Synthetic Fuel Technologies

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Chapter 1

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.

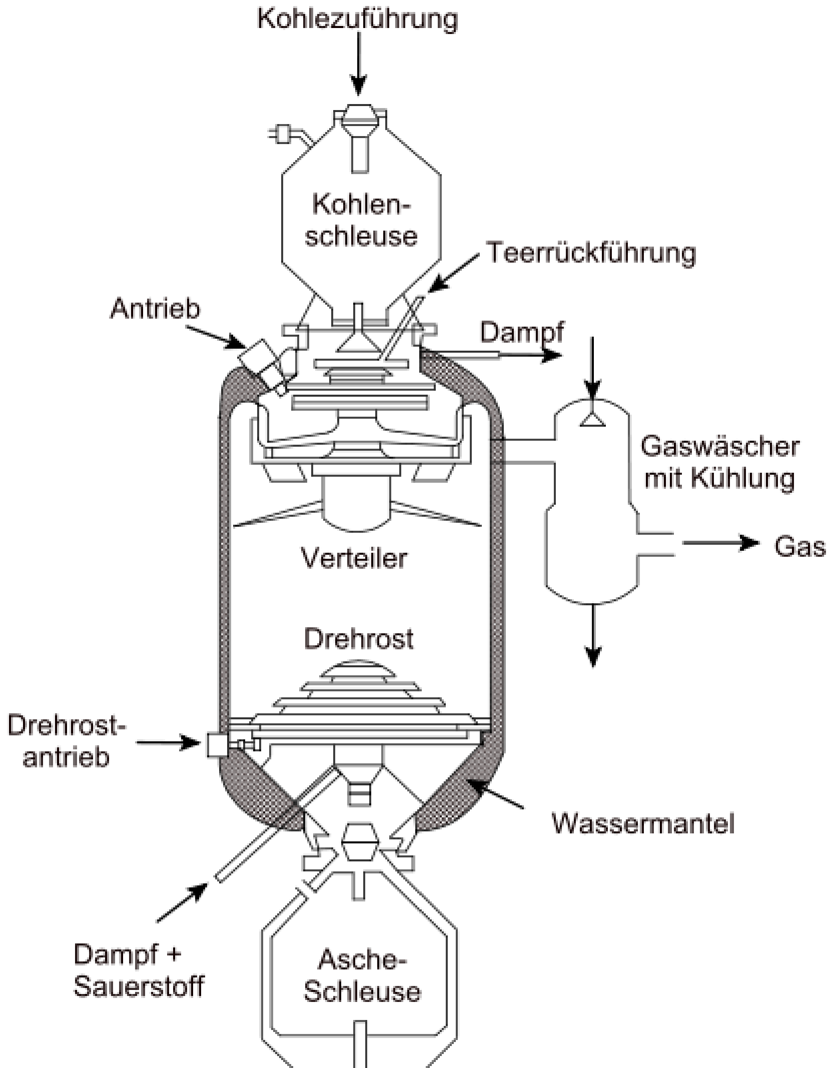
A wide variety of appliances and uses for gas developed over the years. Gas fires, gas cookers, refrigerators, washing machines, hand irons, pokers for fire lighting, gas-heated baths, remotely controlled clusters of gas lights, gas engines of various types and, in later years, gas warm air and hot water 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 2

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

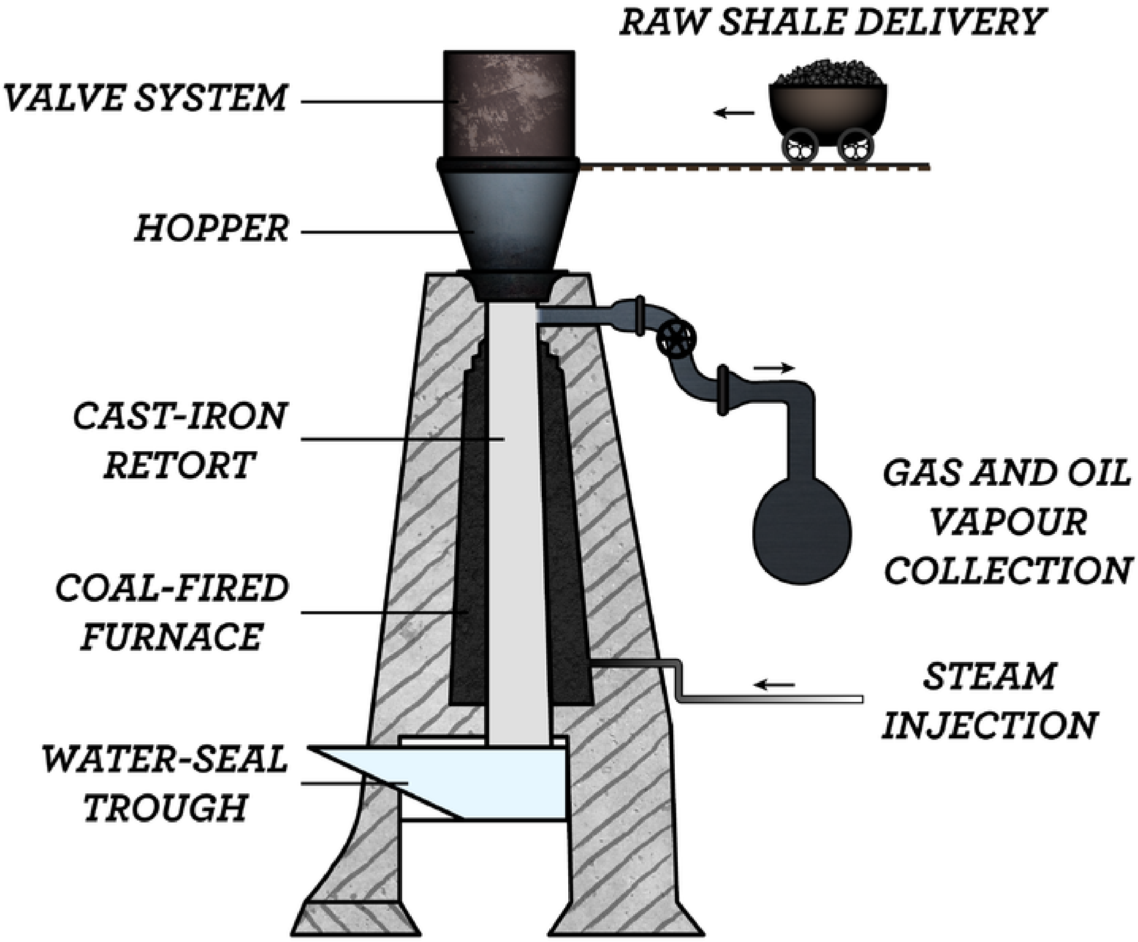
Shale oil extraction is an industrial process for unconventional oil production. This process converts kerogen in oil shale into shale oil by pyrolysis, hydrogenation, or thermal dissolution. The resultant shale oil is used as fuel oil or upgraded to meet refinery feedstock specifications by adding hydrogen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



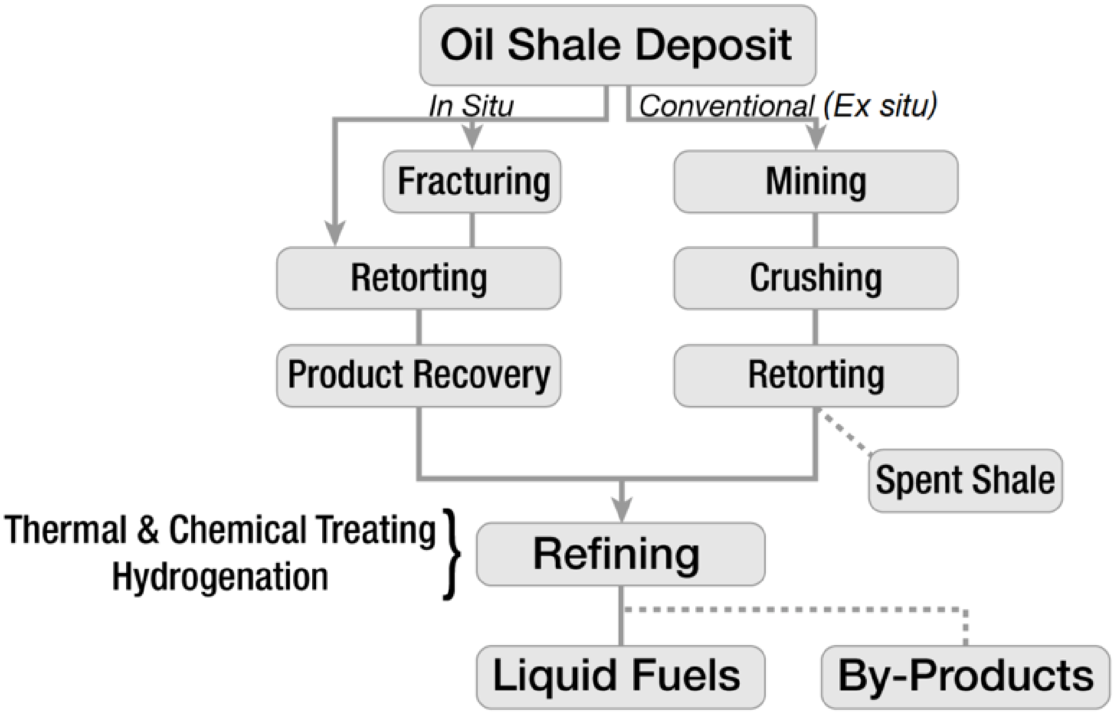
A.C. Kirk's retort, used in the mid-to-late 19th century, was one of the first vertical oil shale retorts. Its design is typical of retorts used in the end of 19th and beginning of 20th century.

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.

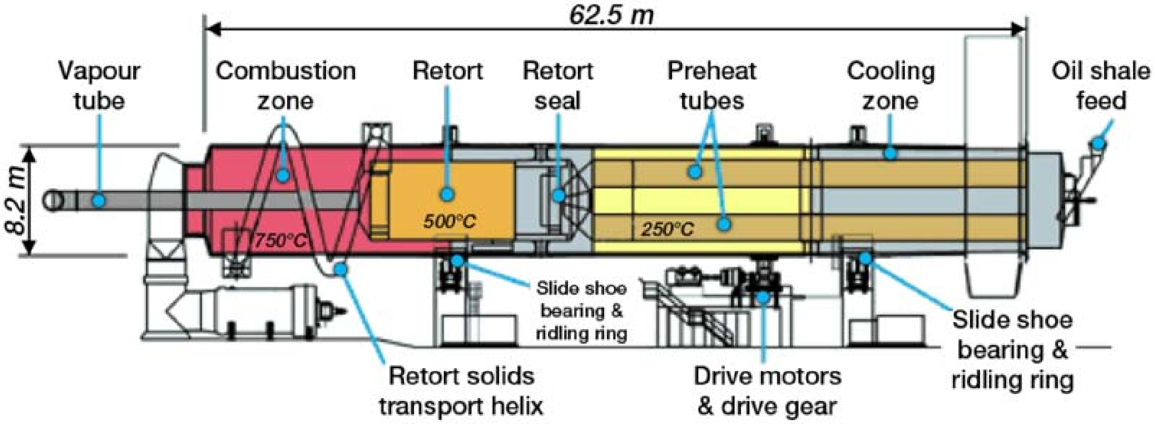
Common drawbacks of internal combustion technologies are that the shale oil gas is diluted by combustion gases and particles smaller than 10 millimeters (0.4 in) can not be processed. Uneven distribution of gas across the retort can result in blockages when hot spots cause particles to fuse or disintegrate.

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.

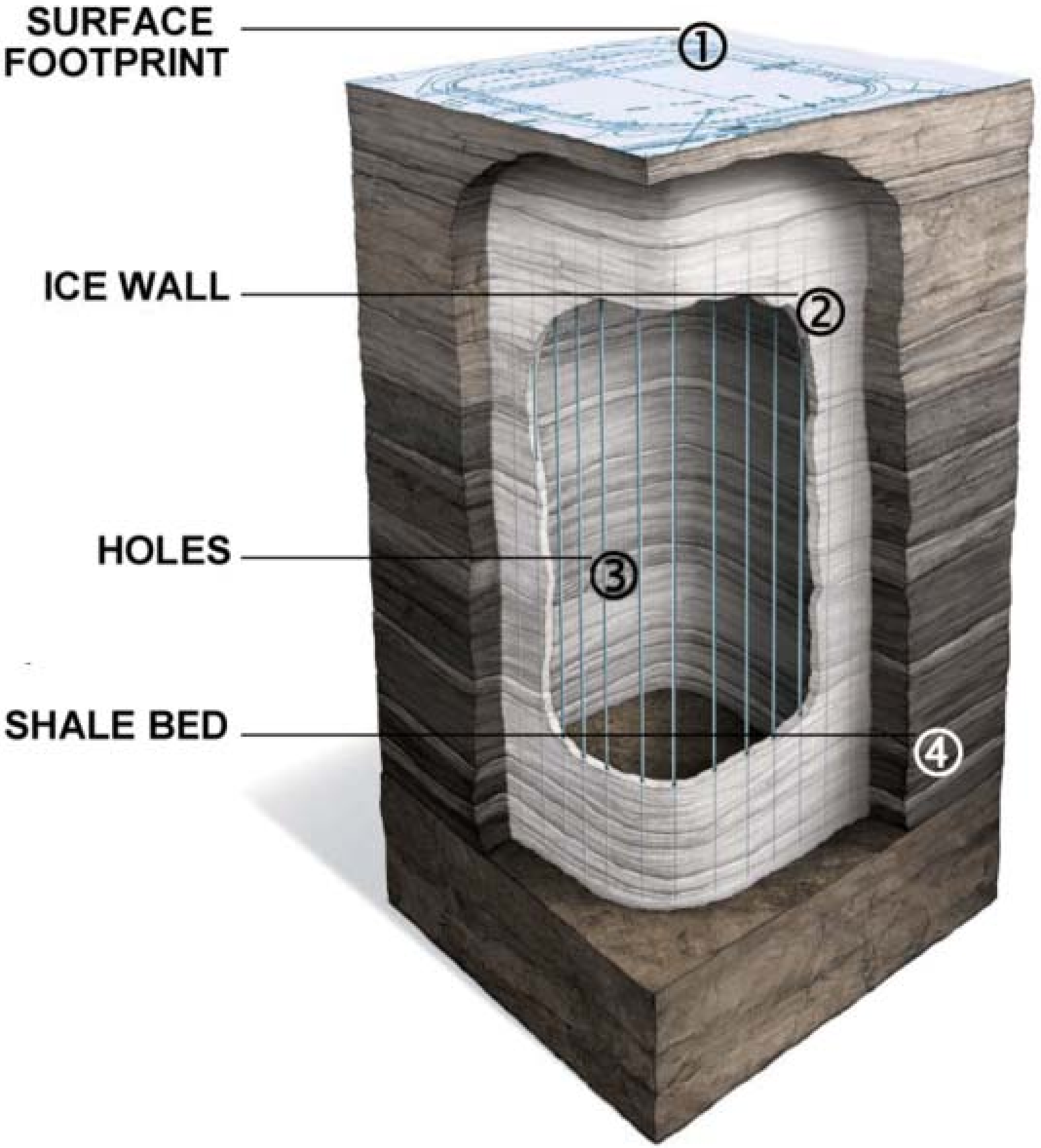
Reactive fluids

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.

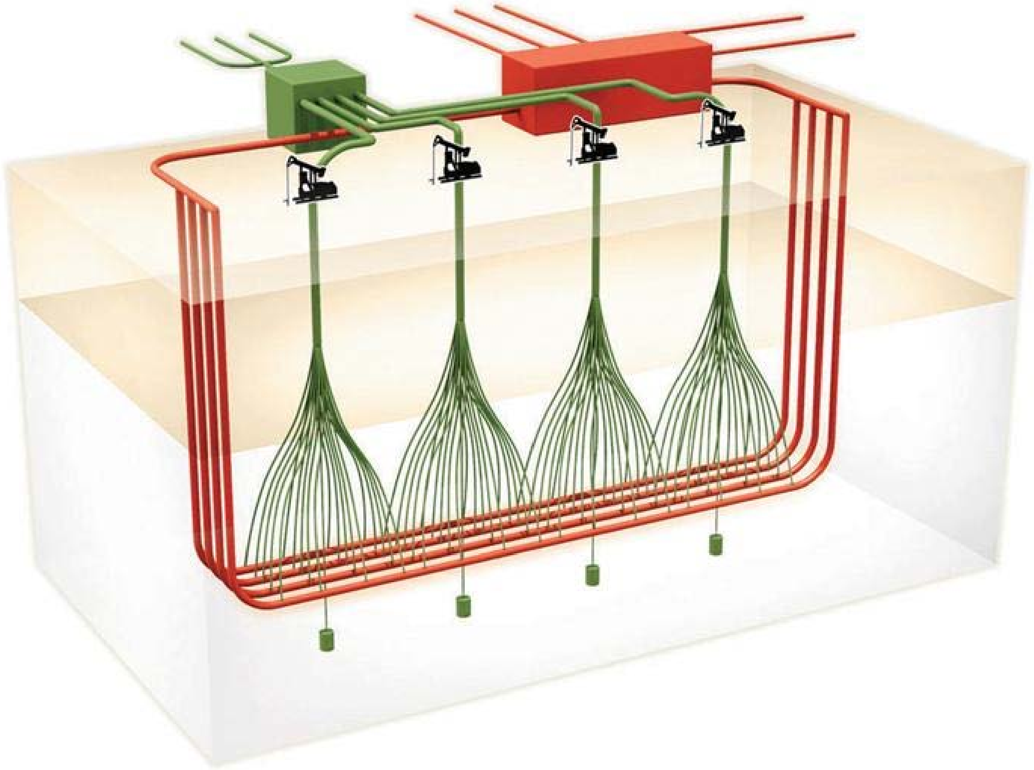
During World War II a modified *in situ* extraction process was implemented without significant success in Germany. One of the earliest successful *in situ* processes was underground gasification by electrical energy (Ljungström method)—a process exploited between 1940 and 1966 for shale oil extraction 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.

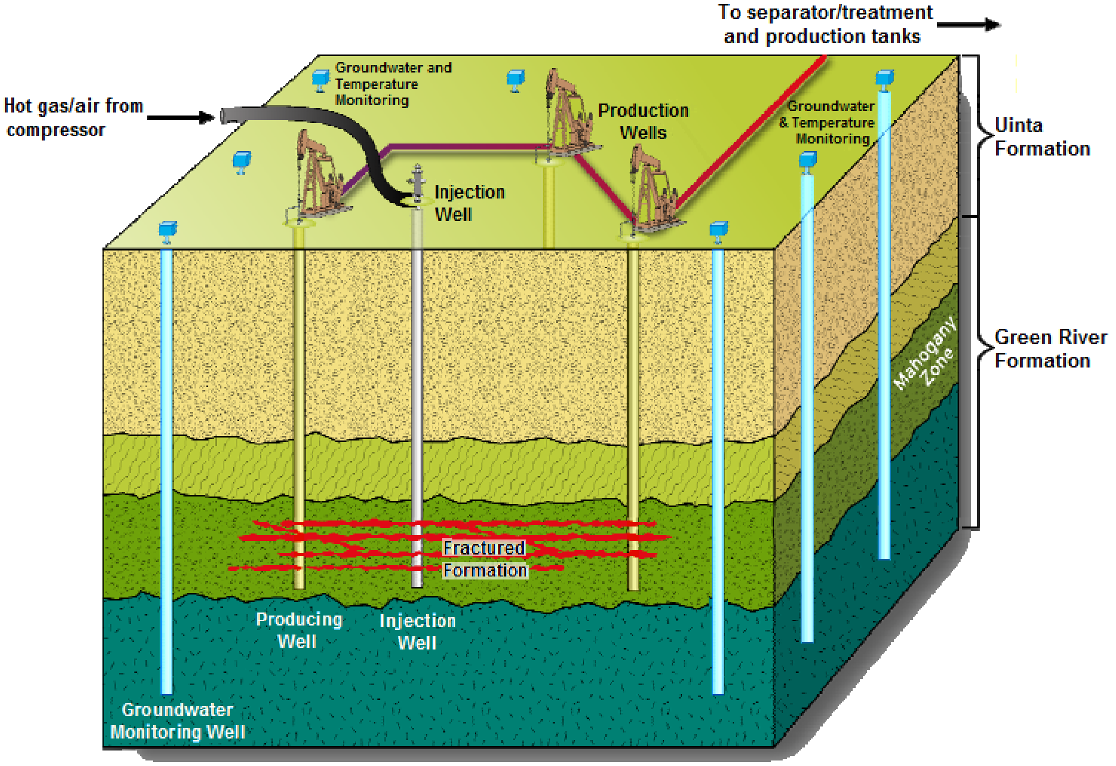


American Shale Oil CCR Process

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



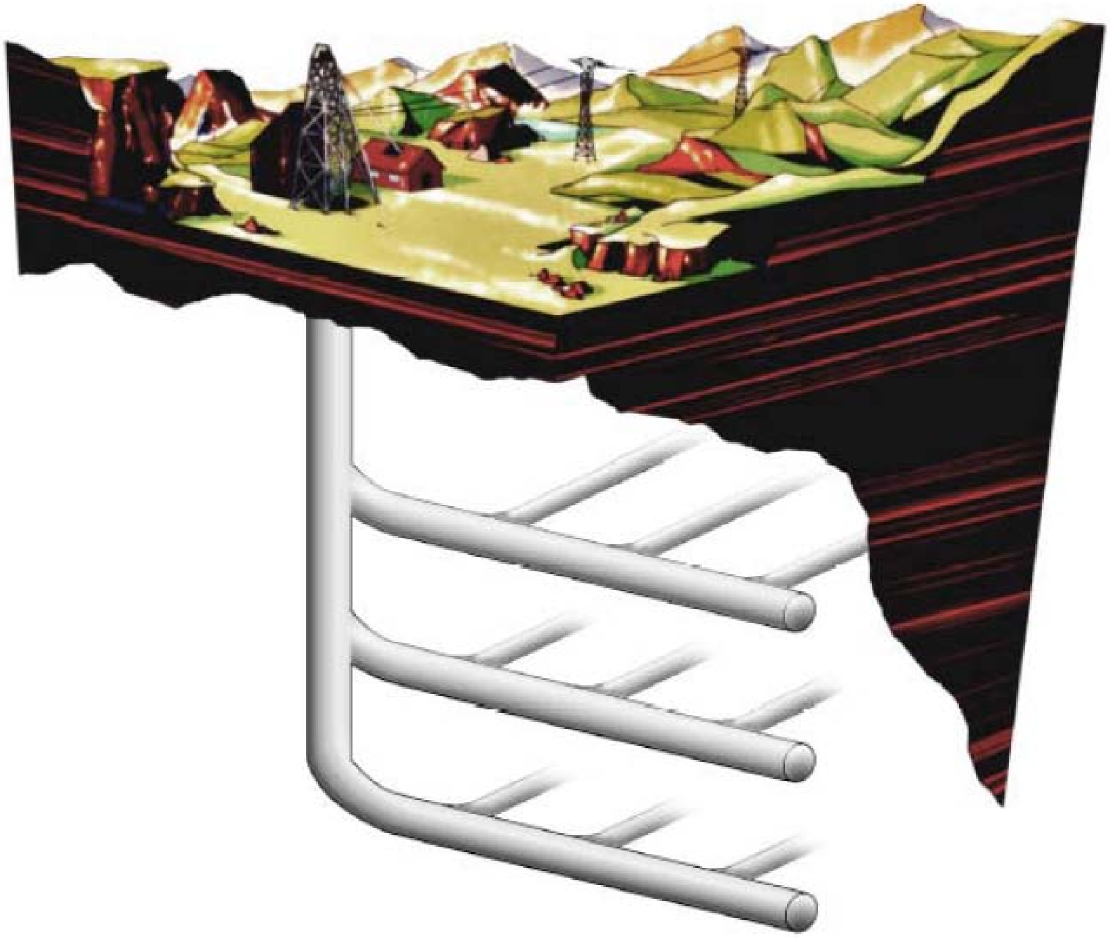
Chevron CRUSH process

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

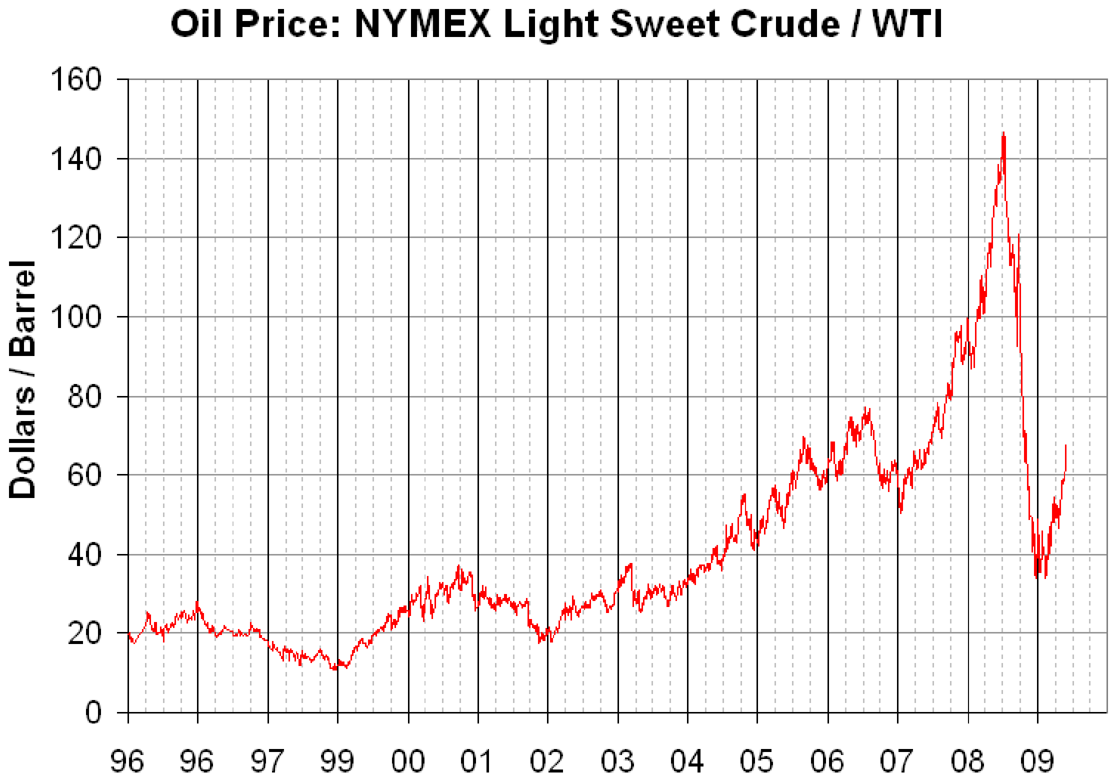


Artist's rendition of a radio wave-based extraction facility

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

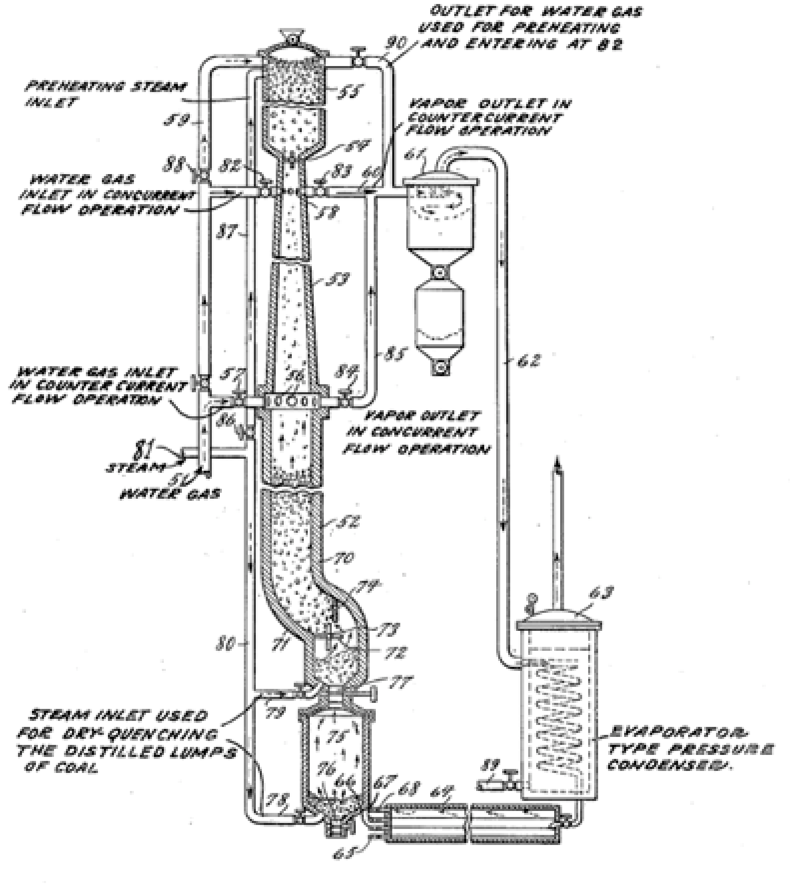
The production and usage of oil shale usually generates more greenhouse gas emissions, including carbon dioxide, than conventional fossil fuels. Depending on the technology and the oil shale composition, shale oil extraction processes may also emit sulfur dioxide, hydrogen sulfide, carbonyl sulfide, 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 3

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 4

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,[:210,224] 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.

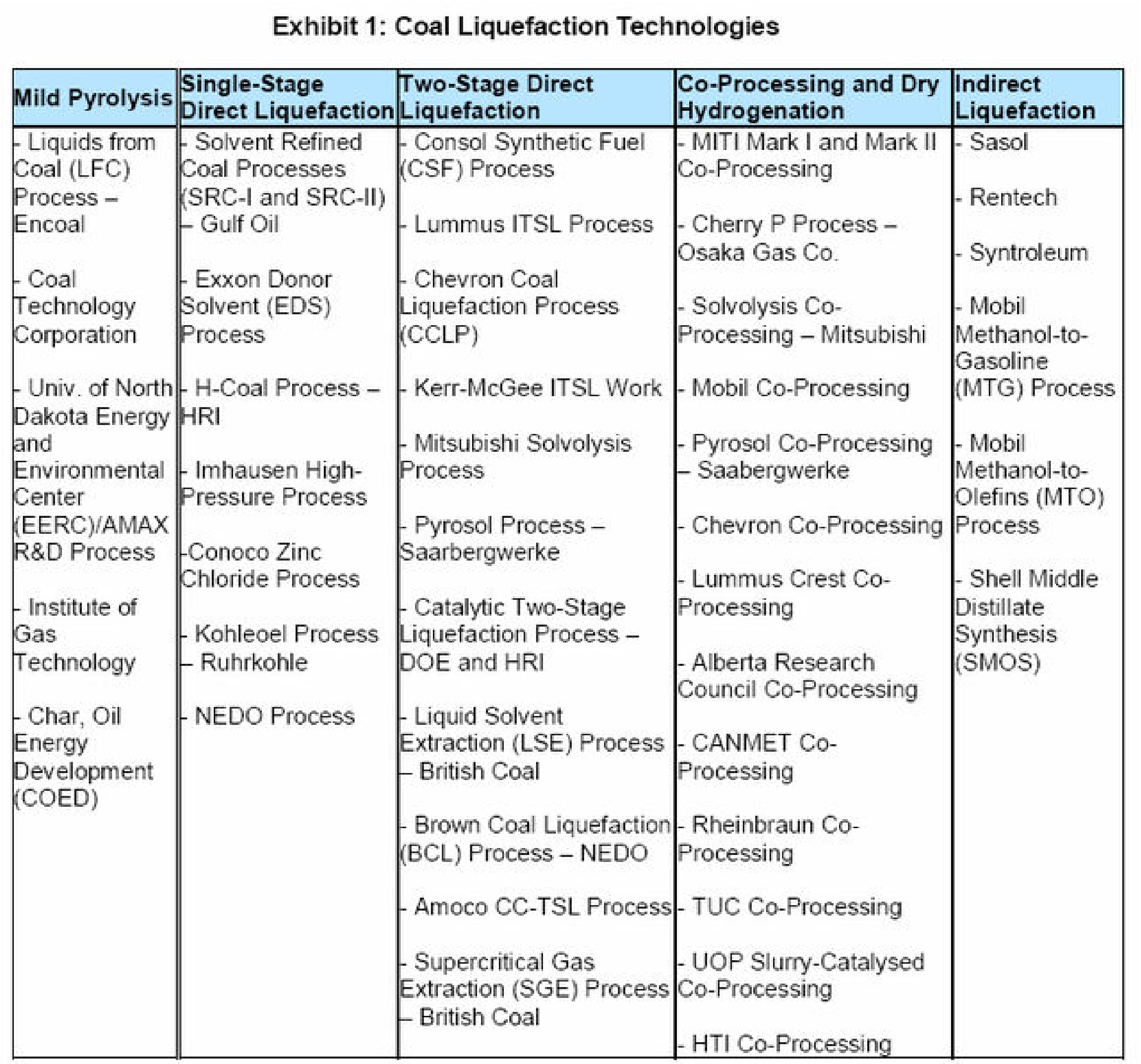


Exhibit 1: Coal Liquefaction Technologies

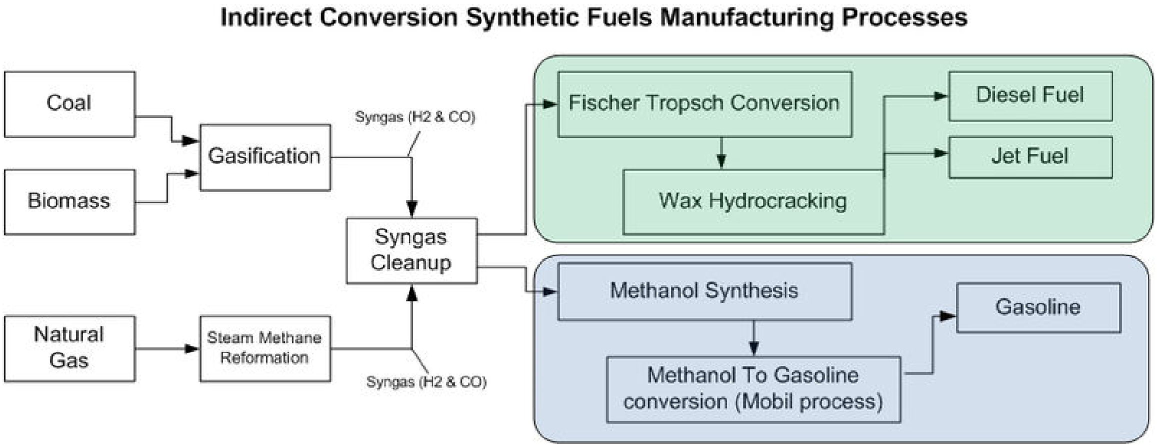
Mild Pyrolysis	Single-Stage Direct Liquefaction	Two-Stage Direct Liquefaction	Co-Processing and Dry Hydrogenation	Indirect Liquefaction
- Liquids from Coal (LFC) Process – Encoal - Coal Technology Corporation - Univ. of North Dakota Energy and Environmental Center (EERC)/AMAX R&D Process - Institute 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:

$$n\mathrm{C} + (n+1)\mathrm{H}_2 \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2}$$

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

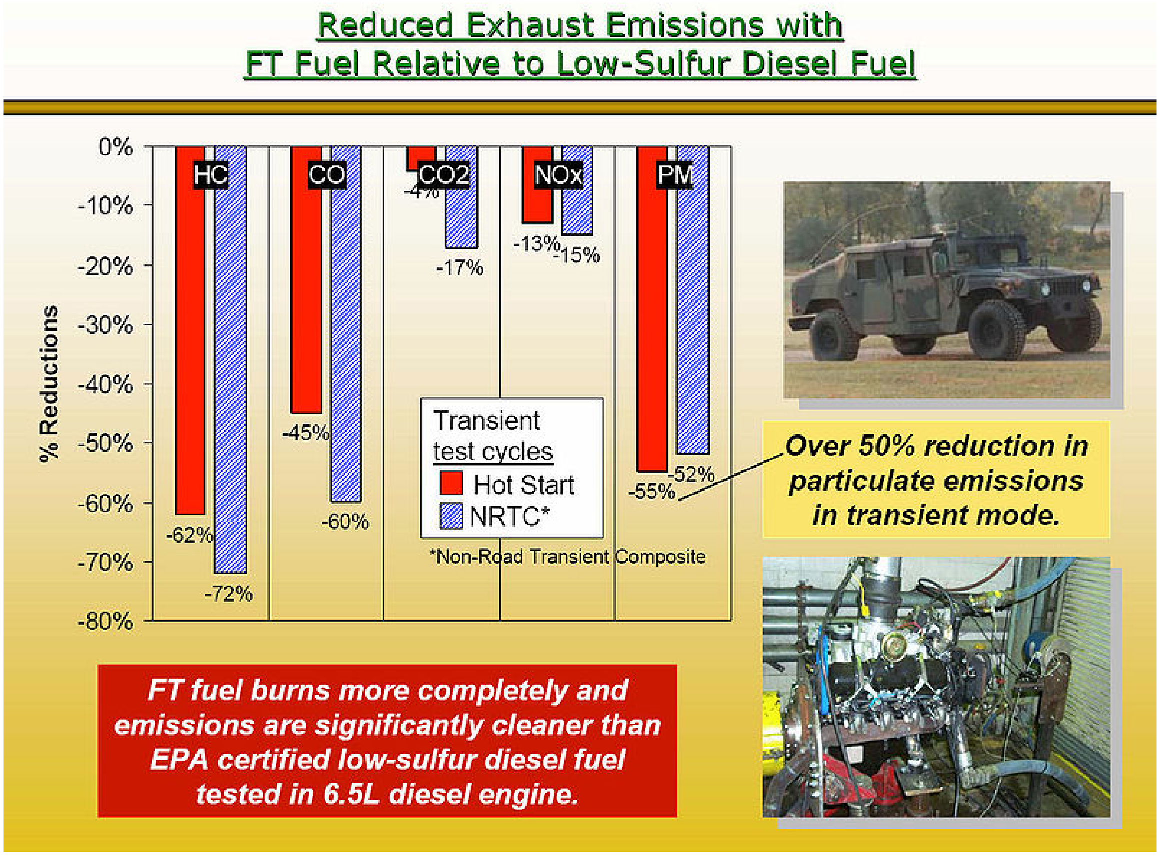
The fuels produced by the various synthetic fuels process also have a wide range of potential environmental performance, though they tend to be very uniform based on the type of synthetic fuels process used (i.e. the tailpipe emissions characteristics of Fischer Tropsch diesel tend to be the same, though 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.

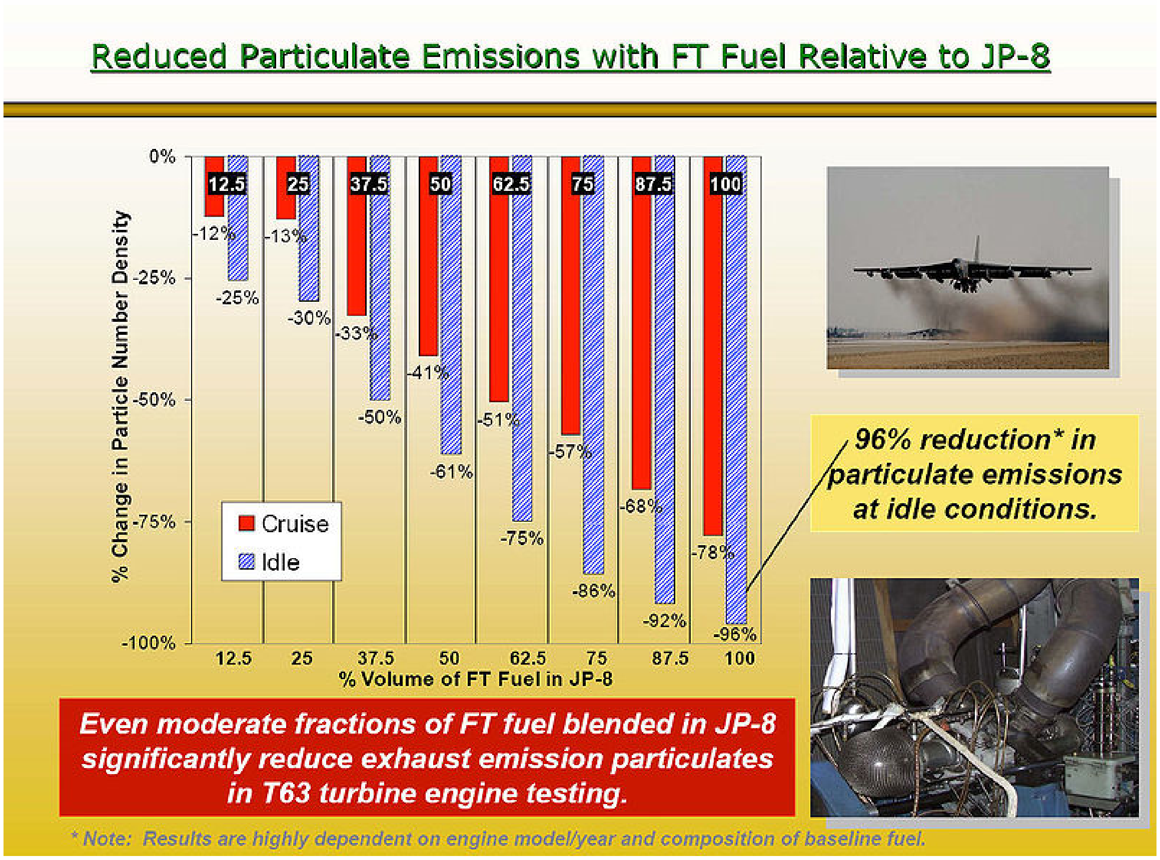


Reduced Exhaust Emissions with FT Fuel Relative to Low-Sulfur Diesel Fuel

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

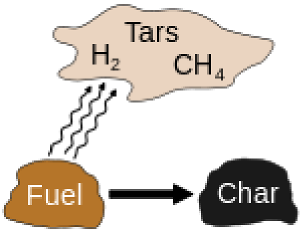
One concern commonly raised about the development of synthetic fuels plants is sustainability. Fundamentally, transitioning from oil to coal or natural gas for transportation fuels production is a transition from one inherently depeleteable geologically limited resource to another.

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 5

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 6

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 7

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 8

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 9

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

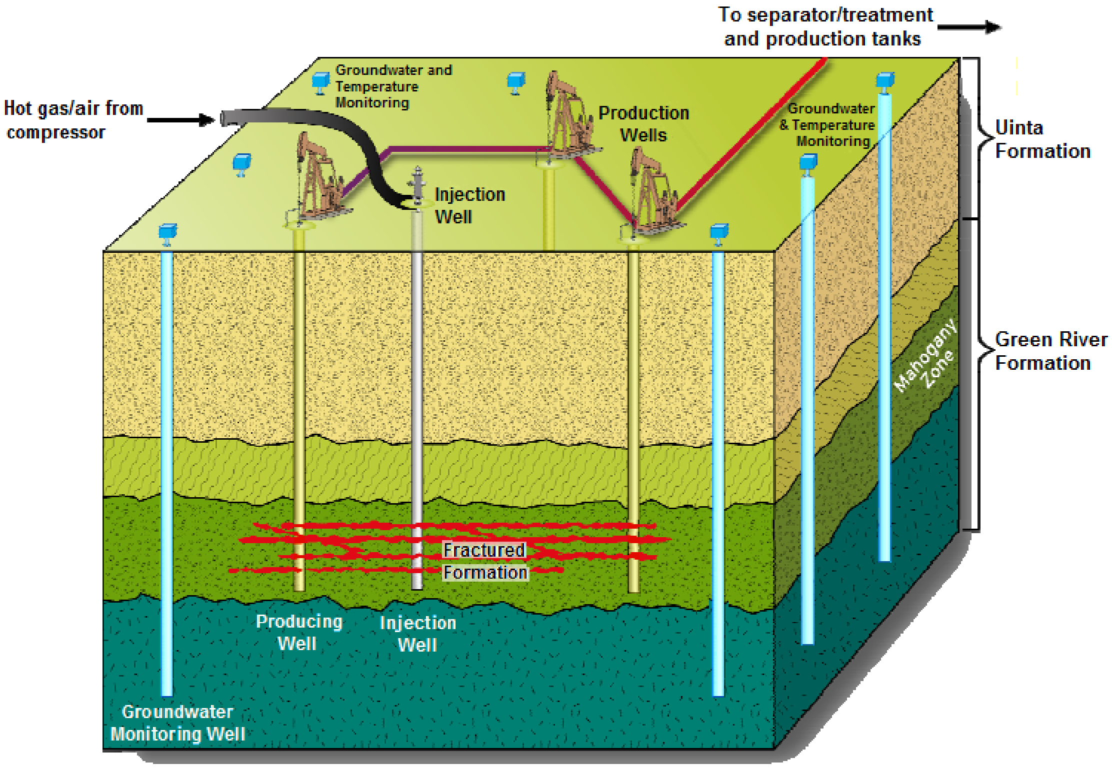
Chevron CRUSH is an *in situ* shale oil extraction technology to convert kerogen in oil shale to shale oil. The name stands for Chevron's Technology for the Recovery and Upgrading of Oil from Shale. It is developed jointly by Chevron Corporation and the Los Alamos National Laboratory.

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

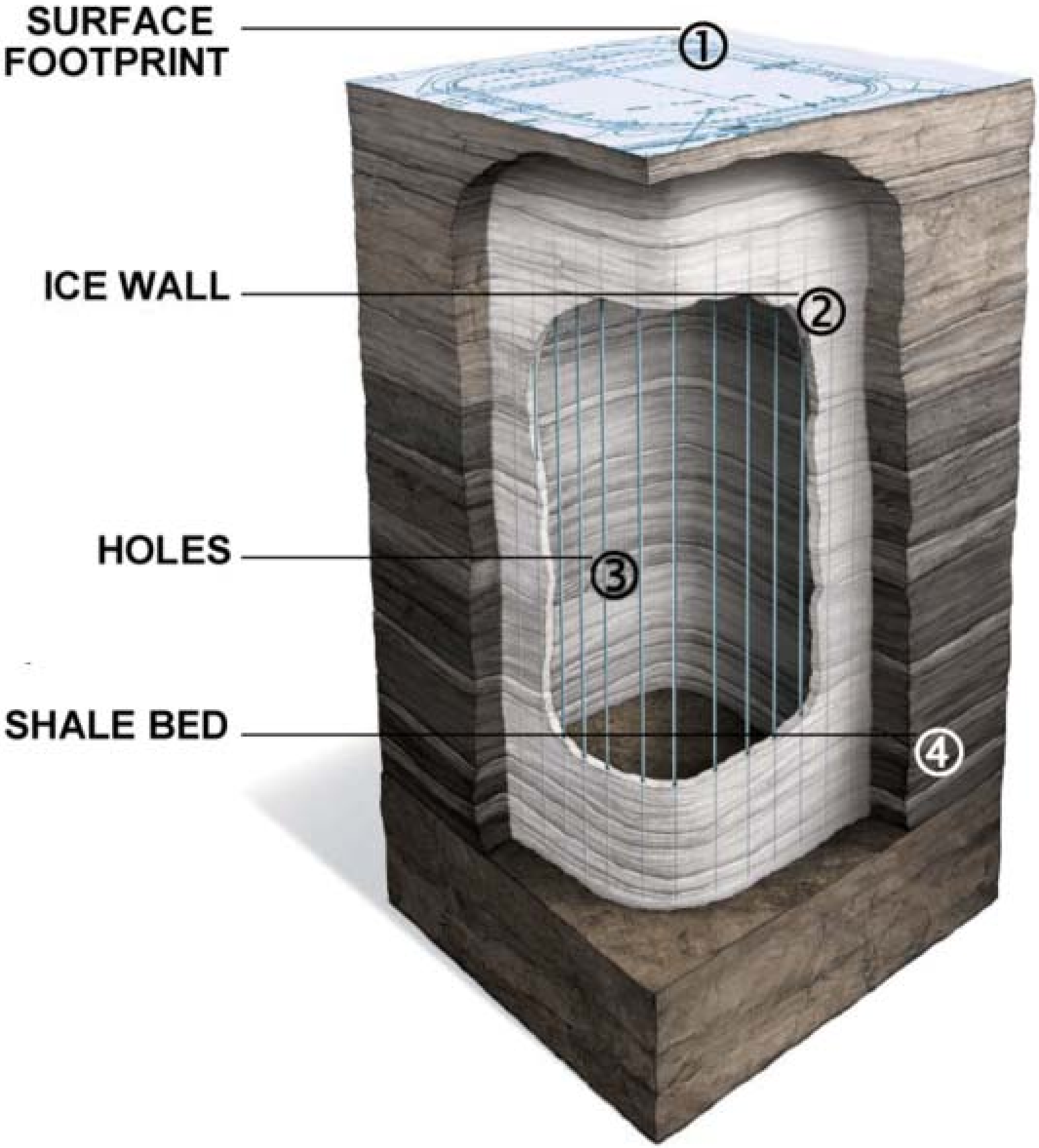
Process type	chemical
Industrial sector(s)	chemical industry, oil industry
Feedstock	oil shale
Product(s)	shale oil
Leading companies	Shell Oil Company
Main facilities	Mahogany Research Project
Developer(s)	Shell Oil Company

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.

Chapter 10

Alberta Taciuk Process & Lurgi-Ruhrgas Process

Alberta Taciuk Process

Alberta Taciuk Process
AOSTRA Taciuk Process

Process type	Chemical
Industrial sector(s)	Chemical industry oil industry
Feedstock	oil shale oil sands organics-bearing materials
Product(s)	shale oil synthetic crude
Leading companies	UMATAC Industrial Processes Queensland Energy Resources United States Environmental Protection Agency
Main facilities	Stuart Oil Shale Plant
Inventor	William Taciuk
Year of invention	1975
Developer(s)	UMATAC Industrial Processes

The **Alberta Taciuk Process** (ATP; known also as the **AOSTRA Taciuk Process**) is an above ground dry thermal retorting technology for extracting oil from oil sands, oil shale and other organics-bearing materials, including oil contaminated soils, sludges and wastes. The technology is named after its inventor William Taciuk and the Alberta Oil Sands Technology and Research Authority.

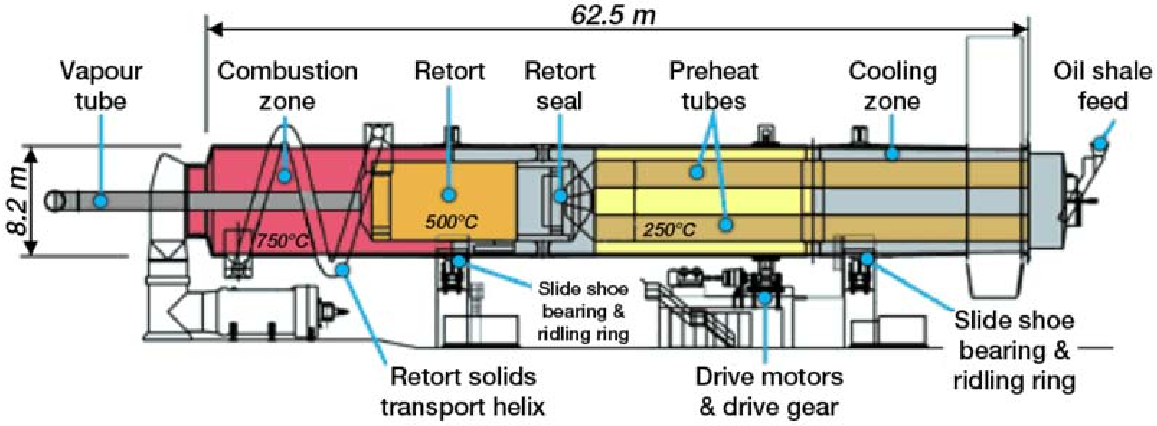
History

The research and development of the ATP technology started in 1970. In 1975, its inventor, William Taciuk, formed the UMATAC Industrial Processes (now part of Polysius) to further its development. The first ATP pilot plant was constructed in 1977.

The ATP was originally developed for pyrolysis of oil sand. However, its first commercial application in 1989 was dedicated to the environmental remediation of contaminated soils. From 1999 to 2004, ATP technology was used for the shale oil extraction at the Stuart Oil Shale Plant in Australia. During that time, 1.5 million barrels (238.48094×10^3 m^3) of shale oil was extracted before the owner, Southern Pacific Petroleum Pty Ltd went into receivership. The subsequent owner, Queenland Energy Resources closed and dismantled the plant.

Technology

The ATP is an above-ground oil-shale retorting technology classified as a hot recycled solids technology. The distinguishing feature of the ATP is that the drying and pyrolysis of the oil shale or other feed, as well as the combustion, recycling, and cooling of spent materials and residues, all occur within a single rotating multi-chamber horizontal retort. Its feed consists of fine particles.



Alberta Taciuk Processor (ATP) retort

In its shale oil applications, fine particles (less than 25 millimetres (1.0 in) in diameter) are fed into the preheat tubes of the retort, where they are dried and preheated to 250 °C (480 °F) indirectly by hot shale ash and hot flue gas. In the pyrolysis zone, oil shale particles are mixed with hot shale ash and the pyrolysis is performed at temperatures between 500 °C (930 °F) and 550 °C (1,020 °F). The resulting shale oil vapor is withdrawn from the retort through a vapour tube and recovered by condensation in other equipment. The char residues, mixed with ash, are moved to the combustion zone, and burnt at about 800 °C (1,470 °F) to form shale ash. Part of the ash is delivered to the pyrolysis zone, where its heat is recycled as a hot solid carrier; the other part is removed and cooled in the cooling zone with the combustion gases by heat transfer to the feed oil shale.

The advantages of the ATP technology for shale oil extraction lie in its simple and robust design, energy self-sufficiency, minimal process water requirements, ability to handle fine particles, and high oil yields. It is particularly suited for processing materials with otherwise low oil yield. The mechanical transfer of solids through the machine does not involve moving parts and it achieves improved process efficiencies through solid-to-solid heat transfer. Most of the process energy (over 80%) is produced by combustion of char and produced oil shale gas; external energy inputs are minimal. The oil yields are about 85-90% of Fischer Assay. The organic carbon content of the process residue (spent shale) is less than 3%. The process produces only small amounts of contaminated water with low concentrations of phenols. These advantages also apply to its oil sands applications, including increased oil yield, a simplified process flow, reduction of bitumen losses to tailings, elimination of the need for tailing ponds, improvement in energy efficiency compared with the hot water extraction process, and elimination of requirements for chemical and other additives.

A complication of the ATP is that retorting operations can reach temperatures at which carbonate minerals within the shale decompose, increasing greenhouse gas emissions.

Operations

As of 2008, ATP was used by the United States Environmental Protection Agency at a PCB-contaminated site near Buffalo, New York, and at the Waukegan Harbor, Illinois.

UMATAC Industrial Processes runs a 5 tons of oil shale per hour pilot processor in Calgary, Alberta for large scale tests of different oil shales. The Fushun Mining Group of China has built a 250 tonnes per hour ATP plant that began commissioning in 2010. Jordan Energy and Mining Ltd plans to use the ATP technology for extracting oil from Al Lajjun and Attarat oil shale deposits in Jordan.

Lurgi-Ruhrgas Process

Lurgi-Ruhrgas process

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

Product(s)	shale oil synthetic fuel
Developer(s)	Lurgi Gesellschaft für Warmetechnik G.m.b.H. Ruhrgas AG

The **Lurgi-Ruhrgas process** is an above-ground coal liquefaction and shale oil extraction technology. It is classified as a hot recycled solids technology.

History

The Lurgi-Ruhrgas process was originally invented in 1940s and further developed in the 1950s for a low-temperature liquefaction of lignite (brown coal). The technology is named after its developers Lurgi Gesellschaft für Warmetechnik G.m.b.H. and Ruhrgas AG. Over a time, the process was used for coal processing in Japan, Germany, the United Kingdom, Argentina, and former Yugoslavia. The plant in Japan processed also cracking petroleum oils to olefins.

In 1947–1949, the Lurgi-Ruhrgas process was used in Germany for shale oil production. In Lukavac, Bosnia and Herzegovina, two retorts for liquefaction of lignite were in operation from 1963 to 1968. The capacity of the plant was 850 ton of lignite per day. The plant in Lincolnshire, the United Kingdom, operated in 1978-1979 with capacity of 900 ton of coal per day. In late 1960s and early 1970s oil shales from different European countries and from the Green River Formation of Colorado, the United States, were tested at the Lurgi's pilot plant in Frankfurt. In the United States, the technology was promoted in cooperation with Dravo Corporation. In 1970s, the technology was licensed to the Rio Blanco Shale Oil Project for construction of a modular retort in combination with the modified *in situ* process. However, this plan was terminated.

In 1980, the Natural Resources Authority of Jordan commissioned from the Klöckner-Lurgi consortium a pre-feasibility study of construction of an oil shale retorting complex in Jordan using Lurgi-Ruhrgas process. However, although the study found the technology feasible, it was never implemented.

Technology

The Lurgi-Ruhrgas process is a hot recycled solids technology, which processes fine particles of coal or oil shale in size of 0.25 to 0.5 inch (6.3 to 12.7 mm). As a heat carrier, it uses spent char or spent oil shale (oil shale ash), mixed with sand or other more durable materials. In this process, crushed coal or oil shale is fed into the top of the retort. In retort, coal or oil shale is mixed with the 550 °C (1,020 °F) heated char or spent oil shale particles in the mechanical mixer (screw conveyor). The heat is transferred from the heated char or spent oil shale to the coal or raw oil shale causing pyrolysis. As a result, oil shale decomposes to shale oil vapors, oil shale gas and spent oil shale. The oil vapor and product gases passes through a hot cyclone for cleaning before sending to the condenser. In condenser, shale oil is separated from product gases.

The spent oil shale, still including residual carbon (char), is burnt at a lift pipe combustor to heat the process. If necessary, additional fuel oil is used for combustion. During the combustion process, heated solid particles in the pipe are moved to the surge bin by pre-heated air that is introduced from the bottom of the pipe. At the surge bin, solids and gases are separated, and solid particles are transferred to the mixer unit to conduct a pyrolysis of the raw oil shale.

One of the disadvantages of this technology is the fact that produced shale oil vapors are mixed with shale ash causing impurities in shale oil. Ensuring the quality of produced shale oil is complicated as compared with other mineral dusts the shale ash is more difficult to collect.

Chapter 11

Fischer–Tropsch Process

The **Fischer–Tropsch process** (or Fischer–Tropsch Synthesis) is a set of chemical reactions that convert a mixture of carbon monoxide and hydrogen into liquid hydrocarbons. The process, a key component of gas to liquids technology, produces a petroleum substitute, typically from coal, natural gas, or biomass for use as synthetic lubrication oil and as synthetic fuel. The F-T process has received intermittent attention as a source of low-sulfur diesel fuel and to address the supply or cost of petroleum-derived hydrocarbons.

Process chemistry

The Fischer–Tropsch process involves a series of chemical reactions that lead to a variety of hydrocarbons. Useful reactions give alkanes:

$$(2n+1)\ H_2 + n\ CO \rightarrow C_nH_{(2n+2)} + n\ H_2O$$

where 'n' is a positive integer. The formation of methane ($n = 1$) is generally unwanted. Most of the alkanes produced tend to be straight-chain alkanes, although some branched alkanes are also formed. In addition to alkane formation, competing reactions result in the formation of alkenes, as well as alcohols and other oxygenated hydrocarbons. Usually, only relatively small quantities of these non-alkane products are formed, although catalysts favoring some of these products have been developed.

Other reactions relevant to the F-T process

Several reactions are required to obtain the gaseous reactants required for F-T catalysis. First, reactant gases entering a F-T reactor must first be desulfurized to protect the catalysts that are readily poisoned. The other major class of reactions are employed to adjust the H_2/CO ratio:

- water gas shift reaction provides a source of hydrogen:

  $H_2O + CO \rightarrow H_2 + CO_2$

- For F-T plants that start with methane, another important reaction is steam reforming, which converts the methane into CO and H_2:

  $H_2O + CH_4 \rightarrow CO + 3\ H_2$

Chemical mechanisms

The conversion of CO to alkanes involves net hydrogenation of CO, the hydrogenolysis of C-O bonds, and the formation of C-C bonds. Such reactions are assumed to proceed via initial formation of surface-bound metal carbonyls. The CO ligand is speculated to undergo dissociation, possibly into oxide and carbide ligands. Other potential intermediates are various C-1 fragments including formyl (CHO), hydroxycarbene (HCOH), hydroxymethyl (CH_2OH), methyl (CH_3), methylene (CH_2), methylidyne (CH), and hydroxymethylidyne (COH). Furthermore, and critical to the production of liquid fuels, are reactions that form C-C bonds, such as migratory insertion. Many related stoichiometric reactions have been simulated on discrete metal clusters, but homogeneous F-T catalysts are poorly developed and of no commercial importance.

Process conditions

Generally, the Fischer–Tropsch process is operated in the temperature range of 150–300 °C (302–572 °F). Higher temperatures lead to faster reactions and higher conversion rates but also tend to favor methane production. As a result, the temperature is usually maintained at the low to middle part of the range. Increasing the pressure leads to higher conversion rates and also favors formation of long-chained alkanes both of which are desirable. Typical pressures range from one to several tens of atmospheres. Even higher pressures would be favorable, but the benefits may not justify the additional costs of high-pressure equipment.

A variety of synthesis gas compositions can be used. For cobalt-based catalysts the optimal H_2:CO ratio is around 1.8-2.1. Iron-based catalysts promote the water-gas-shift reaction and thus can tolerate significantly lower ratios. This reactivity can be important for synthesis gas derived from coal or biomass, which tend to have relatively low H_2:CO ratios (<1).

Product distribution

In general the product distribution of hydrocarbons formed during the Fischer–Tropsch process follows an Anderson-Schulz-Flory distribution, which can be expressed as:

$$W_n/n = (1-\alpha)^2\alpha^{n-1}$$

Where W_n is the weight fraction of hydrocarbon molecules containing n carbon atoms. α is the chain growth probability or the probability that a molecule will continue reacting to form a longer chain. In general, α is largely determined by the catalyst and the specific process conditions.

Examination of the above equation reveals that methane will always be the largest single product; however by increasing α close to one, the total amount of methane formed can be minimized compared to the sum of all of the various long-chained products. Increasing α increases the formation of long-chained hydrocarbons. The very long-chained hydrocarbons are waxes, which are solid at room temperature. Therefore, for production of liquid transportation fuels it may be necessary to crack some of the Fischer-Tropsch products. In order to avoid this, some researchers have proposed using zeolites or other catalyst substrates with fixed sized pores that can restrict the formation of hydrocarbons longer than some characteristic size (usually $n<10$). This way they can drive the reaction so as to minimize methane formation without producing lots of long-chained hydrocarbons. Such efforts have met with only limited success.

Fischer-Tropsch catalysts

A variety of catalysts can be used for the Fischer–Tropsch process, but the most common are the transition metals cobalt, iron, and ruthenium. Nickel can also be used, but tends to favor methane formation ("methanation").

Cobalt-based catalysts are highly active, although iron may be more suitable for low-hydrogen-content synthesis gases such as those derived from coal due to its promotion of the water-gas-shift reaction. In addition to the active metal the catalysts typically contain a number of "promoters," including potassium and copper. Group 1 alkali metals, including potassium, is a poison for cobalt catalysts but is a promoter for iron catalysts. Catalysts are supported on high-surface-area binders/supports such as silica, alumina, or zeolites. Cobalt catalysts are more active for Fischer-Tropsch synthesis when the feedstock is natural gas. Natural gas has a high hydrogen to carbon ratio, so the water-gas-shift is not needed for cobalt catalysts. Iron catalysts are preferred for lower quality feedstocks such as coal or biomass.

Unlike the other metals used for this process (Co, Ni, Ru), which remain in the metallic state during synthesis, iron catalysts tend to form a number of phases, including various oxides and carbides during the reaction. Control of these phase transformations can be important in maintaining catalytic activity and preventing breakdown of the catalyst particles.

Fischer-Tropsch catalysts are sensitive to poisoning by sulfur-containing compounds. The sensitivity of the catalyst to sulfur is greater for cobalt-based catalysts than for their iron counterparts.

Promotors also have an important influence on activity. Alkali metal oxides and copper are common promotors, but the formulation depends on the primary metal, iron vs cobalt.

Alkali oxides on cobalt catalysts generally cause activity to drop severely even with very low alkali loadings. C5+ and CO2 selectivity increase while methane and C2-C4 selectivity decrease. In addition, the olefin to parafin ratio increases.

LTFT and HTFT

High-Temperature Fischer-Tropsch (or HTFT) is operated at temperatures of 330C-350C and uses an iron-based catalyst. This process was used extensively by Sasol in their Coal-to-Liquid plants (CTL). Low-Temperature Fischer-Tropsch (LTFT) is operated at lower temperatures and uses a cobalt based catalyst. This process is best known for being used in the first integrated Gas-to-Liquid (GTL) plant operated and built by Shell in Bintulu, Malaysia.

Gasification

F-T plants associated with coal or related solid feedstocks (sources of carbon) must first convert the solid fuel into gaseous reactants, i.e. CO, H_2, and alkanes. This conversion is called gasification. Synthesis gas obtained from coal gasification tends to have a H_2/CO ratio of ~0.7 compared to the ideal ratio of ~2. This ratio is adjusted via the water-gas shift reaction. Coal-based Fischer–Tropsch plants can produce varying amounts of CO_2, depending upon the energy source of the gasification process. However, most coal-based plants rely on the feed coal to supply all the energy requirements of the F-T process. Ongoing research aims to combine biomass gasification (BG) and Fischer-Tropsch (FT) synthesis to produce renewable transportation fuels (biofuels).

History

Since the invention of the original process by Franz Fischer and Hans Tropsch, working at the Kaiser Wilhelm Institute in the 1920s, many refinements and adjustments have been made. The term "Fischer-Tropsch" now applies to a wide variety of similar processes (**Fischer-Tropsch synthesis** or **Fischer-Tropsch chemistry**). Fischer and Tropsch filed a number of patents, e.g., US patent no. 1,746,464, applied 1926, published 1930. It was commercialized in Germany in 1936. Being petroleum-poor but coal-rich, in Germany the FT-process was used by Nazi Germany and Japan during World War II to produce *ersatz* (German: *substitute*) fuels. F-T production accounted for an estimated 9% of German war production of fuels and 25% of the automobile fuel.

The United States Bureau of Mines, in a program initiated by the Synthetic Liquid Fuels Act, employed seven Operation Paperclip synthetic fuel scientists in a Fischer-Tropsch plant in Louisiana, Missouri in 1946.

In Britain, Alfred August Aicher obtained several patents for improvements to the process in the 1930s and 1940s. Aicher's company was named *Synthetic Oils Ltd*. (Now based in Canada.)

Commercialization

Fluidized bed gasification with FT-pilot in Güssing, Burgenland, Austria

The F-T process has been applied on a large scale in some industrial sectors, although its popularity is hampered by high capital costs, high operation and maintenance costs, the uncertain and volatile price of crude oil, and environmental concerns. In particular, the use of natural gas as a feedstock only becomes practical when using "stranded gas", i.e. sources of natural gas far from major cities which are impractical to exploit with conventional gas pipelines and LNG technology; otherwise, the direct sale of natural gas to consumers would become much more profitable. Several companies are developing the process to enable practical exploitation of so-called stranded gas reserves.

Sasol

The largest scale implementation of F-T technology are in a series of plants operated by Sasol in South Africa, a country with large coal reserves but lacking in oil. Sasol uses coal and now natural gas as feedstocks and produces a variety of synthetic petroleum products, including most of the country's diesel fuel.

Shell Middle Distillate Synthesis

One of the largest implementations of F-T technology is in Bintulu, Malaysia. This Shell facility converts natural gas into low-sulfur diesel fuels and food-grade wax. The scale is 12,000 barrels per day.

Ras Laffan, Qatar

The new LTFT facility scheduled to commission in 2010 at Ras Laffan, Qatar is based on the Sasol technology, using cobalt catalysts at 230 °C. It includes the "Dolphin Gas Project" plant, converting natural gas to petroleum liquids at a rate of 140,000 barrels/day, with additional production of 120,000 barrels of oil equivalent in natural gas liquids and ethane.

UPM (Finland)

In October 2006, Finnish paper and pulp manufacturer UPM announced its plans to produce biodiesel by Fischer–Tropsch process alongside the manufacturing processes at its European paper and pulp plants, using waste biomass resulted by paper and pulp manufacturing processes as source material.

Rentech (Colorado, USA)

A demonstration scale F-T plant is owned and operated by Rentech Inc in partnership with ClearFuels, a company specializing in biomass gasification. Located in Commerce City, Colorado (U.S.), the facility produces about 10 barrels per day of fuels from natural gas. Commercial scale facilities are planned for Rialto, California and Natchez, Mississippi.

Other

In the US, some coal-producing states have invested in F-T plants. In Pennsylvania, Waste Management and Processors Inc. was funded by the state to implement F-T technology licensed from Shell and Sasol to convert so-called waste coal (leftovers from the mining process) into low-sulfur diesel fuel.

Research developments

Choren Industries has built an FT plant in Germany that converts biomass to syngas and fuels using the Shell F-T process.

U.S. Air Force certification

Syntroleum, a publicly traded US company (Nasdaq: SYNM) has produced over 400,000 gallons of diesel and jet fuel from the Fischer–Tropsch process using natural gas and coal at its demonstration plant near Tulsa, Oklahoma. Syntroleum is working to commercialize its licensed Fischer-Tropsch technology via coal-to-liquid plants in the US, China, and Germany, as well as gas-to-liquid plants internationally. Using natural gas as a feedstock, the ultra-clean, low sulfur fuel has been tested extensively by the U.S. Department of Energy and the U.S. Department of Transportation. Most recently, Syntroleum has been working with the U.S. Air Force to develop a synthetic jet fuel blend that will help the Air Force to reduce its dependence on imported petroleum. The Air Force, which is the U.S. military's largest user of fuel, began exploring alternative fuel sources in 1999. On December 15, 2006, a B-52 took off from Edwards AFB, California for the first time powered solely by a 50-50 blend of JP-8 and Syntroleum's FT fuel. The seven-hour flight test was considered a success. The goal of the flight test program is to qualify the fuel blend for fleet use on the service's B-52s, and then flight test and qualification on other aircraft. The test program concluded in 2007. This program is part of the Department of Defense Assured Fuel Initiative, an effort to develop secure domestic sources for the military energy needs. The Pentagon hopes to reduce its use of crude oil from foreign producers and obtain about half of its aviation fuel from alternative sources by 2016. With the B-52 now approved to use the FT blend, the C-17 Globemaster III, the B-1B, and eventually every airframe in its inventory to use the fuel by 2011.

Carbon dioxide reuse

In 2009, chemists working for the U.S. Navy investigated Fischer-Tropsch for generating fuels, obtaining hydrogen by electrolysis of seawater. When combined with the dissolved carbon dioxide using a cobalt-based catalyst, this study produced mostly methane gas. However, when using an iron-based catalyst, it was possible to reduce the methane produced to 30 per cent with the rest being predominantly short-chain hydrocarbons. Further refining of the hydrocarbons produced applying solid acid catalysts, such as zeolites, can potentially lead to the production of kerosene-based jet fuel.

The abundance of CO_2 makes seawater an attractive alternative fuel source. Scientists at the U.S. Naval Research Laboratory stated that, "although the gas forms only a small proportion of air – around 0.04 per cent – ocean water contains about 140 times that concentration". Robert Dorner presented the findings of his work to the American Chemical Society on 16 August 2009, at the Marriott Metro Center in Washington DC. Of course, such a method requires an energy source - since CO_2 is a major product of combustion, converting it back into combustible material is a highly endothermic (energy-absorbing) process. In practice this would probably come from nuclear power, which is in abundant supply aboard nuclear powered ships.

Chapter 12

Gasification

Gasification is a process that converts carbonaceous materials, such as coal, petroleum, biofuel, or biomass, into carbon monoxide and hydrogen by reacting the raw material at high temperatures with a controlled amount of oxygen and/or steam. The resulting gas mixture is called *syngas* (from *synthesis gas*) and is itself a fuel. Gasification is a method for extracting energy from many different types of organic materials.

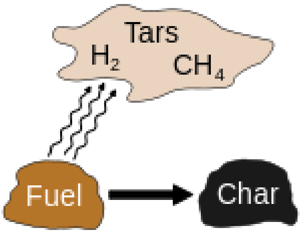
The advantage of gasification is that using the syngas is potentially more efficient than direct combustion of the original fuel because it can be combusted at higher temperatures or even in fuel cells, so that the thermodynamic upper limit to the efficiency defined by Carnot's rule is higher or not applicable. Syngas may be burned directly in internal combustion engines, used to produce methanol and hydrogen, or converted via the Fischer-Tropsch process into synthetic fuel. Gasification can also begin with materials that are not otherwise useful fuels, such as biomass or organic waste. In addition, the high-temperature combustion refines out corrosive ash elements such as chloride and potassium, allowing clean gas production from otherwise problematic fuels.

Gasification of fossil fuels is currently widely used on industrial scales to generate electricity. However, almost any type of organic material can be used as the raw material for gasification, such as wood, biomass, or even plastic waste.

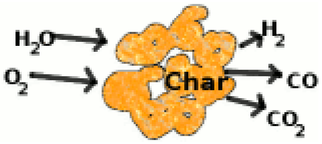
Gasification relies on chemical processes at elevated temperatures >700°C, which distinguishes it from biological processes such as anaerobic digestion that produce biogas.

Chemistry

In a gasifier, the carbonaceous material undergoes several different processes:



Pyrolysis of carbonaceous fuels



Gasification of char

1. The *pyrolysis* (or devolatilization) process occurs as the carbonaceous particle heats up. Volatiles are released and char is produced, resulting in up to 70% weight loss for coal. The process is dependent on the properties of the carbonaceous material and determines the structure and composition of the char, which will then undergo gasification reactions.
2. The *combustion* process occurs as the volatile products and some of the char reacts with oxygen to primariliy form carbon dioxide and small amounts of carbon monoxide, which provides heat for the subsequent gasification reactions. Letting **C** represent a carbon-containing organic compound, the basic reaction here is $\mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2}$
3. The *gasification* process occurs as the char reacts with carbon dioxide and steam to produce carbon monoxide and hydrogen, via the reaction
   $\mathrm{C} + \mathrm{H_2O} \rightarrow \mathrm{H_2} + \mathrm{CO}$
4. In addition, the reversible gas phase water gas shift reaction reaches equilibrium very fast at the temperatures in a gasifier. This balances the concentrations of carbon monoxide, steam, carbon dioxide and hydrogen.
   $\mathrm{CO} + \mathrm{H_2O} \leftrightarrow \mathrm{CO_2} + \mathrm{H_2}$

In essence, a limited amount of oxygen or air is introduced into the reactor to allow some of the organic material to be "burned" to produce carbon monoxide and energy, which drives a second reaction that converts further organic material to hydrogen and additional carbon dioxide. Further reactions occur when the formed carbon monoxide and residual water from the organic material react to form methane and excess carbon dioxide. This third reaction occurs more abundantly in reactors that increase the residence time of the reactive gases and organic materials, as well as heat and pressure. Catalysts are used in more sophisticated reactors to improve reaction rates, thus moving the system closer to the reaction equilibrium for a fixed residence time.

History

Adler Diplomat 3 with gas generator (1941)

The process of producing energy using the gasification method has been in use for more than 180 years. During that time coal and peat were used to power these plants. Initially developed to produce town gas for lighting & cooking in 1800s, this was replaced by electricity and natural gas, it was also used in blast furnaces but the bigger role was played in the production of synthetic chemicals where it has been in use since the 1920s.

During both world wars especially the Second World War the need of gasification produced fuel reemerged due to the shortage of petroleum. Wood gas generators, called Gasogene or Gazogène, were used to power motor vehicles in Europe. By 1945 there were trucks, buses and agricultural machines that were powered by gasification. It is estimated that there were close to 9,000,000 vehicles running on producer gas all over the world.

Gasification processes

Four types of gasifier are currently available for commercial use: counter-current fixed bed, co-current fixed bed, fluidized bed and entrained flow.

The **counter-current fixed bed ("up draft") gasifier** consists of a fixed bed of carbonaceous fuel (e.g. coal or biomass) through which the "gasification agent" (steam, oxygen and/or air) flows in counter-current configuration. The ash is either removed dry or as a slag. The slagging gasifiers have a lower ratio of steam to carbon, achieving temperatures higher than the ash fusion temperature. The nature of the gasifier means that the fuel must have high mechanical strength and must ideally be non-caking so that it will form a permeable bed, although recent developments have reduced these restrictions to some extent. The throughput for this type of gasifier is relatively low. Thermal efficiency is high as the gas exit temperatures are relatively low. However, this means that tar and methane production is significant at typical operation temperatures, so product gas must be extensively cleaned before use. The tar can be recycled to the reactor.

The **co-current fixed bed ("down draft") gasifier** is similar to the counter-current type, but the gasification agent gas flows in co-current configuration with the fuel (downwards, hence the name "down draft gasifier"). Heat needs to be added to the upper part of the bed, either by combusting small amounts of the fuel or from external heat sources. The produced gas leaves the gasifier at a high temperature, and most of this heat is often transferred to the gasification agent added in the top of the bed, resulting in an energy efficiency on level with the counter-current type. Since all tars must pass through a hot bed of char in this configuration, tar levels are much lower than the counter-current type.

In the **fluidized bed reactor**, the fuel is fluidized in oxygen and steam or air. The ash is removed dry or as heavy agglomerates that defluidize. The temperatures are relatively low in dry ash gasifiers, so the fuel must be highly reactive; low-grade coals are particularly suitable. The agglomerating gasifiers have slightly higher temperatures, and are suitable for higher rank coals. Fuel throughput is higher than for the fixed bed, but not as high as for the entrained flow gasifier. The conversion efficiency can be rather low due to elutriation of carbonaceous material. Recycle or subsequent combustion of solids can be used to increase conversion. Fluidized bed gasifiers are most useful for fuels that form highly corrosive ash that would damage the walls of slagging gasifiers. Biomass fuels generally contain high levels of corrosive ash.

In the **entrained flow gasifier** a dry pulverized solid, an atomized liquid fuel or a fuel slurry is gasified with oxygen (much less frequent: air) in co-current flow. The gasification reactions take place in a dense cloud of very fine particles. Most coals are suitable for this type of gasifier because of the high operating temperatures and because the coal particles are well separated from one another. The high temperatures and pressures also mean that a higher throughput can be achieved, however thermal efficiency is somewhat lower as the gas must be cooled before it can be cleaned with existing technology. The high temperatures also mean that tar and methane are not present in the product gas; however the oxygen requirement is higher than for the other types of gasifiers. All entrained flow gasifiers remove the major part of the ash as a slag as the operating temperature is well above the ash fusion temperature. A smaller fraction of the ash is produced either as a very fine dry fly ash or as a black colored fly ash slurry. Some fuels, in particular certain types of biomasses, can form slag that is corrosive for ceramic inner walls that serve to protect the gasifier outer wall. However some entrained bed type of gasifiers do not possess a ceramic inner wall but have an inner water or steam cooled wall covered with partially solidified slag. These types of gasifiers do not suffer from corrosive slags. Some fuels have ashes with very high ash fusion temperatures. In this case mostly limestone is mixed with the fuel prior to gasification. Addition of a little limestone will usually suffice for the lowering the fusion temperatures. The fuel particles must be much smaller than for other types of gasifiers. This means the fuel must be pulverized, which requires somewhat more energy than for the other types of gasifiers. By far the most energy consumption related to entrained bed gasification is not the milling of the fuel but the production of oxygen used for the gasification.

Current applications

In small business and building applications, where the wood source is sustainable, 250-1000 kWe and new zero carbon biomass gasification plants have been installed in Europe that produce tar free syngas from wood and burn it in reciprocating engines connected to a generator with heat recovery. This type of plant is often referred to as a wood biomass CHP unit but is a plant with seven different processes: biomass processing, fuel delivery, gasification, gas cleaning, waste disposal, electricity generation and heat recovery.

Industrial-scale gasification is currently mostly used to produce electricity from fossil fuels such as coal, where the syngas is burned in a gas turbine.

Gasification is also used industrially in the production of electricity, ammonia and liquid fuels (oil) using Integrated Gasification Combined Cycles (IGCC), with the possibility of producing methane and hydrogen for fuel cells. IGCC is also a more efficient method of CO_2 capture as compared to conventional technologies. IGCC demonstration plants have been operating since the early 1970s and some of the plants constructed in the 1990s are now entering commercial service.

Gasification technologies have been developed in recent years that use plastic-rich waste as a feed.

Syngas can be used for heat production and for generation of mechanical and electrical power. Like other gaseous fuels, producer gas gives greater control over power levels when compared to solid fuels, leading to more efficient and cleaner operation.

Gasifiers offer a flexible option for thermal applications, as they can be retrofitted into existing gas fueled devices such as ovens, furnaces, boilers, etc., where syngas may replace fossil fuels. Heating values of syngas are generally around 4-10 MJ/m^3.

Diesel engines can be operated on dual fuel mode using producer gas. Diesel substitution of over 80% at high loads and 70-80% under normal load variations can easily be achieved. Spark ignition engines and SOFC fuel cells can operate on 100% gasification gas. Mechanical energy from the engines may be used for e.g. driving water pumps for irrigation or for coupling with an alternator for electrical power generation.

In 2009 21stCenturyMotorworks was reported on mass media to have developed gasification technology in a prototype pickup truck that could use any biomass materials for fuel. The vehicle was displayed at multiple events including the 2009 Boston Greenfest.

While small scale gasifiers have existed for well over 100 years, there have been few sources to obtain a ready to use machine. Small scale devices are typically DIY projects. However, currently in the United States, several companies offer gasifiers to operate small engines.

Potential for renewable energy

Gasification plant Güssing, Austria (2006)

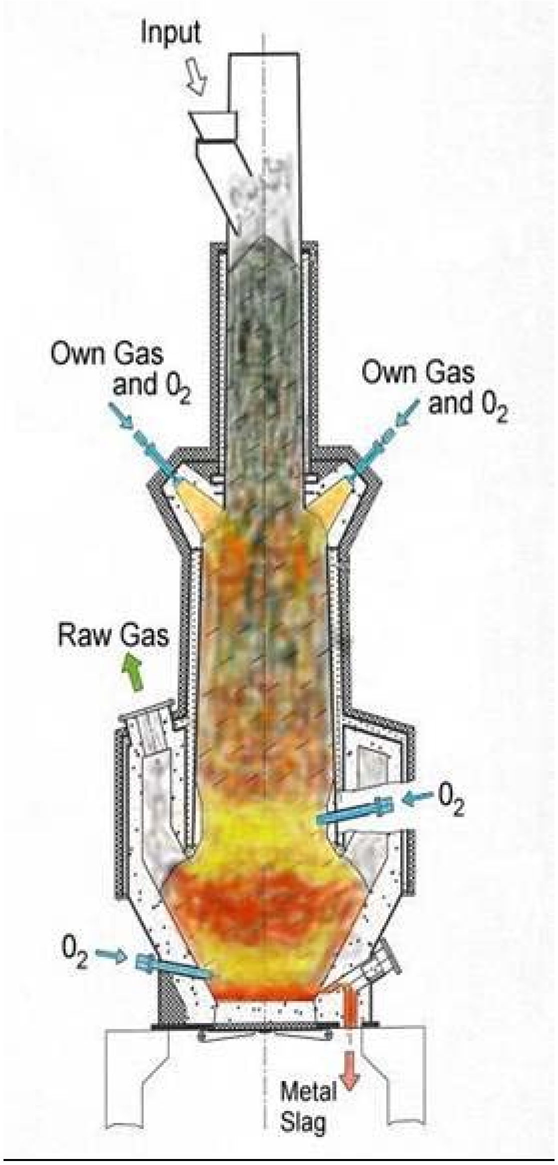
In principle, gasification can proceed from just about any organic material, including biomass and plastic waste. The resulting syngas can be combusted. Alternatively, if the syngas is clean enough, it may be used for power production in gas engines, gas turbines or even fuel cells, or converted efficiently to dimethyl ether (DME) by methanol dehydration, methane via the Sabatier reaction, or diesel-like synthetic fuel via the Fischer-Tropsch process. In many gasification processes most of the inorganic components of the input material, such as metals and minerals, are retained in the ash. In some gasification processes (slagging gasification) this ash has the form of a glassy solid with low leaching properties, but the net power production in slagging gasification is low (sometimes negative) and costs are higher.

Regardless of the final fuel form, gasification itself and subsequent processing neither directly emits nor traps greenhouse gasses such as carbon dioxide. Power consumption in the gasification and syngas conversion processes may be significant though, and may indirectly cause CO_2 emissions; in slagging and plasma gasification, the electricity consumption may even exceed any power production from the syngas. Combustion of syngas or derived fuels emits exactly the same amount of carbon dioxide as would have been emitted from direct combustion of the initial fuel. Biomass gasification and combustion could play a significant role in a renewable energy economy, because biomass production removes the same amount of CO_2 from the atmosphere as is emitted from gasification and combustion. While other biofuel technologies such as biogas and biodiesel are carbon neutral, gasification in principle may run on a wider variety of input materials and can be used to produce a wider variety of output fuels.

There is at present very little industrial scale biomass gasification being done. Examples of demonstration projects include

- Those of the Renewable Energy Network Austria, including a plant using dual fluidized bed gasification that has supplied the town of Güssing with 2 MW of electricity and 4 MW of heat, generated from wood chips, since 2003.
- Chemrec's pilot plant in Piteå that has produced 3 MW of clean syngas since 2006, generated from entrained flow gasification of black liquor.

Waste disposal



HTCW reactor, one of several proposed waste gasification processes. According to the sales and sales management consultants *KBI Group* a pilot plant in Arnstadt implementing this process has completed initial tests.

Waste gasification has several principal advantages over incineration:

- The necessary extensive flue gas cleaning may be performed on the syngas instead of the much larger volume of flue gas after combustion.
- Electric power may be generated in engines and gas turbines, which are much cheaper and more efficient than the steam cycle used in incineration. Even fuel cells may potentially be used, but these have rather severe requirements regarding the purity of the gas.

- Chemical processing of the syngas may produce other synthetic fuels instead of electricity.
- Some gasification processes treat ash containing heavy metals at very high temperatures so that it is released in a glassy and chemically stable form.

A major challenge for waste gasification technologies is to reach an acceptable (positive) gross electric efficiency. The high efficiency of converting syngas to electric power is counteracted by significant power consumption in the waste preprocessing, the consumption of large amounts of pure oxygen (which is often used as gasification agent), and gas cleaning. Another challenge becoming apparent when implementing the processes in real life is to obtain long service intervals in the plants, so that it is not necessary to close down the plant every few months for cleaning the reactor.

Several waste gasification processes have been proposed, but few have yet been built and tested, and only a handful have been implemented as plants processing real waste, and most of the time in combination with fossil fuels.

Since 2008 in Svenljunga, Sweden, a biomass gasification unit generates up to 14 MWth, supplying industries and citizens with process steam and district heating, respectively. The gasifier uses biomass fuels such as CCA or creosote impregnated waste wood and other kinds of recycled wood. In 2011 a similar gasifier, using the same kinds of fuels, is being installed at Munkfors Energy's CHP plant. The CHP plant will generate 2 MWe (electricity) and 8 MWth (district heating).

In 2011 in Green Bay Wisconsin, a deal was made with the Oneida Nation and the city of Green Bay to build a gasification power plant which will supply electricity to over 4,000 homes.

One plant (in Chiba, Japan using the Thermoselect process) has been processing industrial waste since year 2000, but has not yet documented positive net energy production from the process.

Ze-gen is operating a waste gasification demonstration facility in New Bedford, Massachusetts. The facility was designed to demonstrate gasification of specific non-MSW waste streams using *liquid metal gasification*.