residues of incomplete organic pyrolysis, e.g., from cooking fires, are thought to be the key component of the terra preta soils associated with ancient indigenous communities of the Amazon basin. Terra preta is much sought by local farmers for its superior fertility compared to the natural red soil of the region. Efforts are underway to recreate these soils through biochar, the solid residue of pyrolysis of various materials, mostly organic waste.

Biochar improves the soil texture and ecology, increasing its ability to retain fertilizers and release them slowly. It naturally contains many of the micronutrients needed by plants, such as selenium. It is also safer than other "natural" fertilizers such as manure or sewage, since it has been disinfected at high temperature. And, since it releases its nutrients at a slow rate, it greatly reduces the risk of water table contamination.

Biochar is also being considered for carbon sequestration, with the aim of mitigation of global warming. When its volatile and gaseous products are combusted or captured, the biochar process emits primarily water vapor. The solid, carbon-containing char produced can be sequestered in the ground, where it will remain indefinitely.

Coke

Pyrolysis is used on a massive scale to turn coal into coke for metallurgy, especially steelmaking. Coke can also be produced from the solid residue left from petroleum refining.

Those starting materials typically contain hydrogen, nitrogen, or oxygen atoms combined with carbon into molecules of medium to high molecular weight. The coke-making or "coking" process consists of heating the material in closed vessels to very high temperatures (up to 2,000 °C or 3,600 °F) so that those molecules are broken down into lighter volatile substances, which leave the vessel, and a porous but hard residue that is mostly carbon and inorganic ash. The amount of volatiles varies with the source material, but is typically 25-30% of it by weight.

Carbon fiber

Carbon fibers are filaments of carbon that can be used to make very strong yarns and textiles. Carbon fiber items are often produced by spinning and weaving the desired item from fibers of a suitable polymer, and then pyrolyzing the material at a high temperature (from 1,500–3,000 °C or 2,730–5,430 °F).

The first carbon fibers were made from rayon, but polyacrylonitrile has become the most common starting material.

For their first workable electric lamps, Joseph Wilson Swan and Thomas Edison used carbon filaments made by pyrolysis of cotton yarns and bamboo splinters, respectively.

Biofuel

Pyrolysis is the basis of several methods that are being developed for producing fuel from biomass, which may include either crops grown for the purpose or biological waste products from other industries.

Although synthetic diesel fuel cannot yet be produced directly by pyrolysis of organic materials, there is a way to produce similar liquid ("bio-oil") that can be used as a fuel, after the removal of valuable bio-chemicals that can be used as food additives or pharmaceuticals. Higher efficiency is achieved by the so-called flash pyrolysis, in which finely divided feedstock is quickly heated to between 350 and 500 °C (660 and 930 °F) for less than 2 seconds.

Fuel bio-oil resembling light crude oil can also be produced by hydrous pyrolysis from many kinds of feedstock, including waste from pig and turkey farming, by a process called thermal depolymerization (which may, however, include other reactions besides pyrolysis).

Plastic waste disposal

Anhydrous pyrolysis can also be used to produce liquid fuel similar to diesel from plastic waste.

Processes

In many industrial applications, the process is done under pressure and at operating temperatures above 430 °C (806 °F). For agricultural waste, for example, typical temperatures are 450 to 550 °C (840 to 1,000 °F).

Vacuum pyrolysis

In **vacuum pyrolysis**, organic material is heated in a vacuum in order to decrease boiling point and avoid adverse chemical reactions. It is used in organic chemistry as a synthetic tool. In **flash vacuum thermolysis** or **FVT**, the residence time of the substrate at the working temperature is limited as much as possible, again in order to minimize secondary reactions.

Processes for biomass pyrolysis

Since pyrolysis is endothermic, various methods to provide heat to the reacting biomass particles have been proposed:

- Partial combustion of the biomass products through air injection. This results in poor-quality products.

- Direct heat transfer with a hot gas, the ideal one being product gas that is reheated and recycled. The problem is to provide enough heat with reasonable gas flow-rates.
- Indirect heat transfer with exchange surfaces (wall, tubes). It is difficult to achieve good heat transfer on both sides of the heat exchange surface.
- Direct heat transfer with circulating solids: Solids transfer heat between a burner and a pyrolysis reactor. This is an effective but complex technology.

For flash pyrolysis, the biomass must be ground into fine particles and the insulating char layer that forms at the surface of the reacting particles must be continuously removed. The following technologies have been proposed for biomass pyrolysis:

- Fixed beds used for the traditional production of charcoal. Poor, slow heat transfer result in very low liquid yields.
- Augers: This technology is adapted from a Lurgi process for coal gasification. Hot sand and biomass particles are fed at one end of a screw. The screw mixes the sand and biomass and conveys them along. It provides a good control of the biomass residence time. It does not dilute the pyrolysis products with a carrier or fluidizing gas. However, sand must be reheated in a separate vessel, and mechanical reliability is a concern. There is no large-scale commercial implementation.
- Ablative processes: Biomass particles are moved at high speed against a hot metal surface. Ablation of any char forming at the particles surface maintains a high rate of heat transfer. This can be achieved by using a metal surface spinning at high speed within a bed of biomass particles, which may present mechanical reliability problems but prevents any dilution of the products. As an alternative, the particles may be suspended in a carrier gas and introduced at high speed through a cyclone whose wall is heated; the products are diluted with the carrier gas. A problem shared with all ablative processes is that scale-up is made difficult, since the ratio of the wall surface to the reactor volume decreases as the reactor size is increased. There is no large-scale commercial implementation.
- Rotating cone: Pre-heated hot sand and biomass particles are introduced into a rotating cone. Due to the rotation of the cone, the mixture of sand and biomass is transported across the cone surface by centrifugal force. Like other shallow transported-bed reactors relatively fine particles are required to obtain a good liquid yield. There is no largescale commercial implementation.
- Fluidized beds: Biomass particles are introduced into a bed of hot sand fluidized by a gas, which is usually a recirculated product gas. High heat transfer rates from fluidized sand result in rapid heating of biomass particles. There is some ablation by attrition with the sand particles, but it is not as effective as in the ablative processes. Heat is usually provided by heat exchanger tubes through which hot combustion gas flows. There is some dilution of the products, which makes it more difficult to condense

and then remove the bio-oil mist from the gas exiting the condensers. This process has been scaled up by companies such as Dynamotive and Agri-Therm. The main challenges are in improving the quality and consistency of the bio-oil.

- Circulating fluidized beds: Biomass particles are introduced into a circulating fluidized bed of hot sand. Gas, sand, and biomass particles move together, with the transport gas usually being a recirculated product gas, although it may also be a combustion gas. High heat transfer rates from sand ensure rapid heating of biomass particles and ablation stronger than with regular fluidized beds. A fast separator separates the product gases and vapors from the sand and char particles. The sand particles are reheated in fluidized burner vessel and recycled to the reactor. Although this process can be easily scaled up, it is rather complex and the products are much diluted, which greatly complicates the recovery of the liquid products.

Industrial sources

Many sources of organic matter can be used as feedstock for pyrolysis. Suitable plant material includes greenwaste, sawdust, waste wood, woody weeds; and agricultural sources including nut shells, straw, cotton trash, rice hulls, switch grass; and animal waste including poultry litter, dairy manure, and potentially other manures. Pyrolysis is used as a form of thermal treatment to reduce waste volumes of domestic refuse. Some industrial byproducts are also suitable feedstock including paper sludge and distillers grain.

There is also the possibility of integrating with other processes such as mechanical biological treatment and anaerobic digestion.

Industrial products

- syngas (flammable mixture of carbon monoxide and hydrogen): can be produced in sufficient quantities to provide both the energy needed for pyrolysis and some excess production
- solid char that can either be burned for energy or be recycled as a fertilizer (biochar).

Fire protection

Destructive fires in buildings will often burn with limited oxygen supply, resulting in pyrolysis reactions. Thus, pyrolysis reaction mechanisms and the pyrolysis properties of materials are important in fire protection engineering for passive fire protection. Pyrolytic carbon is also important to fire investigators as a tool for discovering origin and cause of fires.

Chapter 15

Union Process & Fushun Process

Union Process

Union process

Process type	Chemical
Industrial sector(s)	Chemical industry oil industry
Feedstock	oil shale
Product(s)	shale oil
Leading companies	Unocal Corporation
Inventor	Unocal Corporation

The **Union process** is an above ground shale oil extraction technology for production of shale oil, a type of synthetic crude oil. The process uses a vertical retort where heating causes decomposition of oil shale into shale oil, oil shale gas and spent residue. The particularity of this process is that oil shale in the retort moved countercurrent from the bottom upward to the top by a mechanism known as a rock pump. The process technology was invented by the American oil company Unocal Corporation in late 1940s and was developed through several decades. The largest oil shale retort ever built was the Union B type retort.

History

Union Oil Company of California (Unocal) started its oil shale activities in 1920s. In 1921, it acquired an oil shale tract in the Parachute Creek area of Colorado, southern Piceance Basin. The development of the Union process began in the late 1940s, when the Union A retort was designed. This technology was tested between 1954 and 1958 at the company-owned tract in the Parachute Creek. During these tests, up to 1,200 tonne per day of oil shale was processed, resulting of 800 barrels per day (130 m^3/d) shale oil, which was refined at a Colorado refinery. More than 13,000 barrels (2,100 m^3) of gasoline and fuels were produced. This production was finally shut down in 1961 due to cost.

In 1974, the Union B process, evolved from the Union A process, was developed. In 1976, Union announced its plans to build a Union B demonstration plant. Construction started in 1981 at Long Ridge in San Miguel County, Colorado, and the plant was started its operations in 1986. It was closed in 1991 after production of 5 million barrels (790×10^3 m^3) shale oil.

Process

The Union process can be operated in two different combustion modes, which are direct and indirect. The Union A (direct) process is similar to the gas combustion retort technology, classified as an internal combustion method, while the Union B (indirect) process is classified as an externally generated hot gas method.

The Union retort is a vertical shaft retort. The main difference to other vertical shaft retorts such as Kiviter, Petrosix, Paraho and Fushun is that crushed oil shale is fed through the bottom of the retort rather than the top. Lumps of oil shale in size of 3.2 to 50.8 millimetres (0.13 to 2.00 in) are moved upwards through the retort by a solids pump (known as a "rock pump"). Hot gases, generated by internal combustion or circulated through the top of the retort, decompose the oil shale while descending. The pyrolysis occurs at the temperature of 510 °C (950.0 °F) to 540 °C (1,004.0 °F). Condensed shale oil and gases are removed from the retort at the bottom. Part of the gases is recirculated for pyrolysis and fueling combustion, while other part could be used as product gas. The spent shale is removed from the top of the retort. After cooling with a water, it is conveyed to the waste disposal.

Advantages

The Union retort design has several advantages. The reducing atmosphere in the retort allows the removal of sulfur and nitrogen compounds through the formation of hydrogen sulfide and ammonia. Oil vapors are cooled by the raw oil, thus minimizing polymer formation among the hydrocarbon fractions.

Fushun Process

Fushun process

Process type	Chemical
Industrial sector(s)	Chemical industry oil industry
Feedstock	oil shale
Product(s)	shale oil

Leading companies	Fushun Mining Group
Main facilities	Fushun Shale Oil Plant

The **Fushun process** is an above-ground retorting technology for shale oil extraction. It is named after the main production site of Fushun, Liaoning province in northeastern China.

History

The Fushun process was developed and utilized for the extraction of shale oil in China during the mid-1920s. The commercial-scale utilization of the process began in 1930 with the construction of "Refinery No. 1". After World War II, the shale oil production was ceased, but 100 Fushun-type oil shale retorts were restored in 1949. In 1950, total 266 retorts were in operation, each with the capacity of 100–200 tons of shale oil per day.

With the discovery of Da Qing oil field in 1960s, the shale oil production declined and Sinopec, an operator of shale oil production these times, shut down its oil shale operations in the beginning of 1990s. At the same time, the Fushun Oil Shale Retorting Plant, using Fushun process technology, was established as a part of the Fushun Mining Group. It started production in 1992. In 2005, China became the largest shale oil producer in the world.

In 1985-1986, Sinopec used the Fushun process for a test processing of Jordan's oil shale from the El Lajjun deposit. Although the process was technically viable, the cooperation was halted due to high operation costs.

Technology

The Fushun process is classified as an internal combustion technology but also includes external gas heating. It uses a vertical cylindrical type shaft retort, with outside steel plate lined with inner fire bricks. The retort has height over 10 metres (33 ft) and its inner diameter is about 3 metres (9.8 ft). Raw oil shale particles with the size of 10 to 75 millimetres (0.4 to 3.0 in) are fed from the top of the retort. At the upper section of the retort oil shale is dried and heated by the ascending hot gases, which pass upward through the descending oil shale causing decomposition of the rock. The pyrolysis takes place at about 500 °C (930 °F). The produced oil vapor and gases exit from the top of the retort; hot gases and oil vapors move from the bottom to the top directly, and not diagonally like in Kiviter process. During the pyrolysis process, oil shale is decomposed to shale coke (char), which together with the ascending air-steam is burnt in the lower part of the retort to heat gases necessary for pyrolysis. These gases are recirculated; after leaving retort, they are cooled in a condensation system, where shale oil is condensed, and re-heated in a heating furnace about 500 °C (930 °F) to 700 °C (1,290 °F) before reinserting into the retort. The shale ash exits from a rotating water dish that acts as a seal and cooler at the bottom of the retort.

Retorts are operated in sets and have a heat carrier preparation unit and rotating water seals designed for the whole set instead of a single retort as in case of the Kiviter retort. Regenerative furnaces are located next to the retorts and they are operating in two cycles – the combustion cycle and the gas heating cycle. During the combustion cycle, a furnace is heated up to 1,000 °C (1,830 °F) by combustion gases. After the combustion cycle, retort gases from the condensation system is inserted into a furnace for their heating. By alternating furnaces, one furnace is always available for heating retort gas. Twenty retorts typically share one condensation system and a set of heating furnances.

Advantages of the Fushun process include small investment and stable operation. The process is characterized by the high thermal efficiency, but due to the addition of air into the retort, the nitrogen dilutes the pyrolysis gas. In addition, the excess oxygen in retort burns out a part of produced shale oil, which reduce the shale oil yield. The oil yield of the Fushun retort accounts for about 65% of Fischer Assay. Disadvantage of this process is a high water consumption amounting to 6–7 barrels of water per barrel of produced shale-oil, and great quantities of waste shale. It is not suitable of ores with small size and oil content lower than 5%.

As the capacity of single retort is limited, Fushun process is suitable for small-scale retorting plants, and for processing lean oil shale with low gas yield.

Commercial use

Fushun process is used only in China. The Fushun Mining Group operates the largest by capacity shale oil plant in the world (Fushun Shale Oil Plant) consisting of 180 Fushun retorts. Each retort processes about 4 tonnes of oil shale per hour.

Chapter 16

Galoter Process & Superior Multimineral Process

Galoter Process

Galoter process Enefit process	
Process type	Chemical
Industrial sector(s)	Chemical industry oil industry
Feedstock	oil shale
Product(s)	shale oil
Leading companies	Eesti Energia VKG Oil
Main facilities	Narva Oil Plant Petroter
Inventor	Krzhizhanovsky Power Engineering Institute
Developer(s)	Eesti Energia Outotec

The **Galoter process** (also known as **TSK**, **UTT**, or **SHC**) is a shale oil extraction technology for a production of shale oil, a type of synthetic crude oil. In this process, the oil shale is decomposed into shale oil, oil shale gas, and spent residue. A decomposition is caused by mixing raw oil shale with a hot oil shale ash, generated by combustion of carbonaceous residue (semi-coke) in the spent residue. The process was developed in 1950s and it is used commercially for the shale oil production in Estonia. There are projects for further development of this technology and for expansion of its usage, e.g. in Jordan.

History

At the laboratory scale, the Galoter process was invented and developed in Russia in 1945–1946. The further research continued in Estonia and the first Galoter-type pilot retorts with a solid heat carrier were built at Kiviõli, Estonia, in 1953 and 1963 (closed in 1963 and 1981 respectively). The Narva Oil Plant, annexed to the Eesti Power Plant and operating two Galoter-type retorts, was commissioned in Estonia in 1980. These retorts were designed and developed in cooperation with the Krzhizhanovsky Power Engineering Institute of Moscow. Started as a pilot plant, the process of converting it to commercial scale plant took about 20 years. During this period, the company has modernized more than 70% of the equipment compared to the initial design.

In 2008, Estonian energy company Eesti Energia, an operator of Galoter retorts in Narva and a developer of this technology, established a joint venture with the Finnish technology company Outotec to develop and commercialize a modified Galoter process–the Enefit process–which combines the current process with circulating fluidized bed technologies.

Technology

Galoter retort

The Galoter process is an above-ground oil-shale retorting technology classified as a hot recycled solids technology. The process uses a horizontal cylindrical rotating kiln-type retort, which is slightly declined. It has similarities with the TOSCO II process.

Before retorting, the oil shale is crushed into fine particles with a size of less than 25 millimetres (1.0 in) in diameter. The crushed oil shale is dried in the fluidized bed drier (aerofountain drier) by contact with hot gases. After drying and pre-heating to 135 °C (275 °F), oil shale particles are separated from gases by cyclonic separation. Oil shale is transported to the mixer chamber, where it is mixed with hot ash of 800 °C (1,470 °F), produced by combustion of spent oil shale in a separate furnace. The ratio of oil shale ash to raw oil shale is 2.8–3:1. The mixture is moved then to the rotating kiln. When the heat transfers from the hot ash to raw oil shale particles, the pyrolysis (chemical decomposition) begins. The temperature of pyrolysis is kept at 520 °C (970 °F). Produced oil vapors and gases are cleaned of solids by cyclones and moved to condensation system (rectification column) where shale oil condense and oil shale gas is separated in gaseous form. Spent shale (semi-coke) is transported then to the separate furnace for combustion to produce hot ash. A portion of the hot ash is separated from the furnace gas by cyclones and recycled to the rotary kiln for pyrolysis. The remaining ash is removed from the combustion gas by more cyclones and cooled and removed for disposal by using water. The cleaned hot gas returns to the oil shale dryer.

The Galoter process has high thermal and technological efficiency, and high oil recovery ratio. Oil yield reaches 85–90% of Fischer Assay and retort gas yield accounts for 48 cubic meters per tonne. Oil quality is considered good, but the equipment is sophisticated and capacity is relatively low. This process creates less pollution than internal combustion technologies, as it uses less water, but it still generates carbon dioxide as also carbon disulfide and calcium sulfide.

Enefit process

Enefit process is a modification of the Galoter process being developed by Enefit Outotec Technology, a joint venture of Eesti Energia and Outotec. In this process, the Galoter technology is combined with proven circulating fluidized bed (CFB) combustion technology used in coal-fired power plants and mineral processing. Oil shale particles and hot oil shale ash are mixed in a rotary drum as in the classical Galoter process. The primary modification is the replacing of the Galoter semi-coke furnace with a CFB furnace. The Enefit process also incorporates fluid bed ash cooler and waste heat boiler commonly used in coal-fired boilers to convert waste heat to steam for power generation. Compared to the traditional Galoter, the Enefit process allows complete combustion of carbonaceous residue, improved energy efficiency by maximum utilization of waste heat, and less water use for quenching. According to promoters, the Enefit process has a lower retorting time compare to the classical Galoter process and therefore its has a greater throughput. Avoidance of moving parts in the retorting zones increases their durability.

Commercial use

Two Galoter retorts built in 1980 are used for oil production by the Narva Oil Plant, a subsidiary of the Estonian energy company Eesti Energia. Both retorts process 125 tonnes per hour of oil shale. The annual shale oil production is 135,000 tonnes and oil shale gas production is 40 million cubic metres per annum (1.4×10^9 cu ft/a). The company is building a new plant exploiting its newer Enefit process with a processing capacity of 2.26 million tonnes of oil shale per year and producing 290,000 tonnes of shale oil and 75 million cubic metres (2.6×10^9 cu ft) of oil shale gas. It is planned to become operational by 2012. In addition, Eesti Energia plans to build a similar Enefit plant in Jordan; the construction is scheduled to begin by 2015.

VKG Oil, a subsidiary of Viru Keemia Grupp, constructed a new Galoter retort (Petroter) at Kohtla-Järve that is similar to the two retorts operating at Narva. The basic engineering of the retort was done by Atomenergoproject of Saint Petersburg. The basic engineering of the condensation and distillation plant was done by Rintekno of Finland. The plant has a processing capacity of 1.1 million tonnes of oil shale per year and it produces 100,000 tonnes of shale oil, 30 million cubic metres (1.1×10^9 cu ft) of oil shale gas, and 150 GWh of steam per year. Operation started in December 2009. The company plans to start construction of the the second Petroter plant in 2012.

Superior Multimineral Process

Superior multimineral process
McDowell–Wellman process

Process type	Chemical
Industrial sector(s)	Chemical industry oil industry
Feedstock	oil shale
Product(s)	shale oil
Leading companies	Superior Oil Company
Developer(s)	Superior Oil Company

The **Superior multimineral process** (also known as the **McDowell–Wellman process** or **circular grate process**) is an above ground shale oil extraction technology designed for production of shale oil, a type of synthetic crude oil. The process heats oil shale in a sealed horizontal segmented vessel (retort) causing its decomposition into shale oil, oil shale gas and spent residue. The particularities of this process is a recovery of saline minerals from the oil shale, and a doughnut-shape of the retort. The process is suitable for processing of mineral-rich oil shales, such as in the Piceance Basin. It has a relatively high reliability and high oil yield. The technology was developed by the American oil company Superior Oil.

History

The multimineral process was developed by Superior Oil Company, now part of ExxonMobil, for processing of the Piceance Basin's oil shale. The technology tests were carried out in pilot plants in Cleveland, Ohio. In 1970s, Superior Oil planned a commercial-size demonstration plant in the northern Piceance Basin area with a capacity of 11,500 to 13,000 barrels (1,830 to 2,100 m^3) of shale oil per day; however, because of low crude oil price these plans were never implemented.

Process

The process was developed to combine the shale oil production with production of sodium bicarbonate, sodium carbonate, and aluminum from nahcolite and dawsonite, occurring in oil shales of the Piceance Basin. In this process, the nahcolite is recovered from the raw oil shale by crushing it to lumps smaller than 8 inches (200 mm). As a result, most of the nahcolite in the oil shale becomes a fine powder what could screened out. Screened oil shale lumps are further crushed to particles smaller than 3 inches (76 mm). Oil shale particles are further processed in a horizontal segmented doughnut-shaped traveling-grate retort in the direct or indirect heating mode. The retort was originally designed by Davy McKee Corporation for iron ore pelletizing and it also known as the **Dravo retort**. In the direct retort, oil shale moves past ducts through which are provided hot inert gas for heating the raw oil shale, air for combustion of carbon residue (char or semi-coke) in the spent oil shale, and cold inert gas for cooling the spent oil shale. The oil pyrolysis takes place in the heating section. To minimize solubility of aluminium compounds in the oil shale, the heat control is a crucial factor. Necessary heat for pyrolysis is generated in the carbon recovery section by combustion of carbon residue (char or semi-coke) remained in the spent oil shale. While blowing inert gases through the spent oil shale, the spent oil shale is cooled and gases are heated to cause pyrolysis. The indirect mode is similar; the difference is that combustion of carbonaceous residue takes place in separate vessel. The last section is for discharging of oil shale ash. Aluminium oxide and sodium carbonate are recovered from calcined dawsonite and calcined nahcolite in the oil shale ash.

Advantages

The traveling-grate retort allows close temperature control, and therefore better control of dawsonite's solubility during the burning stage. During retorting, there is no relative movement of oil shale, which avoids dust creation, and therefore increase the quality of generated products. The oil recovery yields greater than 98% Fischer Assay. The technology has also a relatively high reliability. The sealed system of this process has environmental advantage as it prevents gas and mist leakage.

Chapter 17

Petrosix & Paraho Process

Petrosix

Petrosix process

Process type	Chemical
Industrial sector(s)	Chemical industry oil industry
Feedstock	oil shale
Product(s)	shale oil
Leading companies	Petrobras
Inventor	Petrobras
Developer(s)	Petrobras

Petrosix is currently the world's largest surface oil shale pyrolysis retort with an 11 metres (36 ft) diameter vertical shaft kiln, operational since 1992. It is located in São Mateus do Sul, Brazil, and it is owned and operated by the Brazil energy company Petrobras. Petrosix means also the Petrosix process, an externally generated hot gas technology of shale oil extraction. The technology is tailored to Irati oil shale formation, a Permian formation of the Paraná Basin.

History

Petrobras started oil shale processing activities in 1953 by developing Petrosix technology for extracting oil from oil shale of the Irati formation. A 5.5 metres (18 ft) inside diameter semi-works retort (the Irati Profile Plant) with capacity of 2,400 tons per day, was brought on line in 1972, and began limited commercial operation in 1980. The first retort that used current Petrosix technology was a 0.2 metres (0.7 ft) internal diameter retort pilot plant started in 1982. It was followed by a 2 metres (6.6 ft) retort demonstration plant in 1984. A 11 metres (36 ft) retort was brought into service in

December 1991, and commercial production started in 1992. At present, the company operates two retorts which process 8,500 tons of oil shale daily.

Retort

The Petrosix 11 metres (36 ft) vertical shaft retort is the world's largest operational surface oil shale pyrolysis reactor. It was designed by Cameron Engineers. The retort has the upper pyrolysis section and lower shale coke cooling section. The retort capacity is 6,200 tons of oil shale per day, and it yields a nominal daily output of 3,870 barrels of shale oil, 132 tons of oil shale gas, 50 tons of liquefied oil shale gas, and 82 tons of sulfur.

Process

Petrosix is one of fives technologies of shale oil extraction, which is currently in commercial use. It is an above-ground retorting technology, which uses externally generated hot gas for the oil shale pyrolysis. After mining, the shale is transported by trucks to a crusher and screens, where it is reduced to particles (lump shale). These particles are between 12 millimetres (0.5 in) and 75 millimetres (3.0 in) and have an approximately parallelepipedic shape. These particles are transported on a belt to a vertical cylindrical vessel, where the shale is heated up to about 500 °C (932 °F) for pyrolysis. Oil shale enters through the top of the retort while hot gases are injected into the middle of the retort. The oil shale is heated by the gases as it moves down. As a result, the kerogen in the shale decomposes to yield oil vapor and more gas. Cold gas is injected into the bottom of the retort to cool and recover heat from the spent shale. Cooled spent shale is discharged through a water seal with drag conveyor below the retort. Oil mist and cooled gases are removed through the top of the retort and enter a wet electrostatic precipitator where the oil droplets are coalesced and collected. The gas from the precipitator is compressed and split into three parts.

One part of the compressed retort gas is heated in a furnace to 600 °C (1,112 °F) and recirculated back to the middle of the retort for heating and pyrolyzing the oil shale, and another part is circulated cold into the bottom of the retort, where it cools down the spent shale, heats up itself, and ascends into the pyrolysis section as a supplementary heat source for heating the oil shale. The third part undergoes further cooling for light oil (naphtha) and water removal and then sent to the gas treatment unit, where fuel gas and liquefied petroleum gas (LPG) are produced and sulfur recovered.

One drawback of this process is that the potential heat from the combustion of the char contained in the shale is not utilized. Also oil shale particles smaller than 12 millimetres (0.5 in) can not be processed in the Petrosix retort. These fines may account for 10 to 30 per cent of the crushed feed.

Paraho Process

Paraho process

Process type	Chemical
Industrial sector(s)	Chemical industry oil industry
Feedstock	oil shale
Product(s)	shale oil
Leading companies	Paraho Development Corporation
Inventor	John B. Jones, Jr.
Developer(s)	Development Engineering, Inc.

The **Paraho process** is an above ground retorting technology for shale oil extraction. The name "Paraho" is delivered from the words "*para homem*", which means in Portuguese "for mankind".

History

The Paraho process was invented by John B. Jones, Jr., later president of the Paraho Development Corporation, and developed by Development Engineering, Inc., in late 1960s. Its design was based on a gas combustion retort developed by the United States Bureau of Mines and the earlier Nevada–Texas–Utah Retort. In the late 1940s, these retorts were tested in the Oil Shale Experiment Station at Anvil Points in Rifle, Colorado. In 1971, the Standard Oil of Ohio started to cooperate with Mr. John B. Jones providing financial support for obtaining an oil shale lease at Anvil Points. In May 1972, the lease was approved. Before leasing a track at Anvil Points, a test of using the Paraho Direct process for limestone calcination in cement kilns was carried out.

The consortium for developing the Anvil Points lease – the Paraho Development Corporation – was formed in 1973. In addition to the Standard Oil of Ohio, other participants of the consortium were Atlantic Richfield, Carter Oil, Chevron Research, Cleveland-Cliffs Iron, Gulf Oil, Kerr-McKee, Marathon Oil, Arthur G. McKee, Mobil Research, Phillips Petroleum Company, Shell Development, Southern California Edison, Standard Oil Company (Indiana), Sun Oil, Texaco, and the Webb-Chambers-Gary-McLoraine Group. Shale oil retorting started in 1974 when two operational retorts – pilot plant and semiworks – were put into operation. The semiworks unit achieved a maximum throughput capacity of 290 tons (263 tonnes) of raw oil shale per day. In March 1976, the Paraho Development Corporation tested a modification of its technology – the Paraho Indirect process. The Anvil Points lease was closed in 1978.

In 1976–1978, under the contracts with the United States Navy, Paraho technology was used for production of 100,000 barrels of crude shale oil. It was tested for using as military transportation fuels. The Gary Western Refinery in Fruita, Colorado, refined the Paraho shale oil for production of gasoline, jet fuels, diesel fuel marine, and heavy fuel oil. Paraho JP-4 aviation fuel was tested by the United States Air Force in the T-39 jet aircraft flight, which took a place between the Wright Patterson Air Force Base (Dayton, Ohio) and the Carswell Air Force Base (Fort Worth, Texas). In addition, the Paraho heavy fuel oil was used for fueling a Cleveland-Cliffs Iron ore carrier during its 7-day cruise on Great Lakes. On 13 June 1980, the Department of Energy awarded $4.4 million contract to build a modular demonstration shale oil plant near Vernal, Utah. No commercial-scale Paraho was ever built.

In 1982, Paraho's semi-works plant was torn down when the Anvil Points station was decommissioned, but the pilot plant was moved to a new site.

In 1987, Paraho reorganized as New Paraho and began production of SOMAT asphalt additive used in test strips in 5 States. In 1991, New PARAHO reported successful tests of SOMAT shale oil asphalt additive.

On 28 June 2000, Shale Technologies purchased Paraho Development Corporation and became owner of the proprietary information relating to the Paraho oil shale retorting technologies.

On 14 August 2008, Queensland Energy Resources announced that it will use the Paraho Indirect technology for its Stuart Oil Shale Project.

Technology

The Paraho process can be operated in two different heating modes, which are direct and indirect. The Paraho Direct process evolved from gas combustion retort technology and is classified as an internal combustion method. Accordingly, the Paraho Direct retort is a vertical shaft retort similar to the Kiviter and Fushun retorts, used correspondingly in Estonia and China. However, compared to the earlier gas combustion retorts the Paraho retort's raw oil shale feeding mechanism, gas distributor, and discharge grate have different designs. In the Paraho Direct process, the crushed and screened raw oil shale is fed into the top of the retort through a rotating distributor. The oil shale descends the retort as a moving bed. The oil shale is heated by the rising combustion gases from the lower part of the retort and the kerogen in the shale decomposes at about 500 °C (932 °F) to oil vapour, shale oil gas and spent shale. Heat for pyrolysis comes from the combustion of char in the spent shale. The combustion takes place where air is injected at two levels in the middle of the retort below the pyrolysis section raising the temperature of the shale and the gas to 700 °C (1,292 °F) to 800 °C (1,472 °F). Collecting tubes at the top of the retort carry shale oil mist, evolved gases and combustion gases into the product separation unit, where oil, water and dust are separated from the gases. For combined removal of liquid droplets and particulates, a wet electrostatic precipitator is used. Cleaned gases from the precipitator are compressed in a compressor. Part of the gas from the compressor is recycled to the bottom of the retort to cool the combusted shale (shale ash) and carry the recovered heat back up the retort. Cooled shale ash exits the retort through the discharge grate in the bottom of the retort. After processing, shale ash is disposed of. The liquid oil is separated from produced water and may be further refined into high quality products. The mixure of evolved gases and combustions gases is available for use as a low quality fuel gas for drying or power generation.

The Paraho Indirect is classified as an externally generated hot gas technology . The Paraho Indirect retort configuration is similar to the Paraho Direct except that a part of the gas from the compressor is heated to between 600 °C (1,112 °F) to 800 °C (1,472 °F) in a separate furnace and injected into the retort instead of air. No combustion occurs in the Paraho Indirect retort itself. As a result, the fuel gas from the Paraho Indirect is not diluted with combustion gases and the char remains on the disposed spent shale.

The main advantage of the Paraho process is simplicity in process and design; it has few moving parts and therefore low construction and operating costs compared with more sophisticated technologies. The Paraho retort also consumes no water, which is especially important for oil shale extraction in areas with water scarcity. A disadvantage common to both the Paraho Direct and Paraho Indirect is that neither are able to process oil shale particles smaller than about 12 millimetres (0.5 in). These fines may account for 10 to 30 per cent of the crushed feed.

Operations

Shale Technologies LCC owns and operates a pilot Paraho retort near Rifle, Colorado.

Chapter 18

Chevron CRUSH & Shell in Situ Conversion Process

Chevron CRUSH

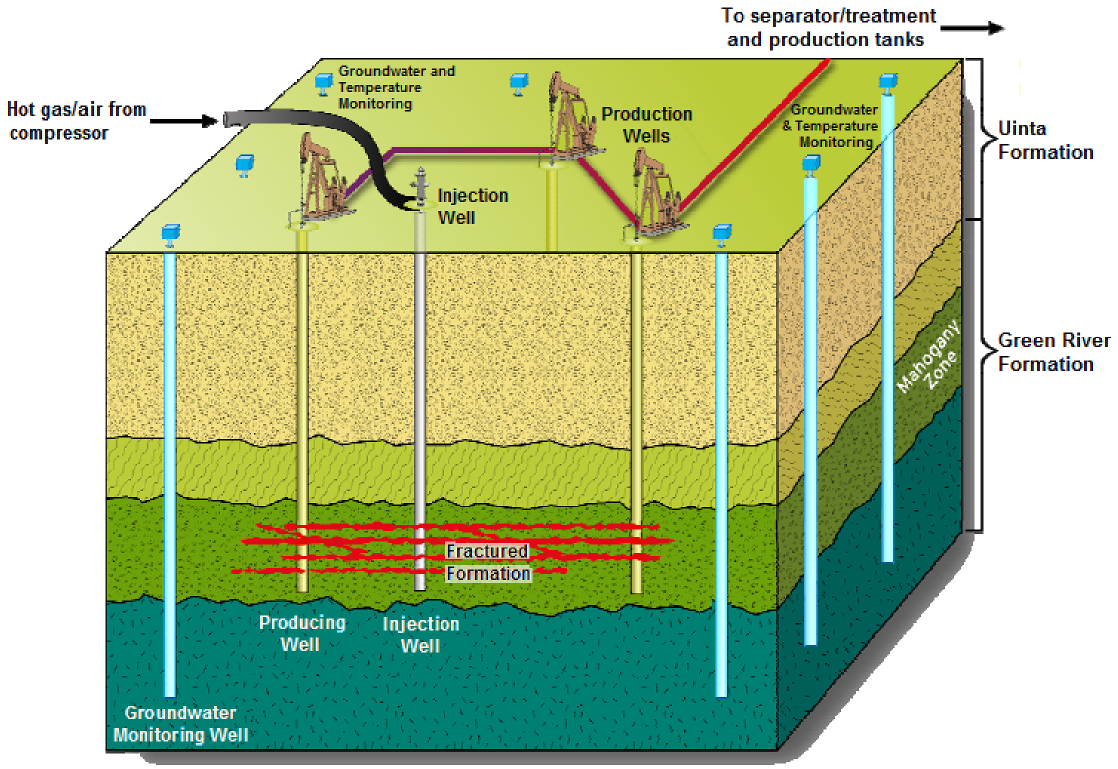
Chevron CRUSH	
Process type	chemical
Industrial sector(s)	chemical industry, oil industry
Feedstock	oil shale
Product(s)	shale oil
Leading companies	Chevron Corporation
Developer(s)	Chevron Research Company

Chevron CRUSH is an *in situ* shale oil extraction technology to convert kerogen in oil shale to shale oil. The name stands for Chevron's Technology for the Recovery and Upgrading of Oil from Shale. It is developed jointly by Chevron Corporation and the Los Alamos National Laboratory.

History

The Chevron CRUSH technology bases on the earlier *in situ* efforts. Sinclair Oil Corporation conducted an experiment using both natural and induced fractures to establish communication between wells and developing an *in situ* combustion process. Geokinetics, the Sandia National Laboratories, and the Laramie Energy Technology Center of the U.S. Department of Energy emploed explosive and hydraulic fracturing technologies. Equity Oil Company, Continental Oil Company and the University of Akron studied the benefit of carbon dioxide as a carrier gas to facilitate a higher yield of shale oil. Based on these works, Chevron Corporation and the Los Alamos National Laboratory started a cooperation in 2006 to improve the recovery of hydrocarbons from oil shale. IN 2006, the United States Department of the Interior issued a research, development and demonstration lease for Chevron's demonstration project on public lands in Colorado’s Piceance Basin.

Process



Chevron CRUSH process

For decomposition kerogen in oil shale, the Chevron CRUSH process uses heated carbon dioxide. The process involves drilling vertical wells into the oil shale formation and applying horizontal fractures induced by injecting carbon dioxide through drilled wells and then pressured through the formation for circulation through the fractured intervals to rubblize the production zone. For further rubblization propellants and explosives may be used. The used carbon dioxide then be routed to the gas generator to be reheated and recycled. The remaining organic matter in previously heated and depleted zones is combusted *in-situ* to generate the heated gases required to process successive intervals. These gases would then be pressured from the depleted zone into the newly fractured portion of the formation and the process would be repeated. The hydrocarbon fluids are brought up in conventional vertical oil wells.

Isolation of groundwater

The processing area is isolated from surrounding groundwater by creating fractured areas ("pockets"), approximately 1 to 5 acres (4,000 to 20,000 m^2) wide and 50 feet (15 m) high within the center of the oil shale deposit. In this way, about 75 feet (23 m) of the confining layer would separate the process area from the water bearing layers above and below, keeping the aquifers out of the production zone.

Shell in situ Conversion Process

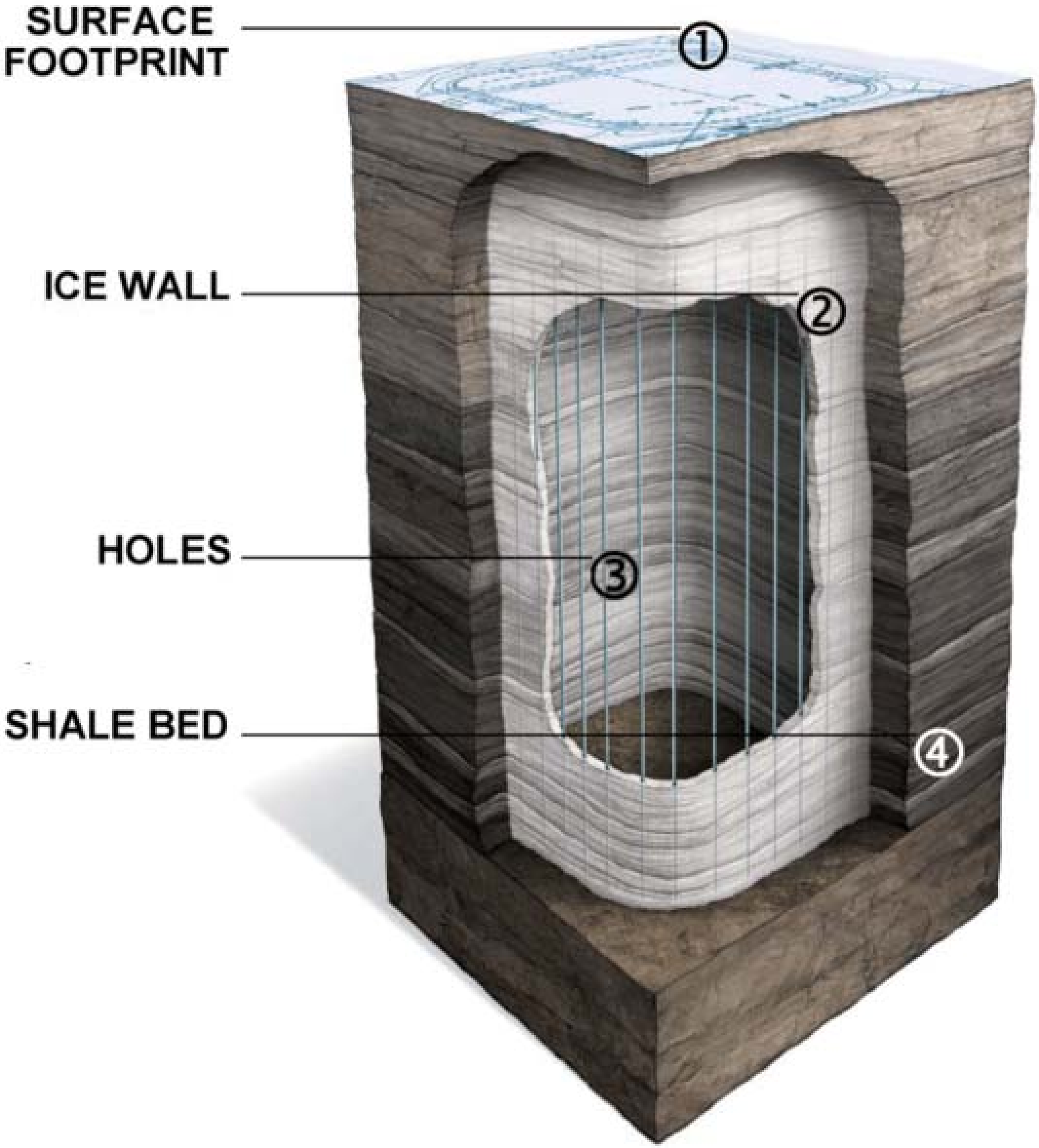
Shell ICP	
Process type	chemical
Industrial sector(s)	chemical industry, oil industry
Feedstock	oil shale
Product(s)	shale oil
Leading companies	Shell Oil Company
Main facilities	Mahogany Research Project
Developer(s)	Shell Oil Company

The **Shell's *in situ* conversion process** (**Shell ICP**) is an *in situ* shale oil extraction technology to convert kerogen in oil shale to shale oil. It is developed by the Shell Oil Company.

History

Shell's *in situ* conversion process has been under development since the early 1980s. In 1997, the first small scale test was conducted on the Mahogany property, located 200 miles (320 km) west of Denver on Colorado's Western Slope in the Piceance Creek Basin. Since 2000, additional research and development activities have carried on as a part of the Mahogany Research Project. The oil shale heating at Mahogany started early 2004.

Process



Shells Freeze Wall for *in situ* shale oil production

The process heats sections of the vast oil shale field *in situ*, releasing the shale oil and oil shale gas from the rock so that it can be pumped to the surface and made into fuel. In this process, a freeze wall is first to be constructed to isolate the processing area from surrounding groundwater. To maximize the functionality of the freeze walls, adjacent working zones will be developed in succession. 2,000 feet (610 m) wells, eight feet apart, are drilled and filled with a circulating super-chilled liquid to cool the ground to −60 °F (−50 °C). Water is then removed from the working zone. Heating and recovery wells are drilled at 40 feet (12 m) intervals within the working zone. Electrical heating elements are lowered into the heating wells and used to heat oil shale to between 650 °F (340 °C) and 700 °F (370 °C) over a period of approximately four years. Kerogen in oil shale is slowly converted into shale oil and gases, which are then flow to the surface through recovery wells.

Energy consumption

An operation producing 100,000 barrels a day would require a dedicated power generating capacity of 1.2 gigawatts. If this amount of electricity to be generated by coal-fired power plant, it would consume five million ton of coal annually. Although this method is energy-intensive, it compares well to heavy oil projects such as oil sands development. Over the project life cycle, Shell estimates that for every unit of energy consumed, three to four units would be produced. The Energy Return on Energy Invested (EROEI) is low compared to conventional crude oil extraction, however the heating process itself creates a byproduct of shale gas that can be used as the energy input.

Environmental impact

This *in situ* method requires minimum disturbance of the surface. Within the pyrolyzed zone the expected surface expressions of heave is about 1.0 to 1.5 inches (25 to 38 mm) and the expected surface expression of subsidence is about 0.5 to 1.0 inch (13 to 25 mm). The footprint of extraction operations is in comparison to conventional oil and gas drilling. Extensive water use and the risk of groundwater pollution are the technology's greatest challenges.