Kirk-Othmer Encyclopedia of Chemical Technology.

FEEDSTOCKS, COAL CHEMICALS

Coal is used in industry both as a fuel and in much lower volume as a source of chemicals. In this respect it is like petroleum and natural gas whose consumption also is heavily dominated by fuel use. Coal was once the principal feedstock for chemical production, but in the 1950s it became more economical to obtain most industrial chemicals from petroleum and gas. Nevertheless, certain chemicals continue to be obtained from coal by traditional routes, and an interest in coal-based chemicals has been maintained in academic and industrial research laboratories. Much of the recent activity in coal conversion has been focused on production of synthetic fuels, but significant progress also has been made on use of coal as a chemical feedstock (see Coal conversion processes).

The term feedstock in this article refers not only to coal, but also to products and coproducts of coal conversion processes used to meet the raw material needs of the chemical industry. This definition distinguishes between use of coal-derived products for fuels and for chemicals, but this distinction is somewhat arbitrary because the products involved in fuel and chemical applications are often identical or related by simple transformations. For example, methanol has been widely promoted and used as a component of motor fuel, but it is also used heavily in the chemical industry. Frequently, some or all of the chemical products of a coal conversion process are not isolated but used as process fuel. This practice is common in the many coke plants that are now burning coal tar and naphtha in the ovens.

Because of the overlapping roles of coal in industry, many of the technologies covered here have been developed for synthetic fuel applications, but they also have been used or have demonstrated potential for production of significant quantities of chemicals. The scope of an article on coal as a chemical source would not be complete without coverage of synfuel processes, but the focus will be on the chemical production potential of the processes, looking toward a future when coal again may become the principal feedstock for chemical production.

1. Coal Chemical Origins

The discovery that useful chemicals could be made from coal tar provided the foundation upon which the modern chemical industry is built. Industrial chemistry expanded rapidly in the late nineteenth century in German laboratories and factories where coal-tar chemicals were refined and used in synthesis of dyes and pharmaceuticals. But coal-tar production has an earlier origin, dating back to the discovery by William Murdock in 1792 that heating coal in the absence of air generated a gas suitable for lighting. Murdock commercialized this technology, and by 1812 the streets of London were illuminated with coal gas (1).

Coal tar is produced as a coproduct during coal gasification. Up until the middle of the nineteenth century coal tar was regarded as a waste product, although John Kidd had isolated naphthalene from coal tar as early as 1819. The German chemist August Wilhelm von Hofmann earned a Ph.D. in 1841 under Liebig with a dissertation on the properties of aniline from coal tar. Hofmann later taught in England at the Royal College of Chemistry in London, where in 1855 he employed seventeen-year-old William Perkin as his assistant. Hofmann's suggestion that the drug quinine might be made from coal-tar chemicals prompted Perkin to undertake experiments to attempt this synthesis. In 1856 Perkin mixed aniline and potassium dichromate, but instead of quinine he isolated a purple compound which proved to be an excellent dye for silk and later became known as the color mauve (1). Perkin obtained a patent on the process at the age of eighteen and left school to start a successful dye business. Hofmann returned to Germany in 1864, and with Baeyer, who synthesized indigo, and other chemists advanced Germany to world leadership in synthetic organic chemistry and established a strong chemical industry (see Dyes and dye intermediates).

Coal feedstocks dominated the chemical industry up until the 1950s. However, the volume of chemicals available from this source was not sufficient to meet wartime demands or keep up with a rapidly expanding chemical industry after the war. The emergence of the petrochemical industry provided the required quantities, and petroleum rapidly became a more economical feedstock for chemical production (see Feedstocks, petrochemical). In Germany, petroleum did not surpass coal as a chemical feedstock until after 1961 (2). Even in the 1990s some aromatic and heterocyclic chemicals are most easily obtained from coal tar. Since the oil supply disruption problems of the 1970s, much work has been done to develop conversion processes that can transform coal economically to liquid and gaseous fuels and chemical products. Methods to accomplish this goal include gasification, direct coal liquefaction, and indirect liquefaction.

Although significant progress has been made in reducing costs of coal conversion processes, the economics of a specific project depend heavily on process complexity, the cost of competing raw materials, and project or site-specific criteria such as desired end product and proximity to raw material supplies. The relatively stable prices of petroleum and natural gas since the 1970s have decreased the urgency of transition to coal-based fuels and chemicals, but competing coal conversion processes stand ready, and will again become favorable if oil and gas prices climb out of proportion to coal feedstocks. Even now, under certain conditions, the advent of modern coal conversion technology has allowed coal to become a significant raw material for chemical manufacture.

2. Coal Carbonization

The thermal degradation of coal in the absence of air is known as pyrolysis or carbonization. This reaction also is referred to as coking because of its large volume use to prepare coke for blast furnaces. The type and quantity of products produced by coal pyrolysis depend on type of coal, rate of heating, and final temperature. In general, rapid heating affords higher liquid yields than slow pyrolysis. Low temperature carbonization or mild gasification is performed at 450–700°C and is used in some areas to prepare smokeless fuels. High temperature carbonization is performed in the range of 900–1100°C and is generally the process used to prepare blast furnace coke. Low temperature carbonization gives fewer gaseous and more liquid products than carbonization at higher temperature (1).

Most coal-tar chemicals are recovered from coproduct coke ovens. Since the primary product of the ovens is metallurgical coke, production of coal chemicals from this source is highly dependent on the level of activity in the steel industry. In past years most large coke producers operated their own coproduct recovery processes. Because of the decline in the domestic steel industry, the recent trend is for independent refiners to collect crude coal tars and light oils from several producers and then separate the marketable products.

When coal is coked at a temperature of approximately 1000°C, about 70–75% of the product is coke. Nearly 20% of the product is a light gas, mostly methane and hydrogen, that typically is used as fuel to heat the ovens. Coal tars amount to about 4% of the product and light oil or naphtha is about 1%. Ammonia is recovered in an amount equal to about 0.3% of the feed coal. The ammonia is usually converted to ammonium sulfate and sold as a fertilizer. Little or no ammonia [7664-41-7] is produced in low temperature carbonization (3).

Many valuable chemicals can be recovered from the volatile fractions produced in coke ovens. For many years coal tar was the primary source for chemicals such as naphthalene [91-20-3], anthracene [120-12-7], and other aromatic and heterocyclic hydrocarbons. The routes to production of important coal-tar derivatives are

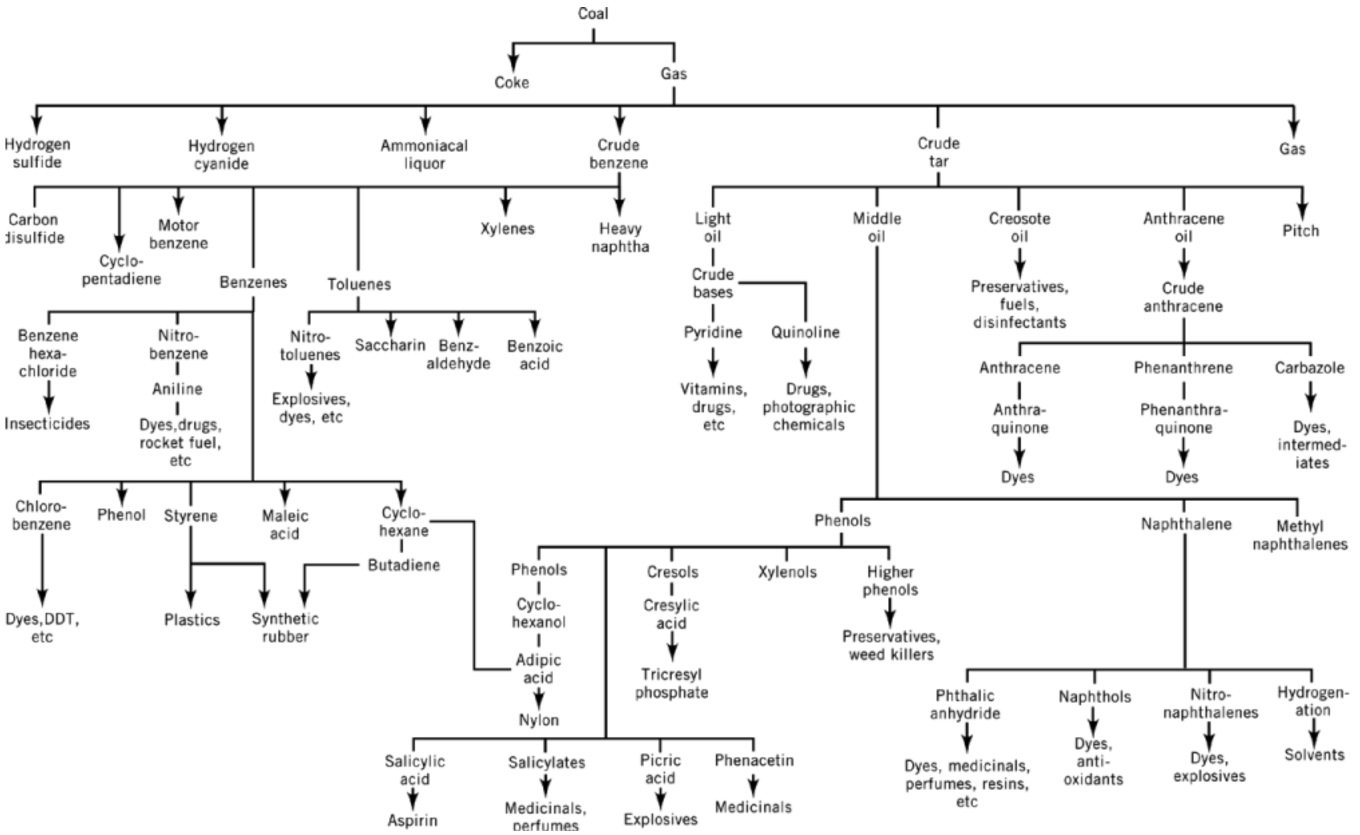


Fig. 1. General pathways for the production of chemicals from coal (4).(Courtesy of Marcel Dekker, Inc.)

shown in Figure 1. Much of the production of these chemicals, especially tar bases such as the pyridines and picolines, is based on synthesis from petroleum feedstocks. Nevertheless, a number of important materials continue to be derived from coal tar.

Benzene [71-43-2], toluene [108-88-3], xylene [1330-20-7], and solvent naphtha are separated from the light oil. Benzene (qv), toluene (qv), and xylene are useful as solvents and chemical intermediates (see Xylenes and ethylbenzene). The crude light oil is approximately 60–70% benzene, 12–16% toluene, 4–8% xylenes, 9–16% other hydrocarbons, and about 1% sulfur compounds (5) (see BTX processing).

Naphthalene, anthracene, carbazole [86-74-8], phenol [108-95-2], and cresylic acids are found in the tar. Phenol and cresylic acids are useful as chemical and resin intermediates. The aromatic chemicals are useful in the manufacture of pharmaceuticals, dyes, fragrances, and pesticides. Various grades of pitch are made from residues of tar refining. Coal-tar pitch is used for roofing and road tar, and as a binder mixed with petroleum coke to produce anodes for the aluminum industry.

Approximately 50–55% of the product from a coal-tar refinery is pitch and another 30% is creosote. The remaining 15–20% is the chemical oil, about half of which is naphthalene. Creosote is used as a feedstock for production of carbon black and as a wood preservative. Because of modifications to modern coking processes, tar acids such as phenol and cresylic acids are contained in coal tar in lower quantity than in the past. To achieve economies of scale, these tar acids are removed from crude coal tar with a caustic wash and sent to a central processing plant where materials from a number of refiners are combined for recovery.

In 1990, U.S. coke plants consumed 3.61×10^7 t of coal, or 4.4% of the total U.S. consumption of 8.12×10^8 t (6). Worldwide, roughly 400 coke oven batteries were in operation in 1988, consuming about 4.5×10^7 t of coal and producing 3.5×10^7 t metallurgical coke. Coke production is in a period of decline because of reduced demand for steel and increasing use of technology for direct injection of coal into blast furnaces (7). The decline in coke production and trend away from recovery of coproducts is reflected in a 70–80% decline in volume of coal-tar chemicals since the 1970s.

In 1990, U.S. production of crude coal tar was 597,000 m^3 (700,000 t) and production of crude light oil was 255,000 m^3 (200,000 t). Crude coal tar and light oil were refined to produce 110,000 m^3 of crude naphthalene (freezing point 76–79°C), 8700 m^3 of crude tar acid oils (tar acid content 5–24%), and 297,000 m^3 of creosote oils. Coal-tar pitch production in 1990 amounted to 600,000 t (8).

In 1980, the last year for which a breakdown has been published, the amount of benzene derived from coal in the United States was 168,000 t or 2.5% of domestic benzene production. Coal-derived toluene was 0.8% of production, and xylenes from coal were only 0.1% of total chemical production (9). The amounts and proportions of BTX components derived from coal in the United States are expected to be nearly the same today as in 1980. Based on information submitted to the International Trade Commission, approximately 25 companies participated in the coal-tar industry in the United States in 1990.

World production of coal tar and light oil in 1987 was estimated to be 15–17 million metric tons and 5×10^6 t, respectively. Approximately 7.5×10^6 t of coal tar were processed by distillation in 1989, affording 950,000 t naphthalene, 20,000 t anthracene, and 10,000 t other two–four ring aromatics (7). Much of this coal-tar processing occurs in Eastern Europe, India, and Japan. In spite of Germany's past activity, only one company (Ruetgers) is known to be engaged in recovery of chemicals from coal tar. The principal producers of coal-tar chemicals in the United States include Allied-Signal, Aristech, Koppers Industries, and Cooper Creek Chemical.

As the economic value of coproducts has decreased, it has become more difficult to provide capital for environmental controls on air emissions and wastewater streams such as toxic phenolic effluents from chemical recovery operations. Some former coke and manufactured gas sites may require remediation to clean up contaminated soil and groundwater. These difficulties will force the shutdown of some operations and discourage recovery of coproducts in future installations.

One challenging problem is control of the approximately 300,000 t SO_2/yr that are emitted from the approximately 30 coke oven plants in the United States. Innovative technology to reduce these emissions is under development by Bethlehem Steel in conjunction with the U.S. Department of Energy's (DOE) Clean Coal Technology Program. The planned demonstration will clean 2.1×10^6 m^3/day (7.4×10^7 SCF/day) of coke oven gas using water produced in the coke oven batteries to absorb ammonia and hydrogen sulfide from the gas. The ammonia will be destroyed in a catalytic converter, and the hydrogen sulfide will be converted to sulfur in a Claus plant. Widespread adoption of this technology would substantially reduce the ammonium sulfate coproduct available from coke oven operations (10).

3. Coal Hydrogenation

Although small amounts of liquids are produced during coal pyrolysis, significant amounts of coal-derived liquids did not become available until after the discovery of coal hydrogenation. This discovery is attributed to Berthelot about 1869, but the first practical process was the Bergius hydrogen donor process, developed in 1913 in Germany. Work was continued at BASF. By the late 1920s a solvent extraction process also was developed (11). In 1927 the first pilot plant was erected at Leuna. At the height of production in Germany, 12 hydrogenation plants were producing 4×10^6 t/yr of fuel (12). Since 1945 only pilot-scale coal hydrogenation facilities have been built and operated. Perhaps the best known is the 200 t/day demonstration plant operated from 1981–1987 by Ruhrkohle AG at Bottrop. This plant, based on the Bergius-Pier process, had typical operating temperature of 450°C and pressure of 31 MPa (306 atm). An inexpensive iron catalyst was slurried with Ruhr coal and solvent in a single-stage process that yielded 66 wt % liquid products (13). Other direct liquefaction processes that reached an advanced stage of development in the 1970s and 1980s include the Exxon Donor Solvent (EDS), H-Coal, and Solvent Refined Coal (SRC I and SRC II) processes (14).

A new generation of coal liquefaction processes has been under study since the 1980s, differing from the previous versions in that a two-stage approach is employed. A two-stage process has the advantage of allowing optimum conditions to be established in separate reactors for the coal dissolution and upgrading reactions, resulting in higher distillate yield, lower gas yield, and higher quality products. All recent direct liquefaction work in the United States has been devoted to study of catalytic two-stage liquefaction. The Wilsonville, Alabama process development unit has been one of the most active facilities for study of coal liquefaction (13). In general, oils produced from direct coal liquefaction are lower boiling, have lower hydrogen content, and higher oxygen and nitrogen content than typical petroleum crudes. Also, they differ from petroleum in that they contain mostly condensed cyclic compounds, few paraffins, and no residuum. Virtually all of the work on coal liquid upgrading has concentrated on study of refining conditions for production of gasoline, diesel, jet fuel, and heating oil. Hydrotreated and hydrocracked naphthas from coal liquids are easy to reform and can be converted to benzene, toluene, and xylenes with yields as high as 70–80% (13). A typical aromatic product distribution from reforming of hydrotreated H-coal process-derived naphtha at 520°C over platinum catalyst is 13% benzene, 26% toluene, 20% xylene, and 15% C-9 aromatics for a total aromatics yield of 74% (5).

4. Synthesis Gas Generation

4.1. Selection of Feedstock

The variety of chemicals available by conversion of synthesis gas is illustrated in Figure 2. Synthesis gas can be produced by steam reforming of natural gas and naphtha, partial oxidation of heavy oil and petroleum coke, and coal gasification. In 1977 the relative ratio of synthesis gas produced by these methods was 87:10:3, respectively (16). Virtually any hydrocarbon source can be used to generate synthesis gas, and the choice of feedstock for a given project can be made only after careful evaluation of all the alternatives. Most economic studies have shown that the cost of producing liquids from synthesis gas is dominated by the cost of producing the gas. This cost can be as high as 60–75% of the overall cost of the final product (16). Because of the high cost of producing synthesis gas from coal under economic conditions prevailing in the early 1990s, coal will be the favored feedstock for chemicals only under special circumstances.

Some of the factors that influence the choice of feedstock and potentially favor coal are feedstock cost, availability, and C/H ratio. The choice is most heavily influenced by the projected balance of raw material and capital costs. The size of the differential between coal and alternative feedstocks determines whether feedstock savings compensate for the increased capital required to install coal-based plants. Concern about the reliability of feedstock supply also enters into the decision, and in many areas of the United States this factor favors abundant, locally available coal. Transportation charges are a significant component of feedstock cost. For a given site, minimization of these charges requires procurement of a feedstock from the closest source. Clearly, this factor favors coal only for users located in coal producing areas. Another important consideration is the relative amount of hydrogen and carbon monoxide produced from different feedstocks. Project economics benefit by direct production of the required hydrogen to CO ratio. The ratio available by gasification of coal closely matches the ratio required for many desirable chemical products.

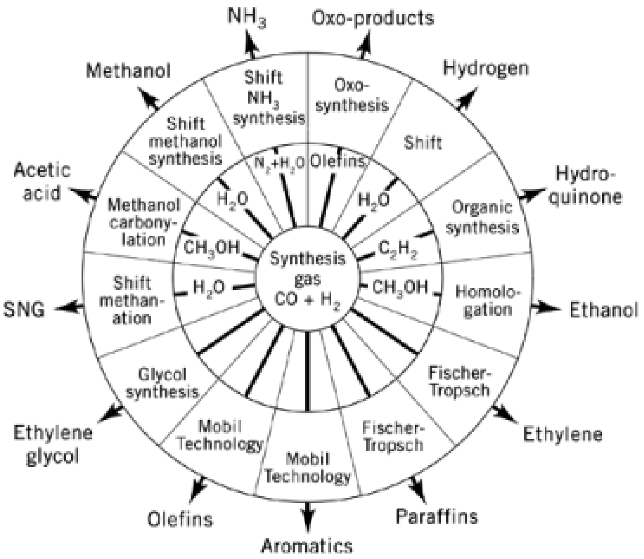


Fig. 2. The use of synthesis gas as a chemical feedstock (15). SNG is substitute natural gas.

Table 1. Calculated Heats of Reaction at 298 K for Selected Gasification Reactions[a]

Reaction	Heat of reaction, kJ/mol[b]
$C + 1/2\ O_2 \longrightarrow CO$	−110.5
$C + O_2 \longrightarrow CO_2$	−393.5
$CO + H_2O \longrightarrow CO_2 + H_2$	−41.2
$C + 2\ H_2 \longrightarrow CH_4$	−74.8
$C + CO_2 \longrightarrow 2\ CO$	172.5
$C + H_2O \longrightarrow CO + H_2$	131.3

[a] Ref. 14.

[b] To convert kJ/mol to kcal/mol, divide by 4.184.

4.2. Gasification Chemistry

Gasification of coal involves many reactions. Some of the prominent reactions in a partial oxidation gasifier are shown in Table 1. For many gasifiers, particularly those operating at higher temperatures, these reactions approach equilibrium, and the product mixture is strongly dependent on the feed composition and gasifier temperature and pressure.

4.3. Coal Gasifier Designs

After many years of development three general gasifier designs have achieved commercial status. These types are fixed-bed, fluidized-bed, and entrained-bed gasifiers. Each design has advantages and disadvantages and may be more suitable than other designs for a given type of coal or process application (see Coal conversion processes, gasification).

The fixed-bed gasifier is fed lump coal through the top of the gasifier. Oxidant and steam are introduced in the bottom of the gasifier and react with the coal generating a hot gas that passes up through the coal bed promoting further gasification reactions and coal pyrolysis. In traditional designs a dry ash removal system is provided at the bottom of the gasifier. A more recent version provides for removal of the ash as a molten slag. The most widely used fixed-bed design is the Lurgi dry ash gasifier.

As a consequence of the countercurrent feed mode, the average temperature gas in a fixed-bed reactor is lower than in alternative gasifier designs. The lower temperature requires longer residence times to achieve satisfactory conversion, but results in a high carbon inventory in the gasifier which provides some safety benefits. Also, the lower gas exit temperature reduces the need for expensive cooling and heat recovery equipment. The product from this type of gasifier has a high methane content and contains some hydrocarbon liquids and coal tars. These undesirable products may be recycled to the gasifier or reformed in a separate process to produce additional synthesis gas.

A fluidized-bed gasifier uses crushed or pulverized coal. The coal and oxidant feeds are injected into a fluidized bed of sand or ash particles maintained at a temperature below the melting point. A high flow of recirculating gas is used to keep the solids in the gasifier fluidized, which contributes to the very even temperature distribution through the reactor. The characteristics of the fluidized bed require that the particle size of the coal feed be tightly controlled, and that entrained char be recycled to obtain high coal conversion. The temperature achieved in fluidized-bed reactors allows most of the tars and liquids to be converted to gas. The High Temperature Winkler (HTW) process is one of the more advanced versions of a fluidized gasifier design.

In an entrained-bed reactor, the coal and oxidant are fed simultaneously at one end of the reactor and pass through the reaction zone together. A short residence time of less than a minute is typical for this type of reactor. Because of the short residence time the coal feed must be ground to a powder to ensure rapid reaction with the oxidant. Coal can be fed as a dry powder or slurried with water and sprayed in the gasifier. These reactors operate at very high temperature, which eliminates all tars and liquids from the product gas. Also, the coal ash is converted to a molten form that forms a glassy, granular slag when removed from the gasifier. Product gas cooling is accomplished either with a combination of radiant and convection coolers or by direct quench with water. In the quench mode, elaborate heat recovery equipment is required for efficient operation. Several entrained-bed processes including Texaco, Dow, Shell, Koppers-Totzek, and Prenflo have been commercialized or demonstrated on a commercial scale.

5. Synthesis Gas Chemicals

5.1. Fischer-Tropsch Process

The literature on the hydrogenation of carbon monoxide dates back to 1902 when the synthesis of methane from synthesis gas over a nickel catalyst was reported (17). In 1923, F. Fischer and H. Tropsch reported the formation of a mixture of organic compounds they called synthol by reaction of synthesis gas over alkalized iron turnings at 10–15 MPa (99–150 atm) and 400–450°C (18). This mixture contained mostly oxygenated compounds, but also contained a small amount of alkanes and alkenes. Further study of the reaction at 0.7 MPa (6.9 atm) revealed that low pressure favored olefinic and paraffinic hydrocarbons and minimized oxygenates, but at this pressure the reaction rate was very low. Because of their pioneering work on catalytic hydrocarbon synthesis, this class of reactions became known as the Fischer-Tropsch (FT) synthesis.

A systematic evaluation of catalysts and reaction conditions by Fischer and others through the 1920s and 1930s revealed that promoted cobalt and nickel catalysts also were active for higher hydrocarbon synthesis. This work led to construction in 1934 of a 1000 t/yr pilot plant by Ruhrchemie AG at Oberhausen-Holten. This pilot plant used a manganese oxide-promoted nickel catalyst. Subsequently, more active cobalt catalysts were developed, and by 1936 four commercial plants with a combined output of 200,000 t/yr were put in operation. Later, a catalyst with the composition Co–ThO_2–MgO–kieselguhr became the standard for nine commercial plants operating between 1938 and 1944 (19) (see Coal conversion processes, liquefaction).

The FT process offers an effective alternative to direct liquefaction of coal for liquid hydrocarbon production and, along with methanol synthesis, represents a coal conversion strategy referred to as indirect coal liquefaction. Although the FT process was developed for fuel production, the value of aliphatic FT products as feedstocks for chemical production was recognized very early. By 1944 almost 40% of the primary FT product from German plants underwent further chemical processing. A process was developed for aromatization of the C-6–C-8 fraction over alkaline aluminum and chromium oxides to produce BTX compounds. The C-10–C-18 paraffin fraction was used for manufacture of lubricants by chlorination and condensation with aromatics, and the olefins were polymerized with aluminum chloride. Detergent feedstocks were produced by sulfochlorination of FT products (2). Although oxo alcohol chemistry was not practiced during the 1940s, the unbranched terminal olefins are particularly suitable feeds for this process.

The Fischer-Tropsch process can be considered as a one-carbon polymerization reaction of a monomer derived from CO. The polymerization affords a distribution of polymer molecular weights that follows the Anderson-Shulz-Flory model. The distribution is described by a linear relationship between the logarithm of product yield vs carbon number. The objective of much of the development work on the FT synthesis has been to circumvent the theoretical distribution so as to increase the yields of gasoline range hydrocarbons.

An enormous amount of research effort has been devoted to improving FT catalysts. Although many metals have been investigated, only iron and cobalt have sufficient activity and selectivity to be of interest. Iron is the preferred catalyst because of its low cost and high selectivity. Also, the water gas shift activity of iron catalysts allows the use of synthesis gas with a low H_2/CO ratio. Slurry-phase FT process and catalyst development work again is beginning to attract attention, and an active effort is underway within the U.S. Department of Energy's Indirect Liquefaction Program (20).

The FT process was used in Germany during World War II to supply motor fuels, and production reached a maximum of about 600,000 t/yr in early 1944 before Allied bombing destroyed much of the capacity. In the 1950s, developments included the Arge process, jointly developed by Ruhrchemie and Lurgi, and the Rheinpreussen-Koppers liquid-phase process. In 1953 a demonstration plant with a hydrocarbon production capacity of 11.5 t/day went into operation using the liquid-phase process. Both advanced processes employed improved iron catalysts that were more flexible and efficient than the previous cobalt catalysts (2). The Sasol facilities in South Africa are the only modern large-scale Fischer-Tropsch plants in operation.

Sasol produces synthetic fuels and chemicals from coal-derived synthesis gas. Two significant variations of this technology have been commercialized, and new process variations are continually under development. Sasol One used both the fixed-bed (Arge) process, operated at about 240°C, as well as a circulating fluidized-bed (Synthol) system operating at 340°C. Each FT reactor type has a characteristic product distribution that includes coproducts isolated for use in the chemical industry. Paraffin wax is one of the principal coproducts of the low temperature Arge process. Alcohols, ketones, and lower paraffins are among the valuable coproducts obtained from the Synthol process.

Recent advances in Fischer-Tropsch technology at Sasol include the demonstration of the slurry-bed Fischer-Tropsch process and the new generation Sasol Advanced Synthol (SAS) Reactor, which is a classical fluidized-bed reactor design. The slurry-bed reactor is considered a superior alternative to the Arge tubular fixed-bed reactor. Commercial implementation of a slurry-bed design requires development of efficient catalyst separation techniques. Sasol has developed proprietary technology that provides satisfactory separation of wax and solid catalyst, and a commercial-scale reactor is being commissioned in the first half of 1993.

The principal advantage of the SAS reactor is that it can be built for approximately half the cost of the previous Synthol reactor design. The SAS reactor concept was proven in commercial operation starting in 1987 when the first full-scale version was commissioned in Sasolburg at Sasol One. This reactor represented a 30-fold scale-up of the demonstration plant. The improved efficiency and operating characteristics of the commercial SAS reactor compared to the conventional circulating reactor design have been confirmed during operation of this plant. Other advantages of the new design are low pressure drop, increased flexibility in choosing flow rates, efficient operation at lower recycle ratio, and better temperature control. Finally, the new reactor is easier to operate and maintain than the conventional version.

5.2. Ammonia and Hydrogen Production

The earliest route for manufacture of ammonia from nitrogen was the cyanamide process commercialized in Italy in 1906. In this process calcium carbide manufactured from coal was treated with nitrogen at 1000°C to form calcium cyanamide, $CaCN_2$. The cyanamide was hydrolyzed with water affording ammonia and calcium carbonate. Production reached 140,000 t/yr in Germany in 1915, but this process was energy intensive and soon was displaced by the more efficient Bosch-Haber process. This process was developed by BASF and commercialized in 1913 and involves the high pressure reaction of nitrogen and hydrogen over an iron catalyst. Most of the world's hydrogen production is used in ammonia synthesis by the Bosch-Haber process. The hydrogen for ammonia synthesis generally is obtained from synthesis gas produced by steam reforming of natural gas or naphtha. Carbon monoxide in the synthesis gas is shifted to produce additional hydrogen, and the resulting carbon dioxide is removed. Several ammonia plants based on synthesis gas from coal are in operation.

5.3. Methanol Production

Like hydrogen production, steam reforming of natural gas is by far the largest source of synthesis gas for methanol [67-56-1]. But alternative feedstocks in use include heavy oil and coal. In 1927, the first methanol plant in the United States to use synthesis gas generated from coal was built by Du Pont in Belle, West Virginia. At least four other methanol plants are operating or have operated on coal in recent times. These facilities include the 165,000 t/yr plant at Eastman in Kingsport and a 250,000 t/yr plant at Leuna in Germany. The Leuna plant reportedly was closed in June 1990, but another 100,000 t/yr plant is operated by RWE-DEA at Wesseling. Finally, a methanol plant is operated in conjunction with ammonia production at AECI in South Africa near Johannesburg. Recently, plans were announced for a new 100,000 t/yr coal-based methanol plant that will be built in China and will use the Texaco gasification process.

Methanol (qv) is one of the 10 largest volume organic chemicals produced in the world, with over 18×10^6 t of production in 1990. The reactions for the synthesis of methanol from CO, CO_2, and H_2 are shown below1,2. The water gas shift reaction2 also is important in methanol synthesis.

$$CO + 2\,H_2 \longrightarrow CH_3OH \qquad -90.6\ \text{kJ/mol}\ (-21.7\ \text{kcal/mol})$$

$$CO_2 + 3\,H_2 \longrightarrow CH_3OH + H_2O \qquad -49.5\ \text{kJ/mol}\ (-11.8\ \text{kcal/mol})$$

All commercial methanol plants use gas-phase heterogeneous catalytic reactors. Two main processes account for the majority of methanol produced; the Lurgi process, which uses a water-cooled, tubular, fixed-bed reactor, and the ICI process, which employs larger fixed-bed reactors with interstage cooling. Copper–zinc oxide alumina catalysts are now the standard for methanol plants, but they are subject to sulfur poisoning if sulfur species in the feed gas are not removed to less than 1 ppm. Until the advent of modern sulfur removal technology, this constraint prevented the use of copper catalysts with coal-derived synthesis gas.

Except in special situations, alternative feedstocks such as coal are not expected to be competitive with gas during the 1990s. As discussed previously, the principal reason for the higher cost of coal-based methanol is the large capital investment required, which has been estimated to be 2.8 to 3.1 times larger than the capital required for an equally sized gas-based plant. Construction of a gas-based plant in a remote location is expected to increase capital costs by about 60% (21). A related analysis by Lurgi suggests that, at somewhat higher gas prices, these infrastructure capital costs combined with transportation costs of $25–30/t raise the cost of remote methanol to a level potentially competitive with coal-based plants in developed plant locations (22).

The price differential at which coal becomes competitive with gas depends on plant size and the cost of capital, but based on estimates by the International Energy Agency (21) the required price ratio for gas to coal in North America falls into the range of 3.1 to 3.7 on an equivalent energy basis ($/MJ). Current prices give a gas/coal cost ratio nearer 1.5 to 2.0. As a result, all projected new methanol capacity is based on natural gas or heavy oil except for the proposed coal-based plant in China.

5.4. Methanol/Higher Alcohol Mixtures

Conversion of synthesis gas directly to higher alcohols or a mixture of methanol and higher alcohols is receiving increasing attention. These alcohols or derivatives are attractive for use as a constituent in reformulated gasoline, but have potential applications in the chemical industry. Processes for higher alcohol synthesis have been developed based on modified high pressure methanol synthesis with alkalized zinc oxide–chromia catalysts (Snamprogetti, Enichem, Haldor-Topsoe, and SEHT), a combination of Fischer-Tropsch and methanol-type chemistry using copper–cobalt oxide catalysts (Institut Francais du Petrol, IFP), modified low pressure methanol synthesis on alkalized copper oxide (Lurgi OCTAMIX), and the Dow/Union Carbide process over alkalized molybdenum sulfide catalysts. Also, an extensive investigation of cesium doped copper–zinc oxide catalysts has been performed at Lehigh University, and a number of rhodium–based catalysts have shown activity for higher alcohol synthesis, particularly ethanol (23).

The alkalized zinc oxide–chromia process developed by SEHT was tested on a commercial scale between 1982 and 1987 in a renovated high pressure methanol synthesis plant in Italy. This plant produced 15,000 t/yr of methanol containing approximately 30% higher alcohols. A demonstration plant for the IFP copper–cobalt oxide process was built in China with a capacity of 670 t/yr, but other higher alcohol synthesis processes have been tested only at bench or pilot-plant scale (23).

Isobutyl alcohol [78-83-1] forms a substantial fraction of the butanols produced by higher alcohol synthesis over modified copper–zinc oxide-based catalysts. Conceivably, separation of this alcohol and dehydration affords an alternative route to isobutylene [115-11-7] for methyl *t*-butyl ether [1624-04-4] (MTBE) production. MTBE is a rapidly growing constituent of reformulated gasoline, but its growth is likely to be limited by available supplies of isobutylene. Thus higher alcohol synthesis provides a process capable of supplying all of the raw materials required for manufacture of this key fuel oxygenate (24) (see Ethers).

5.5. Liquid-Phase Methanol Process

Because of the highly exothermic nature of the methanol synthesis reaction, it would be advantageous to run the process in a liquid-phase slurry-bed reactor. Such a process would provide greater heat removal capability and higher production rates. One slurry-bed process, designated the Liquid-Phase Methanol Process (LPMEOH), has been under development for several years in a joint project sponsored by Air Products, Chem Systems, and the U.S. Department of Energy (DOE). Recent development work on the LPMEOH process has been directed to preparing the process for integration with gasification combined cycle power plants (25). Pilot-plant work on the process has been performed in a 4.5 t/day process development unit at LaPorte, Texas operated by Air Products under a DOE contract.

In this configuration the process employs an entrained slurry reactor in a once-through mode of operation. Synthesis gas from a source such as coal gasification is fed to the reactor without making adjustments to the hydrogen/carbon oxides ratio. The methanol reaction consumes a portion of the hydrogen and carbon monoxide in the feed producing fuel-grade methanol and a CO-rich fuel gas. About 32% of the heating value contained in the synthesis gas feed is contained in the methanol produced by this scheme.

The attractive feature of methanol synthesis for power plant operators is the ability to convert some of the energy produced in a coal gasification plant to a form that can be stored for use during peak generation hours. Alternatively, the methanol produced in the process could be sold to the chemical industry. However, it has been claimed that the LPMEOH process generates a high percentage of by-products, making it difficult to refine the crude methanol to chemical grade (22).

5.6. Dimethyl Ether

Synthesis gas conversion to methanol is limited by equilibrium. One way to increase conversion of synthesis gas is to remove product methanol from the equilibrium as it is formed. Air Products and others have developed a process that accomplishes this objective by dehydration of methanol to dimethyl ether [115-10-6]. Testing by Air Products at the pilot facility in LaPorte has demonstrated a 40% improvement in conversion. The reaction is similar to the liquid-phase methanol process except that a solid acid dehydration catalyst is added to the copper-based methanol catalyst slurried in an inert hydrocarbon liquid (26).

By selection of appropriate operating conditions, the proportion of coproduced methanol and dimethyl ether can be varied over a wide range. The process is attractive as a method to enhance production of liquid fuel from CO-rich synthesis gas. Dimethyl ether potentially can be used as a starting material for oxygenated hydrocarbons such as methyl acetate and higher ethers suitable for use in reformulated gasoline. Also, dimethyl ether is an intermediate in the Mobil MTG process for production of gasoline from methanol.

5.7. Mobil MTG and MTO Process

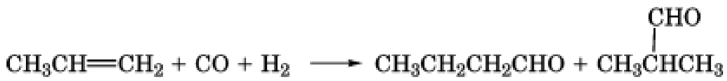
Methanol from any source can be converted to gasoline range hydrocarbons using the Mobil MTG process. This process takes advantage of the shape selective activity of ZSM-5 zeolite catalyst to limit the size of hydrocarbons in the product. The pore size and cavity dimensions favor the production of C-5–C-10 hydrocarbons. The first step in the conversion is the acid-catalyzed dehydration of methanol to form dimethyl ether. The ether subsequently is converted to light olefins, then heavier olefins, paraffins, and aromatics. In practice the ether formation and hydrocarbon formation reactions may be performed in separate stages to facilitate heat removal.

In the early 1980s, the process was commercialized in New Zealand to convert offshore natural gas to 2200 m^3/day (14,000 barrels/day) gasoline. Since then some of the methanol has been diverted from fuel production to chemical-grade methanol production by adding additional methanol refining capacity.

The MTG process accomplishes the same end as the Fischer-Tropsch process, but each method has some advantages. The Fischer-Tropsch process benefits from a cheap, throwaway iron catalyst. The desirable features of the MTG process for high octane liquid fuel production include high selectivity, low methane yield, and high aromatics yield. However, environmental concerns about aromatics in gasoline may offset the octane benefits. It is interesting to note that Fischer-Tropsch technology was selected for the recently completed Mossgas project in South Africa, which also produces liquids from natural gas.

5.8. Oxo Synthesis

All of the synthesis gas reactions discussed to this point are heterogeneous catalytic reactions. The oxo process (qv) is an example of an industrially important class of reactions catalyzed by homogeneous metal complexes. In the oxo reaction(**1**), carbon monoxide and hydrogen add to an olefin to produce an aldehyde with one more carbon atom than the original olefin, eg, for propylene:



$$CH_3CH{=}CH_2 + CO + H_2 \longrightarrow CH_3CH_2CH_2CHO + CH_3\overset{\overset{CHO}{|}}{C}HCH_3$$

Often the aldehyde is hydrogenated to the corresponding alcohol. In general, addition of carbon monoxide to a substrate is referred to as carbonylation, but when the substrate is an olefin it is also known as hydroformylation. The early work on the oxo synthesis was done with cobalt hydrocarbonyl complexes, but in 1976 a low pressure rhodium-catalyzed process was commercialized that gave greater selectivity to linear aldehydes and fewer coproducts.

The only known application of coal-derived synthesis gas for oxo chemicals was the Synthesegasanlage Ruhr (SAR) plant in Germany. Synthesis gas was provided by a 750 t/day Texaco gasification plant. The design was based on the successful 150 t/day demonstration plant operated by Ruhrkohle and Ruhrchemie in Oberhausen-Holten between 1978 and 1985. The plant began production on coal in 1986, but because of the escalating costs of German coal, the plant was converted in 1989 to use heavy oil as feedstock. During over 10,000 hours of operation, the plant gasified 313,000 t of coal.

5.9. Acetic Acid and Anhydride

Synthesis of acetic acid by carbonylation of methanol is another important homogeneous catalytic reaction. The Monsanto acetic acid process3 developed in the late 1960s is the best known variant of the process.

$$CH_3OH + CO \longrightarrow CH_3COOH \qquad -120.5\ \text{kJ/mol}\ (-28.8\ \text{kcal/mol})$$

This reaction is rapidly replacing the former ethylene-based acetaldehyde oxidation route to acetic acid. The Monsanto process employs rhodium and methyl iodide, but soluble cobalt and iridium catalysts also have been found to be effective in the presence of iodide promoters.

The Eastman acetic anhydride [108-24-7] process provides an extension of carbonylation chemistry to carboxylic acid esters. The process is based on technology developed independently in the 1970s by Eastman and Halcon SD. The Eastman acetic anhydride process4 involves carbonylation of methyl acetate [79-20-9] produced from coal-derived methanol and acetic acid [64-19-7].

$$CH_3COOCH_3 + CO \longrightarrow CH_3COOCOCH_3 \qquad -50.6\ \text{kJ/mol}\ (12.1\ \text{kcal/mol})$$

In analogy to the acetic acid process, the acetic anhydride process is a homogeneous rhodium-catalyzed reaction that requires methyl iodide. Two key requirements for the commercial acetic anhydride process are the presence of a reducing agent and an iodide salt. But there are important differences that distinguish the anhydrous acetic anhydride system from the aqueous acetic acid process. A difference with significant process implications is the lower heat of reaction of the methyl acetate carbonylation reaction. The reduced thermodynamic driving force imposes equilibrium limitations on conversion in the acetic anhydride reactors (27).

5.10. Emerging Processes

There is extensive literature on production of chemicals from synthesis gas. In addition to the chemicals described in the foregoing, reports or patents have been published on ethylene glycol, vinyl acetate, aliphatic amines, acrylic acid, and homologation of carboxylic acids (28, 29). The amidocarbonylation reaction is a new procedure for utilization of synthesis gas to introduce amido and carboxylate groups into olefins or aldehydes (30). The reaction is a potentially useful technique for industrial production of amino acids and derivatives. Also, biological conversion offers an alternative route for utilization of synthesis gas to make chemicals. Production of ethanol and acetic acid by bioconversion of synthesis gas are areas under active investigation (31).

6. Carbide Chemicals

The development of technology for production of calcium carbide and acetylene in 1892 provided a means for conversion of coke to chemical products. Further progress in Germany between 1920 and 1930 led to installation of electric arc processes for production of acetylene from coke oven gases. The commercialization of acetylenic chemicals is based on the work of the German chemist Julius Reppe. Both the electric arc process and calcium carbide process were used extensively in Germany during World War II for production of acetylene and derivatives vital to the war effort. Such industrial chemicals as acetaldehyde, acetic acid, ethylene, and butadiene have been made from coal using the acetylene route (32–34) (see Acetylene-derived chemicals).

Calcium carbide has been used in steel production to lower sulfur emissions when coke with high sulfur content is used. The principal use of carbide remains hydrolysis for acetylene (C_2H_2) production. Acetylene is widely used as a welding gas, and is also a versatile intermediate for the synthesis of many organic chemicals. Approximately 450,000 t of acetylene were used annually in the early 1960s for the production of such chemicals as acrylonitrile, acrylates, chlorinated solvents, chloroprene, vinyl acetate, and vinyl chloride. Since then, petroleum-derived olefins have replaced acetylene in these uses. The principal chemicals based on Reppe chemistry today are propargyl alcohol and butyn-1,4-diol and derivatives such as 2-pyrrolidinone, *N*-vinyl-2-pyrrolidinone, polyvinylpyrrolidinone, vinyl ethers, and tetrahydrofuran (33).

The first process for manufacture of calcium carbide [75-20-7] and acetylene [74-86-2] involved the reaction of coke and lime. The carbide process5 operates at a temperature of about 2000°C according to the following reaction:

$$\mathrm{CaO} + 3\ \mathrm{C} \longrightarrow \mathrm{CaC_2} + \mathrm{CO} \qquad -\,464\ \mathrm{kJ/mol}\ (-111\ \mathrm{kcal/mol})$$

A typical large carbide furnace consumes 950 kg of lime, 550 kg of coke, and 15 kg of electrode carbon, and requires about $3200\ \mathrm{kW{\cdot}h}$ of electrical energy per metric ton of carbide produced. This grade of carbide produces about 300 L C_2H_2/kg, and has an analysis of 80.5% CaC_2, 12.9% CaO, 1.3% Si, 1.1% Al, 0.2% Fe, 0.5% S, and 0.3% C (2).

Newer coal-based methods of acetylene manufacture under development include the AVCO process, based on the reaction of coal in a hydrogen plasma. Finely divided coal is passed through a hydrogen plasma arc generating temperature gradients of up to 15,000 K. About 67% of the coal is consumed, yielding char and acetylene in concentrations up to 16%. An energy requirement of $9.5\ \mathrm{kW{\cdot}h/kg}$ acetylene has been reported (33).

7. Commercial Facilities Using Coal as a Chemical Feedstock

7.1. Eastman Coal Chemicals

In 1983 Eastman Chemical Co. became the first chemical producer in the United States to return to coal as a raw material for large-scale manufacture of industrial chemicals (35). In that year, Eastman started manufacturing acetic anhydride from coal. Acetic anhydride is a key intermediate for production of coatings, cellulosic plastics, and cellulose acetate fibers. Acetic anhydride from other sources also is used in the manufacture of pharmaceuticals, starches and sweeteners, and flavors and fragrances.

The Eastman Chemicals from Coal facility is a series of nine complex interrelated plants. These plants include air separation, slurry preparation, gasification, acid gas removal, sulfur recovery, CO/H_2 separation, methanol, methyl acetate, and acetic anhydride. A block flow diagram of the process is shown in Figure 3. The facility covers an area of $2.2 \times 10^5\ \mathrm{m}^2$ (55 acres) at Eastman's main plant site in Kingsport, Tennessee. The air separation plant is owned and operated by Air Products, and provides up to 965 t/day of oxygen for the

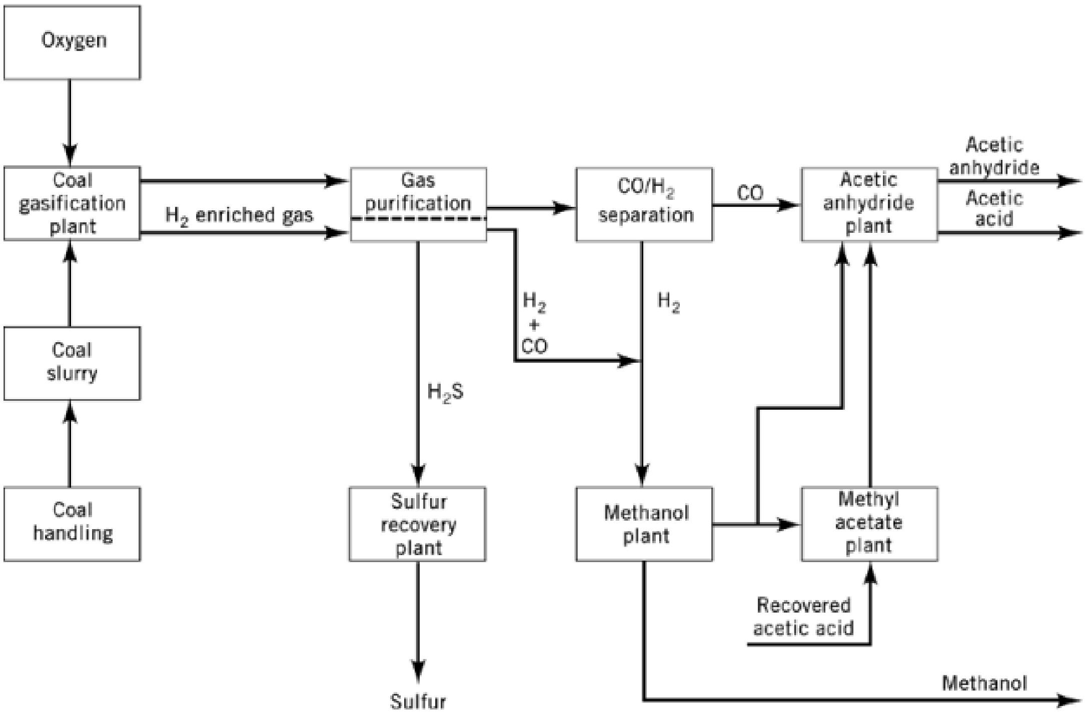


Fig. 3. Overall block flow diagram for Eastman's coal gasification–acetic anhydride complex (35).

gasification plant. The plant contains three complete cryogenic air separation trains to provide reliability for continuous operation.

The slurry preparation plant includes two rod mills to grind run-of-mine coal with sufficient water and additives to produce a fluid slurry with a particle size distribution and viscosity suitable for pumping to the gasifier. The plant produces a slurry that contains approximately 65–70% coal and 30–35% water. The slurry is pumped from holding tanks to the gasifier with high pressure diaphragm pumps designed to handle slurries.

The gasification plant is equipped with two Texaco gasifiers, each capable of producing all of the synthesis gas required for operation of the complex. Eastman chose an entrained-bed gasification process for the Chemicals from Coal project because of three attractive features. The product gas composition using locally available coal is particularly suitable for production of the desired chemicals. Also, the process has excellent environmental performance and generates no liquids or tars. Finally, the process can be operated at the elevated pressure required for the downstream chemical plants.

The gasifiers convert up to 1000 t/day of coal at a temperature of approximately 1260–1370°C and pressure of 6.2–6.9 MPa (900–1000 psi). Normally, one gasifier is in operation while the other is on standby. The gas contains mainly CO, H_2, and CO_2. The sulfur in the coal is converted to H_2S and to a small amount of COS, which are removed and converted to elemental sulfur in a Claus plant. The ash becomes molten in the gasifier and is cooled and solidified in the quench section. The resulting granular slag is removed with a lock hopper and deposited in a landfill.

The crude product from the gasifier contains CO_2 and H_2S, which must be removed before the gas can be used to produce chemicals. The Rectisol process is used to remove these contaminants from the gas. This is accomplished by scrubbing the product with cold methanol which dissolves the CO_2 and H_2S and lets the H_2 and CO pass through the scrubber. The H_2S is sent to a Claus sulfur plant where over 99.7% of the sulfur in the coal feed is recovered in the form of elemental sulfur. A portion of the clean H_2 and CO are separated in a cryogenic distillation process. The main product from the cryogenic distillation is a purified CO stream for use in the acetic anhydride process. The remaining CO and hydrogen are used in the methanol plant.

The chemical complex includes the methanol plant, methyl acetate plant, and acetic anhydride plant. The methanol plant uses the Lurgi process for hydrogenation of CO over a copper-based catalyst. The plant is capable of producing 165,000 t/yr of methanol. The methyl acetate plant converts this methanol, purchased methanol, and recovered acetic acid from other Eastman processes into approximately 440,000 t/yr of methyl acetate.

The acetic anhydride process employs a homogeneous rhodium catalyst system for reaction of carbon monoxide with methyl acetate (36). The plant has capacity to coproduce approximately 545,000 t/yr of acetic anhydride, and 150,000 t/yr of acetic acid. One of the many challenges faced in operation of this plant is recovery of the expensive rhodium metal catalyst. Without a high recovery of the catalyst metal, the process would be uneconomical to operate.

Production of Eastman's entire acetic anhydride requirement from coal allows a reduction of 190,000 m^3/yr (1.2 million barrels/yr) in the amount of petroleum used for production of Eastman chemicals. Now virtually all of Eastman's acetyl products are made in part from coal-based feedstocks. Before the technology was introduced, these chemicals had been made from petroleum-based acetaldehyde. Reduced dependence on petroleum, much of which must be obtained from foreign sources, is important to maintain a strong domestic chemical industry.

7.2. Sasol Chemical Production

The best known and largest coal conversion facilities in the world are those of Sasol in South Africa. Sasol was formed in 1950 as the South African Coal, Oil, and Gas Corp., and began production of liquid transportation fuels from coal in 1955 at Sasolburg. Sasol's entry into the chemical industry began in earnest in 1964 when Sasol began production of styrene and butadiene for synthetic rubber, and ammonia for fertilizers. In 1965 a naphtha cracker for production of ethylene was put in operation. Beginning in the early 1980s, the facilities and product mix were significantly expanded, and at the present time Sasol is a principal producer of chemicals as well as fuel products.

Coal consumption at Sasol One is approximately 7×10^6 t/yr. Originally nine dry ash, oxygen blown Lurgi gasifiers with a diameter of approximately 3.7 m were installed at Sasol One. In 1981 an additional prototype Lurgi gasifier with a diameter of 4.7 m was installed (37). Gas production is approximately 10^7 m^3/day (3.5×10^8 SCF/day) from which liquid fuel production of 850 t/day is obtained. Also, about 1.7×10^6 m^3/day (6×10^7 SCF/d) of 19 MJ/m^3 fuel gas is produced (14).

In 1991, the relatively old and small synthetic fuel production facilities at Sasol One began a transformation to a higher value chemical production facility (38). This move came as a result of declining economics for synthetic fuel production from synthesis gas at this location. The new facilities installed in this conversion will expand production of high value Arge waxes and paraffins to 123,000 t/yr in 1993. Also, a new facility for production of 240,00 t/yr of ammonia will be added. The complex will continue to produce ethylene and process feedstock from other Sasol plants to produce alcohols and higher phenols.

Sasol Two and Sasol Three are essentially identical second generation FT plants located adjacent to one another in Secunda. Sasol Two started up in 1980 and Sasol Three in 1982. Each plant operates 40 Lurgi gasifiers and eight Synthol reactors. The combined coal requirement for gasification and steam production is over 40×10^6 t/yr, and output is approximately 1.5×10^4 m^3/day (100,000 barrels/day) of motor fuels. An approximate distribution of products from one of the second generation Sasol plants is shown in Table 2, and a block flow diagram for chemical and fuel production at Sasol Two is shown in Figure 4.

Secunda discharges no process water effluents. All water streams produced are cleaned and reused in the plant. The methane and light hydrocarbons in the product are reformed with steam to generate synthesis

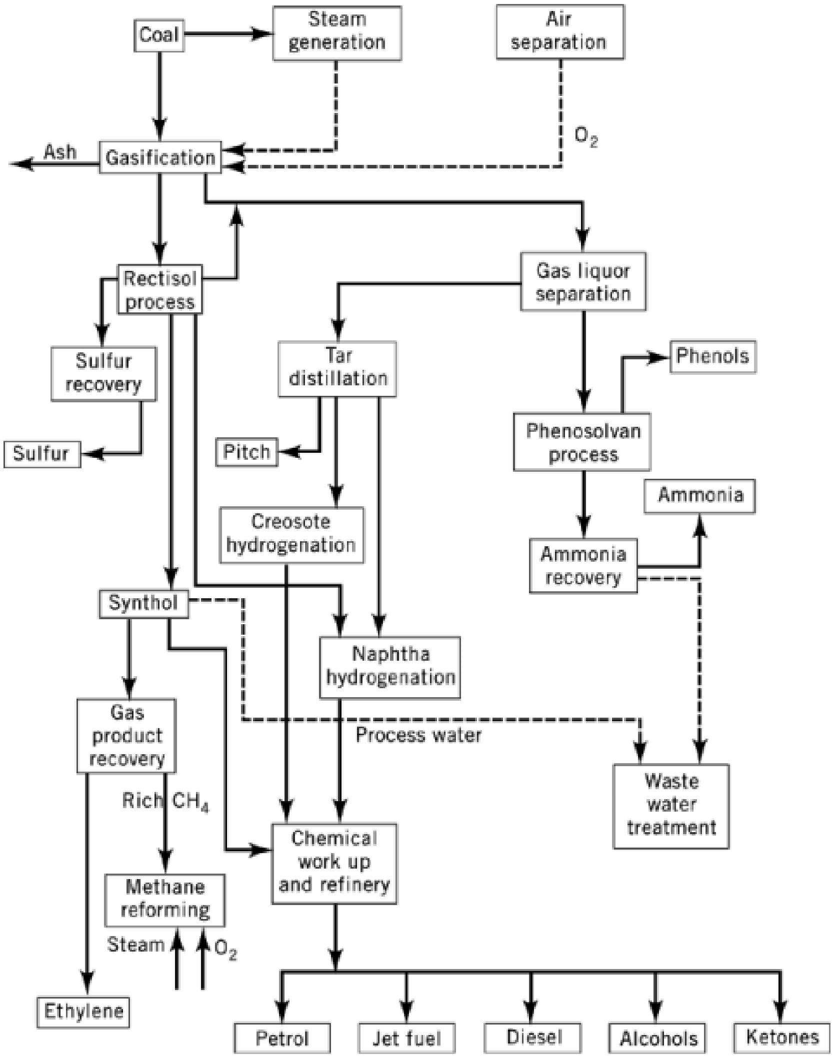


Fig. 4. Sasol Two block flow diagram (38).(Courtesy of Sasol.)

gas for recycle (14). Even at this large scale, the cost of producing fuels and chemicals by the Fischer-Tropsch process is dominated by the cost of synthesis gas production. Sasol has estimated that gas production accounts for 58% of total production costs (39).

Ammonia from coal gasification has been used for fertilizer production at Sasol since the beginning of operations in 1955. In 1964 a dedicated coal-based ammonia synthesis plant was brought on stream. This plant has now been deactivated, and is being replaced with a new facility with three times the production capacity. Nitric acid is produced by oxidation and is converted with additional ammonia into ammonium nitrate fertilizers. The products are marketed either as a liquid or in a solid form known as Limestone Ammonium Nitrate. Also, two types of explosives are produced from ammonium nitrate. The first is a mixture of fuel oil and porous ammonium nitrate granules. The second type is produced by emulsifying small droplets of ammonium nitrate solution in oil.

Table 2. Approximate Product Distribution from Sasol Two[a]

Product	Output, t/yr
motor fuels	1,500,000
ethylene	185,500
chemicals	85,500
tar products	185,500
ammonia (as N)	100,000
sulfur	90,000
Total	*2,146,500*

[a] Ref. 23.

The tar and pitch coproducts from gasification of coal at Sasol are upgraded to a number of higher value products such as wood preservatives and pitch for cellulose fiber pipes. A plant to upgrade pitch to produce electrode coke for the aluminum and iron industries is being commissioned in 1993. The crude tar acid processing facilities have been upgraded to produce higher quality phenol and to add *o*-cresol as well as mixed cresylics to the product spectrum.

A number of chemical products are derived from Sasol's synthetic fuel operations based on the Fischer-Tropsch synthesis including paraffin waxes from the Arge process and several polar and nonpolar hydrocarbon mixtures from the Synthol process. Products suitable for use as hot melt adhesives, PVC lubricants, corrugated cardboard coating emulsions, and polishes have been developed from Arge waxes. Wax blends containing medium and hard wax fractions are useful for making candles, and over 20,000 t/yr of wax are sold for this application.

Synthol coproducts include alcohols, ketones, and lower paraffins. They are used mainly as solvents in the paint and printing industries, although some alcohols are blended into fuels. In 1992 Sasol began producing 17,500 t/yr 1-butanol [71-36-3] from 5-07-acetaldehyde [75-07-0] and planned to start a plant to produce high purity ethanol [64-17-5] in 1993. Acetone [67-64-1] and methyl ethyl ketone [78-93-3] are two ketone coproducts sold as solvents.

The latest of three ethylene recovery plants was started in 1991. Sasol sold almost 300,000 t of ethylene in 1992. Sasol also produces polypropylene at Secunda from propylene produced at Sasol Two. In 1992 Sasol started construction of a linear alpha olefin plant at Secunda to be completed in 1994 (40). Initial production is expected to be 100,000 t/yr pentene and hexene. Sasol also has a project under construction to extract and purify krypton and xenon from the air separation plants at Sasol Two. Other potential new products under consideration at Sasol are acrylonitrile, acetic acid, acetates, and alkylamines.

7.3. Chemical Production at Great Plains

The largest coal conversion facility in the United States is the Dakota Gasification Co. Great Plains plant at Beulah, North Dakota. This facility was constructed in the early 1980s with financing from the Federal Government's now defunct Synthetic Fuels Corp. The facility started operation in 1984, and currently gasifies 15,500 t/day North Dakota lignite in 14 Lurgi dry ash coal gasifiers, producing 4.5×10^6 m^3/day (1.6×10^8 SCF/day) of synthetic natural gas. The plant also produces 64 t/day of ammonia and 45 t/day of sulfur (41). Up until recently all coal liquid coproducts from gasification were burned to generate process steam. Now the company has begun isolating and marketing some coproducts. These products include phenol, cresylic acids, hydrotreated naphtha, anhydrous ammonia, and sulfur. Dakota Gasification's chemical sales exceeded $5 million in 1991. In 1992 Dakota Gasification entered into a contract to supply Merichem with crude cresylic acids. The volume of cresylic acids available from Great Plains coproduct streams has been estimated to correspond to 70% of U.S. and 15% of world demand (42). Potential coproduct yields from Great Plains are shown in Table 3.

Table 3. Coproduct Yields From the Great Plains Plant[a]

Product	Yield, t/day
argon	104
krypton/xenon	0.04
carbon dioxide	11,800
phenol	60
o-cresol	15
m,p-cresol	34
mixed xylenols	29
creosote	320
aromatic naphtha	120
benzene	43
toluene	21
mixed xylenes	9

[a] Ref. 41.

7.4. Coal-Based Ammonia Production

Synthesis gas for the commercial production of ammonia has been made from coal in many locations around the world. The atmospheric pressure Koppers-Totzek coal gasification process was used almost exclusively for synthesis gas generation up until development of pressurized gasification processes, which are more economical because of the savings in synthesis gas compression costs. Between 1951 and 1981 contracts were obtained for approximately 20 Koppers-Totzek based ammonia plants. The largest of these plants is the African Explosives and Chemicals Industry (AECI) plant at Moderfontein in South Africa which started production in 1974. This plant operates six gasifiers with the capacity to produce 2.15×10^6 m^3/day (7.6×10^7 SCF/day) of synthesis gas, 1000 t/day of ammonia, and 100 t/day of methanol. In 1973, Krupp Koppers began development of a pressurized, entrained-flow process (Prenflo) based on Koppers-Totzek gasification.

In 1984, the Ube Ammonia Industry Co. began operating the largest Texaco coal gasification complex to date. This facility is located in Ube City, Japan, and has a rated gasification capacity of 1500 t/day of coal, and production capacity of 1000 t/day of ammonia. The plant has successfully gasified coals from Canada, Australia, South Africa, and China. At the present time the plant uses a mixture of petroleum coke and coal (43).

Ube has a long history of ammonia production from coal, and began operation in 1934 using the Koppers low temperature carbonization process to produce ammonium sulfate for fertilizers from locally mined subbituminous coal. Over the years, Ube's feedstock flexibility has been increased by adding oil gasification and naphtha steam reforming capacity. The oil supply disruptions of the 1970s and 1980s encouraged Ube to return to coal as a principal feedstock for ammonia production.

The Ube plant consists of four complete trains of Texaco quench-type gasifiers. During normal operation, three gasifiers are on line and one is on standby. Each gasifier consumes 500 t/day of coal to generate syngas for 350 t/day of ammonia. Up to the middle of 1990 the Ube plant gasified 2.2 million t of coal and petroleum coke.

8. Planned Coal Chemical Projects

8.1. Texaco Gasification Projects in China

Because of large domestic coal reserves, China is becoming very active in commercialization of coal conversion projects. Two coal gasification projects using the Texaco process are currently under construction, and two additional Texaco gasification projects were announced in early 1992. The Lunan Fertilizer plant in Shandong province is expected to start operation in 1993, and the Shougang plant in Beijing will begin producing fuel gas for industrial use in 1994. The Lunan plant will produce ammonia from 360 t/day of coal. The Shougang plant will have the capacity to gasify 1000 t/day of coal. Newly announced projects are the Shanghai Coking and Chemical Plant town gas production facility and the Weihe Chemical Fertilizer Plant in Shaanxi province.

The Shanghai plant will gasify 1100 t/day of coal to produce 1.7 m^3/day (60 ft^3/day) of town gas, and 200,000 t/yr of methanol. Plans call for the first phase of the new gasification facility to begin operation in 1994. Increased town gas production from this plant will eliminate the need for residents to burn coal for home heating, and reduce air pollution from this source. Also, coal slurry for the gasifier will be prepared using wastewater from existing processes and remove these discharges from the Huangpu River.

When completed in 1996, the Weihe plant will gasify 1500 t/day of coal to produce 300,000 t/yr of ammonia, which will be used to manufacture 520,000 t/yr of urea fertilizer. This project is the eighth Texaco oil or coal gasification plant licensed by Chinese industry.

8.2. TVA Urea Project

In Round 4 of DOE's Clean Coal Technology program, the Tennessee Valley Authority (TVA) proposed construction of a 250 MW IGCC power plant that would coproduce urea and electric power from 730,000 metric tons of coal a year. The project was not selected in Round 4, but is being submitted again for consideration in Round 5, which is expected to give chemical projects favorable treatment. Recently, TVA announced that the Shell coal gasification process has been selected for this plant. TVA has experience in coal gasification, having successfully operated a Texaco gasifier based demonstration plant for ammonia synthesis from coal in the late 1970s and early 1980s.

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