Section 27

Energy Resources, Conversion, and Utilization

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INTRODUCTION

FUELS

HEAT GENERATION

THERMAL ENERGY CONVERSION AND UTILIZATION

HEAT RECOVERY

ELECTROCHEMICAL ENERGY CONVERSION

Nomenclature and Units

Symbol	Definition	SI units	U.S. customary units
A	Area specific resistance	Ω/m^2	Ω/ft^2
c	Heat capacity	J/(kg·K)	Btu/(lb·°F)
E	Activation energy	J/mol	Btu/lb mol
E	Electrical potential	V	V
$\hat{f}$	Fugacity	kPa	psia
F	Faraday constant	C/mol	C/lb mol
ΔG	Free energy of reaction	J/mol	Btu/lb mol
ΔH	Heat of reaction	J/mol	Btu/lb mol
i	Current density	A/m^2	A/ft^2
k	Rate constant	$g/(h \cdot cm^3)$	$lb/(h \cdot ft^3)$
K	Latent heat of vaporization	kJ/kg	Btu/lb
P	Pressure	kPa	psia
Q	Heating value	kJ/kg	Btu/lb
R	Gas constant	J/mol·K	Btu/lb mol·°R
s	Relative density	Dimensionless	Dimensionless
T	Temperature	K	°F
U	Fuel utilization	percent	percent
V	Molar gas volume	m^3/mol	ft^3/lb mol
Z	Compressibility factor	Dimensionless	Dimensionless
	Greek symbols		
ε	Energy conversion efficiency	Percent	Percent

Acronyms and unit prefixes

Symbol	Name	Value
E	Exa	10^{18}
G	Giga	10^9
K	Kilo	10^3
M	Mega	10^6
P	Peta	10^{15}
T	Tera	10^{12}
Z	Zetta	10^{21}

Acronym	Definition
AFBC	atmospheric fluidized bed combustion
AFC	alkaline fuel cell
AGC-21	Advanced Gas Conversion Process
BG/L	British Gas and Lurgi process
COE	cost of electricity
COED	Char Oil Energy Development Process
DOE	U.S. Department of Energy
EDS	Exxon Donor Solvent Process
FBC	fluidized bed combustion
HAO	hydrogenated anthracene oil
HPO	hydrogenated phenanthrene oil
HRI	Hydrocarbon Research, Inc.
HTI	Hydrocarbon Technologies, Inc.
IGCC	integrated gasification combined-cycle
KRW	Kellogg-Rust-Westinghouse process
MCFC	molten carbonate fuel cell
MTG	methanol-to-gasoline process
OTFT	once-through-Fischer-Tropsch process
PAFC	phosphoric acid fuel cell
PC	pulverized coal
PEFC	polymer electrolyte fuel cell
PFBC	pressurized fluidized bed combustion
Quad	10^{15} Btu
SASOL	South African operation of synthetic fuels plants
SMDS	Shell Middle Distillate Synthesis Process
SNG	synthetic natural gas
SOFC	solid oxide fuel cell
SRC	solvent-refined coal

INTRODUCTION

GENERAL REFERENCES: Loftness, *Energy Handbook,* 2d ed., Van Nostrand Reinhold, New York, 1984. Energy Information Administration, *Energy Use and Carbon Emissions: Some International Comparisons,* U.S. Dept. of Energy, DOE/EIA-0579, 1994. Howes and Fainberg (eds.), *The Energy Source Book,* American Institute of Physics, New York, 1991. Johansson, Kelly, Reddy, and Williams (eds.), Burnham (exec. ed.), *Renewable Energy—Sources for Fuels and Electricity,* Island Press, Washington, D.C., 1993. Turner, *Energy Management Handbook,* The Fairmont Press, Lilburn, Ga., 1993. *National Energy Strategy,* U.S. Dept. of Energy, 1991.

Energy is usually defined as the capacity to do work. Nature provides us with numerous sources of energy, some difficult to utilize efficiently (e.g., solar radiation and wind energy), others more concentrated or energy dense and therefore easier to utilize (e.g., fossil fuels). Energy sources can be classified also as *renewable* (solar and nonsolar) and *nonrenewable.* Renewable energy resources are derived in a number of ways: gravitational forces of the sun and moon, which create the tides; the rotation of the earth combined with solar energy, which generates the currents in the ocean and the winds; the decay of radioactive minerals and the interior heat of the earth, which provide geothermal energy; photosynthetic production of organic matter; and the direct heat of the sun. These energy sources are called renewable because they are either continuously replenished or, for all practical purposes, are inexhaustible.

Nonrenewable energy sources include the fossil fuels (natural gas, petroleum, shale oil, coal, and peat) as well as uranium. Fossil fuels are both energy dense and widespread, and much of the world's industrial, utility, and transportation sectors rely on the energy contained in them. Concerns over global warming notwithstanding, fossil fuels will remain the dominant fuel form for the foreseeable future. This is so for two reasons: (1) the development and deployment of new technologies able to utilize renewable energy sources such as solar, wind, and biomass are uneconomic at present, in most part owing to the diffuse or intermittent nature of the sources; and (2) concerns persist over storage and/or disposal of spent nuclear fuel and nuclear proliferation.

Fossil fuels, therefore, remain the focus of this section; their principal use is in the generation of heat and electricity in the industrial, utility, and commercial sectors, and in the generation of shaft power in transportation. The material in this section deals primarily with the conversion of the chemical energy contained in fossil fuels to heat and electricity. Material from *Perry's Chemical Engineers' Handbook,* 6th ed., Sec. 9, has been updated and condensed, and, in addition, new material on electrochemical energy conversion in fuel cells has been introduced. Even though the principles of energy conversion in fuel cells were known before internal combustion engines were developed, only recent improvements in materials and manufacturing methods have allowed fuel cells to be considered for stationary and transportation power generation.

FUELS

RESOURCES AND RESERVES

Proven worldwide energy resources are large. The largest remaining known reserves of crude oil, used mainly for producing transportation fuels, are located in the Middle East, along the equator, and in the former Soviet Union. U.S. proven oil reserves currently account for only about 3 percent of the world's total. Large reserves of natural gas exist in the former Soviet Union and the Middle East. Coal is the most abundant fuel on earth and the primary fuel for electricity in the United States, which has the largest proven reserves. Annual world consumption of energy is still currently less than 1 percent of combined world reserves of fossil fuels. The resources and reserves of the principal fossil fuels in the United States—coal, petroleum, and natural gas—follow.

	ZJ*		
Fuel	Proven reserves	Estimated undiscovered recoverable reserves	Estimated identified and undiscovered resources
Coal	7.3		110
Petroleum	0.15	0.31	
Natural gas	0.19	0.43	

*ZJ = 10^{21} J. (To convert to 10^{18} Btu, multiply by 0.948.)

The energy content of fossil fuels in commonly measured quantities is as follows.

	Energy content	
Bituminous and anthracite coal	30.2 MJ/kg	26×10^6 Btu/US ton
Lignite and subbituminous coal	23.2 MJ/kg	20×10^6 Btu/US ton
Crude oil	38.5 MJ/L	5.8×10^6 Btu/bbl
Natural-gas liquids	25.2 MJ/L	3.8×10^6 Btu/bbl
Natural gas	38.4 MJ/m^3	1032 Btu/ft^3

1 bbl = 42 US gal = 159 L = 0.159 m^3

SOLID FUELS

Coal

General References: Lowry (ed.), *Chemistry of Coal Utilization,* Wiley, New York, 1945; suppl. vol., 1963; 2d suppl. vol., Elliott (ed.), 1981. Van Krevelen, *Coal,* Elsevier, Amsterdam, 1961.

Origin Coal originated from the arrested decay of the remains of trees, bushes, ferns, mosses, vines, and other forms of plant life, which flourished in huge swamps and bogs many millions of years ago during prolonged periods of humid, tropical climate and abundant rainfall. The precursor of coal was peat, which was formed by bacterial and chemical action on the plant debris. Subsequent actions of heat, pressure, and other physical phenomena metamorphosed the peat to the various ranks of coal as we know them today. Because of the various degrees of the metamorphic changes during this process, coal is not a uniform substance; no two coals are ever the same in every respect.

Classification Coals are classified by rank, i.e., according to the degree of metamorphism in the series from lignite to anthracite. Table 27-1 shows the classification system adopted by the American Society for Testing and Materials, D388-92A. The heating value on the moist *mineral-matter-free* (mmf) basis, and the fixed carbon, on the dry mmf basis, are the bases of this system. The lower-rank coals are classified according to the heating value, kJ/kg (Btu/lb), on a moist mmf basis. The agglomerating character is used to differentiate between adjacent groups. Coals are considered agglomerating if the coke button remaining from the test for volatile matter will support a weight of 500 g or if the button swells or has a porous cell structure.

The Parr formulas, Eqs. (27-1) to (27-3), or the approximation formulas, Eqs. (27-4) and (27-5), are used for classifying coals according to rank. The Parr formulas are employed in litigation cases.

$$F' = \frac{100\,(F - 0.15S)}{100 - (M + 1.08A + 0.55S)} \qquad (27\text{-}1)$$

$$V' = 100 - F' \qquad (27\text{-}2)$$

TABLE 27-1 Classification of Coals by Rank*

	Fixed carbon limits (dry, mineral-matter-free basis), %		Volatile matter limits (dry, mineral-matter-free basis), %		Gross calorific value limits (moist, mineral-matter-free basis)†				
					MJ/kg		Btu/lb		
Class/group	Equal or greater than	Less than	Greater than	Equal or less than	Equal or greater than	Less than	Equal or greater than	Less than	Agglomerating character
Anthracitic:									
Meta-anthracite	98	—	—	2	—	—	—	—	Nonagglomerating
Anthracite	92	98	2	8	—	—	—	—	
Semianthracite‡	86	92	8	14	—	—	—	—	
Bituminous:									
Low-volatile bituminous coal	78	86	14	22	—	—	—	—	Commonly agglomerating¶
Medium-volatile bituminous coal	69	78	22	31	—	—	—	—	
High-volatile A bituminous coal	—	69	31	—	32.6	—	14,000§	—	
High-volatile B bituminous coal	—	—	—	—	30.2	32.6	13,000§	14,000	
High-volatile C bituminous coal	—	—	—	—	26.7	30.2	11,500	13,000	
					24.4	26.7	10,500	11,500	Agglomerating
Subbituminous:									
Subbituminous A coal	—	—	—	—	24.4	26.7	10,500	11,500	Nonagglomerating
Subbituminous B coal	—	—	—	—	22.1	24.4	9,500	10,500	
Subbituminous C coal	—	—	—	—	19.3	22.1	8,300	9,500	
Lignitic:									
Lignite A	—	—	—	—	14.7	19.3	6,300	8,300	
Lignite B	—	—	—	—	—	14.7	—	6,300	

Data from 1994 Annual Book of ASTM Standards, vol. 5 D 388 (1994). Copyright ASTM. Reprinted with permission.

*This classification does not apply to certain coals.

†*Moist* refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.

‡If agglomerating, classify in low-volatile group of the bituminous class.

§Coals having 69 percent or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of gross calorific value.

¶It is recognized that there may be nonagglomerating varieties in these groups of the bituminous class and that there are notable exceptions in the high-volatile C bituminous group.

$$Q' = \frac{100\,(Q - 50S)}{100 - (M + 1.08A + 0.55S)} \tag{27-3}$$

$$F' = \frac{100F}{100 - (M + 1.1A + 0.1S)} \tag{27-4}$$

$$Q' = \frac{100Q}{100 - (1.1A + 0.1S)} \tag{27-5}$$

where M, F, A, and S are weight percentages, on a moist basis, of moisture, fixed carbon, ash, and sulfur, respectively; F' and V' are weight percentages, on a dry mmf basis, of fixed carbon and volatile matter, respectively; Q and Q' are calorific values (Btu/lb), on a moist non-mmf basis and a moist mmf basis, respectively. (Btu/lb = 2326 J/kg)

Composition and Heating Value The composition of coal is reported in two different ways: the proximate analysis and the ultimate analysis, both expressed in weight percent. The *proximate analysis* is the determination by prescribed methods of moisture, volatile matter, fixed carbon, and ash.

The moisture in coal consists of inherent moisture, also called equilibrium moisture, and surface moisture. Free moisture is that moisture lost when coal is air-dried under standard low-temperature conditions.

The *volatile matter* is the portion of coal which, when the coal is heated in the absence of air under prescribed conditions, is liberated as gases and vapors. Volatile matter does not exist by itself in coal, except for a little absorbed methane, but results from thermal decomposition of the coal substance.

Fixed carbon, the residue left after the volatile matter is driven off, is calculated by subtracting from 100 the percentages of moisture, volatile matter, and ash of the proximate analysis. In addition to carbon, it may contain several tenths of a percent of hydrogen and oxygen, 0.4 to 1.0 percent nitrogen, and about half of the sulfur that was in the coal.

Ash is the inorganic residue that remains after the coal has been burned under specified conditions, and it is composed largely of compounds of silicon, aluminum, iron, and calcium, and minor amounts of compounds of magnesium, sodium, potassium, phosphorous, sulfur, and titanium. Ash may vary considerably from the original mineral matter, which is largely kaolinite, illite, montmorillonite, quartz, pyrites, and gypsum.

The *ultimate analysis* is the determination by prescribed methods of the ash, carbon, hydrogen, nitrogen, sulfur, and (by difference) oxygen. Along with these analyses, the *heating value,* expressed as kJ/kg (Btu/lb), is also determined. This is the heat produced at constant volume by the complete combustion of a unit quantity of coal in an oxygen-bomb calorimeter under specified conditions. The result includes the latent heat of vaporization of the water in the combustion products and is called the gross heating or *high heating value* (HHV), Q_h. The heating value when the water is not condensed is called the *low heating value* (LHV), Q_l, and is obtained from

$$Q_l = Q_h - K \cdot W \tag{27-6}$$

where W = weight of water formed/weight of fuel burned. The factor K is the latent heat of vaporization at the partial pressure of the vapor in the exit gas. The value of K ranges from 2396 to 2512 kJ/kg of water (1030 to 1080 Btu/lb). Q_h in Btu/lb (×2.326 = kJ/kg) can be approximated by a formula developed by the Institute of Gas Technology:

$$Q_h = 146.58\,C + 568.78\,H + 29.4\,S - 6.58\,A - 51.53\,(O + N) \tag{27-7}$$

where C, H, S, A, O, and N are the weight percentages on a dry basis of carbon, hydrogen, sulfur, ash, oxygen, and nitrogen, respectively. The standard deviation for 775 coal samples is 127 Btu/lb.

Coal analyses are reported on several bases, and it is customary to select the basis best suited to the application. The *as-received* basis represents the weight percentage of each constituent in the sample as received in the laboratory. The sample itself may be coal as fired, as mined, or as prepared for a particular use. The *moisture-free* (dry) basis is generally the most useful basis because performance calculations can be easily corrected for the actual moisture content at the point of use. The *dry, ash-free* basis is frequently used to approximate the rank and source of a coal. For example, the heating value of coals of a given source and rank is remarkably constant when calculated on this basis.

Laboratory procedures for proximate and ultimate analyses are given in the *Annual Book of ASTM Standards* (Sec. 5, American Society for Testing and Materials, Conshohocken, Pa., 1994) and in *Methods of Analyzing and Testing Coal and Coke* (U.S. Bureau of Mines Bulletin 638, 1967).

Sulfur Efforts to abate atmospheric pollution have drawn considerable attention to the sulfur content of coal, since the combustion of coal results in the discharge to the atmosphere of sulfur oxides. Sulfur occurs in coal in three forms: as pyrite (FeS_2); as organic sulfur, which is a part of the coal substance; and as sulfate. Sulfur as sulfate comprises at the most only a few hundredths of a percent of the coal. The organic sulfur may comprise from 20 to 80 percent of the total sulfur. Since organic sulfur is chemically bound to the coal substance in a complex manner, drastic treatment is necessary to break the chemical bonds before the sulfur can be removed. There is no economical method known at present that will remove organic sulfur, although so-called chemical treatment methods for cleaning coal can reduce the sulfur content. Pyritic sulfur can be partially removed by using standard coal-washing equipment. The degree of pyrite removal depends on the size of the coal and the size and distribution of the pyrite particles.

The sulfur content of U.S. coals varies widely, ranging from a low of 0.2 percent to as much as 7 percent by weight, on a dry basis. The estimated remaining U.S. coal reserves of all ranks, by sulfur content, are shown in Fig. 27-1. Extensive data on sulfur and sulfur reduction potential, including washability, in U.S. coals are given in *Sulfur and Ash Reduction Potential and Selected Chemical and Physical Properties of United States Coal* (U.S. Dept. of Energy, DOE/PETC, TR-90/7, 1990; TR-91/1 and TR-91/2, 1991).

Coal-Ash Characteristics and Composition When coal is to be burned, used in steelmaking, or gasified, it is important to determine the ash fusibility, comprising the initial deformation, softening, and fluid temperatures. The difference between the softening and initial deformation temperatures is called the *softening interval,* and that between the fluid temperature and the softening temperature is called the *fluid interval.* The procedure for determining the fusibility of coal ash is prescribed by ASTM D 1857 (American Society for Testing and Materials, op. cit., 1994). The softening temperature is most

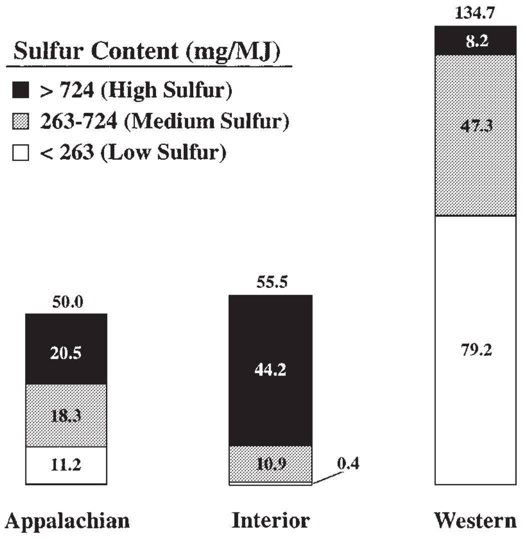


FIG. 27-1 Estimates of recoverable U.S. coal reserves in Gt by sulfur ranges and region. To convert tonnes to US tons, multiply by 1.102; and mg/MJ to lb/10^{16} Btu, multiply by 2.321. (*Source:* U.S. Coal Reserves: An Update by Heat and Sulfur Content, *Energy Information Administration, DOE/EIA-0529(92), February 1993.*)

often used as a rough qualitative guide to the behavior of ash on a grate and on furnace heat-transfer surfaces, with respect to the tendency to form large masses of sintered or fused ash, which impair heat transfer and impede gas flow. Likewise, the fluid temperature and the fluid interval are qualitative guides to the "flowability" of ash in slag-tap and cyclone furnaces. However, because ash fusibility is not an infallible index of ash behavior in practice, care is needed in using fusibility data for designing and operating purposes. There is an excellent discussion on this subject in *Steam: Its Generation and Use* (40th ed., Babcock & Wilcox Co., New York, 1992).

The composition of coal ash varies widely. Calculated as oxides, the composition (percent by weight) varies as follows:

SiO_2	20–60
Al_2O_3	10–35
Fe_2O_3	5–35
CaO	1–20
MgO	0.3–4
TiO_2	0.5–2.5
Na_2O and K_2O	1–4
SO_3	0.1–12

Knowledge of the composition of coal ash is useful for estimating and predicting coal performance in coke making and, to a limited extent, the fouling and corrosion of heat-exchange surfaces in pulverized-coal-fired furnaces.

Multiple correlations for ash composition and ash fusibility are discussed in the *Coal Conversion Systems Technical Data Book* (part IA, U.S. Dept. of Energy, 1984).

The slag viscosity-temperature relationship for completely melted slag is

$$\text{Log viscosity} = \frac{10^7 M}{(T - 150)^2 + C} \qquad (27\text{-}8)$$

where viscosity is in poises (×0.1 = Pa·s), $M = 0.00835\ (SiO_2) + 0.00601(Al_2O_3) - 0.109$, $C = 0.0415\ (SiO_2) + 0.0192\ (Al_2O_3) + 0.0276$ (equivalent Fe_2O_3) + 0.0160 (CaO) − 3.92, and T = temperature, K.

The oxides in parentheses are the weight percentages of these oxides when $SiO_2 + Al_2O_3 + Fe_2O_3 + CaO + MgO = 100$.

Physical Properties The *free-swelling index* (FSI) measures the tendency of a coal to swell when burned or gasified in fixed or fluidized beds. Coals with a high FSI (greater than 4) can usually be expected to cause difficulties in such beds. Details of the test are given by the ASTM D 720 (American Society for Testing and Materials, op. cit.) and U.S. Bureau of Mines Report of Investigations 3989.

The *Hardgrove grindability index* (HGI) indicates the ease (or difficulty) of grinding coal and is complexly related to physical properties such as hardness, fracture, and tensile strength. The Hardgrove machine is usually employed (ASTM D 409, American Society for Testing and Materials, op. cit.). It determines the relative grindability or ease of pulverizing coal in comparison with a standard coal, chosen as 100 grindability (see Sec. 20 of this handbook). The FSI and HGI of some U.S. coals are given in Bureau of Mines Information Circular 8025 for FSI and HGI data for 2812 and 2339 samples, respectively.

The *bulk density* of broken coal varies according to the specific gravity, size distribution, and moisture content of the coal and the amount of settling when the coal is piled. Following are some useful approximations of the bulk density of various ranks of coal.

	kg/m^3	lb/ft^3
Anthracite	800–930	50–58
Bituminous	670–910	42–57
Lignite	640–860	40–54

Size stability refers to the ability of coal to withstand breakage during handling and shipping. It is determined by twice dropping a 23-kg (50-lb) sample of coal from a height of 1.8 m (6 ft) onto a steel plate. From the size distribution before and after the test, the size stability is reported as a percentage factor (see ASTM D 440). The *friability* test measures the tendency of coal to break during repeated handling. It is actually the complement of size stability and is determined by the standard tumbler test (ASTM D 441-36).

Spier's *Technical Data on Fuels* gives the *specific heat* of dry, ash-free coal as follows.

	kJ/(kg·K)	Btu/(lb·°F)
Anthracite	0.92–0.96	0.22–0.23
Bituminous	1.0–1.1	0.24–0.25

The relationships between specific heat and water content and between specific heat and ash content are linear. Given the specific heat on a dry, ash-free basis, it can be corrected to an as-received basis. The specific heat and enthalpy of coal to 1366 K (2000°F) are given in *Coal Conversion Systems Technical Data Book* (part 1A, U.S. Dept. of Energy, 1984).

The *mean specific heat* of coal ash and slag, which is used for calculating heat balances on furnaces, gasifiers, and other coal-consuming systems, follows.

Temperature range		Mean specific heat	
K	°F	kJ/(kg·K)	Btu/(lb·°F)
273–311	32–100	0.89	0.21
273–1090	32–1500	0.94	0.22
273–1310	32–1900	0.97	0.23
273–1370	32–2000	0.98	0.24
273–1640	32–2500	1.1	0.27

Coke Coke is the solid, cellular, infusible material remaining after the carbonization of coal, pitch, petroleum residues, and certain other carbonaceous materials. The varieties of coke generally are identified by prefixing a word to indicate the source, if other than coal, (e.g., *petroleum* coke) or the process by which a coke is manufactured (e.g., *oven* coke).

The mechanism of the formation of coke when coal is carbonized is a complex of physical and chemical phenomena that are not perfectly understood. Some of the physical changes, which are interrelated when certain ranks of coal or blends are heated, are softening, devolatilization, swelling, and resolidification. Some of the accompanying chemical changes are cracking, depolymerization, polymerization, and condensation. More detailed theoretical information is given in the general references listed in the beginning of the section on coal.

High-Temperature Coke (1173 to 1423 K or 1652 to 2102°F.) This type is most commonly used in the United States; nearly 20 percent of the total bituminous coal consumed is used to make high-temperature coke for metallurgical applications. About 99 percent of this type of coke is made in slot-type recovery ovens. Blast furnaces use about 90 percent of the production, the rest going mainly to foundries and gas plants.

A U.S. Bureau of Mines survey of 12 blast-furnace coke plants, whose capacity is 30 percent of the total production in the United States, provides an excellent picture of the acceptable chemical and physical properties of metallurgical coke. The ranges of properties are given in Table 27-2.

TABLE 27-2 Chemical and Physical Properties of High-Temperature Cokes Used in the United States*

Property	Range
Volatile matter	0.6–1.4 wt %, as received
Ash	7.5–10.7 wt %, as received
Sulfur	0.6–1.1 wt %, as received
Stability factor	39–58 (1-in tumbler)
Hardness factor	60–68 (¼-in tumbler)
Apparent specific gravity (water = 1.0)	0.80–0.99

**Comparison of Properties of Coke Produced by BM-AGA and Industrial Methods,* U.S. Bur. Mines Rep. Invest. 6354. To convert inches to centimeters, multiply by 2.54.

The typical by-product yields per US ton (909 kg) of dry coal from high-temperature carbonization in ovens with inner-wall temperatures from 1273 to 1423 K (1832 to 2102°F) are: coke, 653 kg (1437 lb); gas, 154 kg (11,200 ft^3); tar, 44 kg (10 gal); water, 38 kg (10 gal); light oil, 11 kg (3.3 gal); and ammonia, 2.2 kg (4.8 lb).

Foundry Coke This coke has different requirements from blast-furnace coke. The volatile matter should not exceed 2.0 percent, the sulfur should not exceed 0.7 percent, the ash should not exceed 12.0 percent, and the size should exceed 76 mm (3 in).

Low- and Medium-Temperature Coke (773 to 1023 K or 932 to 1382°F.) Cokes of this type are no longer produced in the United States to a significant extent. However, there is some interest in low-temperature carbonization as a source of both hydrocarbon liquids and gases to supplement petroleum and natural-gas resources.

The *Fischer assay* is an arbitrary but precise analytical tool for determining the yield of products from low-temperature carbonization. A known weight of coal is heated at a controlled rate in the absence of air to 773 K (932°F), and the products are collected and weighed. Table 27-3 gives the approximate yields of products for various ranks of coal.

Pitch Coke and Petroleum Coke Pitch coke is made from coal-tar pitch, and petroleum coke is made from petroleum residues from petroleum refining. Pitch coke has about 1.0 percent volatile matter, 1.0 percent ash, and less than 0.5 percent sulfur on the as-received basis. There are two kinds of petroleum coke: delayed coke and fluid coke. Delayed coke is produced by heating a gas oil or heavier feedstock to 755 to 811 K (900 to 1000°F) and spraying it into a large vertical cylinder where cracking and polymerization reactions occur. Water jets are used to cut the coke from one drum while the other drum is being charged. Fluid coke is made in a fluidized-bed reactor where preheated feed is sprayed onto a fluidized bed of coke particles. Coke product is continuously withdrawn by size classifiers in the solids loop of the reactor system. Since it contains the impurities from the original crude oil, the sulfur is usually high, and appreciable quantities of vanadium salts may be present. Ranges of composition and properties are as follows.

Composition and properties	Delayed coke	Fluid coke
Volatile matter, wt %	8–18	3.7–7.0
Ash, wt %	0.05–1.6	0.1–2.8
Sulfur, wt %	—	1.5–10.0
Grindability index	40–60	20–30
True density, g/cm^3	1.28–1.42	1.5–1.6

Other Solid Fuels

Coal Char This type of char is the nonagglomerated, nonfusible residue from the thermal treatment of coal. Coal chars are obtained as a residue or a coproduct from low-temperature carbonization processes and from processes being developed to convert coal to liquid and gaseous fuels and to chemicals. Such chars have a substantial heating value. The net amount of char from a conversion process varies widely; in some instances, it may represent between about 30 and 55 percent of the weight of the coal feed; in others, no net or excess char is produced; i.e., the entire char yield is consumed as in-plant fuel. The volatile matter, sulfur, and heating values of the chars are lower, and the ash is higher, than in the original coal. Chars typically have higher volatile matter contents (7 to 12 wt %) than low- and medium-temperature cokes (2.5 to 6 wt %), but this is both process and feed-coal dependent.

Peat Peat is partially decomposed plant matter that has accumulated underwater or in a water-saturated environment. It is the precursor of coal but is not classified as coal. Sold under the term *peat moss* or *moss peat*, peat is used in the United States mainly for horticultural and agricultural applications, but interest is growing in its use as a fuel in certain local areas (e.g., North Carolina). Peat is used extensively as a fuel primarily in Ireland and the former Soviet Union. Although analyses of peat vary widely, a typical high-grade peat has 90 percent water, 3 percent fixed carbon, 5 percent volatile matter, 1.5 percent ash, and 0.10 percent sulfur. The moisture-free heating value is approximately 20.9 MJ/kg (9000 Btu/lb).

Wood Typical higher heating values are 20 MJ/kg (8600 Btu/lb) for oven-dried hardwood and 20.9 MJ/kg for oven-dried softwood. These values are accurate enough for most engineering purposes. U.S. Department of Agriculture Handbook 72 (revised 1974) gives the specific gravity of the important softwoods and hardwoods, useful if heating value on a volume basis is needed.

Charcoal Charcoal is the residue from the destructive distillation of wood. It absorbs moisture readily, often containing as much as 10 to 15 percent water. In addition, it usually contains about 2 to 3 percent ash and 0.5 to 1.0 percent hydrogen. The heating value of charcoal is about 27,912 to 30,238 kJ/kg (12,000 to 13,000 Btu/lb).

Solid Wastes and Biomass Large and increasing quantities of solid wastes are a significant feature of affluent societies. In the United States in 1993 the rate was about 1.8 kg (4 lb) per capita per day or nearly 190 Tg (2.07 × 10^8 U.S. tons) per year, but the growth rate has slowed in recent years as recycling efforts have increased. Table 27-4 shows that the composition of miscellaneous refuse is surprisingly uniform, but size and moisture variations cause major difficulties in efficient, economical disposal.

The fuel value of most solid wastes is usually sufficient to enable self-supporting combustion, leaving only the incombustible residue and reducing the volume of waste eventually consigned to sanitary landfills to only 10 to 15 percent of the original volume. The heat released by the combustion of waste can be recovered and utilized, although the cost of the recovery equipment or the distance to a suitable point of use for the heat may make its recovery economically infeasible.

Wood, wood scraps, bark, and wood product plant waste streams are a major element of biomass, industrial, and municipal solid waste fuels. In 1991, about 1.7 EJ (1.6 × 10^{15} Btu [quads]) of energy were obtained from wood and wood wastes, representing about 60 percent of the total biomass-derived energy in the United States. *Bagasse* is the solid residue remaining after sugarcane has been crushed by pressure rolls. It usually contains from 40 to 50 percent water. The dry bagasse has a heating value of 18.6 to 20.9 MJ/kg (8000 to 9000 Btu/lb).

TABLE 27-3 Fischer-Assay Yields from Various Ranks of Coal (As-Received Basis)

ASTM classification by rank		Coke, wt %	Tar, gal/ton	Light oil, gal/ton	Gas, ft^3/ton	Water, wt %
Class	Group					
Bituminous	1. Low-volatile bituminous	90	8.6	1.0	1760	3
	2. Medium-volatile bituminous	83	18.9	1.7	1940	4
	3. High-volatile A bituminous	76	30.9	2.3	1970	6
	4. High-volatile B bituminous	70	30.3	2.2	2010	11
	5. High-volatile C bituminous	67	27.0	1.9	1800	16
Subbituminous	1. Subbituminous A	59	20.5	1.7	2660	23
	2. Subbituminous B	58	15.4	1.3	2260	28
Lignite	1. Lignite A	37	15.2	1.2	2100	44

NOTE: To convert gallons per ton to liters per kilogram, multiply by 0.004; to convert cubic feet per ton to cubic meters per kilogram, multiply by 3.1 × 10^{-5}.

TABLE 27-4 Waste Fuel Analysis

Type of waste	Heating value, Btu/lb	Percentage composition by weight					Density, $\mathrm{lb/ft}^3$
		Volatiles	Moisture	Ash	Sulfur	Dry combustible	
Paper	7,572	84.6	10.2	6.0	0.20		
Wood	8,613	84.9	20.0	1.0	0.05		
Rags	7,652	93.6	10.0	2.5	0.13		
Garbage	8,484	53.3	72.0	16.0	0.52		
Coated fabric: rubber	10,996	81.2	1.04	21.2	0.79	78.80	23.9
Coated felt: vinyl	11,054	80.87	1.50	11.39	0.80	88.61	10.7
Coated fabric: vinyl	8,899	81.06	1.48	6.33	0.02	93.67	10.1
Polyethylene film	19,161	99.02	0.15	1.49	0	98.51	5.7
Foam: scrap	12,283	75.73	9.72	25.30	1.41	74.70	9.1
Tape: resin-covered glass	7,907	15.08	0.51	56.73	0.02	43.27	9.5
Fabric: nylon	13,202	100.00	1.72	0.13	0	99.87	6.4
Vinyl scrap	11,428	75.06	0.56	4.56	0.02	95.44	23.4

SOURCE: From Hescheles, *MECAR Conference on Waste Disposal,* New York, 1968; and *Refuse Collection Practice,* 3d ed., American Public Works Association, Chicago, 1966.

To convert British thermal units per pound to joules per kilogram, multiply by 2326; to convert pounds per cubic foot to kilograms per cubic meter, multiply by 16.02.

LIQUID FUELS

Liquid Petroleum Fuels The principal liquid fuels are made by fractional distillation of crude petroleum (a mixture of hydrocarbons and hydrocarbon derivatives ranging from methane to heavy bitumen). As many as one-quarter to one-half of the molecules in crude may contain sulfur atoms, and some contain nitrogen, oxygen, vanadium, nickel, or arsenic. Desulfurization, hydrogenation, cracking (to lower molecular weight), and other refining processes may be performed on selected fractions before they are blended and marketed as fuels. Viscosity/gravity/boiling-range relationships of common fuels are shown in Fig. 27-2.

Specifications The American Society for Testing and Materials has developed specifications (*Annual Book of ASTM Standards,* Conshohocken, Pa., updated annually) that are widely used to classify fuels. Table 27-5 shows fuels covered by ASTM D 396, Standard Specification for Fuel Oils. D 396 omits kerosenes (low-sulfur, clean-burning No. 1 fuels for lamps and freestanding flueless domestic heaters), which are covered separately by ASTM D 3699.

In drawing contracts and making acceptance tests, refer to the pertinent ASTM standards. *ASTM Standards* contain specifications (classifications) and test methods for burner fuels (D 396), motor and aviation gasolines (D 4814 and D 910), diesel fuels (D 975), and aviation and gas-turbine fuels (D 1655 and D 2880). ASTM D 4057 contains procedures for sampling bulk oil in tanks, barges, etc.

Fuel specifications from different sources may differ in test limits on sulfur, density, etc., but the same general categories are recognized worldwide: kerosene-type vaporizing fuel, distillate (or "gas oil") for atomizing burners, and more viscous blends and residuals for commerce and heavy industry. Typical specifications are as follows.

Specifier	Number	Category
Canadian Government Specification Board, Department of Defense Production, Ottawa, Canada	3-GP-2	Fuel oil, heating
Deutschen Normenauschusses, Berlin 15	DIN 51603	Heating (fuel) oils
British Standards Institution, British Standards House, 2 Park Street, London, WIA 2BS	B.S. 2869	Petroleum fuels for oil engines and burners
Japan	JIS K2203 JIS K2204 JIS K2205	Kerosene Gas oil Fuel oils
Federal specifications, United States	ASTM D 396	Fuel oil, burner

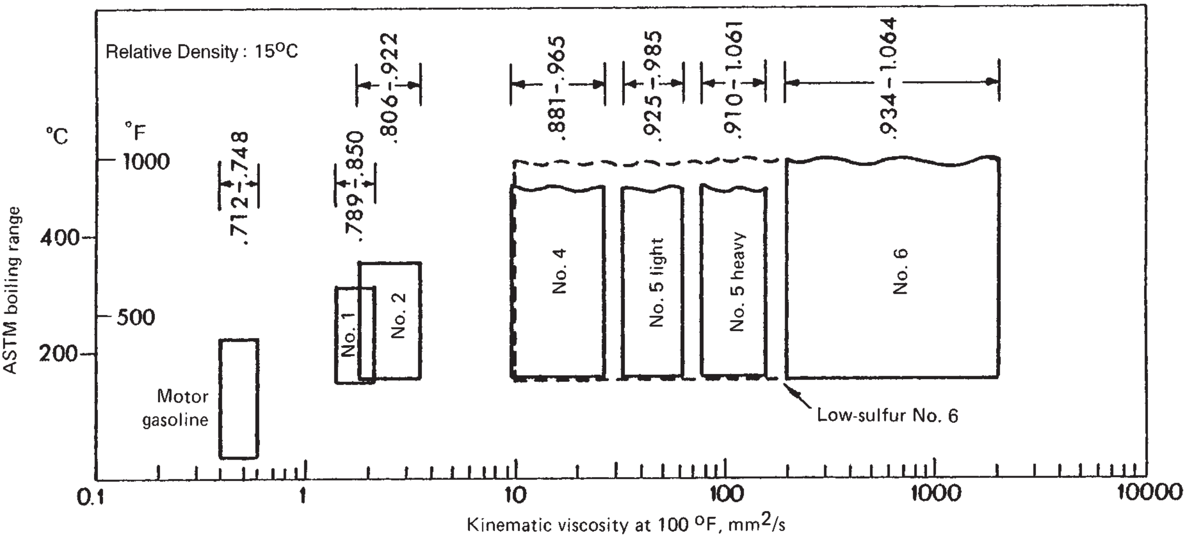


FIG. 27-2 Viscosity, boiling-range, and gravity relationships for petroleum fuels.

TABLE 27-5 Detailed Requirements for Fuel Oils[a]

Property	ASTM test method[b]	No. 1	No. 2	Grade No. 4 (light)	No. 4	No. 5 (light)	No. 5 (heavy)	No. 6
Flash point, °C, min.	D 93	38	38	38	55	55	55	60
Water and sediment, % vol. max.	D 1796	0.05	0.05	(0.50)[c]	(0.50)[c]	(1.00)[c]	(1.00)[c]	(2.00)[c]
Distillation temperature, °C	D 86							
10% vol. recovered, max.		215	—	—	—	—	—	—
90% vol. recovered, min.			282	—	—	—	—	—
max.		288	338	—	—	—	—	—
Kinematic viscosity at 40°C (104°F), mm^2/s	D 445	—	—	—	—	—	—	—
min.		1.3	1.9	1.9	>5.5	—	—	—
max.		2.1	3.4	5.5	24.0[d]	—	—	—
Kinematic viscosity at 100°C (212°F), mm^2/s								
min.	—	—	—	—	—	5.0	9.0	15.0
max.	—	—	—	—	—	8.9[d]	14.9[d]	50.0[d]
Ramsbottom carbon residue on 10% distillation residue, % mass, max.	D 524	0.15	0.35	—	—	—	—	—
Ash, % mass, max.	D 482	—	—	0.05	0.10	0.15	0.15	—
Sulfur, % mass max[e]	D 129	0.50	0.50	—	—	—	—	—
Copper strip corrosion rating, max., 3 h at 50°C	D 130	No. 3	No. 3	—	—	—	—	—
Density at 15°C, kg/m^3	D 1298							
min.		—	—	>876[f]	—	—	—	—
max.		850	876	—	—	—	—	—
Pour point °C, max[g]	D 97	−18	−6	6	−6	—	—	[h]

[a] Source ASTM D 396-92. It is the intent of these classifications that failure to meet any requirement of a given grade does not automatically place an oil in the next lower grade unless in fact it meets all requirements of the lower grade. However, to meet special operating conditions modifications of individual limiting requirements may be agreed upon among the purchaser, seller, and manufacturer. Copyright ASTM. Reprinted with permission.

[b] The test methods indicated are the approved referee methods. Other acceptable methods are indicated in Section 2 and 5.1.

[c] The amount of water by distillation by Test Method D 95 plus the sediment by extraction by Test Method D 473 shall not exceed the value shown in the table. For Grade No. 6 fuel oil, the amount of sediment by extraction shall not exceed 0.5 mass % and a deduction in quantity shall be made for all water and sediment in excess of 1.0 mass %.

[d] Where low sulfur fuel oil is required, fuel oil falling in the viscosity range of a lower-numbered grade down to and including No. 4 can be supplied by agreement between the purchaser and supplier. The viscosity range of the initial shipment shall be identified and advance notice shall be required when changing from one viscosity range to another. This notice shall be in sufficient time to permit the user to make the necessary adjustments.

[e] Other sulfur limits may apply in selected areas in the United States and in other countries.

[f] This limit assures a minimum heating value and also prevents misrepresentation and misapplication of this product as Grade No. 2.

[g] Lower or higher pour points can be specified whenever required by conditions of storage or use. When a pour point less than −18°C is specified, the minimum viscosity at 40°C for grade No. 2 shall be 1.7 mm^2/s and the minimum 90% recovered temperature shall be waived. (Add 273 to °C to obtain K.)

[h] Where low sulfur fuel oil is required, Grade No. 6 fuel oil will be classified as *low pour* (+15°C max.) or *high pour* (no max.). Low-pour fuel oil should be used unless tanks and lines are heated.

Foreign specifications are generally available from the American National Standards Institute, New York; United States federal specifications, at Naval Publications and Forms, Philadelphia.

Equipment manufacturers and large-volume users often write fuel specifications to suit particular equipment, operating conditions, and economics. Nonstandard test procedures and restrictive test limits should be avoided; they reduce the availability of fuel and increase its cost.

Bunker-fuel specifications for merchant vessels are described by ASTM D 2069, Standard Specification for Marine Fuels. Deep draft vessels carry residual (e.g., No. 6 fuel oil) or distillate-residual blend for main propulsion, plus distillate for start-up, shutdown, maneuvering, deck engines, and diesel generators. Main-propulsion fuel is identified principally by its viscosity in centistokes at 373 K. Obsolete designations include those based on Redwood No. 1 seconds at 100°F (311 K) (e.g., "MD 1500") and the designations "Bunker A" for No. 5 fuel oil and "Bunker B" and "Bunker C" for No. 6 fuel oil in the lower- and upper-viscosity ranges, respectively.

Chemical and Physical Properties Petroleum fuels contain paraffins, isoparaffins, naphthenes, and aromatics, plus organic sulfur, oxygen, and nitrogen compounds that were not removed by refining. Olefins are absent or negligible except when created by severe refining. Vacuum-tower distillate with a final boiling point equivalent to 730 to 840 K (850 to 1050°F) at atmospheric pressure may contain from 0.1 to 0.5 ppm vanadium and nickel, but these metal-bearing compounds do not distill into No. 1 and 2 fuel oils.

Black, viscous residuum directly from the still at 410 K (390°F) or higher serves as fuel in nearby furnaces or may be cooled and blended to make commercial fuels. Diluted with 5 to 20 percent distillate, the blend is No. 6 fuel oil. With 20 to 50 percent distillate, it becomes No. 4 and No. 5 fuel oils for commercial use, as in schools and apartment houses. Distillate-residual blends also serve as diesel fuel in large stationary and marine engines. However, distillates with inadequate solvent power will precipitate asphaltenes and other high-molecular-weight colloids from *visbroken* (severely heated) residuals. A blotter test, ASTM D 4740, will detect sludge in pilot blends. Tests employing centrifuges, filtration (D 4870), and microscopic examination have also been used.

No. 6 fuel oil contains from 10 to 500 ppm vanadium and nickel in complex organic molecules, principally porphyrins. These cannot be removed economically, except incidentally during severe hydrodesulfurization (Amero, Silver, and Yanik, *Hydrodesulfurized Residual Oils as Gas Turbine Fuels,* ASME Pap. 75-WA/GT-8). Salt, sand, rust, and dirt may also be present, giving No. 6 a typical ash content of 0.01 to 0.5 percent by weight.

Ultimate analyses of some typical fuels are shown in Table 27-6.

The hydrogen content of petroleum fuels can be calculated from density with the following formula, with an accuracy of about 1 percent for petroleum liquids that contain no sulfur, water, or ash:

$$H = 26 - 15s \tag{27-9}$$

where H = percent hydrogen and s = relative density at 15°C (with respect to water), also referred to as specific gravity. Schmidt (*Fuel Oil Manual,* 3d ed., Industrial Press, New York, 1969) claims improved precision of the formula by replacing 26 with different constants.

Relative density (288 K)	API gravity	Constant
1.0754–1.0065	0–9	24.50
1.0065–0.9935	10–20	25.00
0.9935–0.8757	21–30	25.20
0.8757–0.8013	31–45	25.45

Relative density is usually determined at ambient temperature with specialized hydrometers. In the United States these hydrometers commonly are graduated in an arbitrary scale termed *degrees API.* This scale relates inversely to relative density s (at 60°F) as follows (see also the abscissa scale of Fig. 27-3):

TABLE 27-6 Typical Ultimate Analyses of Petroleum Fuels

Composition, %	No. 1 fuel oil (41.5° A.P.I.)	No. 2 fuel oil (33° A.P.I.)	No. 4 fuel oil (23.2° A.P.I.)	Low sulfur, No. 6 F.O. (12.6° A.P.I.)	High sulfur, No. 6 (15.5° A.P.I.)
Carbon	86.4	87.3	86.47	87.26	84.67
Hydrogen	13.6	12.6	11.65	10.49	11.02
Oxygen	0.01	0.04	0.27	0.64	0.38
Nitrogen	0.003	0.006	0.24	0.28	0.18
Sulfur	0.09	0.22	1.35	0.84	3.97
Ash	<0.01	<0.01	0.02	0.04	0.02
C/H Ratio	6.35	6.93	7.42	8.31	7.62

NOTE: The C/H ratio is a weight ratio.

$$\text{Degrees API} = \frac{141.5}{s} - 131.5 \qquad (27\text{-}10)$$

For practical engineering purposes, relative density at 15°C (288 K), widely used in countries outside the United States, is considered equivalent to specific gravity at 60°F (288.6 K). With the adoption of SI units, the American Petroleum Institute favors absolute density at 288 K instead of degrees API.

The hydrogen content, heat of combustion, specific heat, and thermal conductivity data herein were abstracted from Bureau of Standards Miscellaneous Publication 97, *Thermal Properties of Petroleum Products*. These data are widely used, although other correlations have appeared, notably that by Linden and Othmer (*Chem. Eng.* **54**[4, 5], April and May, 1947).

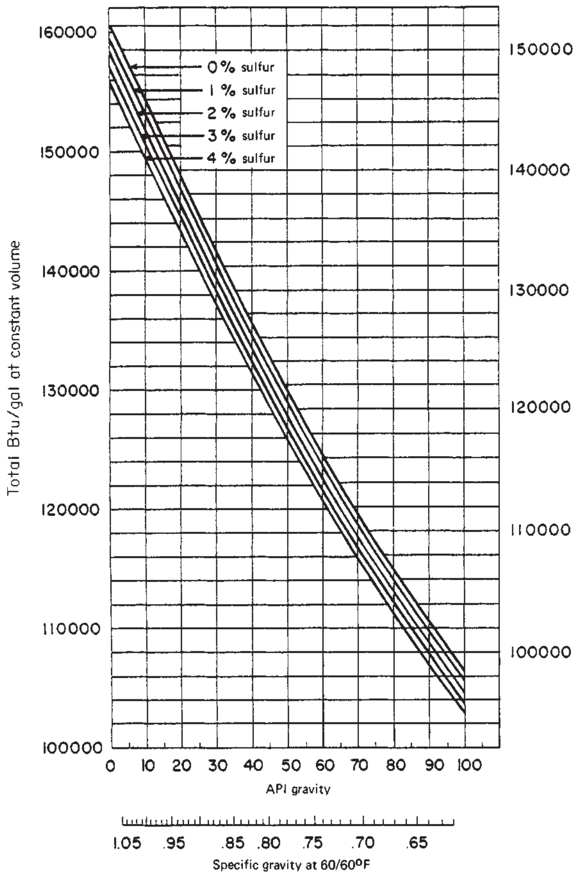


FIG. 27-3 Heat of combustion of petroleum fuels. To convert Btu/US gal to kJ/m^3, multiply by 278.7.

Heat of combustion can be estimated within 1 percent from the relative density of the fuel by using Fig. 27-3. Corrections for water and sediment must be applied for residual fuels, but they are insignificant for clean distillates.

Pour point ranges from 213 K (−80°F) for some kerosene-type jet fuels to 319 K (115°F) for waxy No. 6 fuel oils. *Cloud point* (which is not measured on opaque fuels) is typically 3 to 8 K higher than pour point unless the pour has been depressed by additives. Typical petroleum fuels are practically newtonian liquids between the cloud point and the boiling point and at pressures below 6.9 MPa (1000 psia).

Fuel systems for No. 1 (kerosene) and No. 2 fuel oil (diesel, home heating oil) are not heated. Systems for No. 6 fuel oil are usually designed to preheat the fuel to 300 to 320 K (90 to 120°F) to reduce viscosity for handling and to 350 to 370 K (165 to 200°F) to reduce viscosity further for proper atomization. No. 5 fuel oil may also be heated, but preheating is usually not required for No. 4. (See Table 27-5.) Steam or electric heating is employed as dictated by economics, climatic conditions, length of storage time, and frequency of use. Pressure relief arrangements are recommended on sections of heated pipelines when fuel could be inadvertently trapped between valves.

The *kinematic viscosity* of a typical No. 6 fuel oil declines from 5000 mm^2/s (0.054 ft^2/s) at 298 K (77°F) to about 700 mm^2/s (0.0075 ft^2/s) and 50 mm^2/s (0.000538 ft^2/s) on heating to 323 K (122°F) and 373 K (212°F), respectively. Viscosity of 1000 mm^2/s or less is required for manageable pumping. Proper boiler atomization requires a viscosity between 15 and 65 mm^2/s.

Thermal expansion of petroleum fuels can be estimated as volume change per unit volume per degree. ASTM-IP Petroleum Measurement Tables (ASTM D 1250 IP 200) are used for volume corrections in commercial transactions.

Heat capacity (specific heat) of petroleum liquids between 0 and 205°C (32 and 400°F), having a relative density of 0.75 to 0.96 at 15°C (60°F), can be calculated within 2 to 4 percent of the experimental values from the following equations:

$$c = \frac{1.685 + (0.039 \times {}^\circ\text{C})}{\sqrt{s}} \qquad (27\text{-}11)$$

$$c' = \frac{0.388 + (0.00045 \times {}^\circ\text{F})}{\sqrt{s}} \qquad (27\text{-}12)$$

where c is heat capacity, kJ/(kg·°C) or kJ/(kg·K), and c' is heat capacity, Btu/(lb·°F). Heat capacity varies with temperature, and the arithmetic average of the values at the initial and final temperatures can be used for calculations relating to the heating or cooling of oil.

The *thermal conductivity* of liquid petroleum products is given in Fig. 27-4. Thermal conductivities for asphalt and paraffin wax in their solid states are 0.17 and 0.23 W/(m·K), respectively, for temperatures above 273 K (32°F) (1.2 and 1.6 Btu/[h·ft^2][°F/in]).

Commercial Considerations Fuels are sold in gallons and in multiples of the 42-gal barrel (0.159 m^3) in the United States, while a weight basis is used in other parts of the world. Transactions exceeding about 20 to 40 m^3 (5000 to 10,000 US gal) usually involve volume corrections to 288 K (60°F) for accounting purposes. Fuel passes through an air eliminator and mechanical meter when loaded into or dispensed from trucks. Larger transfers such as pipeline, barge, or tanker movements are measured by fuel depth and *strapping tables* (calibration tables) in tanks and vessels, but positive-displacement

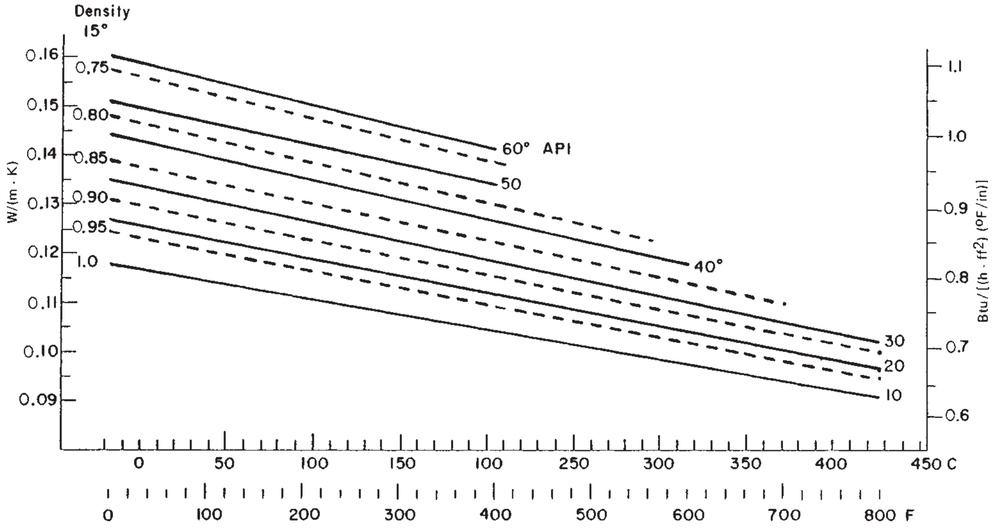


FIG. 27-4 Thermal conductivity of petroleum liquids. The solid lines refer to density expressed as degrees API; the broken lines refer to relative density at 288 K (15°C). (K = [°F + 459.7]/1.8)

meters that are *proved* (calibrated) frequently are gaining acceptance. After an appropriate settling period, water in the tank bottom is measured with a plumb bob or stick smeared with water-detecting paste.

Receipts of tank-car quantities or larger are usually checked for gravity, appearance, and flash point to confirm product identification and absence of contamination.

Safety Considerations Design and location of storage tanks, vents, piping, and connections are specified by state fire marshals, underwriters codes, and local ordinances. In NFPA 30, *Flammable and Combustible Liquids Code, 1993* (published by the National Fire Protection Association, Quincy, Mass.), liquid petroleum fuels are classified as follows for safety in handling:

Class I (flammable) liquid has a flash point below 311 K (100°F) and a vapor pressure not exceeding 0.28 MPa at 311 K (40 psia at 100°F).

Class IA includes those liquids having flash points below 296 K (73°F) and boiling points below 311 K (100°F).

Class IB liquids have flash points below 296 K (73°F) and boiling points at or above 311 K (100°F).

Class IC includes those liquids having flash points at or above 296 K (73°F) and below 311 K (100°F).

Class II combustible liquids have flash points at or above 311 K (100°F) and below 333 K (140°F).

Class IIIA combustible liquids have flash points at or above 333 K (140°F) and below 366 K (200°F).

Class IIIB liquids flash at or above 366 K (200°F).

NFPA 30 details the design features and safe placement of handling equipment for flammable and combustible liquids.

Crude oils with flash points below 311 K (100°F) have been used in place of No. 6 fuel oil. Different pumps may be required because of low fuel viscosity.

Nonpetroleum Liquid Fuels

Tar Sands Canadian tar sands are strip-mined and extracted with hot water to recover heavy oil (bitumen). The oil is processed into naphtha, kerosene, and gasoline fractions (which are hydrotreated), in addition to gas (which is recovered). Tar sands are being developed in Utah also.

Oil Shale Oil shale is nonporous rock containing organic kerogen. Raw shale oil is extracted from mined rock by pyrolysis in a surface retort, or in situ by steam injection after breaking up the rock with explosives. Pyrolysis cracks the kerogen, yielding raw shale oil high in nitrogen, oxygen, and sulfur. *Shale oil* has been hydrotreated and refined in demonstration tests into relatively conventional fuels. Refining in petroleum facilities is possible, and blending with petroleum is most likely.

Coal-Derived Fuels Liquid fuels derived from coal range from highly aromatic coal tars to liquids resembling petroleum. Raw liquids from different hydrogenation processes show variations that reflect the degree of hydrogenation achieved. Also, the raw liquids can be further hydrogenated to refined products. Properties and cost depend on the degree of hydrogenation and the boiling range of the fraction selected. A proper balance between fuel upgrading and equipment modification is essential for the most economical use of coal liquids in boilers, industrial furnaces, diesels, and stationary gas turbines.

Coal-tar fuels are high-boiling fractions of crude tar from pyrolysis in coke ovens and coal retorts. Grades range from free-flowing liquids to pulverizable pitch. Low in sulfur and ash, they contain hydrocarbons, phenols, and heterocyclic nitrogen and oxygen compounds. Being more aromatic than petroleum fuels, they burn with a more luminous flame. From 288 to 477 K (60 to 400°F) properties include:

Heat capacity	1.47–1.67 kJ/(kg·K) (0.35–0.40 Btu/[lb·°F])
Thermal conductivity	0.14–0.15 W/(m·K) (0.080–0.085 Btu/[h·ft·°F])
Heat of vaporization	349 kJ/kg (150 Btu/lb)
Heat of fusion	Nil

Table 27-7 shows representative data for liquid fuels from tar sands, oil shale, and coal.

GASEOUS FUELS

Natural Gas Natural gas is a combustible gas that occurs in porous rock of the earth's crust and is found with or near accumulations of crude oil. It may occur alone in separate reservoirs, but more commonly it forms a gas cap entrapped between petroleum and an impervious, capping rock layer in a petroleum reservoir. Under high-pressure conditions, it is mixed with or dissolved in crude oil. Natural gas termed *dry* has less than 0.013 dm^3/m^3 (0.1 gal/1000 ft^3) of gasoline. Above this amount, it is termed *wet.*

The proven reserves of natural gas in the United States total about 4.58 Tm^3 (1.62×10^{14} ft^3). Production in 1993 was about 0.51 Tm^3 (1.8×10^{13} ft^3). Revisions and adjustments to the existing resource base, together with modest new additions to proven reserves, have held the recent decline in reserves to about 1.6 percent per year.

Natural gas consists of hydrocarbons with a very low boiling point.

TABLE 27-7 Characteristics of Typical Nonpetroleum Fuels

	Conventional coal-tar fuels from retorting[a]		Typical coal-derived fuels with different levels of hydrogenation[b]					Synthetic crude oils, by hydrogenation	
	CTF 50	CTF 400	Minimal		Mild	Mild[c]	Severe	Oil shale	Tar sands[d]
Distillation range, °C			175–280	280–500	160–415	175–400	125–495		
Density, kg/m³, 15°C	1.018	1.234	0.974	1.072	0.964	0.9607	0.914	0.817	0.864
lb U.S. gal, 60°F	8.5	10.3	8.1	8.9	8.0	8.0	7.6	6.8	7.2
Viscosity, mm²/s	2–9	9–18	3.1–3.4	50–90	3.6	—	2.18		
	At 38°C	At 121°C	At 38°C	At 38°C	At 38°C	—	At 38°C		
Ultimate analysis, %									
Carbon	87.4	90.1	86.0	89.1	87.8	89.6	89.0	86.1	87.1
Hydrogen	7.9	5.4	9.1	7.5	9.7	10.1	11.1	13.84	12.69
Oxygen	3.6	2.4	3.6–4.3	1.4–1.8	2.4	0.3	0.5	0.12	0.04
Nitrogen	0.9	1.4	0.9–1.1	1.2–1.4	0.6	0.04	0.09	0.01	0.07
Sulfur	0.2	0.7	<0.2	0.4–0.5	0.07	0.004	0.04	0.02	0.10
Ash[e]	Trace	0.15	<0.001	[f]					
C/H ratio, weight	11.0	16.5	9.4	11.9	9.1	8.9	8.0	6.2	6.9
Gross calorific value, MJ/kg	38.4–40.7	36.8–37.9							
Btu/lb	16,500–17,500	15,800–16,300							

[a] CTF 50 and 400 indicate approximate preheat temperature, °F, for atomization of fuel in burners (terminology used in British Standard B.S. 1469).

[b] Properties depend on distillation range, as shown, and to a lesser extent on coal source.

[c] Using recycle-solvent process.

[d] Tar sands, although a form of petroleum, are included in this table for comparison.

[e] Inorganic mineral constituents of coal tar fuel:
5 to 50 ppm: Ca, Fe, Pb, Zn (Na, in tar treated with soda ash)
0.05 to 5 ppm: Al, Bi, Cu, Mg, Mn, K, Si, Na, Sn
Less than 0.05 ppm: As, B, Cr, Ge, Ti, V, Mo
Not detected: Sb, Ba, Be, Cd, Co, Ni, Sr, W, Zr

[f] Inherent ash is "trace" or "<0.1%," although entrainment in distillation has given values as high as 0.03 to 0.1%.

Methane is the main constituent, with a boiling point of 119 K (−245°F). Ethane, with a boiling point of 184 K (−128°F) may be present in amounts up to 10 percent; propane, with a boiling point of 231 K (−44°F), up to 3 percent. Butane, pentane, hexane, heptane, and octane may also be present. Physical properties of these hydrocarbons are given in Sec. 2.

Although there is no single composition that may be called "typical" natural gas, Table 27-8 shows the range of compositions in large cities in the United States.

Most natural gas is substantially free of sulfur compounds; the terms *sweet* and *sour* are used to denote the absence or presence of H_2S. Some wells, however, deliver gas containing levels of hydrogen sulfide and other sulfur compounds (e.g., thiophenes, mercaptans, and organic sulfides) that must be removed before transfer to commercial pipelines. Pipeline-company contracts typically specify maximum allowable limits of impurities; H_2S and total sulfur compounds seldom exceed 0.023 and 0.46 g/m³ (1.0 and 20.0 gr/100 std ft³), respectively. The majority of pipeline companies responding to a 1994 survey limited H_2S to less than 0.007 g/m³ (0.3 gr/100 std ft³), but a slightly smaller number continued specifying 0.023 g/m³, in accord with an American Gas Association 1971 recommendation.

TABLE 27-8 Analysis of Natural Gas*

	Range†	
	Low	High
Composition, vol %		
Methane	86.3	95.2
Ethane	2.5	8.1
Propane	0.6	2.8
Butanes	0.13	0.66
Pentanes	0	0.44
Hexanes plus	0	0.09
CO_2	0	1.1
N_2	0.31	2.47
He	0.01	0.06
Heating value MJ/m³ (Btu/ft³)	38.15(1024)	40.72(1093)
Specific gravity Ref.: Air at 288 K (60°F)	0.586	0.641

[*] Adapted from *Gas Engineers Handbook,* American Gas Association, Industrial Press, New York, 1965.

[†] Ranges are the high and low values of annual averages reported by 13 utilities (1954 data).

Compressibility of Natural Gas All gases deviate from the perfect gas law at some combinations of temperature and pressure, the extent depending on the gas. This behavior is described by a dimensionless compressibility factor Z that corrects the perfect gas law for real-gas behavior, $PV = ZRT$. Any consistent units may be used. Z is unity for an ideal gas, but for a real gas, Z has values ranging from less than 1 to greater than 1, depending on temperature and pressure. The compressibility factor is described further in Secs. 2 and 4 of this handbook.

Because the value of Z for natural gas is significantly less than unity at ambient temperatures and at pressures greater than 1 MPa (145 psia), the compressibility must be taken into account in gas measurement: gas purchased at high line pressure will give a greater volume when the pressure is reduced than it would if the gas were ideal. Natural gas pipeline operators use a *supercompressibility* factor, also called *Z,* but defined as

$$Z = \left(\frac{RT}{PV}\right)^{1/2} \tag{27-13}$$

which is convenient for use with differential pressure flowmeters but sometimes a source of confusion. For determining compressibility factors of natural-gas mixtures, see *Manual for the Determination of Supercompressibility Factors for Natural Gas*, American Gas Association, New York, 1963; and A.G.A Gas Measurement Committee Report No. 3, 1969.

Liquefied Natural Gas The advantages of storing and shipping natural gas in liquefied form (LNG) derive from the fact that 0.035 m³ (1 ft³) of liquid methane at 111 K (−260°F) equals about 18 m³ (630 ft³) of gaseous methane. Temperatures higher than 111 K can be used if the liquid is stored under pressure. For example, the liquid state is maintained at 2.24 MPa (325 psia) and 170 K (−155°F). The critical temperature of methane is 191 K (−160°F), and the corresponding critical pressure is 4.64 MPa (673 psia). One cubic meter (264 US gal) weighs 412 kg (910 lb) at 109 K (−263°F). The heating value is about 24 GJ/m³ (86,000 Btu/US gal).

The heat of vaporization of LNG at 0.1 MPa (1 bar) is 232 MJ/m³

(832 Btu/US gal) of liquid. On a product gas basis, the heat required is about 0.3 kJ/m^3 (10 Btu/std ft^3) of gas produced.

LNG is stored in metal double-wall or prestressed concrete tanks, frozen earth, or mined quarries or caverns.

Liquefied Petroleum Gas The term *liquefied petroleum gas* (LPG) is applied to certain specific hydrocarbons which can be liquefied under moderate pressure at normal temperatures but are gaseous under normal atmospheric conditions. The chief constituents of LPG are propane, propylene, butane, butylene, and isobutane. LPG produced in the separation of heavier hydrocarbons from natural gas is mainly of the paraffinic (saturated) series. LPG derived from oil-refinery gas may contain varying low amounts of olefinic (unsaturated) hydrocarbons.

LPG is widely used for domestic service, supplied either in tanks or by pipelines. It is also used to augment natural-gas deliveries on peak days and by some industries as a standby fuel.

Other Gaseous Fuels

Hydrogen Hydrogen is used extensively in the production of ammonia and chemicals, in the hydrogenation of fats and oils, and as an oven reducing atmosphere. It is also used as a fuel in industrial cutting and welding operations. There are no resources of uncombined hydrogen as there are of the other fuels. It is made industrially by the steam reforming of natural gas, as the by-product of industrial operations such as the thermal cracking of hydrocarbons and the production of chlorine, and, to a lesser extent, by the electrolysis of water, which is a practically inexhaustible source.

Hydrogen is seen as the ultimate nonpolluting form of energy; when electrochemically combined with oxygen in fuel cells, only water, heat, and electricity are produced. Means for transforming the world's fossil energy economy into a hydrogen economy are being considered as a long-term option. Hydrogen can be stored in gaseous, liquid, or solid forms; however, currently available technologies are not suited to meet mass energy market needs. Technologies for economically producing, storing, and utilizing hydrogen are being researched in the United States, Europe, and Japan.

Acetylene Acetylene is used primarily in operations requiring high flame temperature, such as welding and metal cutting. To transport acetylene, it is dissolved in acetone under pressure and drawn into small containers filled with porous material.

Miscellaneous Fuels A variety of gases have very minor market shares. These include reformed gas, oil gases, producer gas, blue water gas, carbureted water gas, coal gas, and blast-furnace gas. The heating values of these gases range from 3.4 to 41 MJ/m^3 (90 to 1100 Btu/ft^3). They are produced by pyrolysis, the water gas reaction, or as by-products of pig-iron production.

Hydrogen sulfide in manufactured gases may range from approximately 2.30 g/m^3 (100 gr/100 ft^3) in blue and carbureted water gas to several hundred grains in coal- and coke-oven gases. Another important sulfur impurity is carbon disulfide, which may be present in amounts varying from 0.007 to 0.07 percent by volume. Smaller amounts of carbon oxysulfide, mercaptans, and thiophene may be found. However, most of the impurities are removed during the purification process and either do not exist in the finished product or are present in only trace amounts.

FUEL AND ENERGY COSTS

Fuel costs vary widely from one area to another because of the cost of the fuel itself and the cost of transportation. Any meaningful cost comparison between fuels requires current costs based on such factors as the amounts used at a particular geographical location, utilization efficiencies or energy-ratio data for the equipment involved, and the effects of "form value." Although the costs given in Table 27-9 do not apply to specific locations, they give fuel-cost trends.

COAL CONVERSION

Coal is the most abundant fossil fuel, and it will be available long after petroleum and natural gas are scarce. However, because liquids and gases are more desirable fuel forms, technologies to convert coal into synthetic liquid and gaseous fuels have been developed. Current research, development, and demonstration efforts are aimed toward technical and economic improvements in some of the old, or first-generation, technologies and toward seeking new ways to accomplish the same ends: inexpensive and "clean" coal-conversion processes. However, as long as the price of petroleum remains near current levels, coal gasification and liquefaction technologies will remain uneconomic.

TABLE 27-9 Time-Price Relationships for Fossil Fuels

Year	Bituminous coal and lignite, \$/Mg (\$/US ton)	Natural gas at the wellhead, \$/1000 m^3 (\$/1000 std ft^3)	Crude oil, domestic first purchase price, \$/m^3 (\$/bbl)
1975	21.15 (19.23)	15.55 (0.44)	48.23 (7.67)
1980	26.97 (24.52)	56.18 (1.59)	135.79 (21.59)
1985	27.61 (25.10)	88.69 (2.51)	151.51 (24.09)
1990	23.88 (21.71)	60.42 (1.71)	125.91 (20.03)
1993	21.77 (19.79)	71.73 (2.03)	89.62 (14.25)

SOURCE: *Annual Energy Review 1994,* Energy Information Administration, July 1995. Prices are national averages in current-year U.S. dollars for the year cited.

South Africa has the only commercial plant producing liquid transportation fuels and other products from coal. This technology will be described later.

Bodle, Vyas, and Talwalker (*Clean Fuels from Coal Symposium II,* Institute of Gas Technology, Chicago, 1975) presented the chart in Fig. 27-5, which shows very simply the different routes from coal to clean gases and liquids.

Coal Gasification

GENERAL REFERENCES: *Fuel Gasification Symp.*, 152d American Chemical Society Mtg., Sept. 1966. *Chemistry of Coal Utilization,* suppl. vol., Lowry (ed.), Wiley, New York, 1963; and 2d suppl. vol., Elliot (ed.), 1981. *Coal Gasification Guidebook: Status, Applications, and Technologies,* Electric Power Research Institute, EPRI TR-102034, Palo Alto, Calif., 1993. Notestein, *Commercial Gasifier for IGCC Applications Study Report,* U.S. Dept. of Energy, DOE/METC-91/6118, Morgantown Energy Technology Center, Morgantown, W. Va., 1990.

Background Converting coal to combustible gas has been practiced commercially since the early nineteenth century. The first gas-producing companies were chartered in 1812 in England and in 1816 in the United States to produce gas for illumination by the heating or pyrolysis of coal. This method of producing gas is still in use: the gas is a by-product of the carbonization of coal to manufacture coke for metallurgical purposes.

The advantages of a gaseous fuel as a source of heat and power increased the demand for gas and led to the invention of other methods of coal gasification. In the gas producer, introduced in the second half of the century, a downward-moving bed of coal or coke is reacted at atmospheric pressure with air and steam to create a fuel gas with a low heat value, in the range 3.4 to 6.0 MJ/m^3 (90 to 160 Btu/ft^3). Producer gas, as the product was named, soon enjoyed extensive industrial use, especially in steel manufacture. Gas producers, largely displaced by twentieth-century technology, are still employed in steel mills. A small version enhanced with modern handling and other technical improvements, the Wellman-Galusha producer, enjoys substantial use in small industry.

Driven by the same impetus, the development of the cyclic water-gas process in 1873 permitted the continuous production of gas of higher thermal content, about 13.0 MJ/m^3 (350 Btu/ft^3). Adding oil to the reactor increased the thermal content of the gas to 20.5 MJ/m^3 (550 But/ft^3). This type of fuel gas, carbureted water gas, was distributed in urban areas of the United States for residential and commercial uses until its displacement by lower-cost natural gas began in the 1940s. At approximately that time, development of oxygen-based gasification processes was initiated in the United States and in other countries. An early gasification process developed by Lurgi Kohle u Mineralöltechnik GmbH, which operated at elevated pressure, is still in use. Compositions of the coal gases produced by these methods,

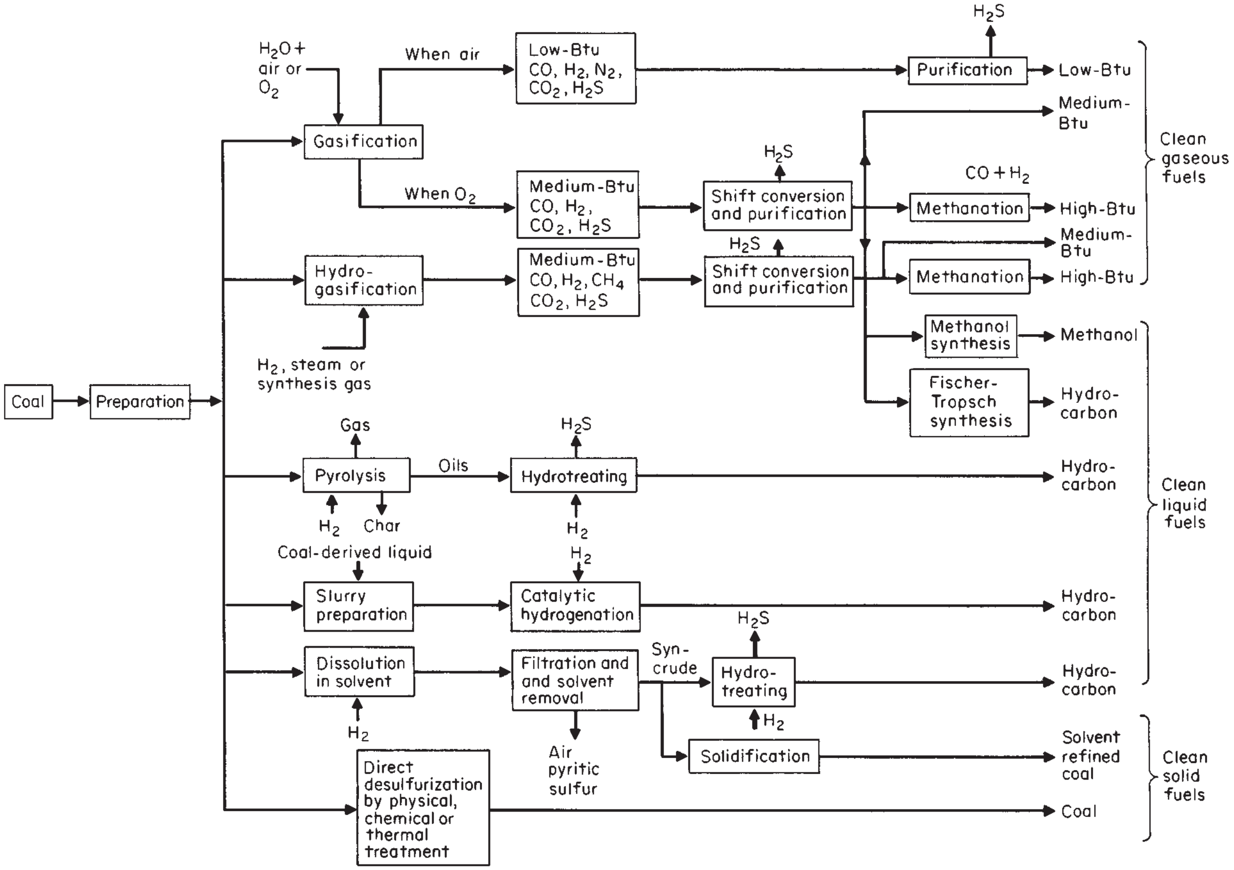


FIG. 27-5 The production of clean fuels from coal. (*Based on W. Bodle, K. Vyas, and A. Talwalker,* Clean Fuels from Coal Symposium II, *Institute of Gas Technology, Chicago, 1975.*)

which are referred to as the first-generation gasifiers, are listed in Table 27-10. There are a number of later-generation gasification technologies, as will be described in an ensuing subsection. The compositions of the gases produced by some of them are listed in Table 27-11.

Theoretical Considerations The chemistry of coal gasification can be depicted by conveniently assuming coal as carbon and by listing the several well-known reactions involved; see Table 27-12. Reaction (27-14) is the combustion of carbon and oxygen, which is highly exothermic. This reaction supplies most of the thermal energy for the gasification process. The oxygen may be pure or contained in air. Reactions (27-16) and (27-17) are endothermic and represent the conversion of carbon to combustible gases. These are driven by the heat energy supplied by reaction (27-14).

Hydrogen and carbon monoxide are produced by the gasification reaction, and they react with each other and with carbon. The reaction of hydrogen with carbon as shown in reaction (27-15) is exothermic and can contribute heat energy. Similarly, the methanation reaction (27-19) can contribute heat energy to the gasification. These equations are interrelated by the water-gas-shift reaction (27-18), the equilibrium of which controls the extent of reactions (27-16) and (27-17).

Several authors have shown (cf. Gumz, *Gas Producers and Blast Furnaces,* Wiley, New York, 1950; and Elliott and von Fredersdorff,

TABLE 27-10 Properties of Coal-Derived Gases

	Coke-oven gas	Producer gas	Water gas	Carbureted water gas	Synthetic coal gas
Reactant system	Pyrolysis	Air + steam	Steam (cyclic-air)	Steam + oil (cyclic-air)	Oxygen plus steam at pressure
Analysis, volume %*					
Carbon monoxide, CO	6.8	27.0	42.8	33.4	15.8
Hydrogen, H_2	47.3	14.0	49.9	34.6	40.6
Methane, CH_4	33.9	3.0	0.5	10.4	10.9
Carbon dioxide, CO_2	2.2	4.5	3.0	3.9	31.3
Nitrogen, N_2	6.0	50.9	3.3	7.9	
Other†	3.8	0.5	0.5	9.8	2.4
Fuel value, MJ/m^3	22.0	5.6	11.5	20.0	10.8
Btu/ft^3	(590)	(150)	(308)	(536)	290
Uses	Fuel, chemicals	Fuel	Fuel, chemicals	Fuel	Fuel, chemicals

*Analyses and fuel values vary with the type of coal and operating conditions.
†Other contents include hydrocarbon gases other than methane, hydrogen sulfide, and small amounts of other impurities.

TABLE 27-11 Coal-Derived Gas Compositions

Developer	Lurgi[*]	Texaco[†][a]	BG/L[†][b]	KRW[*]	KRW[*]	Shell[†][c]
Type of bed	Moving	Entrained	Moving	Fluid	Fluid	Entrained
Coal feed form	Dry coal	Coal slurry	Dry coal	Dry coal	Dry coal	Dry coal
Coal type	Illinois #6	Illinois #6	Illinois #6	Illinois #6	Illinois #6	Illinois #5
Oxidant	Oxygen	Oxygen	Oxygen	Air	Oxygen	Oxygen
Pressure, MPa (psia)	0.101 (14.7)	4.22 (612)	2.82 (409)	2.82 (409)	2.82 (409)	2.46 (357)
Ash form	Slag	Slag	Slag	Agglomerate	Agglomerate	Slag
Composition, vol %						
H_2	52.2	30.3	26.4	15.7	27.7	26.7
CO	29.5	39.6	45.8	24.9	54.6	63.1
CO_2	5.6	10.8	2.9	5.3	4.7	1.5
CH_4	4.4	0.1	3.8	0.8	5.8	0.03
Other hydrocarbons	0.3	—	0.2	<0.01	<0.01	—
H_2S	0.9	1.0	1.0	—	1.3	1.3
COS	0.04	0.02	0.1	—	0.1	0.1
$N_2 + Ar$	1.5	1.6	3.3	47.0	1.7	5.2
H_2O	5.1	16.5	16.3	6.2	4.4	2.0
$NH_3 + HCN$	0.5	0.1	0.2	0.02	0.08	0.02
HCl	—	0.02	0.03	—	—	0.03
H_2S:COS	20:1	42:1	11:1	8:1	9:1	9:1

[*] Rath, "Status of Gasification Demonstration Plants," *Proc. 2d Annu. Fuel Cells Contract Review Mtg.*, DOE/METC-9090/6112, p. 91.
[†] *Coal Gasification Guidebook: Status, Applications, and Technologies*, Electric Power Research Institute, EPRI TR-102034, 1993. (*a*) page 5-28; (*b*) page 5-58; (*c*) page 5-48.

Chemistry of Coal Utilization, 2d suppl. vol., Lowry [ed.], Wiley, New York, 1963) that there are three fundamental reactions: the Boudouard reaction (27-17), the heterogeneous water-gas reaction (27-18), and the hydrogasification reaction (27-15). The equilibrium constants for these reactions are sufficient to calculate all the reactions listed.

It is not possible, however, to calculate accurately actual gas composition by using the relationships of reactions (27-14) to (27-19) in Table 27-12. Since the gasification of coal always takes place at elevated temperatures, thermal decomposition (pyrolysis) takes place as coal enters the gasification reactor. Reaction (27-15) treats coal as a compound of carbon and hydrogen and postulates its thermal disintegration to produce carbon (coke) and methane. Reaction (27-21) assumes the stoichiometry of hydrogasifying part of the carbon to produce methane and carbon.

It is possible to utilize these reactions and their relationships with each other for predicting the effects of changes in the operating parameters of gasification. At higher temperatures, endothermic reactions are favored at the expense of exothermic reactions. Methane production will decrease as reactions (27-15) and (27-19) proceed at a lower rate, CO production will be favored, and all reaction rates will increase in the direction in which heat absorption takes place. An increase in pressure will favor those reactions in which the number of moles of products is less than the number of moles of reactants. At higher pressures, production of CO_2 will be favored as well as that of methane. The knowledge of stoichiometry, equilibrium conditions, and rates for these gasification reactions provides a sound basis for modeling and extrapolating gasification systems.

A great deal depends on the gasifier system, coal reactivity and particle size, and method of contacting coal with gaseous reactants (steam and air or oxygen). It is generally believed that oxygen reacts completely in a very short distance from the point at which it is mixed or comes in contact with coal or char. The heat evolved acts to pyrolyze the coal, and the char formed then reacts with carbon dioxide, steam, or other gases formed by combustion and pyrolysis. The assumption made in Table 27-12 that the solid reactant is carbon is probably close to being correct. The conversion of coal to char and the type of char formed affect the kinetics of gas-solid reactions. While the reaction rate does vary with temperature, as in all chemical reactions, the overall rate of reaction is controlled probably by the chemical reaction rate below 1273 K (1832°F). Above this, pore diffusion has an overriding effect, and at very high temperatures surface-film diffusion probably controls. Thus, for many gasification processes the reactivity of the char is quite important. This may depend not only on parent-coal characteristics but also on the method of heating, rate of heating, and particle-gas dynamics.

The importance of these concepts can be illustrated by the extent to which the pyrolysis reactions contribute to gas production. In a moving-bed gasifier (e.g., producer-gas gasifier), the particle is heated through several distinct thermal zones. At the initial heat-up zone, coal carbonization or devolatilization dominates. In the successively hotter zones, char devolatilization, char gasification, and fixed carbon

TABLE 27-12 Chemical Reactions in Coal Gasification

Reaction	Reaction heat, kJ/(kg·mol)	Process	Number
	Solid-gas reactions		
$C + O_2 \rightarrow CO_2$	+393,790	Combustion	(27-14)
$C + 2H_2 \rightarrow CH_4$	+74,900	Hydrogasification	(27-15)
$C + H_2O \rightarrow CO + H_2$	−175,440	Steam-carbon	(27-16)
$C + CO_2 \rightarrow 2CO$	−172,580	Boudouard	(27-17)
	Gas-phase reaction		
$CO + H_2O \rightarrow H_2 + CO_2$	+2,853	Water-gas shift	(27-18)
$CO + 3H_2 \rightarrow CH_4 + H_2O$	+250,340	Methanation	(27-19)
	Pyrolysis and hydropyrolysis		
CH_x	$\left(1 - \frac{X}{4}\right)C + \left(\frac{X}{4}\right)CH_4$	Pyrolysis	(27-20)
$CH_x + m\ H_2$	$\left[1 - \left(\frac{X+2m}{4}\right)\right]C + \left(\frac{X+2m}{4}\right)CH_4$	Hydropyrolysis	(27-21)

combustion are the dominant processes. About 17 percent of total gas production occurs during the coal devolatilization phase, and about 23 percent is produced during char devolatilization. The balance, typically about 60 percent of the total, is produced during the char gasification and combustion phases. This emphasizes the importance of coal quality or reactivity.

Gasifier Types and Characteristics The fundamental chemistry and physics of gasification motivate the design of existing and advanced gasifiers. The equations listed in Table 27-12 show that an appropriate means of contacting a solid particle with a gaseous reactant is expedient, that the transfer of heat within the gasifier (and to the gasifier) is a critical parameter, and that variations in pressure and temperature alter the composition of the gas produced. In addition, the type of coal and the composition of both organic and inorganic constituents have a strong influence on gas composition and applicability of various gasification systems.

The three main types of reactors shown in Fig. 27-6 are in actual commercial use: the moving bed, the fluidized bed, and the entrained bed. The moving bed is often referred to as a *fixed* bed because the coal bed is kept at a constant height. These differ in size, coal feed, reactant and product flows, residence time, and reaction temperature.

Gasification-Based Power Systems Today's single most important driving force for the coal gasification market development is gasification-based power generation, named the *integrated gasification combined-cycle* (IGCC) power system (Fig. 27-7). The coal is crushed prior to gasification and partially burned, through the addition of steam and air or oxygen, to produce the high-temperature (1033 to 2255 K [1400 to 3600°F], depending on the type of gasifier) reducing environment necessary for gasification. The fuel gas passes through a heat recovery and cleanup section where particulate (dust) and sulfur are removed. After cleanup, the fuel gas, composed primarily of hydrogen and carbon oxides, is burned with compressed air and expanded through a gas turbine to generate electricity. Heat is recovered from the turbine's hot exhaust gas to produce steam (at subcritical conditions), which is expanded in a steam turbine for additional electricity generation.

The three basic types of gasifiers already mentioned have been incorporated into IGCC plant designs. Within each gasifier type, the oxidant can be air or oxygen, and the coal feed can be dry or in slurry form. Furthermore, the gas cleanup (i.e., particulate and sulfur removal) can be performed at high temperature (i.e., hot-gas cleanup) or lower temperature (cold-gas cleanup). The constituents of the fuel gas, as well as the pressure and temperature conditions at the gasifier exit, are determined by the type of gasifier employed. The efficiency and economics of an IGCC power system are highly dependent on the various parameters described above.

There are three unique features of the power system depicted in Fig. 27-7. These features assure that the IGCC-based power system is

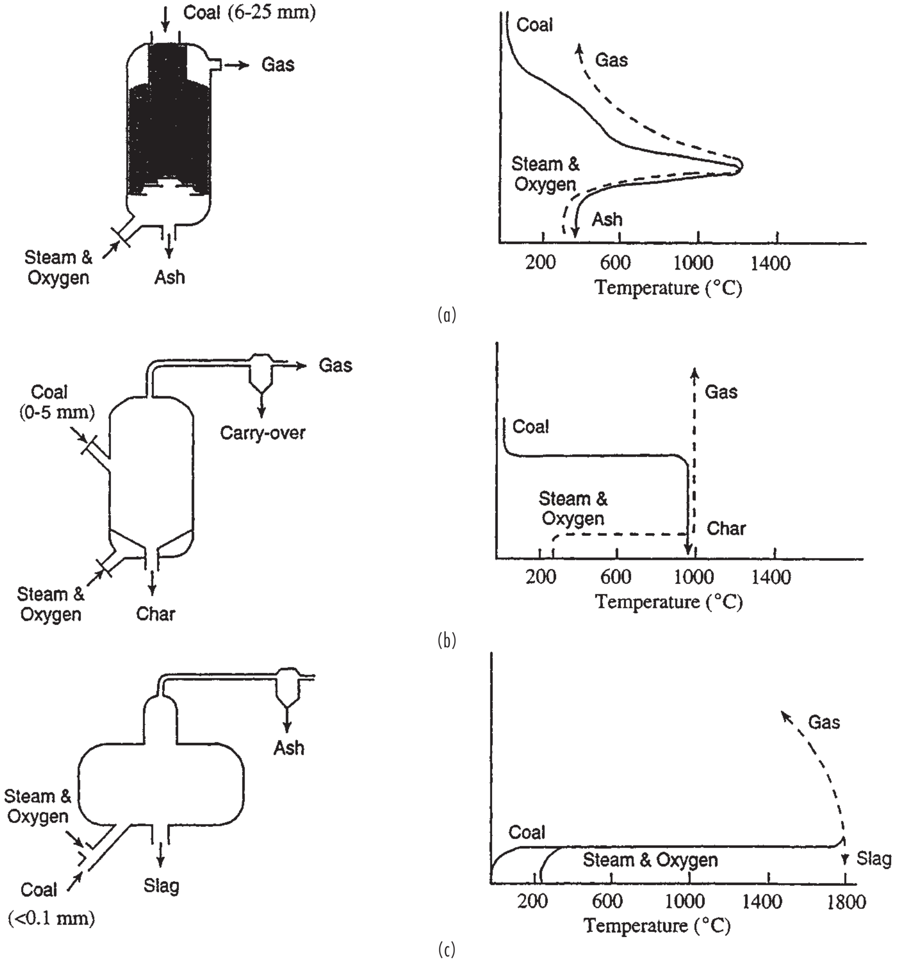


FIG. 27-6 Gasifier types and temperature profiles: (*a*) fixed bed (nonslagging); (*b*) fluidized bed; (*c*) entrained flow. (°C = K − 273)

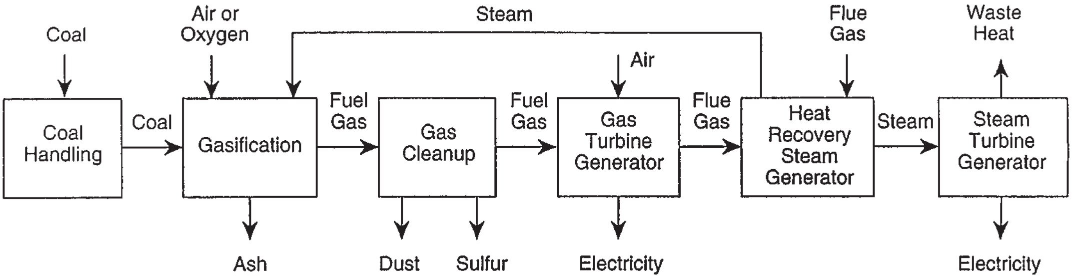


FIG. 27-7 Integrated gasification combined-cycle block diagram.

lower in cost and more thermally efficient than a conventional pulverized-coal combustion system and that it is environmentally superior to it. First, the gas mass flow rate from a gasifier is about one fourth that from a combustor because the former is oxygen-blown and operates substoichiometrically, and the combustor is air-blown and operates with excess air. Because of the elevated operating pressure, the volumetric gas flow to the hydrogen sulfide conversion unit is actually 60 times less than the volumetric flow to the flue gas desulfurization unit, and this lowers the capital cost of the gas cleanup system. Second, the sulfur in coal-derived fuel gas is present as hydrogen sulfide, which can more readily be separated from the fuel gas than sulfur dioxide can be separated from flue gas. Additionally, hydrogen sulfide can be easily converted to elemental sulfur, a more valuable by-product than the calcium sulfate produced when lime is used to remove sulfur dioxide from combustion flue gas. Third, the IGCC system generates electricity by both gas and steam turbines—corresponding to Brayton (gas) and Rankine (steam) cycles—compared to the conventional power plant's steam-only generating system.

Current Status The U.S. Department of Energy (DOE) and its private-sector collaborators have substantially advanced the development of gasification-based power systems during the last decade. This section describes the current status for the various types of gasifiers used.

Moving Bed Depending on the temperature at the base of the coal bed, the ash can either be dry or in the form of molten slag. If excess steam is added, the temperature can be kept below the ash fusion point. In that case the coal bed rests on a rotating grate which allows the dry ash to fall through for removal. To reduce the steam usage, a slagging bottom gasifier has been developed in Scotland by British Gas and Lurgi (BG/L) in which the ash is allowed to melt and drain off through a slag tap. This gasifier has over twice the capacity per unit area of the dry-bottom gasifier. The gas composition from a BG/L gasifier is listed in Table 27-11.

The capacity of the demonstration gasifier in Scotland depends on coal quality; the gasifier can handle a coal input of 750 GJ/h, equivalent to more than 25,000 kg/h (55,115 lb/h) of coal or 70,000 m^3/h (2,500,000 ft^3/h) of gas production. The Clean Energy Demonstration Project, cost-shared by the DOE under the Clean Coal Technology Program, will test the scale-up of the BG/L oxygen-blown, slagging gasifier from demonstration to commercial size. Multiple BG/L units will provide coal gas for a 477-MW IGCC plant to be located on an eastern U.S. site.

Fluidized Bed The possibility of coal and ash agglomeration is eliminated by a fluidized-bed gasifier developed by Westinghouse and M. W. Kellogg. Char and ash that exit the gasifier with the product gas are recycled to the hot agglomerating and jetting zone where temperatures are high enough to pyrolyze fresh coal that is introduced there, gasify the char, and soften the ash particles. The ash particles stick together and fall to the base of the gasifier, where they are cooled and removed. Agglomerating gasifiers achieve better carbon conversion than conventional fluidized-bed gasifiers. The compositions of two gas streams based on air-blown and oxygen-blown gasifiers are listed in Table 27-11.

The agglomerating fluid-bed gasifier can be blown by either air or oxygen at 2.8 MPa (406 psia) pressure. Pressurized operation has several advantages: slightly higher methane formation, resulting in higher heating value of the gas; increased heat from the methanation reactions, which reduces the amount of oxygen needed; reduced heat losses through the wall and, consequently, improved efficiency; and higher generating capacity. Limestone can be added to remove a major portion of the sulfur contained in the coal.

The advanced pressurized fluid-bed gasifiers currently ready for demonstration have internal diameters of around 3.6 m (12 ft) and are 20 to 28 m (66 to 92 ft) in height. Production of more than 100,000 m^3/h of gas (at gasifier temperature and pressure) is achieved by the advanced gasifiers, equivalent to 33,260 kg/h of bituminous coal (air blown).

The KRW (Kellogg-Rust-Westinghouse) gasification process uses an agglomerating-ash fluidized-bed gasifier in which crushed limestone can be injected with the coal for sulfur capture. The Piñon Pine 100-MW IGCC plant built near Reno, Nevada, uses the KRW gasifier. This IGCC plant, scheduled to begin commercial operation in 1997, is being built with U.S. DOE sponsorship under the Clean Coal Technology Program.

Another fluidized-bed gasification technology is the Tampella U-Gas gasifier. This technology was developed by the Institute of Gas Technology (IGT) in Chicago and licensed by the Finnish boiler manufacturer, Tampella. Like the KRW gasifier, it is an air-blown, agglomerating-ash gasifier that uses limestone for in-bed sulfur capture. The two primary differences between the KRW and Tampella gasifiers are the way the gas velocity and temperature in the agglomerating zone are controlled and how the ash and spent limestone discharge is controlled.

Entrained Bed The two primary examples of oxygen-blown, dry-feed, entrained-flow gasifiers are Shell and PRENFLO. These two gasifiers share common roots and are very similar. The gas composition from a Shell gasifier is listed in Table 27-11. An advantage of Shell coal gasification technology is the lack of feed coal limitations. A wide variety of coals (from anthracite to brown coal) have been successfully tested. As with other entrained-flow gasifiers, disadvantages of the Shell process include a high oxygen requirement and a high waste heat recovery duty. However, the ability to feed dry coal reduces the oxygen requirement below that of single-stage entrained-flow gasifiers that use slurry feed and makes the Shell gasifier somewhat more efficient. The penalty for this small efficiency improvement is a more complex coal-feeding system. Like the Shell, the PRENFLO gasification process uses pressurized, dry-feed, entrained-flow technology with water-cooled gasifier vessels. The primary difference between the two processes is in the design of the syngas cooler. While the Shell process uses cooled recycle gas to partially cool the hot syngas before heat recovery, the PRENFLO process uses a radiant water-wall boiler with fins (to increase the surface area for heat transfer) that is connected directly to the gasifier. The PRENFLO gasifier was selected for a 300-MW IGCC project in Puertollano, Spain, to begin operation in 1996. The project is funded by power companies from several European countries and by the European Community.

Cost of Gasification-Based Power Systems In the U.S. power industry the capital cost is usually reported in dollars per kilowatt ($/kW) and the cost of electricity (COE) in mills per kilowatt-hour (a mill is one thousandth of a dollar). Estimation of capital cost and COE is more complex than it seems. The power industry is a regulated industry that uses a different approach than one used by a typical chemical process industry. This approach, an accepted standard procedure in the power industry, is well documented in the *Technical Assessment Guide* (Electric Power Research Institute, EPRI TR-102276-V1 R7, Palo Alto, Calif., 1993). As part of the standard procedure, the assignment of the capital formation structure (i.e., the percentages of bonds, common stock, preferred stock), inflation rate, escalation rate, and assumptions in process and project contingencies are not necessarily the same as those used in the process industry. Process industry practitioners are urged to consult the *Technical Assessment Guide* for more in-depth understanding of capital cost and cost of electricity, as well as meaningful comparisons of different power systems. Comparison of power systems is further complicated by the many different parameters assumed in the cost determination. Cost of coal; sulfur content, moisture content, and other properties of coal; ambient temperature; level of integration between various component units; model of gas turbine; gas cleanup method; year of estimation—all these and other factors may have significant impacts on cost.

While comparison of the absolute capital costs and costs of electricity among different power systems is difficult and uncertain, the structure of these costs is rather typical, and the costs of component units are usually within known ranges. For an oxygen-blown IGCC power system, the breakdown of the capital cost for the four component units is: air separation plant (11 to 17 percent), fuel gas plant (33 to 42 percent), combined-cycle unit (32 to 39 percent), and balance of plant (2 to 21 percent). The breakdown of the cost of electricity is: capital charge (52 to 56 percent), operating and maintenance (14 to 17 percent), and fuel (28 to 32 percent).

The capital investment required for gasification-based power systems is 1400 to 1600 \$/kW (1994 US dollars) and is projected to become less than 1200 \$/kW in the year 2000 because of the higher efficiency associated with gas-turbine combined-cycles currently being designed by turbine vendors.

Development is under way for a gasification-based power system using a cascaded humidified advanced turbine. The power system is the same as the IGCC system in the front end (i.e., the gasification section without heat recovery and the gas-cleanup section) but differs from IGCC in the back end (i.e., the power generation section). Instead of combined steam and gas cycles as used in the IGCC system, the humidified turbine system uses only the gas turbine, eliminating the steam cycle. Because of this simplification and the corresponding elimination of the expensive coal-gas cooler, the power system based on the advanced humidified turbine offers further reduction in the capital investment requirement. Depending upon how the advanced turbine system is configured with the front end section, the capital investment requirement is expected to be on the order of 1000 \$/kW.

Direct Coal Liquefaction

GENERAL REFERENCES: *Chemistry of Coal Utilization*, suppl. vol., Lowry (ed.), Wiley, New York, 1963, and 2d suppl. vol., Elliott (ed.), 1981. Wu and Storch, *Hydrogenation of Coal and Tar*, U.S. Bur. Mines Bull. 633, 1968. Srivastava, McIlvried, Gray, Tomlinson, and Klunder, *American Chemical Society Fuel Chemistry Division Preprints*, Chicago, 1995.

Background The primary objective of any coal-liquefaction process is to increase the hydrogen-to-carbon ratio and remove sulfur, nitrogen, oxygen, and ash. Table 27-13 shows the hydrogen-to-carbon ratios in proceeding from coal to crude petroleum to gasoline, together with the four techniques for accomplishing coal liquefaction. Direct coal liquefaction refers to any process in which coal and hydrogen are directly reacted at high pressure and temperature. A hydrogen donor solvent and/or catalyst may also be present. The first two techniques in Table 27-13 (direct hydrogenation and solvent extraction) follow this approach. A pyrolysis process is included in Table 27-13 for comparison. The fourth technique, catalytic hydrogenation of carbon monoxide, or indirect liquefaction (discussed later in this subsection), first converts coal to synthesis gas, which is purified and reacted over a catalyst to form liquid products. One version of the indirect-liquefaction route converts purified synthesis gas to methanol, for direct fuel use or for conversion to gasoline.

TABLE 27-13 Basic Approaches of Coal Conversion to Liquid Hydrocarbons

1. Direct hydrogenation at elevated temperature and pressure, with or without catalysts
2. Solvent extraction (hydrogen donor)
3. Pyrolysis
4. Catalytic hydrogenation of carbon monoxide

	Bituminous coal	Lignite	Crude petroleum	Gasoline
H/C	0.8	0.7	1.8	1.9

The technology for coal liquefaction to synthetic fuels is not new. In 1913 Dr. Friedrich Bergius discovered the technique of adding hydrogen to coal at a pressure of 20.3 MPa (2940 psia) and a temperature of about 723 K (842°F). Under these conditions most oxygen was hydrogenated to water, some nitrogen to ammonia, and most sulfur to hydrogen sulfide. Hydrogen was also chemically combined with the coal to produce a liquid similar to petroleum. Production of synthetic liquid fuels and chemicals from coal in Germany increased in the mid-1920s, and by 1939 gasoline was being produced by coal hydrogenation in Germany at 910 Gg/a (1×10^6 US ton/a) and in England at 136 Gg/a (150,000 US ton/a). In the early 1950s, the U.S. Bureau of Mines constructed and operated a demonstration plant at Louisiana, Missouri, using the technology of catalytic hydrogenation of coal to produce liquid fuels.

The oil price shocks of the 1970s accelerated the U.S. development of direct coal liquefaction processes to the pilot plant stage (up to 227 Mg/d [250 US ton/d] coal feed rate) of several competing designs, such as the solvent-refined coal (SRC), Exxon donor solvent (EDS), and H-Coal processes. These are discussed briefly in a following subsection. Both the SRC and H-Coal process designs include equipment for generating products ranging from heavy boiler fuels to higher-grade transportation fuels.

In the United States, it became clear after the return of low oil prices in the 1980s that the existing processes would not be able to compete economically, and research proceeded on a smaller scale to improve the efficiency of coal liquefaction for the production of high-value distillate fuels. Key aspects of the process improvement are more effective hydrogen utilization through catalysis and better solids rejection technology. A two-stage concept has been developed that tailors reaction conditions in the first stage to coal solubilization with some cracking, and in the second stage to production of additional liquids with product upgrading. Both supported Ni/Mo catalysts and slurry catalysts are being tested to maximize yields of distillate products that are completely compatible with the existing refinery infrastructure.

A nearer-term variant of direct coal liquefaction is the coprocessing of mixtures of coal and heavy petroleum residua. The coal solids are thought to preferentially "getter" the nickel and vanadium contaminants, typically present in low-value residua, that rapidly poison supported catalysts during conventional resid upgrading. The petroleum component acts as a slurry vehicle for pumping the coal into the reactors, thereby avoiding process recycle requirements. A further advantage is the lowered hydrogen uptake per unit of product. The coprocessing concept can be extended to mixtures of coal and municipal waste such as mixed plastics. Landfill disposal costs are avoided, while, at the same time, carbon values from the waste contribute to the transportation fuel supply.

Direct-Liquefaction Kinetics All direct-liquefaction processes consist of three basic steps: (1) coal slurrying in a vehicle solvent, (2) coal dissolution under high pressure and temperature, and (3) transfer of hydrogen to the dissolved coal. However, the specific reaction pathways and associated kinetics are not known in detail. Overall reaction schemes and semiempirical relationships have been generated by the individual process developers, but applications are process specific and limited to the range of the specific data bases. More extensive research into liquefaction kinetics has been conducted on the laboratory scale, and these results are discussed below.

Depending on its rank, coal can be dissolved in as little as one minute in the temperature range of 623 to 723 K (662 to 842°F) in suitable solvents, which are assumed to promote thermal cracking of the coal into smaller, more readily dissolved fragments. These fragments may be stabilized through reactions with one another or with hydrogen supplied either by a donor solvent or from a gas phase.

Data on Illinois No. 6 and Kentucky No. 9 coals were used by Wen and Han (*Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **20**(1): 216–233, 1975) to obtain a rate equation for coal dissolution under hydrogen pressure. These data included a temperature range of 648 to 773 K (705 to 930°F) and pressures up to 13.8 MPa (2000 psia). An empirical rate expression was proposed as

$$r_A = k_0 \left[\exp\left(\frac{-E}{RT}\right) \cdot \exp\left(0.0992\, P_{H_2}\right) \right] (C_{so})\,(1-x)\left(\frac{C}{S}\right) \tag{27-22}$$

where r_A = rate of dissolution, g/(h·cm³ reactor volume)
C_{so} = weight fraction of organics in original coal
k_0 = rate constant, g/(h·cm³) reactor volume
P_{H_2} = hydrogen partial pressure, MPa
x = conversion, solid organics/solid organics in original coal
C/S = coal-solvent weight ratio
E = energy of activation, kcal/(g·mol)
R = universal gas constant, 1.987×10^{-3} kcal/(g mol·K)
T = temperature, K.

Calculated and measured conversions agreed when the Arrhenius temperature dependency indicated in Eq. (27-22) was used with the following values for the parameters:

Constant	Illinois No. 6	Kentucky No. 9
k_0, g/(h·cm³)	2125	15.3
E, kcal/g·mol)	11	4.5

The low activation energies suggested that the dissolution rate is controlled by counterdiffusion of organic components from the coal surface and dissolved hydrogen from the solvent. Also, the rate of dissolution appeared to depend exponentially on hydrogen partial pressure.

A free-radical mechanism has been proposed for coal dissolution in hydrogen donor solvents. Solvents and high temperatures facilitate degradation of coal to form relatively low-molecular-weight free radicals, which may be stabilized by hydrogen transfer from a hydroaromatic solvent. Initial dissolution is considered to be a thermal process, with a net rate dependent upon the type of solvent and its effectiveness in stabilizing free radicals. The greater a solvent's hydrogen donor capability, the more effective it is in terminating radicals. In continuous recycle process configurations, the overall rate-limiting step appears to be rehydrogenation of the donor solvent, which is a function of the dissolved hydrogen and catalyst. Nitrogen and sulfur removal and the formation of light liquid products are considered to result primarily from catalytic effects.

The conversion reaction from coal to oil has been modeled as a series of steps:

$$\text{Coal} + \text{solvent} \rightarrow \text{preasphaltene} \rightarrow \text{asphaltene} \rightarrow \text{oil}$$

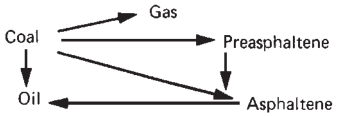
with some gas formation accompanying each step. In a study using Illinois No. 6 coal and 505 to 727 K (450 to 850°F) boiling-range process-derived heavy distillate, data were obtained at 13.8 MPa (2000 psia) and 673 to 748 K (750 to 885°F). Activation energies for the steps of the reaction series were determined to be:

Reaction step	Activation energy, kcal/g·mol
Preasphaltene → asphaltene	15
Asphaltene → oil	21
Coal → preasphaltene	32

At 723K (843°F), stoichiometries for the reaction steps were represented as:

$$\text{Coal} + 3\ \text{solvent} \rightarrow \text{preasphaltene}$$
$$\text{Preasphaltene} \rightarrow 2\ \text{asphaltene}$$
$$\text{Asphaltene} \rightarrow 3\ \text{oil}$$

A more complex reaction model was proposed from the results of a kinetic study of thermal liquefaction of subbituminous coal. Data were obtained over a temperature range of 673 to 743 K (752 to 878°F) at 13.8 MPa (2000 psia) by using two solvents, hydrogenated anthracene oil (HAO), and hydrogenated phenanthrene oil (HPO), at a coal-solvent ratio of 1:15. Results were correlated with the following model:



Activation energies and frequency factors for the various steps of this model were determined as follows:

Reaction	Rate constant	Activation energy, kcal/(g·mol)		Frequency factor, min^{-1}	
		Coal-HAO	Coal-HPO	Coal-HAO	Coal-HPO
Coal → oil	k_o	14.1	28.9	3.11×10^3	2.1×10^8
Coal → preasphaltene	k_p	13.8	4.3	2.81×10^3	4.94
Coal → asphaltene	k_a	15.6	8.6	1.12×10^4	9.63×10^1
Coal → gas	k_g	21.5	10.5	8.72×10^5	3.85×10^2
Preasphaltene → asphaltene	k_{pa}	12.8	33.9	9.66×10^2	2.48×10^9
Asphaltene → oil	k_{ao}	16.0	25.6	1.42×10^3	1.53×10^7

Magnitudes of k_g, k_p, k_a, and k_o indicate the importance of direct reactions with coal, where k_{pa} and k_{ao} are for hydrocracking reactions in the conversion process. Data for k_o and k_{ao} from the experiments with HPO indicate that oil production from coal is increased by the use of a good hydrogen donor solvent.

Direct-Liquefaction Processes Figure 27-8 presents a simplified process flow diagram of a typical direct coal liquefaction plant. Specific processes are described in the following paragraphs.

Solvent-Refined Coal (SRC) This processing concept was initiated by the Pittsburgh & Midway Coal Mining Co. in the early 1960s. The *SRC-I process* operating mode is designed to produce a solid fuel for utility applications. Typical operating conditions and product yields for SRC-I are shown in Table 27-14.

The *SRC-II process* is an improved version of the SRC process that recycles a portion of the reactor effluent slurry in place of the distillate solvent of the SRC-I process. The primary product is a liquid distillate fuel with a 490 to 728 K (423 to 851°F) boiling range. This is achieved in part by increased severity of operating conditions, but also by establishing a higher concentration of resid reactant and catalytic mineral matter in the reactor through slurry recycle. The net reactor effluent slurry is passed to a vacuum-flash unit for separation of the distillate product from the mineral matter and undissolved coal, thereby avoiding the filtration step. Typical operating conditions and product yields for SRC-II are shown in Table 27-14.

Exxon Donor Solvent (EDS) Process The EDS process, developed by the Exxon Research and Engineering Co., liquefies coal by use of a hydrogen donor solvent under hydrogen pressure in an upflow, plug-flow reactor. The solvent is a catalytically hydrogenated recycle stream, fractionated from the middle boiling range, 474 to 728 K (395 to 850°F), of the liquid product. Hydrogenation of the recycle solvent is conducted in a conventional fixed-bed catalytic reactor using hydrotreating catalysts, such as cobalt molybdate or nickel molybdate. Coal conversion and liquid yield strongly depend on the molecular composition, boiling-point range, and other properties of the solvent. Exxon uses its proprietary Solvent Quality Index (SQI) as the main criterion of solvent quality and correlates product yields with SQI. Typical operating conditions and product yields are shown in Table 27-14.

Vacuum distillation is used to remove the residue from the distillate product. Additional heavy oil may be recovered from the vacuum bottoms by employing Exxon's Flexicoking process.

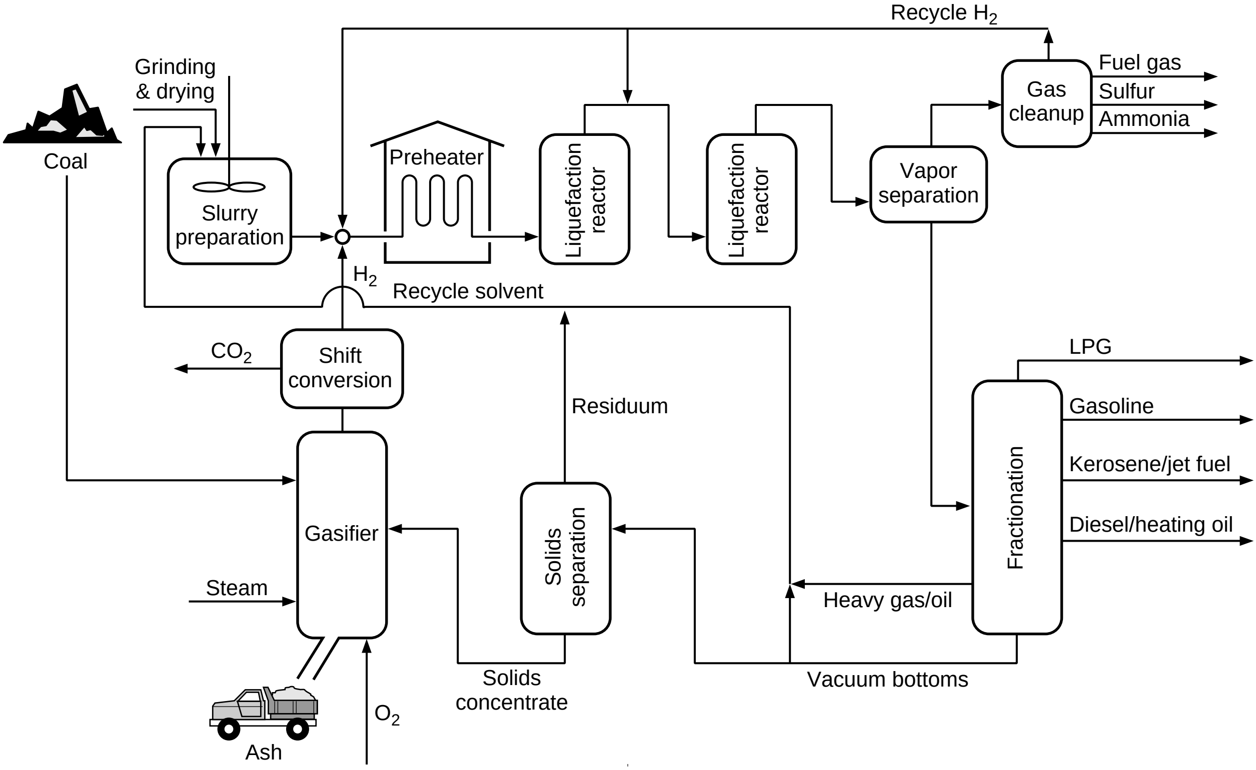


FIG. 27-8 Direct liquefaction of coal.

H-Coal Process The H-Coal process, based on H-Oil technology, was developed by Hydrocarbon Research, Inc. (HRI). Depending on the type of products desired, the process can be operated in either a fuel-oil mode or a syncrude mode by adjusting operating severity. The heart of the process is a three-phase fluidized reactor (ebullated-bed) in which catalyst pellets are fluidized by the upward flow of slurry and gas through the reactor. Catalyst activity in the reactor is maintained by the withdrawal of small quantities of spent catalyst and the addition of fresh catalyst. The reactor contains an internal tube for recirculating the reaction mixture through the catalyst bed.

Solids separation is accomplished by vacuum distillation in the syncrude mode. Table 27-14 shows the product yields obtained in PDU tests with an Illinois No. 6 bituminous coal.

Two-Stage Liquefaction This is an advanced process that provides improved, lower-cost technology by the more efficient and specific application of catalysis in the reaction stages. Higher yields of better-quality products are obtained by recovering and recycling heavy intermediates to extinction. Unconverted coal and mineral matter are removed by conventional technology such as supercritical solvent extraction or vacuum distillation. Several variations of this approach have been tested at the Advanced Coal Liquefaction R&D Facility (5.4 Mg/d or 6 US ton/d scale) in Wilsonville, Alabama. Distillate yields as high as 78 percent (moisture and ash-free basis) have been achieved. Wilsonville operating and product data are shown in Table 27-14. An economic evaluation is given in a later section.

Further development of staged-liquefaction technology options is being conducted by Hydrocarbon Technologies, Inc. (HTI, formerly HRI) in their 2.7-Mg/d (3-US ton/d) proof-of-concept unit (Lawrenceville, New Jersey), and more advanced concepts are being researched by HTI and others at the bench scale. Recent HTI results are presented in Table 27-14. Coal-derived product quality has been improved dramatically (less than 50 ppm nitrogen content, for example) through use of in-line fixed-bed hydrotreating of the product stream. Slurry catalysts are being employed in addition to the more conventional supported catalysts as a means of simplifying reactor designs and removing process constraints.

Coal-Oil Coprocessing In this approach, coal is slurried in petroleum resid rather than recycle solvent, and both coal and petroleum components are converted to high-quality fuels in the reaction stages. This variation offers the potential for significant cost reduction by eliminating or reducing internal recycle oil streams. More important, fresh hydrogen requirements are reduced because the petroleum resid feedstock component has a higher initial hydrogen content. As a result, plant capital investment is reduced substantially. It also offers the opportunity for accelerating the introduction of coal-derived liquid fuels into the marketplace by utilizing, to a much greater degree, existing petroleum refining facilities and technology.

Other carbonaceous materials such as municipal waste plastics, cellulosics, and used motor oils may also serve as cofeedstocks with coal in this technology.

Coal Pyrolysis Coal pyrolysis produces synthetic crude oil, gas, and char. In the COED process, crushed coal is dried and heated to successively higher temperatures in a series of fluidized-bed reactors. In each stage, a portion of the coal's volatile matter is released. Typically, four stages at 589, 727, 811, and 1089 K (600, 850, 1000, and 1500°F), respectively, are used, but operations vary owing to the need to stay below the coal agglomeration temperature. Process heat is generated by burning char in the last stage and circulating hot char and gases to the other stages. Volatile products are condensed in a recovery system and the pyrolysis oil is filtered to remove fines.

Typical pyrolysis yields and oil qualities for two bituminous coals, Utah A and Illinois No. 6, are presented in Table 27-15. The major problem with any pyrolysis process is the high yield of char.

Flash Pyrolysis Coal is rapidly heated to elevated temperatures for a brief period of time to produce oil, gas, and char. The increase in hydrogen content in the gases and liquids is the result of removing carbon from the process as a char containing a significantly reduced amount of hydrogen. Several processes have been tested on a rela-

TABLE 27-14 Direct Liquefaction Process Conditions and Product Yields

Developer	Gulf[a]	Gulf	Exxon	HRI	SCS,[b] EPRI, Amoco	HTI
Process	SRC-I	SRC-II	EDS	H-Coal	Two-stage	Two-stage
Coal type	Kentucky 9 & 14	Illinois No. 6	Illinois No. 6	Illinois No. 6	Illinois No. 6	Illinois No. 6
Operating conditions						
Nominal reactor residence time, h	0.5	0.97	0.67			
Coal space velocity per stage, kg/(h·m^3) (lb/[h·ft^3])				530 (33.1)	825[c] (51.7)	310 (19.4)
1st stage						
Temperature, K (°F)	724 (842)	730 (855)	722 (840)	726 (847)	695 (791)	680 (765)
Total pressure, MPa (psia)	10.3 (1500)	13.4 (1950)	10.3 (1500)			19.2 (2790)
H_2 partial pressure, MPa (psia)	9.7 (1410)	12.6 (1830)		12.6 (1827)	18.3 (2660)	
Catalyst type	Coal minerals	Coal minerals	Coal minerals	Supported catalyst (Co/Mo)	AKZO-AO-60 (Ni/Mo)	AKZO-AO-60 (Ni/Mo)
Catalyst replacement rate, kg/kg (lb/US ton) mf coal					7.5×10^{-4} (1.5)	8×10^{-4} (1.6)
2d Stage						
Temperature, K (°F)					705 (809)	705 (810)
Total pressure, MPa (psia)						18.6 (2700)
H_2 partial pressure, MPa (psia)					17.0 (2470)	
Catalyst type					AKZO-AO-60 (Ni/Mo)	AKZO-AO-60 (Ni/Mo)
Catalyst replacement rate kg/kg (lb/US ton) mf coal					7.5×10^{-4} (1.5)	1.5×10^{-3} (3.0)
Product yields, wt % maf coal						
H_2	–2.4	–4.7	–4.3	–5.9	–6.0	–7.2
H_2O	—	—	12.2[d]	8.3	9.7	9.8
H_2S, CO_x, NH_3	—	—	4.2[e]	5.0	5.2	5.2
C_1-C_3	3.7[f]	15.8[f]	7.3	11.3	6.5	5.6
C_4^+ distillate	13.5[g]	47.3[g]	38.8	53.1	65.6	73.3
Bottoms[h]	68.4	28.0	41.8	28.2	19.0	13.3
Unreacted coal[i]	5.4	5.0	—	6.4	7.0	5.0
Distillate end point, K (°F)	727 (850)	727 (850)	911 (1180)	797 (975)	797 (975)	524 (975)

[a] In partnership with Pittsburg & Midway Coal Mining Co.
[b] Southern Company Services, Inc., prime contractor for Wilsonville Facility.
[c] Coal space velocity is based on settled catalyst volume.
[d] CO_x is included.
[e] CO_x is excluded.
[f] C_4 is included.
[g] C_4 is excluded.
[h] Unreacted coal is included.
[i] "Unreacted coal" is actually insoluble organic matter remaining after reaction.

TABLE 27-15 Pyrolysis Data

	Illinois No. 6 seam	Utah A seam
Net yields, wt % dry coal		
Char	59.5	54.5
Oil	19.3	21.5
Gas	15.1	18.3
Liquor	6.1	5.7
Net process yields		
Char, kg/kg (lb/US ton)	0.595 (1190)	0.545 (1090)
Oil, m^3/kg (bbl/US ton)	1.92×10^{-4} (1.10)	2.15×10^{-4} (1.23)
Gas, m^3/kg (std ft^3/US ton)	0.274 (8810)	0.266 (8545)
Liquor, dm^3/kg (gal/US ton)	0.061 (14.6)	0.057 (13.7)
Oil properties		
Elemental Analysis, wt %, dry		
Carbon	79.6	83.8
Hydrogen	7.1	9.5
Nitrogen	1.1	0.9
Sulfur	2.8	0.4
Oxygen	8.5	5.0
Ash	0.9	0.3
Relative density, 288 K (°API, 60°F)	1.110 (–4)	1.105 (–3.5)
Moisture, wt %	0.8	0.5
Pour point, K (°F)	311 (100)	311 (100)
Kinematic viscosity, mm^2/s, 372 K (SUS 210°F)	300 (1333)	87.5 (390)
Solids, wt %, dry basis	4.0	3.8
Higher heating value, MJ/kg (Btu/lb)	35.0 (15,050)	37.4 (16,100)

tively small scale. None have demonstrated economic potential, although the technical concepts appear to be valid.

Indirect Coal Liquefaction

General References: Dry, *The Fischer-Tropsch Synthesis, Catalysis Science and Technology,* vol. 1, Springer-Verlag, New York, 1981. Anderson, *The Fischer-Tropsch Synthesis,* Academic Press, New York, 1984. Sheldon, *Chemicals from Synthesis Gas,* D. Reidel Publishing Co., Dordrecht, Netherlands, 1983. Rao, Stiegel, Cinquegrane, and Srivastava, "Iron-based Catalyst for Slurry-phase Fischer-Tropsch Process: Technology Review," *Fuel Processing Technology* **30:** 83–151, 1992.

Background Indirect coal liquefaction differs fundamentally from direct coal liquefaction in that the coal is first converted to a synthesis gas (a mixture of H_2 and CO) which is then converted over a catalyst to the final product. Figure 27-9 presents a simplified process flow diagram for a typical indirect coal liquefaction process. The synthesis gas is produced in a gasifier (see a description of coal gasifiers earlier in this section), where the coal is partially combusted at high temperature and moderate pressure with a mixture of oxygen and steam. In addition to H_2 and CO, the raw synthesis gas contains other constituents (such as CO_2, H_2S, NH_3, N_2, and CH_4), as well as particulates.

Before being fed to the synthesis reactor, the synthesis gas must first be cooled and then passed through particulate removal equipment. Following this, depending on the catalyst being used, it may be necessary to adjust the H_2/CO ratio. Modern high-efficiency gasifiers typically produce a ratio between 0.45 and 0.7, which is lower than stoichiometric for the synthesis reaction. Some catalysts, particularly iron catalysts, possess water gas shift conversion activity and permit

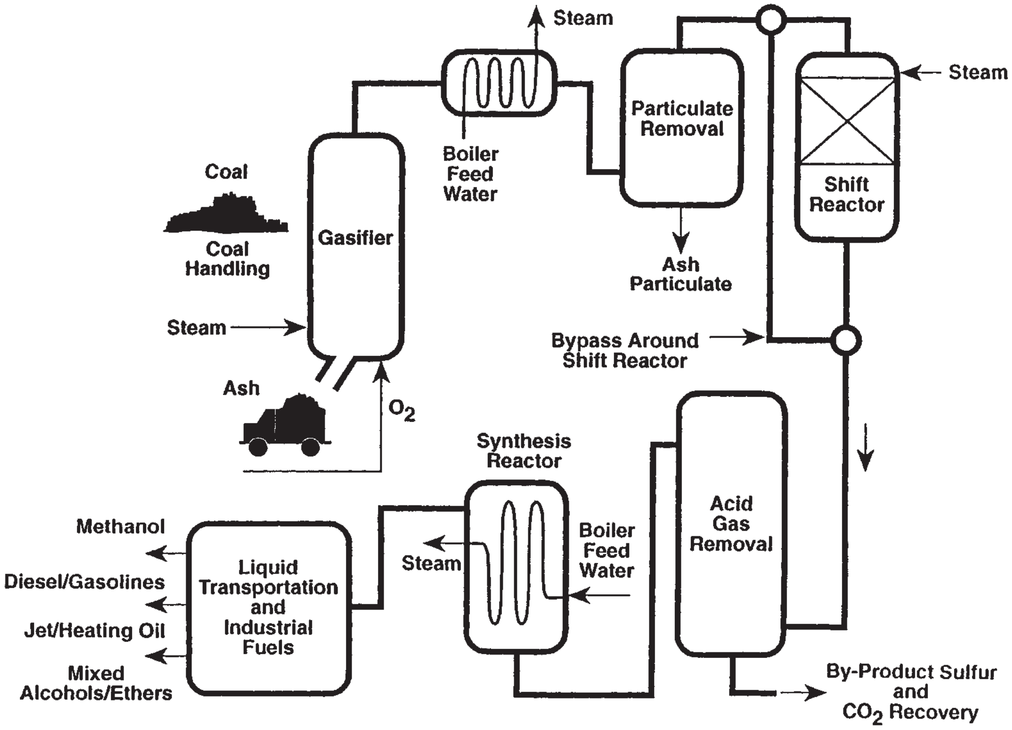


FIG. 27-9 Indirect liquefaction of coal.

operation with a low H_2/CO ratio. Other catalysts possess little shift activity, however, and require a ratio adjustment before the synthesis reactor.

After shift conversion, acid gases (CO_2 and H_2S) are scrubbed from the synthesis gas. A guard chamber is sometimes used to remove the last traces of H_2S. The cleaned gas is sent to the synthesis reactor, where it is converted at moderate temperature and pressure, typically 498 to 613 K (435 to 645°F) and 1.52 to 6.08 MPa (220 to 880 psia). Products from the process depend on operating conditions and the catalyst employed, as well as reactor design. Typical products include hydrocarbons (mainly straight chain paraffins from methane through n-C_{50} and higher), oxygenates (methanol, higher alcohols, ethers), and other chemicals (olefins).

Fischer-Tropsch Synthesis The best-known technology for producing hydrocarbons from synthesis gas is the Fischer-Tropsch synthesis. This technology was first demonstrated in Germany in 1902 by Sabatier and Senderens when they hydrogenated carbon monoxide (CO) to methane, using a nickel catalyst. In 1926 Fischer and Tropsch were awarded a patent for the discovery of a catalytic technique to convert synthesis gas to liquid hydrocarbons similar to petroleum.

The basic reactions in the Fischer-Tropsch synthesis are:

Paraffins:

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \tag{27-23}$$

Olefins:

$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O \tag{27-24}$$

Alcohols:

$$2nH_2 + nCO \rightarrow C_nH_{2n+1}OH + (n-1)H_2O \tag{27-25}$$

Other reactions may also occur during the Fischer-Tropsch synthesis, depending on the catalyst employed and the conditions used:

Water-gas shift:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{27-26}$$

Boudouard disproportionation:

$$2CO \rightarrow C(s) + CO_2 \tag{27-27}$$

Surface carbonaceous deposition:

$$\left(\frac{2x+y}{2}\right) H_2 + xCO \rightarrow C_xH_y + xH_2O \tag{27-28}$$

Catalyst oxidation-reduction:

$$yH_2O + xM \rightarrow M_xO_y + yH_2 \tag{27-29}$$

$$yCO_2 + xM \rightarrow M_xO_y + yCO \tag{27-30}$$

Bulk carbide formation:

$$yC + xM \rightarrow M_xC_y \tag{27-31}$$

where M represents a catalytic metal atom.

The production of hydrocarbons using traditional Fischer-Tropsch catalysts is governed by chain growth or polymerization kinetics. The equation describing the production of hydrocarbons, commonly referred to as the Anderson-Schulz-Flory equation, is:

$$\log\left(\frac{W_n}{n}\right) = n \log \alpha + \log\left[\frac{(1-\alpha)^2}{\alpha}\right] \tag{27-32}$$

where W_n = weight fraction of products with carbon number n, and α = chain growth probability, i.e., the probability that a carbon chain on the catalyst surface will grow by adding another carbon atom rather than terminating. In general, α is dependent on temperature, pressure, and catalyst composition but independent of chain length. As α increases, the average carbon number of the product also increases. When α equals 0, only methane is formed. As α approaches 1, the product becomes predominantly wax.

Figure 27-10 provides a graphical representation of Eq. (27-32) showing the weight fraction of various products as a function of the chain growth parameter α. This figure shows that there is a particular α that will maximize the yield of a desired product, such as gasoline or

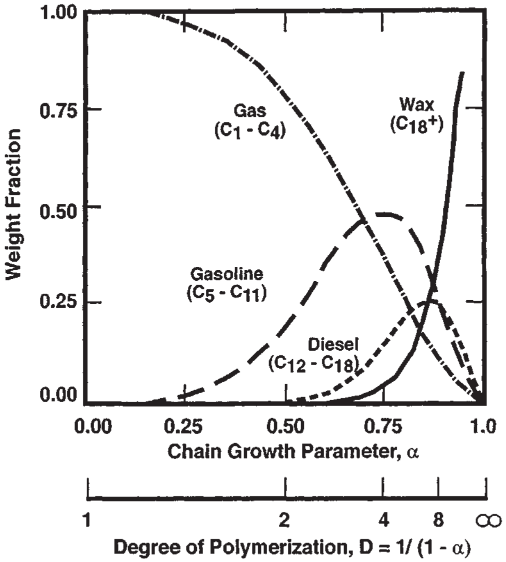


FIG. 27-10 Product yield in Fischer-Tropsch synthesis.

diesel fuel. The weight fraction of material between carbon numbers m and n, inclusive, is given by:

$$W_{mn} = m\alpha^{m-1} - (m-1)\alpha^{m} - (n+1)\alpha^{n} + n\alpha^{n+1} \qquad (27\text{-}33)$$

The α to maximize the yield of the carbon number range from m to n is given by:

$$\alpha_{\text{opt}} = \left(\frac{m^2 - m}{n^2 + n}\right)^{\frac{1}{n-m+1}} \qquad (27\text{-}34)$$

Additional gasoline and diesel fuel can be produced through further refining, such as hydrocracking or catalytic cracking of the wax product.

The Fischer-Tropsch reaction is highly exothermic. Therefore, adequate heat removal is critical. High temperatures result in high yields of methane, as well as coking and sintering of the catalyst. Three types of reactors (tubular fixed bed, fluidized bed, and slurry) provide good temperature control, and all three types are being used for synthesis gas conversion. The first plants used tubular or plate-type fixed-bed reactors. Later, SASOL, in South Africa, used fluidized-bed reactors, and most recently, slurry reactors have come into use.

Fischer-Tropsch synthesis reactor operation can be classified into one of two categories: high-temperature, 613 K (645°F), or low-temperature, 494 to 544 K (430 to 520°F), operation. The Synthol reactor developed by SASOL is typical of high-temperature operation. Using an iron-based catalyst, this process produces a very good gasoline product having high olefinicity and a low boiling range. The olefin fraction can readily be oligomerized to produce diesel fuel. Low-temperature operation, typically in fixed-bed reactors, produces a much more paraffinic and straight-chain product. Selectivity can be tailored to give the desired chain growth parameter. The primary diesel fraction, as well as the diesel-range product from hydrocracking of the wax, is an excellent diesel fuel.

Oxygenates and Chemicals A whole host of oxygenated products, i.e., fuels, fuel additives, and chemicals, can be produced from synthesis gas. These include such products as methanol, ethylene, isobutanol, dimethyl ether, dimethyl carbonate, and many other hydrocarbons and oxyhydrocarbons. Typical oxygenate-producing reactions are:

$$CO + 2H_2 \rightarrow CH_3OH \qquad (27\text{-}35)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (27\text{-}36)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad (27\text{-}37)$$

Reaction (27-37) can occur in parallel with the methanol reactions, thereby overcoming the equilibrium limitation on methanol formation. Higher alcohols can also be formed, as illustrated by Reaction (27-25), which is applicable to the formation of either linear or branched alcohols.

The production of methyl acetate from synthesis gas is currently being practiced commercially. Following methanol synthesis, as shown by Reaction (27-35), the reactions are:

$$CH_3OH + CO \rightarrow CH_3COOH \qquad (27\text{-}38)$$

$$CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O \qquad (27\text{-}39)$$

Acrylates and methacrylates, which are critical to the production of polyesters, plastics, latexes, and synthetic lubricants, can also be produced from these oxygenated intermediates.

Status of Indirect Liquefaction Technology The only commercial indirect coal liquefaction plants for the production of transportation fuels are operated by SASOL in South Africa. Construction of the original plant was begun in 1950, and operations began in 1955. This plant employs both fixed-bed (Arge) and entrained-bed (Synthol) reactors. Two additional plants were later constructed with start-ups in 1980 and 1983. These latter plants employ dry-ash Lurgi Mark IV coal gasifiers and entrained-bed (Synthol) reactors for synthesis gas conversion. These plants currently produce 45 percent of South Africa's transportation fuel requirements, and, in addition, they produce more than 120 other products from coal.

SASOL has pursued the development of alternative reactors to overcome specific operational difficulties encountered with the fixed-bed and entrained-bed reactors. After several years of attempts to overcome the high catalyst circulation rates and consequent abrasion in the Synthol reactors, a bubbling fluidized-bed reactor 1 m (3.3 ft) in diameter was constructed in 1983. Following successful testing, SASOL designed and constructed a full-scale commercial reactor 5 m (16.4 ft) in diameter. The reactor was successfully commissioned in 1989 and remains in operation.

SASOL and others, including Exxon, Statoil, Air Products and Chemicals, Inc., and the U.S. Department of Energy, have engaged in the development of slurry bubble column reactors for Fischer-Tropsch and oxygenate synthesis. SASOL, in fact, commissioned a slurry reactor with a 5-m diameter in 1993. It doubled the wax capacity of the SASOL I facility. The development work on this kind of reactor shows that it has several advantages over competing reactor designs: (1) excellent heat transfer capability resulting in isothermal reactor operations, (2) high catalyst and reactor productivity, (3) ease of catalyst addition and withdrawal, (4) simple construction, and (5) ability to process hydrogen-lean synthesis gas successfully. Because of the small particle size of the catalyst used in the slurry reactor, however, effective separation of catalyst from the products is difficult but is crucial to successful operation.

The United States has two commercial facilities that convert coal to fuels and chemicals by indirect liquefaction. The Great Plains Synfuels Plant, located in Beulah, North Dakota, produces synthetic natural gas (SNG) from North Dakota lignite by Lurgi dry-ash gasification technology and methanation. Operated by Dakota Gasification Company (DGC), the plant converts approximately 15.4 Gg (17,000 US tons) of lignite per day to about 4.7×10^6 Nm^3 (166×10^6 std ft^3) of pipeline-quality gas in 14 Lurgi gasifiers. Aromatic naphtha and tar oil are also produced in the gasification section. The plant operates at 120 percent of its original design capacity. In addition to SNG, there is a wide assortment of other products, e.g., anhydrous ammonia, sulfur, phenol, cresylic acid, naphthas, and krypton/xenon.

Eastman Chemical Company has operated a coal-to-methanol plant in Kingsport, Tennessee, since 1983. Two Texaco gasifiers (one is a backup) process 34 Mg/h (37 US ton/h) of coal to synthesis gas. The synthesis gas is converted to methanol by use of ICI methanol technology. Methanol is an intermediate for producing methyl acetate and acetic acid. The plant produces about 225 Gg/a (250,000 US ton/a) of acetic anhydride. As part of the DOE Clean Coal Technology Program, Air Products and Chemicals, Inc., and Eastman Chemical Company are constructing a 9.8-Mg/h (260-US ton/d) slurry-phase reactor for the conversion of synthesis gas to methanol and dimethyl ether. Construction is expected to be completed in November 1996. Despite the success of SASOL, most of the commercial interest in Fischer-Tropsch synthesis technology is based on natural gas, and it is likely to remain so as long as the gas is abundant and inexpensive. In 1985, Mobil commercialized its Methanol-to-Gasoline (MTG) technology in New Zealand, natural gas being the feedstock. This fixed-bed process converts synthesis gas to 4 Gg (4400 US tons) of methanol per day; the methanol can then be converted to 2290 m^3/d (14,400 bbl/d) gasoline. Owing to economic factors, the plant is used primarily for the production of methanol.

Shell Gas B.V. has constructed a 1987 m^3/d (12,500 bbl/d) Fischer-Tropsch plant in Malaysia, start-up occurring in 1994. The Shell Middle Distillate Synthesis (SMDS) process, as it is called, uses natural gas as the feedstock to fixed-bed reactors containing cobalt-based catalyst. The heavy hydrocarbons from the Fischer-Tropsch reactors are converted to distillate fuels by hydrocracking and hydroisomerization. The quality of the products is very high, the diesel fuel having a cetane number in excess of 75.

Exxon Research and Engineering Company has developed a process for converting natural gas to high-quality refinery feedstock, the AGC-21 Advanced Gas Conversion Process. The technology involves three highly integrated process steps: fluid-bed synthesis gas generation; slurry-phase Fischer-Tropsch synthesis; and mild fixed-bed hydroisomerization. The process was demonstrated in the early 1990s with a slurry-phase reactor having a diameter of 1.2 m (4 ft) and a capacity of about 32 m^3/d (200 bbl/d).

The largest Fischer-Tropsch facility based on natural gas is the Mossgas plant located in Mossel Bay, South Africa. Natural gas is converted to synthesis gas in a two-stage reformer and subsequently converted to hydrocarbons by SASOL's Synthol technology. The plant, commissioned in 1992, has a capacity of 7155 m^3/d (45,000 bbl/d).

Economics of Coal Liquefaction Bechtel developed conceptual commercial designs (greenfield), based on 1993 costs and representing current state-of-the-art technologies, for both direct and indirect coal liquefaction facilities feeding Illinois and Wyoming coals. The direct liquefaction design focuses on producing hydrotreated distillate products. The conceptual baseline plant is designed to process about 26.3 Gg/d (29,000 US ton/d) of coal while producing about 11,130 m^3/d (70,000 bbl/d) of distillate products. The design employs Texaco gasifiers for hydrogen production, supercritical solvent deashing for removing unconverted coal and mineral matter from the products, and high-pressure ebullated-bed reactors for coal hydrogenation. Table 27-16 presents the capital and operating costs. As shown, the crude oil equivalent price for direct liquefaction products is approximately \$215/m^3 (\$34/bbl). Additional cases were evaluated to assess the impact on product costs of technological advances through continued R&D. The final column in Table 27-16 shows the impact of such advances as improvements in product yields, space velocity, catalyst recovery, and hydrogen production on the cost of production. A required selling price of \$176/m^3 (\$28/bbl) (1993 US dollars) is believed to be achievable following further R&D.

The indirect liquefaction baseline design is for a plant of similar size. Unlike the direct liquefaction baseline, the design focuses on producing refined transportation fuels by use of Shell gasification technology. Table 27-17 shows that the crude oil equivalent price is approximately \$216/m^3 (\$34/bbl). Additional technological advances in the production of synthesis gas, the Fischer-Tropsch synthesis, and product refining have the potential to reduce the cost to \$171/m^3 (\$27/bbl) (1993 US dollars), as shown in the second column of Table 27-17.

Coproduction of electricity along with synthesis gas conversion offers the potential for significant cost savings. The once-through liquid-phase methanol technology was developed specifically for this

TABLE 27-16 Estimated Costs of Direct Coal Liquefaction Plant (1993 US dollars)

Elements of cost	Baseline costs[*] \$ million	Improved design due to R&D effort[†]
Coal handling	222	226
Liquefaction	942	823
Gas cleanup/by-product recovery	297	297
Product hydrotreating	107	113
De-ashing unit	46	43
Gasification	334	302
Air separation	244	220
Inside boundary limits field costs	2192	2024
Outside boundary limits field costs	978	968
Total field cost	3170	2992
Total capital	3889	3670
Refined product costs,[‡] \$/m^3		
Capital[§]	148.49	129.12
Coal	49.31	47.23
Catalyst	16.16	1.45
Natural gas	22.58	16.92
Labor	10.44	9.50
Other O&M	2.08	1.89
By-product credits	(26.29)	(20.44)
Required Selling Price	227.77	183.77
Quality premium	(7.48)	(7.48)
Crude oil equivalent price (\$/bbl)[¶]	215.28 (34.22)	176.29 (28.02)
Plant output, Mm^3/a (M bbl/a)	3.85 (24.2)	4.23 (26.6)

[*] Costs based on plant processing 26,105 Mg/d (28,776 US ton/d) of Illinois No. 6 coal. Source: *Direct Coal Liquefaction Baseline Design and Systems Analysis,* prepared by Bechtel and Amoco under DOE contract no. DE-AC22-90PC89857, March 1993.

[†] Source: Klunder and McIlvried, unpublished DOE Pittsburgh Energy Technology Center data.

[‡] To obtain \$/bbl from \$/m^3, multiply by 0.1590.

[§] Includes maintenance materials, taxes, and insurance.

[¶] The difference between the required selling price and the crude oil equivalent price represents the enhanced value of the coal liquids, due to their all-distillate and low-heteroatom character.

TABLE 27-17 Estimated Costs of Indirect Coal Liquefaction Plant (1993 US Dollars)

Elements of cost	Baseline costs,[*] \$ million	Costs with R&D improvements	Once-through Fischer-Tropsch
Coal handling	207	207	207
Gasification	1018	1018	1018
Air separation	466	323	453
Gas cleaning/by-product recovery	195	195	192
Fischer-Tropsch synthesis	331	190	286
Synthesis gas recycle loop	403	352	79
Product refining	209	131	155
Inside battery limits field cost	2829	2416	2390
Power generation	119	254	419
Outside battery limits field cost	488	481	452
Total field cost	3436	3151	3261
Total plant cost	4283	3927	4063
Total capital	4620	4231	4346
Refined product costs,[†] \$/m^3			
Capital[‡]	155.91	147.55	193.02
Coal	63.90	61.57	84.03
Catalyst	12.45	12.01	16.95
Other O&M	34.47	30.94	42.52
Power	7.80	–12.83	–118.74
Required selling price	274.53	229.25	217.17
Crude oil equivalent price (\$/bbl)[§]	216.04 (34.34)	170.75 (27.14)	158.68 (25.23)
Plant output, Mm^3/a (Mbbl/a)	3.77 (23.7)	3.91 (24.6)	2.86 (18.0)
Power, MW			1176

SOURCE: *Proc. Coal Liquefaction and Gas Conversion Contractors Review Conf.*, CONF-9508133, Pittsburgh Energy Technology Center, Pittsburgh, Pa., 1995.

[*] Costs based on plant processing 26,105 Mg/d (28,776 US ton/d) of Illinois No. 6 coal.

[†] To obtain \$/bbl from \$/m^3, multiply by 0.1590.

[‡] Includes maintenance, materials, taxes, and insurance.

[§] The difference between the required selling price and the crude oil equivalent price represents the enhanced value of the coal liquids, due to their all-distillate and low-heteroatom character.

objective to be realized in *integrated gasification combined cycle* (IGCC) power plants. *Once-through Fischer-Tropsch* (OTFT) in conjunction with IGCC has a similar potential, as indicated by the final column in Table 27-17. This concept has the potential for reducing the cost of products from Fischer-Tropsch to a crude oil equivalent price of \$159/m^3 (\$25/bbl).

For the related gas-based technology, Shell and SASOL have separately estimated that their technologies, on large scale and with natural-gas feedstock, can compete with crude oil priced at \$126 to 145/m^3 (\$20 to 23/bbl). The cost of production for each plant is sensitive to plant location and the price of the natural-gas feedstock.

At the current stage of development, direct and indirect liquefaction technologies look equally attractive economically, and both have the potential for significant cost improvements.

HEAT GENERATION

General References: Stultz and Kitto (eds.), *Steam: Its Generation and Use,* 40th ed., Babcock and Wilcox, Barberton, Ohio, 1992. *North American Combustion Handbook,* 3d ed., vols. I and II, North American Manufacturing Company, Cleveland, Ohio, 1996. Singer (ed.), *Combustion: Fossil Power Systems,* 4th ed., Combustion Engineering, Inc., Windsor, Conn., 1991. Cuenca and Anthony (eds.), *Pressurized Fluidized Bed Combustion,* Blackie Academic & Professional, London, 1995. Basu and Fraser, *Circulating Fluidized Bed Boilers: Design and Operations,* Butterworth and Heinemann, Boston, 1991. *Proceedings of International FBC Conference(s),* ASME, New York, 1991, 1993, 1995. *Application of FBC for Power Generation,* Electric Power Research Institute, EPRI PR-101816, Palo Alto, Calif., 1993. Boyen, *Thermal Energy Recovery,* 2d ed., Wiley, New York, 1980.

COMBUSTION BACKGROUND

Basic Principles

Theoretical Oxygen and Air for Combustion The amount of oxidant (oxygen or air) just sufficient to burn the carbon, hydrogen, and sulfur in a fuel to carbon dioxide, water vapor, and sulfur dioxide is the *theoretical* or *stoichiometric oxygen* or *air* requirement. The chemical equation for complete combustion of a fuel is

$$C_xH_yO_zS_w + \left(\frac{4x + y - 2z + 4w}{4}\right) O_2 = xCO_2 + \left(\frac{y}{2}\right) H_2O + wSO_2 \qquad (27\text{-}40)$$

x, y, z, and w being the number of atoms of carbon, hydrogen, oxygen, and sulfur, respectively, in the fuel. For example, 1 mol of methane (CH_4) requires 2 mol of oxygen for complete combustion to 1 mol of carbon dioxide and 2 mol of water. If air is the oxidant, each mol of oxygen is accompanied by 3.76 mol of nitrogen.

The volume of theoretical oxygen (at 0.101 MPa and 298 K) needed to burn any fuel can be calculated from the ultimate analysis of the fuel as follows:

$$24.45\left(\frac{C}{12} + \frac{H}{4} - \frac{O}{32} + \frac{S}{32}\right) = m^3 O_2/\text{kg fuel} \qquad (27\text{-}41)$$

where C, H, O, and S are the decimal weights of these elements in 1 kg of fuel. (To convert to ft^3 per lb of fuel, multiply by 16.02.) The mass of oxygen (in kg) required can be obtained by multiplying the volume by 1.31. The volume of theoretical air can be obtained by using a coefficient of 116.4 in Eq. (27-41) in place of 24.45.

Figure 27-11 gives the theoretical air requirements for a variety of combustible materials on the basis of fuel higher heating value (HHV). If only the fuel lower heating value is known, the HHV can be calculated from Eq. (27-6). If the ultimate analysis is known, Eq. (27-7) can be used to determine HHV.

Excess Air for Combustion More than the theoretical amount of air is necessary in practice to achieve complete combustion. This excess air is expressed as a percentage of the theoretical air amount. The *equivalence ratio* is defined as the ratio of the actual fuel-air ratio to the stoichiometric fuel-air ratio. Equivalence ratio values less than 1.0 correspond to fuel-*lean* mixtures. Conversely, values greater than 1.0 correspond to fuel-*rich* mixtures.

Products of Combustion For lean mixtures, the *products of combustion* (POC) of a sulfur-free fuel consist of carbon dioxide, water vapor, nitrogen, oxygen, and possible small amounts of carbon monoxide and unburned hydrocarbon species. Figure 27-12 shows the effect of fuel-air ratio on the flue gas composition resulting from the combustion of natural gas. In the case of solid and liquid fuels, the POC may also include solid residues containing ash and unburned carbon particles.

Equilibrium combustion product compositions and properties may be readily calculated using thermochemical computer codes which minimize the Gibbs free energy and use thermodynamic databases

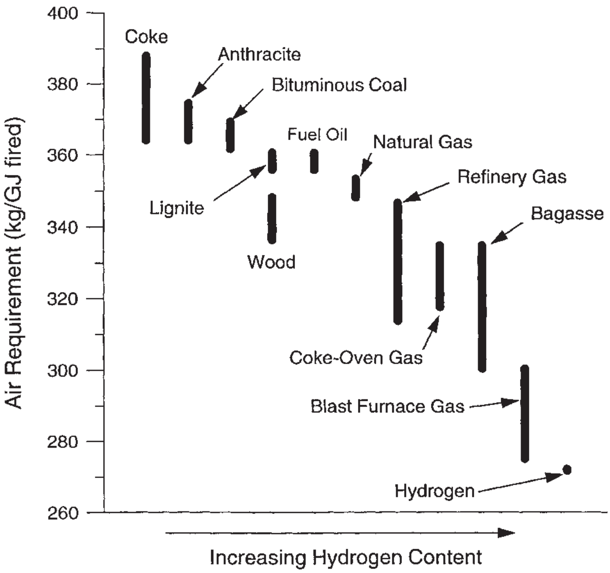


FIG. 27-11 Combustion air requirements for various fuels at zero excess air. To convert from kg air/GJ fired to lb air/10^6 Btu fired, multiply by 2.090.

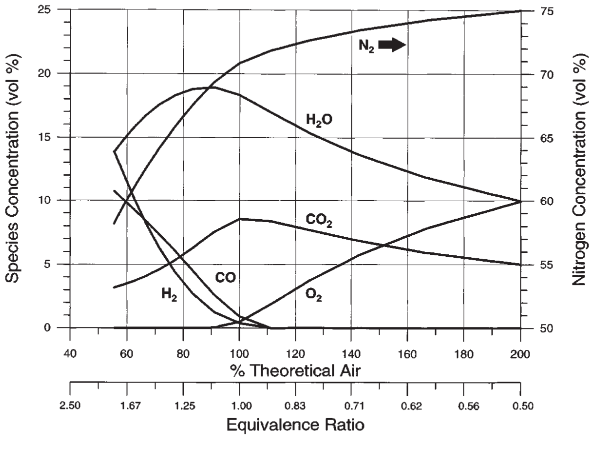


FIG. 27-12 Effect of fuel-air ratio on flue-gas composition for a typical U.S. natural gas containing 93.9% CH_4, 3.2% C_2H_6, 0.7% C_3H_8, 0.4% C_4H_{10}, 1.5% N_2 and 1.1% CO_2 by volume.

containing polynomial curve-fits of physical properties. Two widely used versions are those developed at NASA Lewis (Gordon and McBride, NASA SP-273, 1971) and at Stanford University (Reynolds, *STANJAN Chemical Equilibrium Solver,* Stanford University, 1987).

Flame Temperature The heat released by the chemical reaction of fuel and oxidant heats the POC. Heat is transferred from the POC, primarily by radiation and convection, to the surroundings, and the resulting temperature in the reaction zone is the flame temperature. If there is no heat transfer to the surroundings, the flame temperature equals the theoretical, or adiabatic, flame temperature.

Figure 27-13 shows the *available heat* in the products of combustion for various common fuels. The available heat is the total heat released during combustion minus the flue-gas heat loss (including the heat of vaporization of any water formed in the POC).

Flammability Limits There are both upper (or rich) and lower (or lean) limits of flammability of fuel-air or fuel-oxygen mixtures. Outside these limits, a self-sustaining flame cannot form. Flammability limits for common fuels are listed in Table 27-18.

Flame Speed Flame speed is defined as the velocity, relative to the unburned gas, at which an adiabatic flame propagates normal to itself through a homogeneous gas mixture. It is related to the combustion reaction rate and is important in determining burner flashback and blow-off limits. In a premixed burner, the flame can *flash back* through the flameholder and ignite the mixture upstream of the burner head if the mixture velocity at the flameholder is lower than the flame speed. Conversely, if the mixture velocity is significantly higher than the flame speed, the flame may not stay attached to the flameholder and is said to *blow off.* Flame speed is strongly dependent on fuel/air ratio, passing from nearly zero at the lean limit of flammability through a maximum and back to near zero at the rich limit of flammability. Maximum flame speeds for common fuels are provided in Table 27-18.

Pollutant Formation and Control in Flames Key combustion-generated air pollutants include nitrogen oxides (NO_x), sulfur oxides (principally SO_2), particulate matter, carbon monoxide, and unburned hydrocarbons.

Nitrogen Oxides Three reaction paths, each having unique characteristics (see Fig. 27-14), are responsible for the formation of NO_x during combustion processes: (1) *thermal* NO_x, which is formed by the combination of atmospheric nitrogen and oxygen at high temperatures; (2) *fuel* NO_x, which is formed from the oxidation of fuel-bound nitrogen; and (3) *prompt* NO_x, which is formed by the reaction of fuel-derived hydrocarbon fragments with atmospheric nitrogen. (NO_x is

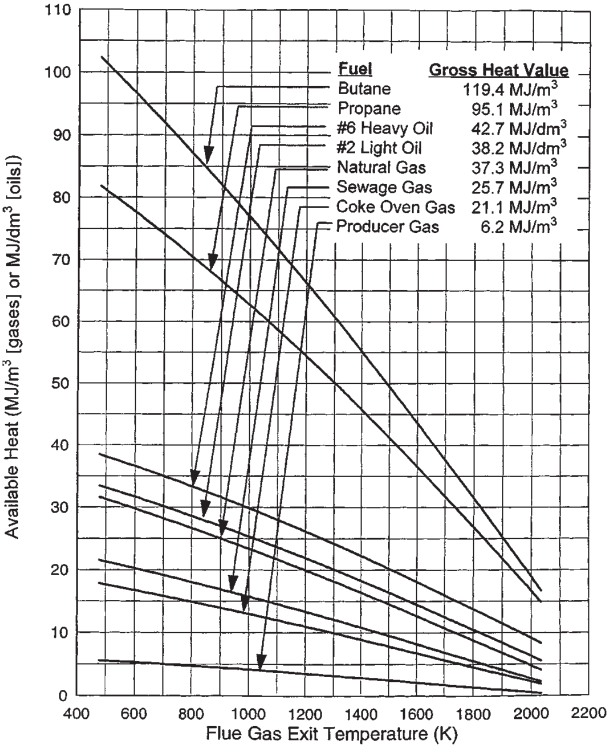


FIG. 27-13 Available heats for some typical fuels. The fuels are identified by their gross (or higher) heating values. All available heat figures are based upon complete combustion and fuel and air initial temperature of 288 K (60°F). To convert from MJ/Nm^3 to Btu/ft^3, multiply by 26.84. To convert from MJ/dm^3 to Btu/gal, multiply by 3588.

TABLE 27-18 Combustion Characteristics of Various Fuels*

Fuel	Minimum ignition temp., K/°F	Calculated flame temperature,† K/°F		Flammability limits, % fuel gas by volume in air		Maximum flame velocity, m/s and ft/s		% theoretical air for max. flame velocity
		in air	in O_2	lower	upper	in air	in O_2	
Acetylene, C_2H_2	578/581	2905/4770	3383/5630	2.5	81.0	2.67/8.75	—	83
Blast furnace gas	—	1727/2650	—	35.0	73.5	—	—	—
Butane, commercial	753/896	2246/3583	—	1.86	8.41	0.87/2.85	—	—
Butane, n-C_4H_{10}	678/761	2246/3583	—	1.86	8.41	0.40/1.3	—	97
Carbon monoxide, CO	882/1128	2223/3542	—	12.5	74.2	0.52/1.7	—	55
Carbureted water gas	—	2311/3700	3061/5050	6.4	37.7	0.66/2.15	—	90
Coke oven gas	—	2261/3610	—	4.4	34.0	0.70/2.30	—	90
Ethane, C_2H_4	745/882	2222/3540	—	3.0	12.5	0.48/1.56	—	98
Gasoline	553/536	—	—	1.4	7.6	—	—	—
Hydrogen, H_2	845/1062	2318/4010	3247/5385	4.0	74.2	2.83/9.3	—	57
Hydrogen sulfide, H_2S	565/558	—	—	4.3	45.5	—	—	—
Mapp gas, (allene) C_3H_4	728/850	—	3200/5301	3.4	10.8	—	4.69/15.4	—
Methane, CH_4	905/1170	2191/3484	—	5.0	15.0	0.45/1.48	4.50/14.76	90
Methanol, CH_3OH	658/725	2177/3460	—	6.7	36.0	—	0.49/1.6	—
Natural gas	—	2214/3525	2916/4790	4.3	15.0	0.30/1.00	4.63/15.2	100
Producer gas	—	1927/3010	—	17.0	73.7	0.26/0.85	—	90
Propane, C_3H_8	739/871	2240/3573	3105/5130	2.1	10.1	0.46/1.52	3.72/12.2	94
Propane, commercial	773/932	2240/3573	—	2.37	9.50	0.85/2.78	—	—
Propylene, C_3H_6	—	—	3166/5240	—	—	—	—	—
Town gas (brown coal)	643/700	2318/3710	—	4.8	31.0	—	—	—

*For combustion with air at standard temperature and pressure. These flame temperatures are calculated for 100 percent theoretical air, disassociation considered. Data from *Gas Engineers Handbook,* Industrial Press, New York, 1965.

†Flame temperatures are theoretical—calculated for stoichiometric ratio, dissociation considered.

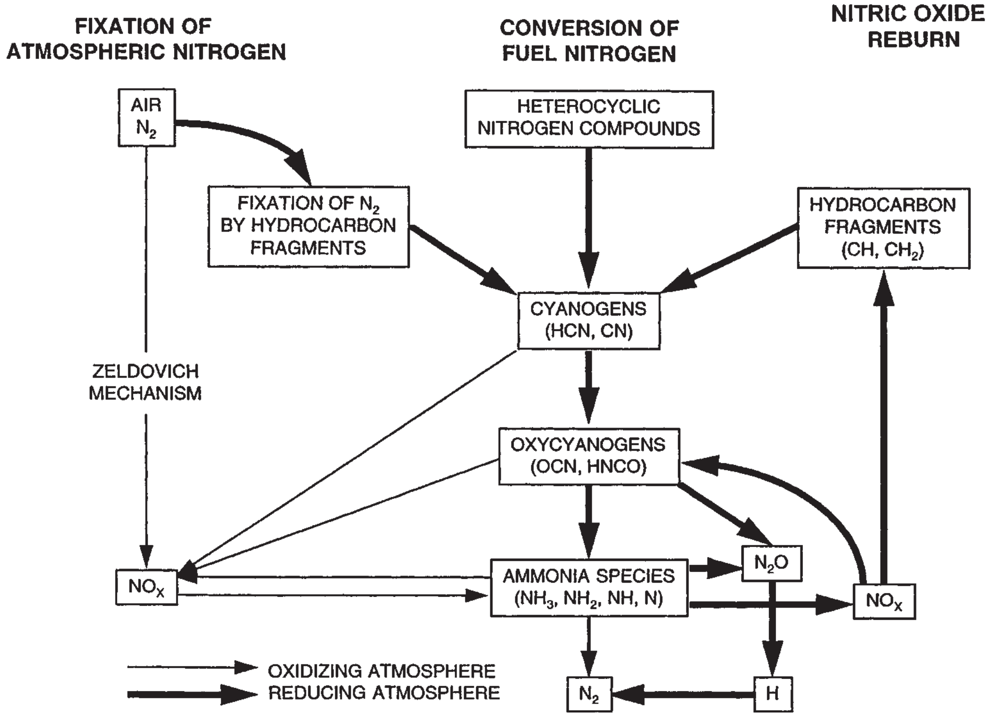


FIG. 27-14 Nitrogen oxide formation pathways in combustion.

used to refer to NO + NO_2. NO is the primary form in combustion products [typically 95 percent of total NO_x]. NO is subsequently oxidized to NO_2 in the atmosphere.)

Thermal NO_x The formation of thermal NO_x is described by the Zeldovich mechanism:

$$N_2 + O \rightleftharpoons NO + N \tag{27-42}$$

$$N + O_2 \rightleftharpoons NO + O \tag{27-43}$$

$$N + OH \rightleftharpoons NO + H \tag{27-44}$$

The first of these reactions is the rate-limiting step. Assuming that O and O_2 are in partial equilibrium, the NO formation rate can be expressed as follows:

$$\frac{d[NO]}{dt} = A[N_2][O_2]^{1/2} \exp\left(\frac{-E}{RT}\right) \tag{27-45}$$

As indicated, the rate of NO formation increases exponentially with temperature, and, of course, oxygen and nitrogen must be available for thermal NO_x to form. Thus, thermal NO_x formation is rapid in high-temperature lean zones of flames.

Fuel NO_x Fuel-bound nitrogen (FBN) is the major source of NO_x emissions from combustion of nitrogen-bearing fuels such as heavy oils, coal, and coke. Under the reducing conditions surrounding the burning droplet or particle, the FBN is converted to fixed nitrogen species such as HCN and NH_3. These, in turn, are readily oxidized to form NO if they reach the lean zone of the flame. Between 20 and 80 percent of the bound nitrogen is typically converted to NO_x, depending on the design of the combustion equipment. With prolonged exposure (order of 100 ms) to high temperature and reducing conditions, however, these fixed nitrogen species may be converted to molecular nitrogen, thus avoiding the NO formation path.

Prompt NO_x Hydrocarbon fragments (such as C, CH, CH_2) may react with atmospheric nitrogen under fuel-rich conditions to yield fixed nitrogen species such as NH, HCN, H_2CN, and CN. These, in turn, can be oxidized to NO in the lean zone of the flame. In most flames, especially those from nitrogen-containing fuels, the prompt mechanism is responsible for only a small fraction of the total NO_x. Its control is important only when attempting to reach the lowest possible emissions.

NO_x Emission Control It is preferable to minimize NO_x formation through control of the mixing, combustion, and heat-transfer processes rather than through postcombustion techniques such as selective catalytic reduction. Four techniques for doing so, illustrated in Fig. 27-15, are air staging, fuel staging, flue-gas recirculation, and lean premixing.

Air Staging Staging the introduction of combustion air can control NO_x emissions from all fuel types. The combustion air stream is split to create a fuel-rich primary zone and a fuel-lean secondary zone. The rich primary zone converts fuel-bound nitrogen to molecular nitrogen and suppresses thermal NO_x. Heat is removed prior to addition of the secondary combustion air. The resulting lower flame temperatures (below 1810 K [2800°F]) under lean conditions reduce the rate of formation of thermal NO_x. This technique has been widely applied to furnaces and boilers and it is the preferred approach for burning liquid and solid fuels. Staged-air burners are typically capable of reducing NO_x emissions by 30 to 60 percent, relative to uncontrolled levels. Air staging can also be accomplished by use of overfire air systems in boilers.

Fuel Staging Staging the introduction of fuel is an effective approach for controlling NO_x emissions when burning gaseous fuels. The first combustion stage is very lean, resulting in low thermal and prompt NO_x. Heat is removed prior to injection of the secondary fuel. The secondary fuel entrains flue gas prior to reacting, further reducing flame temperatures. In addition, NO_x reduction through reburning reactions may occur in the staged jets. This technique is the favored approach for refinery- and chemical plant–fired heaters utilizing gaseous fuels. Staged-fuel burners are typically capable of reducing NO_x emissions by 40 to 70 percent, relative to uncontrolled levels.

Flue Gas Recirculation Flue gas recirculation, alone or in combination with other modifications, can significantly reduce thermal NO_x. Recirculated flue gas is a diluent that reduces flame temperatures. External and internal recirculation paths have been applied: internal

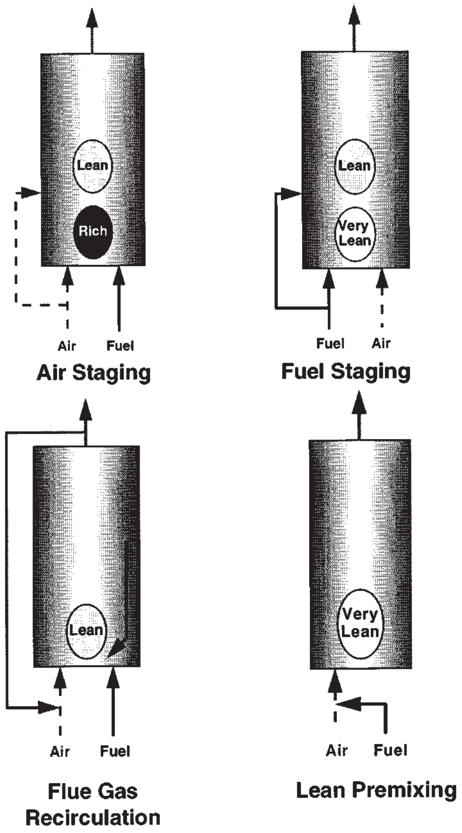


FIG. 27-15 Combustion modifications for NO_x control.

recirculation can be accomplished by jet entrainment using either combustion air or fuel jet energy; external recirculation requires a fan or a jet pump (driven by the combustion air). When combined with staged-air or staged-fuel methods, NO_x emissions from gas-fired burners can be reduced by 50 to 90 percent. In some applications, external flue-gas recirculation can decrease thermal efficiency. Condensation in the recirculation loop can cause operating problems and increase maintenance requirements.

Lean Premixing Very low NO_x emissions can be achieved by premixing gaseous fuels (or vaporized liquid fuels) with air and reacting at high excess air. The uniform and very lean conditions in such systems favor very low thermal and prompt NO_x. However, achieving such low emissions requires operating near the lean stability limit. This is an attractive NO_x control approach for gas turbines, where operation at high excess air does not incur an efficiency penalty. In this application, NO_x emissions have been reduced by 75 to 95 percent.

Sulfur Oxides Sulfur occurs in fuels as inorganic minerals (primarily pyrite, FeS_2), organic structures, sulfate salts, and elemental sulfur. Sulfur contents range from parts per million in pipeline natural gas, to a few tenths of a percent in diesel and light fuel oils, to 0.5 to 5 percent in heavy fuel oils and coals. Sulfur compounds are pyrolized during the volatilization phase of oil and coal combustion and react in the gas phase to form predominantly SO_2 and some SO_3. Conversion of fuel sulfur to these oxides is generally high (85 to 90 percent) and is relatively independent of combustion conditions. From 1 to 4 percent of the SO_2 is further oxidized to SO_3, which is highly reactive and extremely hygroscopic. It combines with water to form sulfuric acid aerosol, which can increase the visibility of stack plumes. It also elevates the dew point of water so that, to avoid back-end condensation and resulting corrosion, the flue-gas discharge temperature must be raised to about 420 K (300°F), reducing heat recovery and thermal efficiency. This reaction is enhanced by the presence of fine particles, which serve as condensation nuclei. Some coals may contain ash with substantial alkali content. In combustion of these fuels, the alkali may react to form condensed phase compounds (such as sulfates), thereby reducing the amount of sulfur emitted as oxides. Reductions in SO_2 emissions may be achieved either by removing sulfur from the fuel before and/or during combustion, or by postcombustion flue-gas desulfurization (wet scrubbing using limestone slurry, for example).

Particulates Combustion-related particulate emissions may consist of one or more of the following types, depending on the fuel.

Mineral matter derived from ash constituents of liquid and solid fuels can vaporize and condense as sub-micron-size aerosols. Larger mineral matter fragments are formed from mineral inclusions which melt and resolidify downstream.

Sulfate particles formed in the gas phase can condense. In addition, sulfate can become bound to metals and can be adsorbed on unburned carbon particles.

Unburned carbon includes unburned char, coke, cenospheres, and soot.

Particles of char are produced as a normal intermediate product in the combustion of solid fuels. Following initial particle heating and devolatilization, the remaining solid particle is termed *char.* Char oxidation requires considerably longer periods (ranging from 30 ms to over 1 s, depending on particle size and temperature) than the other phases of solid fuel combustion. The fraction of char remaining after the combustion zone depends on the combustion conditions as well as the char reactivity.

Cenospheres are formed during heavy oil combustion. In the early stages of combustion, the oil particle is rapidly heated and evolves volatile species, which react in the gas phase. Toward the end of the volatile-loss phase, the generation of gas declines rapidly and the droplet (at this point, a highly viscous mass) solidifies into a porous coke particle known as a *cenosphere.* This is called *initial coke.* For the heaviest oils, the initial coke particle diameter may be 20 percent larger than the initial droplet diameter. For lighter residual oils, it may be only one third of the original droplet diameter. After a short interval, the initial coke undergoes contraction to form *final coke.* Final coke diameter is ~80 percent of the initial droplet diameter for the heaviest oils. At this time the temperature of the particle is approximately 1070 to 1270 K (1470 to 1830°F). Following coke formation, the coke particles burn out in the lean zone, but the heterogeneous oxidation proceeds slowly. Final unburned carbon levels depend on a balance between the amount of coke formed and the fraction burned out. Coke formation tends to correlate with fuel properties such as asphaltene content, C:H ratio, or Conradson Carbon Residue. Coke burnout depends on combustion conditions and coke reactivity. Coke reactivity is influenced by the presence of combustion catalysts (e.g., vanadium) in the cenospheres.

Formation of *soot* is a gas-phase phenomenon that occurs in hot, fuel-rich zones. Soot occurs as fine particles (0.02 to 0.2 μm), often agglomerated into filaments or chains which can be several millimeters long. Factors that increase soot formation rates include high C:H ratio, high temperature, very rich conditions, and long residence times at these conditions. Pyrolysis of fuel molecules leads to soot precursors such as acetylene and higher analogs and various polyaromatic hydrocarbons. These condense to form very small (<2 nm) particles. The bulk of solid-phase material is generated by *surface growth*—attachment of gas-phase species to the surface of the particles and their incorporation into the particulate phase. Another growth mechanism is *coagulation,* in which particles collide and coalesce. Soot particle formation and growth is typically followed by soot oxidation to form CO and CO_2. Eventual soot emission from a flame depends on the relative balance between the soot-formation and oxidation reactions.

Carbon Monoxide Carbon monoxide is a key intermediate in the oxidation of all hydrocarbons. In a well-adjusted combustion system, essentially all the CO is oxidized to CO_2 and final emission of CO is very low indeed (a few parts per million). However, in systems which have low temperature zones (for example, where a flame impinges on a wall or a furnace load) or which are in poor adjustment (for example, an individual burner fuel-air ratio out of balance in a multiburner installation or a misdirected fuel jet which allows fuel to bypass the main flame), CO emissions can be significant. The primary method of CO control is good combustion system design and practice.

Unburned Hydrocarbons Various unburned hydrocarbon species may be emitted from hydrocarbon flames. In general, there are two classes of unburned hydrocarbons: (1) small molecules that are the intermediate products of combustion (for example, formaldehyde) and (2) larger molecules that are formed by pyro-synthesis in hot, fuel-rich zones within flames, e.g., benzene, toluene, xylene, and various polycyclic aromatic hydrocarbons (PAHs). Many of these species are listed as Hazardous Air Pollutants (HAPs) in Title III of the Clean Air Act Amendment of 1990 and are therefore of particular concern. In a well-adjusted combustion system, emission of HAPs is extremely low (typically, parts per trillion to parts per billion). However, emission of certain HAPs may be of concern in poorly designed or maladjusted systems.

COMBUSTION OF SOLID FUELS

There are three basic modes of burning solid fuels, each identified with a furnace design specific for that mode: in suspension, in a bed at rest[*] on a grate (fuel-bed firing), or in a fluidized bed. Although many variations of these generic modes and furnace designs have been devised, the fundamental characteristics of equipment and procedure remain intact. They will be described briefly.

Suspension Firing Suspension firing of pulverized coal (PC) is commoner than fuel-bed or fluidized-bed firing of coarse coal in the United States. This mode of firing affords higher steam-generation capacity, is independent of the caking characteristics of the coal, and responds quickly to load changes. Pulverized coal firing accounts for approximately 55 percent of the power generated by electric utilities in the United States. It is rarely used on boilers of less than 45.4 Mg/h (100,000 lb/h) steam capacity because its economic advantage decreases with size.

A simplified model of PC combustion includes the following sequence of events: (1) on entering the furnace, a PC particle is heated rapidly, driving off the volatile components and leaving a char particle; (2) the volatile components burn independently of the coal particle; and (3) on completion of volatiles combustion, the remaining char particle burns. While this simple sequence may be generally correct, PC combustion is an extremely complex process involving many interrelated physical and chemical processes.

Devolatilization The volatiles produced during rapid heating of coal can include H_2, CH_4, CO, CO_2, and C_2-C_4 hydrocarbons, as well as tars, other organic compounds, and reduced sulfur and nitrogen species. The yield of these various fractions is a function of both heating rate and final particle temperature. The resulting char particle may be larger in diameter than the parent coal particle, owing to swelling produced by volatiles ejection. The particle density also decreases.

Char oxidation dominates the time required for complete burnout of a coal particle. The heterogeneous reactions responsible for char oxidation are much slower than the devolatilization process and gas-phase reaction of the volatiles. Char burnout may require from 30 ms to over 1 s, depending on combustion conditions (oxygen level, temperature), and char particle size and reactivity. Char reactivity depends on parent coal type. The rate-limiting step in char burnout can be chemical reaction or gaseous diffusion. At low temperatures or for very large particles, chemical reaction is the rate-limiting step. At higher temperatures boundary-layer diffusion of reactants and products is the rate-limiting step.

Pulverized-Coal Furnaces In designing and sizing PC furnaces, particular attention must be given to the following fuel-ash properties:

- Ash fusion temperatures, including the spread between initial deformation temperature and fluid temperature
- Ratio of basic (calcium, sodium, potassium) to acidic (iron, silicon, aluminum) ash constituents, and specifically iron-to-calcium ratio
- Ash content
- Ash friability

These characteristics influence furnace plan area, furnace volume, and burning zone size required to maintain steam production capacity for a given fuel grade or quality.

Coal properties influence pulverizer capacity and the sizing of the air heater and other heat-recovery sections of a steam generator. Furnace size and heat-release rates are designed to control slagging characteristics. Consequently, heat-release rates in terms of the ratio of net heat input to plan area range from 4.4 MW/m^2 (1.4 × 10^6 Btu/[h·ft^2]) for severely slagging coals to 6.6 MW/m^2 (2.1 × 10^6 Btu/[h·ft^2]) for low-slagging fuels.

The various burner and furnace configurations for PC firing are shown schematically in Fig. 27-16. The U-shaped flame, designated as *fantail vertical firing* (Fig. 27-16*a*), was developed initially for pulverized coal before the advent of water-cooled furnace walls. Because a large percentage of the total combustion air is withheld from the fuel stream until it projects well down into the furnace, this type of firing is well suited for solid fuels that are difficult to ignite, such as those with less than 15 percent volatile matter. Although this configuration is no longer used in central-station power plants, it may find favor again if low-volatile chars from coal-conversion processes are used for steam generation or process heating.

Modern central stations use the other burner-furnace configurations shown in Fig. 27-16, in which the coal and air are mixed rapidly in and close to the burner. The primary air, used to transport the pulverized coal to the burner, comprises 10 to 20 percent of the total combustion air. The secondary air comprises the remainder of the total air and mixes in or near the burner with the primary air and coal. The velocity of the mixture leaving the burner must be high enough to prevent flashback in the primary air-coal piping. In practice, this velocity is maintained at about 31 m/s (100 ft/s).

In *tangential firing* (Fig. 27-16*b*), the burners are arranged in vertical banks at each corner of a square (or nearly square) furnace and directed toward an imaginary circle in the center of the furnace. This results in the formation of a large vortex with its axis on the vertical centerline. The burners consist of an arrangement of slots one above the other, admitting, through alternate slots, primary air-fuel mixture and secondary air. It is possible to tilt the burners upward or downward, the maximum inclination to the horizontal being 30°, enabling the operator to selectively utilize in-furnace heat-absorbing surfaces, especially the superheater.

The circular burner shown in Fig. 27-17 is widely used in horizontally fired furnaces and is capable of firing coal, oil, or gas in capacities as high as 174 GJ/h (1.65 × 10^8 Btu/h). In such burners the air is often swirled to create a zone of reverse flow immediately downstream of the burner centerline, which provides for combustion stability.

Low-NO_x burners are designed to delay and control the mixing of coal and air in the main combustion zone. A typical low-NO_x air-staged burner is illustrated in Fig. 27-18. This combustion approach can reduce NO_x emissions from coal burning by 40 to 50 percent. Because of the reduced flame temperature and delayed mixing in a low-NO_x burner, unburned carbon emissions may increase in some applications and for some coals. *Overfire air* is another technique for staging the combustion air to control NO_x emissions when burning coal in suspension-firing systems. Overfire air ports are installed above the top level of burners on wall- and tangential-fired boilers. Use of overfire air can reduce NO_x emissions by 20 to 30 percent. *Reburn* is a NO_x control strategy that involves diverting a portion of the fuel from the burners to a second combustion zone (reburn zone) above the main burners. Completion air is added above the reburn zone to complete fuel burnout. The reburn fuel can be natural gas, oil, or pulverized coal, though natural gas is used in most applications. In this approach, the stoichiometry in the reburn zone is controlled to be slightly rich (equivalence ratio of ~1.15), under which conditions a portion (50 to 60 percent) of the NO_x is converted to molecular nitrogen.

Pulverizers The pulverizer is the heart of any solid-fuel suspen-

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[*] The burning fuel bed may be moved slowly through the furnace by the vibrating action of the grate or by being carried on a traveling grate.

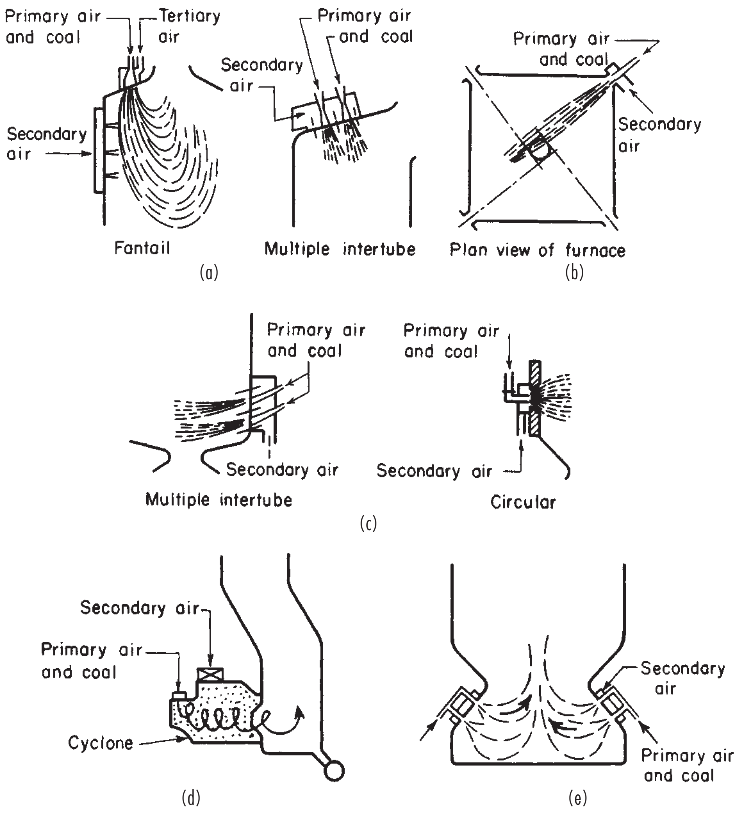


FIG. 27-16 Burner and furnace configurations for pulverized-coal firing: (*a*) vertical firing; (*b*) tangential firing; (*c*) horizontal firing; (*d*) cyclone firing; (*e*) opposed-inclined firing.

sion-firing system. Air is used to dry the coal, transport it through the pulverizer, classify it, and transport it to the burner, where the transport air provides part of the air for combustion. The pulverizers themselves are classified according to whether they are under positive or negative pressure and whether they operate at slow, medium, or high speed.

Pulverization occurs by impact, attrition, or crushing. The capacity of a pulverizer depends on the grindability of the coal and the fineness desired, as shown by Fig. 27-19. Capacity can also be seriously reduced by excessive moisture in the coal, but it can be restored by increasing the temperature of the primary air. Figure 27-20 indicates the temperatures needed. For PC boilers, the coal size usually is 65 to 80 percent through a 200-mesh screen, which is equivalent to 74 μm. Several kinds of available pulverizers and their characteristics are discussed in Sec. 20.

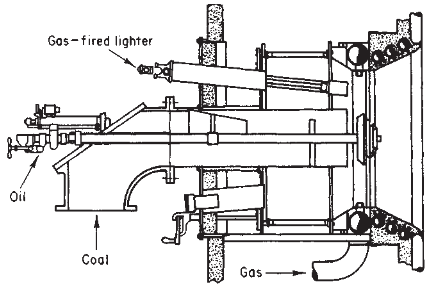


FIG. 27-17 Circular burner for pulverized coal, oil, or gas. (*From* Marks' Standard Handbook for Mechanical Engineers, *8th ed., McGraw-Hill, New York, 1978.*)

Cyclone Furnaces In *cyclone firing* (Fig. 27-16*d*) the coal is not pulverized but is crushed to 4-mesh (4.76-mm) size and admitted tangentially with primary air to a horizontal cylindrical chamber, called a *cyclone furnace,* which is connected peripherally to a boiler furnace. Secondary air also is admitted, so that almost all of the coal burns within the chamber. The combustion gas then flows into the boiler furnace. In the cyclone furnace, finer coal particles burn in suspension and the coarser ones are thrown centrifugally to the chamber wall, where most of them are captured in a sticky wall coating of molten slag. The secondary air, admitted tangentially along the top of the cyclone furnace, sweeps the slag-captured particles and completes their combustion. A typical firing rate is about 18.6 GJ/(h·m^3) (500,000 Btu/[h·ft^3]). The slag drains continuously into the boiler furnace and thence into a quenching tank. Figure 27-21 shows a cyclone furnace schematically.

Fuel-Bed Firing Fuel-bed firing is accomplished with mechanical stokers, which are designed to achieve continuous or intermittent fuel feed, fuel ignition, proper distribution of the combustion air, free release of the gaseous combustion products, and continuous or intermittent disposal of the unburned residue. These aims are met with two classes of stokers, distinguished by the direction of fuel feed to the bed: underfeed and overfeed. Overfeed stokers are represented by two types, distinguished by the relative directions of fuel and air flow (and also by the manner of fuel feed): crossfeed, also termed mass-burning, and spreader. The principles of these three methods of fuel-bed firing are illustrated schematically in Fig. 27-22.

Underfeed Firing Both fuel and air have the same relative

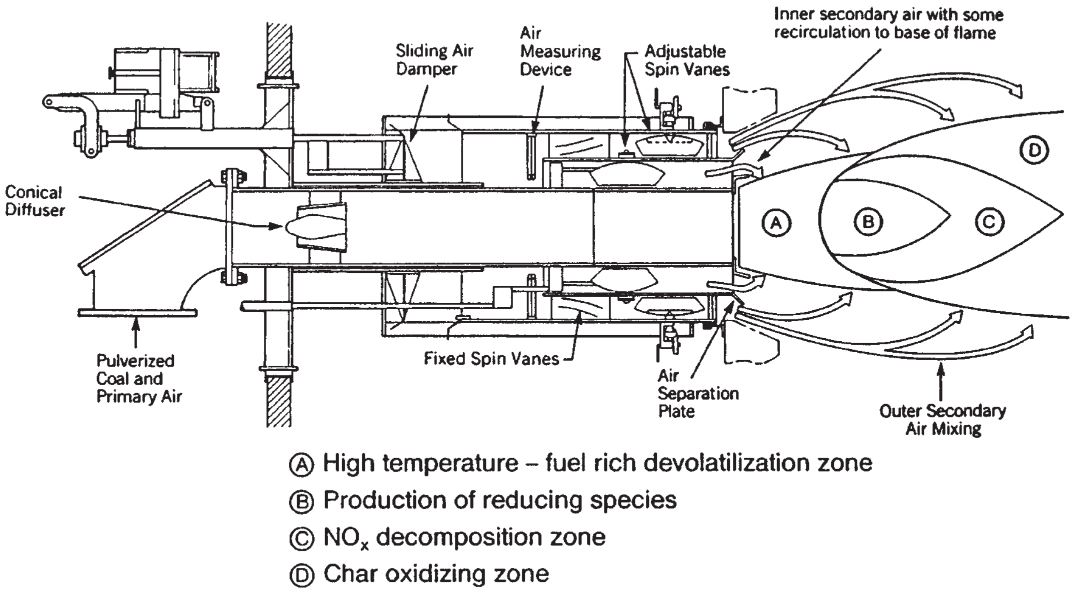


FIG. 27-18 Low-NO$_x$ pulverized coal burner. (*Babcock & Wilcox Co.*)

direction in the underfeed stoker, which is built in single-retort and multiple-retort designs. In the *single-retort,* side-dump stoker, a ram pushes coal into the retort toward the end of the stoker and upward toward the tuyere blocks, where air is admitted to the bed. This type of stoker will handle most bituminous coals and anthracite, preferably in the size range 19 to 50 mm (¾ to 2 in) and no more than 50 percent through a 6-mm (¼-in) screen. Overfire air or steam jets are frequently used in the bridgewall at the end of the stoker to promote turbulence.

In the *multiple-retort stoker,* rams feed coal to the top of sloping grates between banks of tuyeres. Auxiliary small sloping rams perform

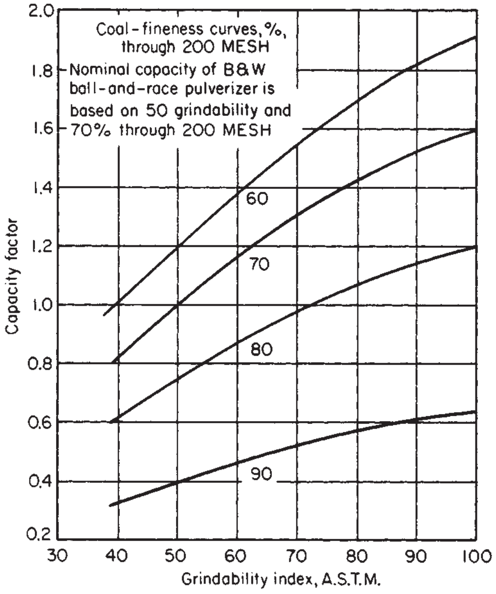


FIG. 27-19 Variation of pulverizer capacity with the grindability of the coal and the fineness to which the coal is ground. (*Babcock & Wilcox Co.*)

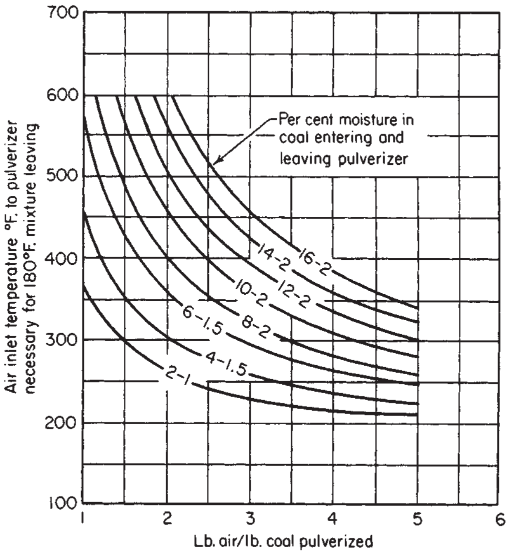


FIG. 27-20 Effect of moisture in coal on pulverizer capacity. Sufficient drying can be accomplished to restore capacity if air temperatures are high enough. [K = (°F + 459.7)/1.8] (Combustion Engineer, *Combustion Engineering Inc., New York, 1966.*)

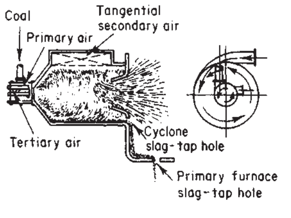


FIG. 27-21 Cyclone furnace. (*From* Marks' Standard Handbook for Mechanical Engineers, *9th ed., McGraw-Hill, New York, 1987.*)

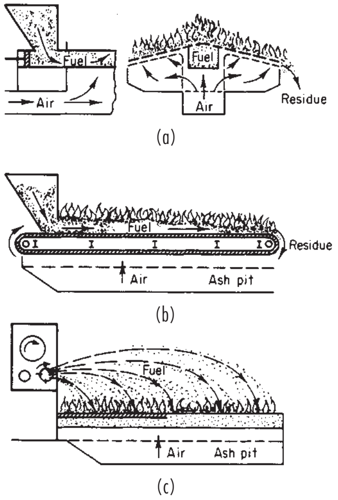


FIG. 27-22 Basic types of mechanical stokers: (*a*) underfeed; (*b*) crossfeed; (*c*) overfeed (spreader stoker).

the same function as the pusher rods in the single retort. Air is admitted along the top of the banks of tuyeres, and on the largest units the tuyeres themselves are given a slight reciprocating action to agitate the bed further. This type of stoker operates best with caking coals having a relatively high ash-softening temperature. Coal sizing is up to 50 mm (2 in) with 30 to 50 percent through a 6-mm (¼-in) screen.

Overfeed Firing: Crossfeed (Mass-Burning) Stokers Crossfeed stokers are also termed mass-burning stokers because the fuel is dumped by gravity from a hopper onto one end of a moving grate, which carries it into the furnace and down its length. Because of this feature, crossfeed stokers are commonly called *traveling-grate* stokers. The grate may be either of two designs: *bar grate* or *chain grate.* Alternatively, the burning fuel bed may be conveyed by a vibratory motion of the stoker (*vibrating-grate*).

The fuel flows at right angles to the air flow. Only a small amount of air is fed at the front of the stoker, to keep the fuel mixture rich, but as the coal moves toward the middle of the furnace, the amount of air is increased, and most of the coal is burned by the time it gets halfway down the length of the grate. Fuel-bed depth varies from 100 to 200 mm (4 to 8 in), depending on the fuel, which can be coke breeze, anthracite, or any noncaking bituminous coal.

Overfeed Firing: Spreader Stokers Spreader stokers burn coal (or other fuel) by propelling it into the furnace. A portion of the coal burns in suspension (the percentage depending on the coal fineness), while the rest burns on a grate. In most units, coal is pushed off a plate under the storage hopper onto revolving paddles (either overthrow or underthrow) which distribute the coal on the grate (Fig. 27-22*c*). The angle and speed of the paddles control coal distribution. The largest coal particles travel the farthest, while the smallest ones become partially consumed during their trajectory and fall on the forward half of the grate. The grate may be stationary or traveling. The fuel and air flow in opposite directions.

Some spreaders use air to transport the coal to the furnace and distribute it, while others use mechanical means to transport the coal to a series of pneumatic jets.

The performance of spreader stokers is affected by changes in coal sizing. The equipment can distribute a wide range of fuel sizes, but it distributes each particle on the basis of size and weight. Normal size specifications call for 19-mm (¾-in) nut and slack with not more than 30 percent less than 6.4 mm (¼ in).

Typically, approximately 30 to 50 percent of the coal is burned in suspension. If excessive fines are present, more coal particles will be carried out of the furnace and burned in suspension, and very little ash will be available to provide a protective cover for the grate surface. On the other hand, if sufficient fines are not present, not all the fuel will be burned on the grate, resulting in derating of the unit and excessive dumping of live coals to the ash hopper.

Excess air is usually 30 to 40 percent for stationary and dumping grates, while traveling grates are operated with from 22 to 30 percent excess air. Preheated air can be supplied for all types of grates but the temperature is usually limited to 395 to 422 K (250 to 300°F) to prevent excessive slagging of the fuel bed.

Overfire air nozzles are located in the front wall underneath the spreaders and in the rear wall from 0.3 to 0.9 m (1 to 3 ft) above the grate level. These nozzles use air directly from a fan or inspirate air with steam to provide turbulence above the grate for most effective mixing of fuel and air. They supply about 15 percent of the total combustion air.

Comparison of Suspension and Fuel-Bed Firing A major factor to consider when comparing a stoker-fired boiler with a PC boiler is the reduction in efficiency due to carbon loss. The carbon content of the ash passing out of a spreader stoker furnace varies from 30 to 50 percent. Overall efficiency of the stoker can be increased by reburning the ash: it is returned to the stoker grate by gravity or a pneumatic feed system. A continuous-ash-discharge spreader-stoker-fired unit will typically have a carbon loss of 4 to 8 percent, depending on the amount of ash reinjection. A properly designed PC boiler, on the other hand, can maintain an efficiency loss due to unburned carbon of less than 0.4 percent.

A difference between these firing methods may also be manifested in the initial fuel cost. For efficient operation of a spreader-stoker-fired boiler, the coal must consist of a proper mixture of coarse and fine particles. Normally, double-screened coal is purchased because less expensive run-of-mine coal does not provide the optimum balance of coarse and fine material.

An advantage of a stoker-fired furnace is its easy adaptability to firing almost any unsized solid fuels. Bark, bagasse, or refuse can normally be fired on a stoker to supplement the coal with a minimum amount of additional equipment. Thus, such supplementary waste fuels may be able to contribute a higher percentage of the total heat input in a stoker-fired furnace than in a PC furnace without expensive equipment modifications.

Fluidized-Bed Combustion The principles of gas-solid fluidization and their application to the chemical process industry are treated in Section 17. Their general application to combustion is reviewed briefly here, and their more specific application to fluidized-bed boilers is discussed later in this section.

In fluidized-bed combustion (FBC) fuel is burned in a bed of particles supported in an agitated state by an upward flow of air introduced via an air distributor. The bed particles may be sand or ash derived from the fuel, but usually they are a sulfur sorbent, like limestone or dolomite. Fluidized beds have inherently good heat-transfer characteristics, and these ensure even temperatures within the combustor and high flux rates to steam/water cooling circuits. The good gas-solids contacting promotes effective sulfur capture and allows high combustion efficiency to be achieved at temperatures significantly lower than those of a pulverized coal furnace (typically 1116 K [1550°F] compared to over 1589 K [2400°F]). These lower temperatures also result in reduced slagging and fouling problems and significantly lower NO_x formation. This latter benefit, in conjunction with the reduced SO_2 emissions, constitutes one of the great advantages of fluidized-bed combustors: in situ pollution control. Having this control built into the furnace eliminates the need for back-end cleanup and reduces plant capital cost while increasing thermal efficiency.

There are two types of FBC unit distinguished by their operating flow characteristics: *bubbling* and *circulating.* These two types operate at atmospheric pressure, AFBC, or at elevated pressure, PFBC. Pressures for PFBC are in the range 0.6 to 1.6 MPa (90 to 240 psia). Typical superficial fluidizing velocities are tabulated as follows.

	Atmospheric	Pressurized
Bubbling	1.5–2.7 m/s (5–9 ft/s)	1–1.2 m/s (3–4 ft/s)
Circulating	3.7–7.3 m/s (12–24 ft/s)	3.7–4.3 m/s (12–14 ft/s)

Bubbling Beds In bubbling beds a large proportion of the noncombustible feedstock, mainly sorbent derived, remains in the combustor, forming the bed. Bed depth is maintained by draining off excess material. Most of the gas in excess of that required for minimum fluidization appears as bubbles (voids), and these carry particles upward in their wake, promoting the rapid vertical mixing within the bed that results in the even temperatures characteristic of FBC units. Bed temperature is controlled by heat transfer to in-bed boiler tubes and/or to the water-wall tubes used to enclose the furnace. Some units have experienced metal loss from these tube surfaces, a combined effect of erosion and abrasion, and suitable protection needs to be provided. Protective measures include surface coatings such as plasma-sprayed metal coatings incorporating silicon carbide, and metal fins to disrupt the solids-flow pattern.

In AFBC units, heat is removed from the flue gas by a convection-pass tube bank. The particulates leaving the boiler with the flue gas consist of unreacted and spent sorbent, unburned carbon, and ash. Multiclones after the convection pass remove much of the particulate matter and recycle it to the combustor, increasing the in-furnace residence time and improving combustion efficiency and sulfur retention performance. Bubbling PFBC units do not have convection-pass tube banks and do not recycle solids to the boiler.

Circulating Beds These fluidized beds operate at higher velocities, and virtually all the solids are elutriated from the furnace. The majority of the elutriated solids, still at combustion temperature, are captured by reverse-flow cyclone(s) and recirculated to the foot of the combustor. This recycle stage is incorporated into AFBC and PFBC units, but only the AFBC unit has a convection pass downstream of the cyclone. The foot of the combustor is a potentially very erosive region, as it contains large particles not elutriated from the bed, and they are being fluidized at high velocity. Consequently, the lower reaches of the combustor do not contain heat-transfer tubes and the water walls are protected with refractory. Some combustors have experienced damage at the interface between the water walls and the refractory, and measures similar to those employed in bubbling beds have been used to protect the tubes in this region.

The furnace temperature is controlled by heat transfer through the exposed upper water-wall tubes. As the units increase in size, more heat-transfer surface is required than is provided by the walls. Surface can be added by wrapping horizontal tubing over the walls of the upper furnace, or by added *wing walls,* sections of water wall extending short distances into the furnace enclosure. In some designs, tubes are extended across the upper furnace where, although the fluidizing velocity is still high, the erosion potential is low because the solids are finer and their concentration is lower. In some designs, heat is removed from the recirculated solids by passing them through a bubbling-bed heat exchanger before returning them to the furnace.

In the bubbling version, all the air is introduced through the distributor plate, but for the circulating units, 30 to 40 percent is introduced above the distributor. This staged entry results in the lower reaches operating substoichiometrically, which helps to reduce NO_x emissions but tends to reduce the fluidizing velocity at the base of the combustor. To compensate for this and increase the mixing by increasing the local gas velocity, the portion of the combustor below the secondary air entry points is tapered. Staging is not generally employed on bubbling units because the oxygen deficiency in the bed tends to accelerate corrosion of the in-bed tube bank.

Fuel Flexibility An advantage of FBC designs is fuel flexibility: a single unit can burn a wider range of fuels than a PC furnace, thus offering owners an improved bargaining position to negotiate lower fuel prices. Among the fuels fired are bituminous and subbituminous coals, anthracite culm, lignite, petroleum coke, refuse-derived fuel, biomass, industrial and sewage sludges, and shredded tires. But fuel flexibility can be achieved only if the unit is designed for the range of fuels intended to be burned. For example, to maintain the same firing rate, a feed system designed for a certain fuel must be capable of feeding a lower calorific fuel at a higher rate. Similarly, to maintain the same degree of sulfur capture, feeders must be capable of delivering sorbent over a range of rates matching the sulfur contents of the fuels likely to be fed.

Sulfur Emissions Sulfur present in a fuel is released as SO_2, a known contributor to acid rain deposition. By adding limestone or dolomite to a fluidized bed, much of this can be captured as calcium sulfate, a dry nonhazardous solid. As limestone usually contains over 40 percent calcium, compared to only 20 percent in dolomite, it is the preferred sorbent, resulting in lower transportation costs for the raw mineral and the resulting ash product. Moreover, the high magnesium content of the dolomite makes the ash unsuitable for some building applications and so reduces its potential for utilization. Whatever sorbent is selected, for economic reasons it is usually from a source local to the FBC plant. If more than one sorbent is available, plant trials are needed to determine the one most suitable, as results from laboratory-scale reactivity assessments are unreliable.

At atmospheric pressure, calcium carbonate almost completely calcines to free lime, and it is this that captures the sulfur dioxide. As the free lime is not completely sulfated, the resulting sorbent ash is very alkaline, consisting primarily of $CaSO_4$ and CaO, with small amounts of $CaCO_3$.

$$CaCO_3 \rightleftharpoons CaO + CO_2 \tag{27-46}$$

$$CaO + SO_2 + [O] \rightleftharpoons CaSO_4 \tag{27-47}$$

The sulfation reaction has an optimum at a mean bed temperature of around 1116 K (1550°F).

At elevated pressure, the partial pressure of carbon dioxide inhibits calcination, and sulfur dioxide is captured by displacement of the carbonate radical. The overall effect is similar except, as no free lime is formed, the resulting sorbent ash is less alkaline, consisting solely of $CaSO_4$ and $CaCO_3$.

$$CaCO_3 + SO_2 + [O] \rightleftharpoons CaSO_4 + CO_2 \tag{27-48}$$

The sulfation reaction does not have an optimum reaction temperature under pressurized operating conditions and the higher partial pressure of oxygen results in increased conversion of sulfur dioxide to sulfur trioxide.

$$SO_2 + [O] \rightleftharpoons SO_3 \tag{27-49}$$

Under normal operating conditions, the concentration of the trioxide is unlikely to exceed 10 ppmv, but this is sufficient to elevate the acid dew point to around 422 K (300°F). This places a limit on the lowest acceptable back-end temperature if acid condensation and resulting corrosion problems are to be avoided.

Nitrogen Oxide Emissions FBC units achieve excellent combustion and sulfur emission performance at relatively modest combustion temperatures in the range 1060 to 1172 K (1450 to 1650°F). At these temperatures no atmospheric nitrogen is converted to NO_x and only a small percentage of the fuel nitrogen is converted. Typical NO_x emissions, consisting of around 90 percent NO and 10 percent NO_2, are in the range 86 to 129 mg/MJ (0.2 to 0.3 lb/10^6 Btu). In circulating AFBCs and in bubbling PFBCs, these values have been reduced to as low as 21 mg/MJ (0.05 lb/10^6 Btu) by injecting ammonia into the boiler freeboard to promote selective noncatalytic reduction (SNCR) reactions. In AFBC units, the prime variables influencing NO_x formation are excess air, mean bed temperature, the nitrogen content of the fuel, and the Ca/S molar ratio. With respect to the latter, high sorbent feed rates increase the free lime content, which catalyzes NO_x formation. In PFBC units, only excess air and fuel nitrogen content have an influence, and there appears to be no effect of pressure.

Particulate Emissions To meet environmental regulations, AFBC boilers, and some PFBC boilers, use a back-end particulate collector, such as a baghouse or an electrostatic precipitator (ESP). Compared to PC units, the ash from FBCs has higher resistivity and is finer because the flue-gas path contains cyclones. Both factors result in reduced ESP collection efficiency with AFBC units, but good performance has been achieved with PFBC units, where the SO_3 present in the flue gas lowers the ash resistivity. In general, however, baghouses are the preferred collection devices for both AFBC and PFBC applications.

FBC ash is irregular, whereas PC ash, because it melts at the elevated operating temperatures, is spherical. This difference in shape influences baghouse design in three ways: (1) FBC ash does not flow from the collection hoppers as readily and special attention has to be given to their design; (2) FBC ash forms a stronger cake, requiring more frequent and more robust cleaning mechanisms, e.g., shake-deflate and pulse-jet technologies; and (3) this more robust action in conjunction with the more abrasive, irregular particles results in filter bags being more prone to failure in FBC systems. Careful selection of bag materials (synthetic felts generally perform best) and good installation and maintenance practices minimize the latter problem.

Some PFBC boiler designs incorporate high-temperature, high-pressure (HTHP) filter devices in the flue-gas stream. These are installed primarily to protect the gas turbine from erosion damage by the fine particles that escape the cyclones, but as the filters remove virtually all the suspended particulates, they also eliminate the need for back-end removal. The commonest HTHP filter elements used are rigid ceramic candles.

COMBUSTION OF LIQUID FUELS

Oil is typically burned as a suspension of droplets generated by atomizing the fuel. As the droplets pass from the atomizer into the flame zone, they are heated both by radiation from the flame and by convection from the hot gases that surround them, and the lighter fuel components vaporize. The vapors mix with surrounding air and ignite. Depending on the fuel type, the fuel droplet may be completely vaporized or it may be partially vaporized, leaving a residual char or coke particle.

Fuel oils can contain a significant amount of sulfur: in the case of high-sulfur No. 6, it may be as much as 4 percent (Table 27-6). SO_2 is the principal product of sulfur combustion with stoichiometric or leaner fuel-air mixtures, but with the excess air customarily used for satisfactory combustion, SO_3 can form and then condense as sulfuric acid at temperatures higher than the normally expected dew point. Thus air preheaters and other heat recovery equipment in the flue-gas stream can be endangered. Figure 27-23 shows the maximum safe upper limits for dew points in the stacks of furnaces burning sulfur-containing oil and emitting unscrubbed flue gas.

Atomizers Atomization is the process of breaking up a continuous liquid phase into discrete droplets. Figure 27-24 shows the idealized process by which the surface area of a liquid sheet is increased until it forms droplets. Atomizers may be classified into two broad groups (see Fig. 27-25): pressure atomizers, in which fuel oil is injected at high pressure, and twin-fluid atomizers, in which fuel oil is injected at moderate pressure and a compressible fluid (steam or air) assists in the atomization process. Low oil viscosity (less than 15 mm²/s) is required for effective atomization (i.e., small droplet size). Light oils, such as No. 2 fuel oil, may be atomized at ambient temperature. However, heavy oils must be heated to produce the desired viscosity. Required preheats vary from approximately 373 K (212°F) for No. 6 oil to 623 K (480°F) for vacuum bottoms.

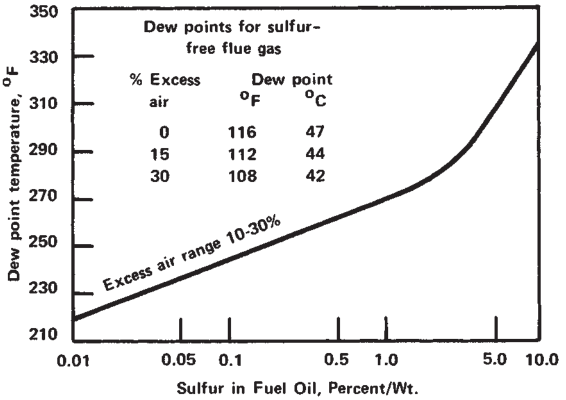


FIG. 27-23 Maximum flue-gas dew point versus percent of sulfur in typical oil fuels. (K = [°F + 459.7]/1.8)

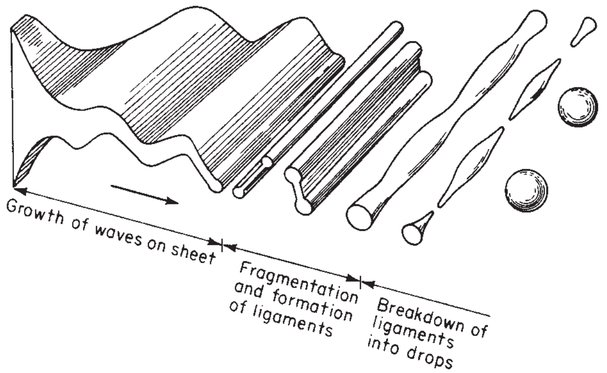


FIG. 27-24 Idealized process of drop formation by breakup of a liquid sheet. (*After Dombrowski and Johns,* Chem. Eng. Sci. ***18:*** *203, 1963.*)

Pressure Atomizers The commonest type of pressure atomizer is the swirl-type (Fig. 27-26). Entering a small cup through tangential orifices, the oil swirls at high velocity. The outlet forms a dam around the open end of the cup, and the oil spills over the dam in the form of a thin conical sheet, which subsequently breaks up into thin filaments and then droplets. Depending on the fuel viscosity, operating pressures range from 0.69 to 6.9 MPa (100 to 1000 psia) and the attainable turndown ratio is approximately 4:1. Pressure atomization is most effective for lighter fuel oils.

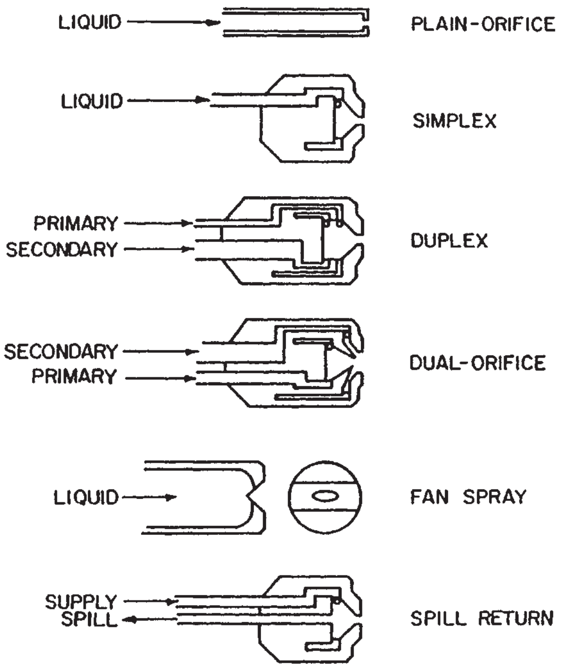


FIG. 27-25*a* Common types of atomizers: pressure atomizers. (*From Lefebvre,* Atomization and Sprays, *Hemisphere, New York, 1989. Reproduced with permission. All rights reserved.*)

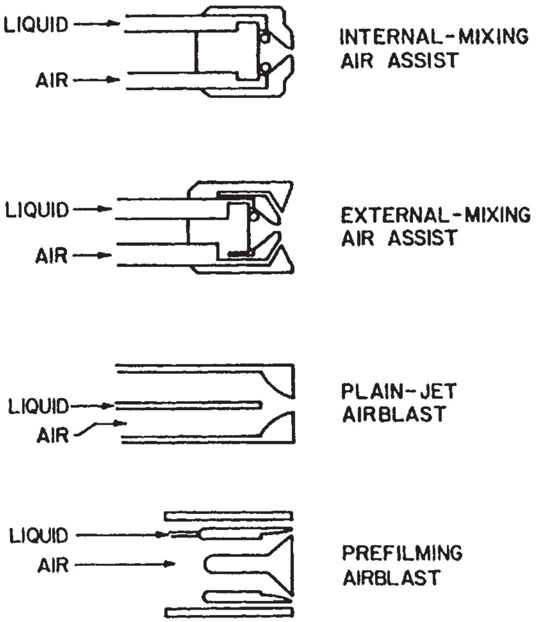


FIG. 27-25*b* Common types of atomizers: twin-fluid atomizers. (*From Lefebvre,* Atomization and Sprays, *Hemisphere, New York, 1989. Reproduced with permission. All rights reserved.*)

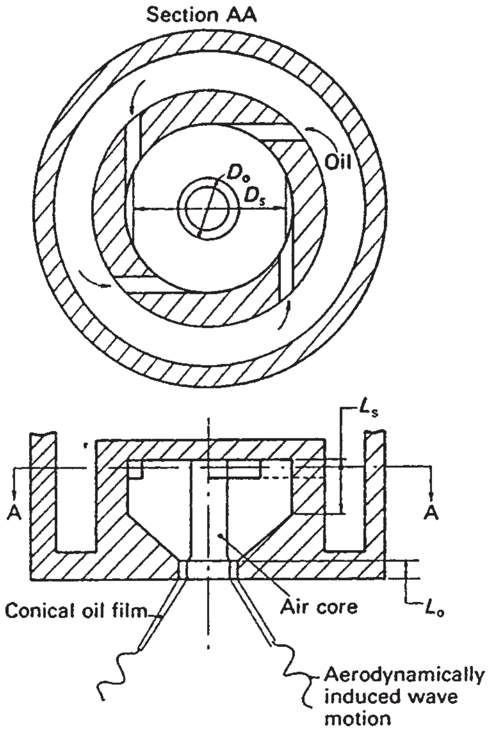


FIG. 27-26 Swirl pressure-jet atomizer. (*From Lefebvre,* Atomization and Sprays, *Hemisphere, New York, 1989. Reproduced with permission. All rights reserved.*)

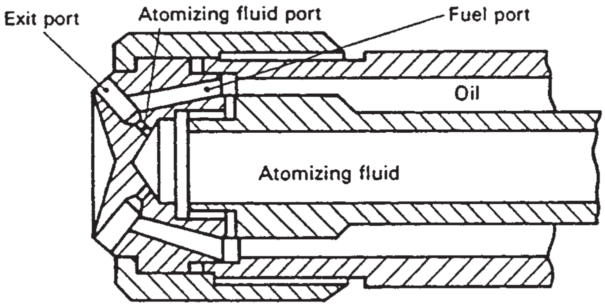


FIG. 27-27 Y-jet twin-fluid atomizer. (*From Lefebvre,* Atomization and Sprays, *Hemisphere, New York, 1989. Reproduced with permission. All rights reserved.*)

Twin-Fluid Atomizers In a twin-fluid atomizer, the fuel stream is exposed to a stream of air or steam flowing at high velocity. In the internal-mixing configuration (Fig. 27-27), the liquid and gas mix inside the nozzle before discharging through the outlet orifice. In the external-mixing nozzle, the oil stream is impacted by the high-velocity gas stream outside the nozzle. The internal type requires lower flows of secondary fluid. In industrial combustion systems, steam is the preferred atomizing medium for these nozzles. In gas turbines, compressed air is more readily available. Maximum oil pressure is about 0.69 MPa (100 psia), with the steam or air pressure being maintained about 0.14 to 0.28 MPa (20 to 40 psia) in excess of the oil pressure. The mass flow of atomizing fluid varies from 5 to 30 percent of the fuel flow rate, and represents only a modest energy consumption. Turndown performance is better than for pressure atomizers and may be as high as 20:1.

A well-designed atomizer will generate a cloud of droplets with a mean size of about 30 to 40 μm and a top size of about 100 μm for light oils such as No. 2 fuel oil. Mean and top sizes are somewhat larger than this for heavier fuel oils.

Oil Burners The structure of an oil flame is shown in Fig. 27-28, and Fig. 27-29 illustrates a conventional circular oil burner for use in boilers. A combination of stabilization techniques is used, typically including swirl. It is important to match the droplet trajectories to the combustion aerodynamics of a given burner to ensure stable ignition and good turndown performance.

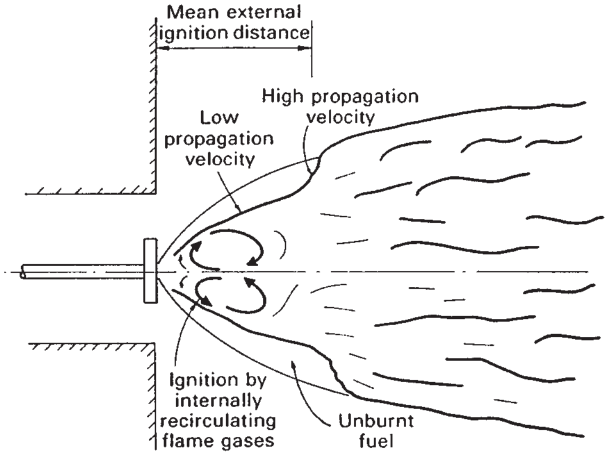


FIG. 27-28 Structure of typical oil flame. (*From Lawn,* Principles of Combustion Engineering for Boilers, *Academic Press, London, 1987. Reprinted with permission.*)

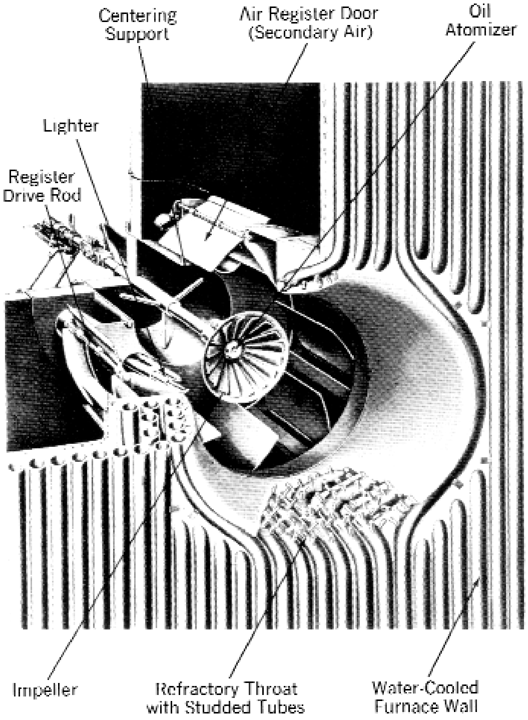


FIG. 27-29 Circular register burner with water-cooled throat for oil firing. (*Babcock & Wilcox Co.*)

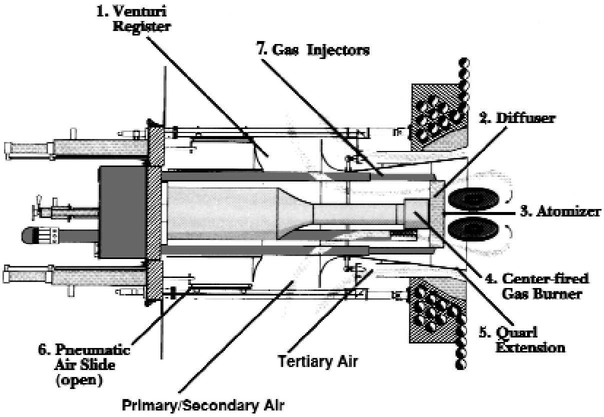


FIG. 27-30 Low-NO$_x$ combination oil/gas forced-draft boiler burner. (*Todd Combustion, Inc.*)

Many oil burners are designed as combination gas/oil burners. An example of a modern low-NO$_x$ oil/gas forced-draft burner is shown in Fig. 27-30. This is an air-staged design, with the air divided into primary, secondary, and tertiary streams. An air-staged natural draft process heater oil/gas burner is illustrated in Fig. 27-31.

Emissions of unburned carbon (primarily coke cenospheres) may be reduced by (1) achieving smaller average fuel droplet size (e.g., by heating the fuel to lower its viscosity or by optimizing the atomizer geometry), (2) increasing the combustion air preheat temperature, or (3) firing oils with high vanadium content (vanadium appears to catalyze the burnout of coke).

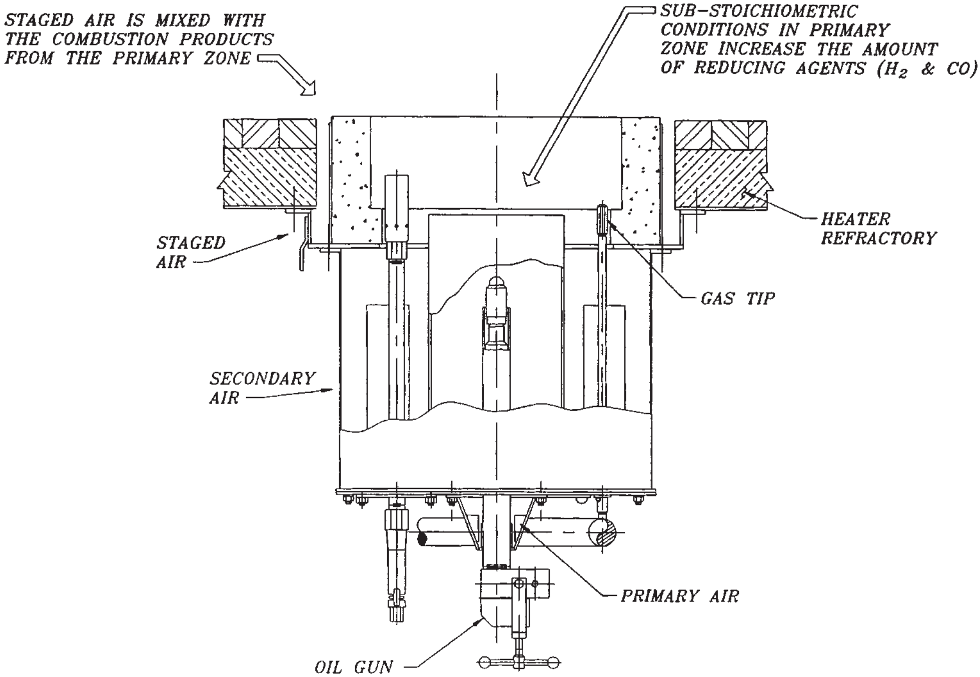


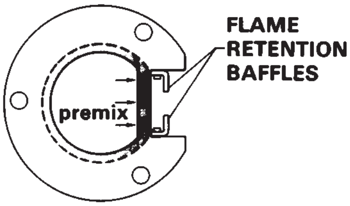
FIG. 27-31 Air-staged natural-draft combination oil/gas burner. (*Callidus Technologies, Inc.*)

COMBUSTION OF GASEOUS FUELS

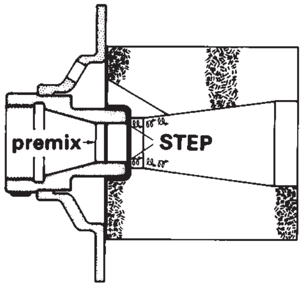
Combustion of gas takes place in two ways, depending upon when gas and air are mixed. When gas and air are mixed before ignition, as in a Bunsen burner, burning proceeds by hydroxylation. The hydrocarbons and oxygen form hydroxylated compounds that become aldehydes; the addition of heat and additional oxygen breaks down the aldehydes to H_2, CO, CO_2, and H_2O. Inasmuch as carbon is converted to aldehydes in the initial stages of mixing, no soot can be developed even if the flame is quenched.

Cracking occurs when oxygen is added to hydrocarbons after they have been heated, decomposing the hydrocarbons into carbon and hydrogen, which, when combined with sufficient oxygen, form CO_2 and H_2O. Soot and carbon black are formed if insufficient oxygen is present or if the combustion process is arrested before completion.

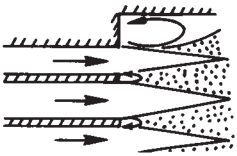
Gas Burners Gas burners may be classified as premixed or nonpremixed. Many types of flame stabilizer are employed in gas burners (see Fig. 27-32). Bluff body, swirl, and combinations thereof are the predominant stabilization mechanisms.



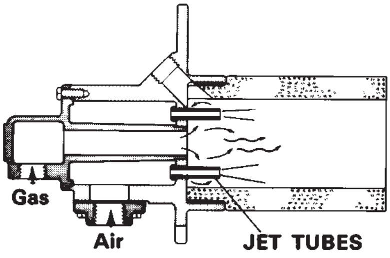
(a) continuous flame line burner (premix)



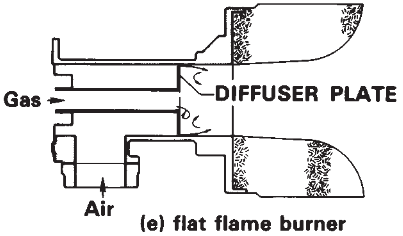
(b) "tunnel" premix burner



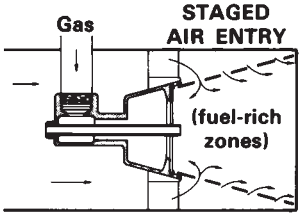
(c) generalized flow field for industrial nozzle-mix burner



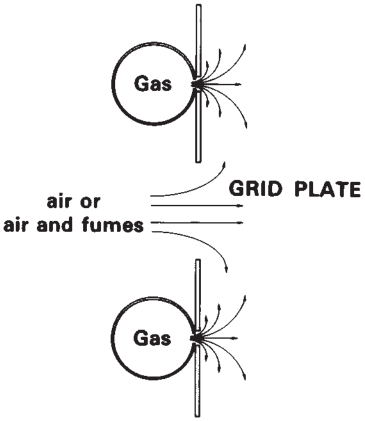
(d) general-purpose burner



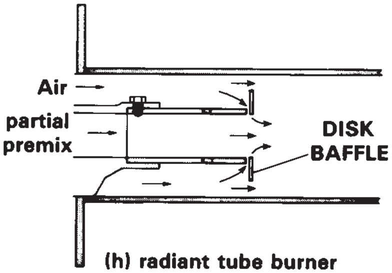
(e) flat flame burner



(f) air heating induct burner



(g) fume-incinerating burner



(h) radiant tube burner

FIG. 27-32 Flame-holding arrangements. Cases (*a*) through (*f*) are various forms of bluff bodies, creating recirculation and fine-scale turbulence in their wake. Cases (*d*) through (*g*) constitute air jets blasting through a relatively quiescent volume of raw gas. Case (*f*) may be cylindrical, as in a gas turbine burner, or trough-like. (*From* North American Combustion Handbook, *3d ed., North American Manufacturing Company, Cleveland, 1996.*)

Fully Premixed Burners A fully premixed burner includes a section for completely mixing the fuel and air upstream of the burner. The burner proper consists essentially of a flame holder; see for example, Fig. 27-32*a, b.* The porting that admits the mixture to the combustion chamber is designed to produce a fairly high velocity through a large number of orifices to avoid the possibility of the flame flashing back through the flame holder and igniting the mixture upstream of the burner.

Surface combustion devices are designed for fully premixing the gaseous fuel and air and burning it on a porous radiant surface. The close coupling of the combustion process with the burner surface results in low flame temperatures and, consequently, low NO_x formation. Surface materials can include ceramic fibers, reticulated ceramics, and metal alloy mats. This approach allows the burner shape to be customized to match the heat transfer profile with the application.

Partially Premixed Burners These burners have a premixing section in which a mixture that is flammable but overall fuel-rich is generated. Secondary combustion air is then supplied around the flame holder. The fuel gas may be used to aspirate the combustion air or vice versa, the former being the commoner. Examples of both are provided in Figs. 27-33 and 27-34.

Nozzle-Mix Burners The most widely used industrial gas burners are of the nozzle-mix type. The air and fuel gas are separated until they are rapidly mixed and reacted after leaving the ports. Figure 27-32*c, d, e, f, h* shows some examples of the variety of nozzle-mix designs in use. These burners allow a wide range of fuel-air ratios, a wide variety of flame shapes, and multifuel firing capabilities. They can be used to generate special atmospheres by firing at very rich conditions (50 percent excess fuel) or very lean conditions (1000 percent excess air). By changing nozzle shape and degree of swirl, the flame profile and mixing rates can be varied widely, from a rapid-mixing short flame ($L/D = 1$), to a conventional flame ($L/D = 5$ to 10), to a slow-mixing long flame ($L/D = 20$ to 50).

Staged Burners As was pointed out earlier under "Pollutant Formation and Control in Flames," the proper staging of fuel or air in the combustion process is one technique for minimizing NO_x emissions. Gas burners that achieve such staging are available.

Air-Staged Burners Low-NO_x air-staged burners for firing gas (or oil) are shown in Figs. 27-30 and 27-31. A high-performance, low-NO_x burner for high-temperature furnaces is shown in Fig. 27-35. In this design, both air-staging and external flue-gas recirculation are used to achieve extremely low levels of NO_x emissions (approximately 90 percent lower than conventional burners). The flue gas is recirculated by a jet-pump driven by the primary combustion air.

Fuel-Staged Burners Use of fuel-staged burners is the preferred combustion approach for NO_x control because gaseous fuels typically contain little or no fixed nitrogen. Figure 27-36 illustrates a fuel-staged natural draft refinery process heater burner. The fuel is split into primary (30 to 40 percent) and secondary (60 to 70 percent) streams. Furnace gas may be internally recirculated by the primary gas jets for additional NO_x control. NO_x reductions of 80 to 90 percent have been achieved by staging fuel combustion.

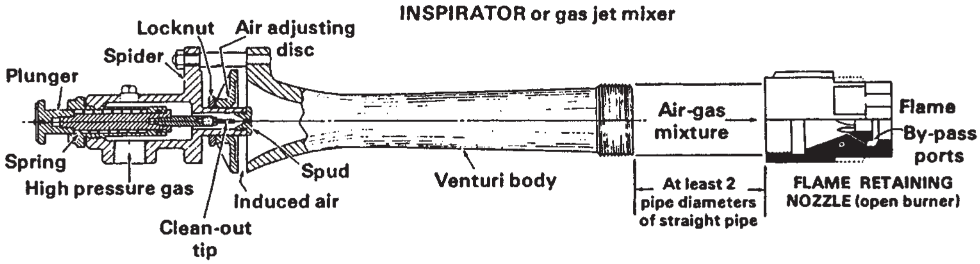


FIG. 27-33 Inspirator (gas-jet) mixer feeding a large port premix nozzle of the flame retention type. High-velocity gas emerging from the spud entrains and mixes with air induced in proportion to the gas flow. The mixture velocity is reduced and pressure is recovered in the venturi section. (*From* North American Combustion Handbook, *3d ed., North American Manufacturing Company, Cleveland, 1996.*)

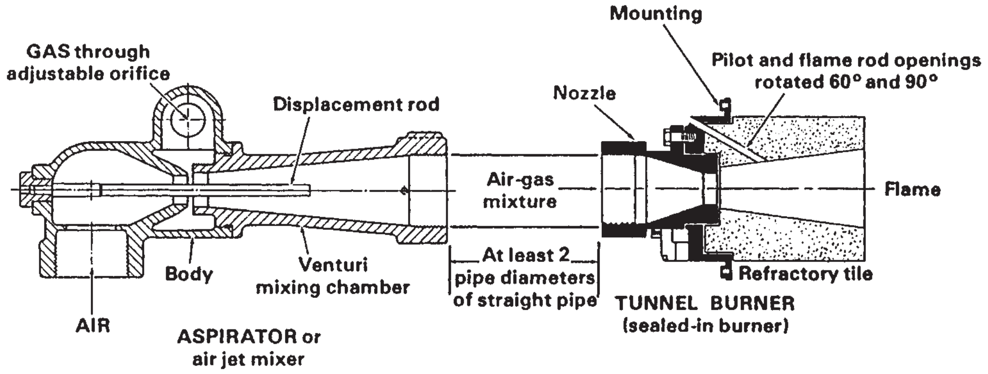


FIG. 27-34 Aspirator (air-jet) mixer feeding a sealed-in large port premix tunnel burner. Blower air enters at lower left. Gas from an atmospheric regulator is pulled into the air stream from the annular space around the venturi throat in proportion to the air flow. (*From* North American Combustion Handbook, *3d ed., North American Manufacturing Company, Cleveland, 1996.*)

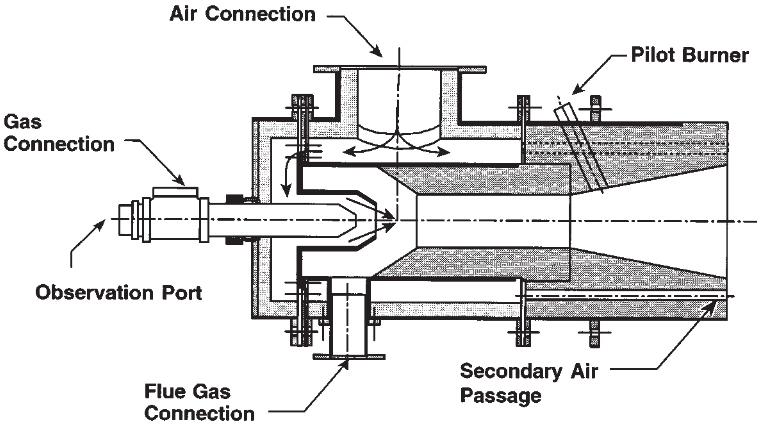


FIG. 27-35 Low-NO_x burner with air-staging and flue-gas recirculation for use in high-temperature furnaces. (*Hauck Manufacturing Company. Developed and patented by the Gas Research Institute.*)

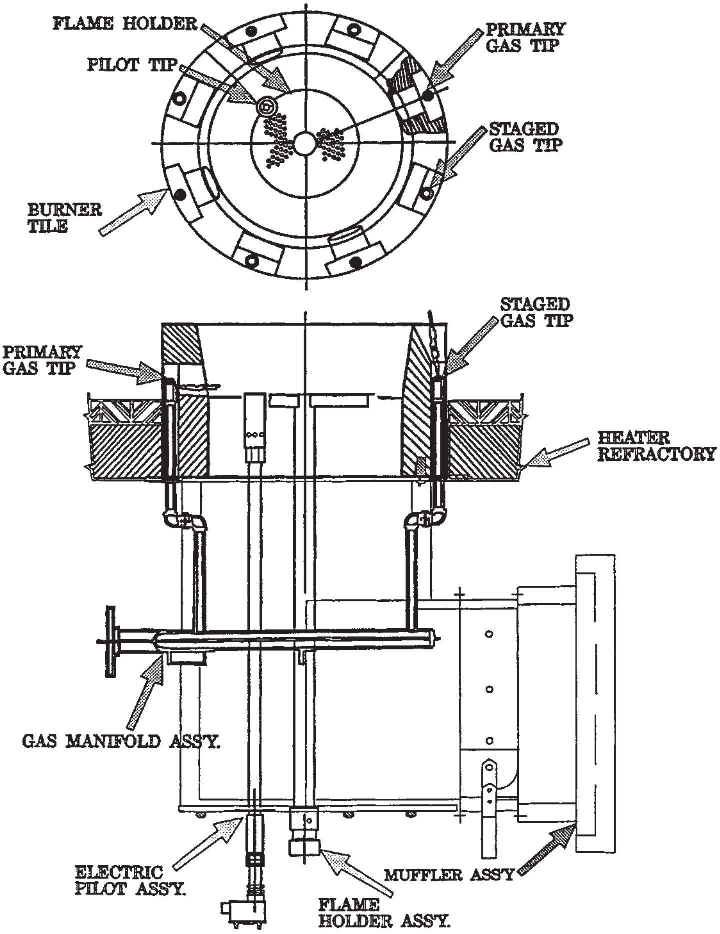


FIG. 27-36 Low-NO_x fuel-staged burner for a natural draft refinery process heater. (*Callidus Technologies, Inc.*)

THERMAL ENERGY CONVERSION AND UTILIZATION

BOILERS

Steam generators are designed to produce steam for process requirements, for process needs along with electric power generation, or solely for electric power generation. In each case, the goal is the most efficient and reliable boiler design for the least cost. Many factors influence the selection of the type of steam generator and its design, and some of these will be treated later in discussions of industrial and utility boilers.

Figure 27-37 shows the chief operating characteristics of a range of boilers, from small-scale heating systems to large-scale utility boilers.

In the industrial market, boilers have been designed to burn a wide range of fuels and operate at pressures up to 12.4 MPa (1800 psia) and steaming rates extending to 455,000 kg/h (1,000,000 lb/h). High-capacity shop-assembled boilers (package boilers) range in capacity from 4545 kg/h (10,000 lb/h) to about 270,000 kg/h (600,000 lb/h). These units are designed for operation at pressures up to 11.4 MPa (1650 psia) and 783 K (950°F). Figure 27-38 shows a gas- or liquid-fuel-fired unit. While most shop-assembled boilers are gas- or oil-fired, designs are available to burn pulverized coal. A field-erected coal-fired industrial boiler is shown in Fig. 27-39.

Boilers designed for service in electric power utility systems operate at both subcritical-pressure (pressures below 22.1 MPa [3205 psia]) and supercritical-pressure steam conditions. Subcritical-pressure boilers range in design pressures up to about 18.6 MPa (2700 psia) and in steaming capacities up to about 2955 Mg/h (6,500,000 lb/h). Supercritical-pressure boilers have been designed to operate at pressures up to 34.5 MPa (5000 psia). The 24.1 MPa (3500 psia) cycle has been firmly established in the utility industry, and boilers with steaming capacities up to 4227 Mg/h (9,300,000 lb/h) and superheat and reheat temperatures of 814 K (1005°F) are in service. The furnace of a large coal-fired steam generator absorbs half of the heat released, so that the gas temperature leaving the furnace is about 1376 K (2000°F).

Boiler Design Issues Boiler design involves the interaction of many variables: water-steam circulation, fuel characteristics, firing systems and heat input, and heat transfer. The furnace enclosure is one of the most critical components of a steam generator and must be conservatively designed to assure high boiler availability. The furnace configuration and its size are determined by combustion requirements, fuel characteristics, emission standards for gaseous effluents and particulate matter, and the need to provide a uniform gas flow and temperature entering the convection zone to minimize ash deposits and excessive superheater metal temperatures. Discussion of some of these factors follows.

Circulation and Heat Transfer Circulation, as applied to a steam generator, is the movement of water or steam or a mixture of both through the heated tubes. The circulation objective is to absorb heat from the tube metal at a rate that assures sufficient cooling of the furnace-wall tubes during all operating conditions, with an adequate margin of reserve for transient upsets. Adequate circulation prevents excessive metal temperatures or temperature differentials that would cause failures due to overstressing, overheating, or corrosion.

The rate of heat transfer from the tubes to the fluid depends primarily on turbulence and the magnitude of the heat flux itself. Turbulence is a function of mass velocity of the fluid and tube roughness. Turbulence has been achieved by designing for high mass velocities, which ensure that nucleate boiling takes place at the inside surface of the tube. If sufficient turbulence is not provided, *departure from nucleate boiling* (DNB) occurs. DNB is the production of a film of steam on the tube surface that impedes heat transfer and results in tube overheating and possible failure. This phenomenon is illustrated in Fig. 27-40.

Satisfactory performance is obtained with tubes having helical ribs on the inside surface, which generate a swirling flow. The resulting centrifugal action forces the water droplets toward the inner tube surface and prevents the formation of a steam film. The internally rifled tube maintains nucleate boiling at much higher steam temperature and pressure and with much lower mass velocities than those needed in smooth tubes. In modern practice, the most important criterion in drum boilers is the prevention of conditions that lead to DNB.

Utility Steam Generators

Steam-Generator Circulation System Circulation systems for utility application are generally classified as natural circulation and forced or pump-assisted circulation in drum-type boilers, and as once-through flow in subcritical- and supercritical-pressure boilers. The

Boiler Service	Fuel	Capacity (kg/h)	Outlet Pressure (MPa)	Steam Temp. (K)	Reheat Temp. (K)	Feedwater Temp. (K)
Heating	Oil	27,000	1.0	Sat	-	373
Small Industrial	Oil	45,000	4.6	673	-	423
Medium Industrial	Coal	115,000	4.6	673	-	403
Large Industrial	Coal	270,000	10.4	745	-	408
Large Utility	Coal	1,700,000	18.2	811	811	522

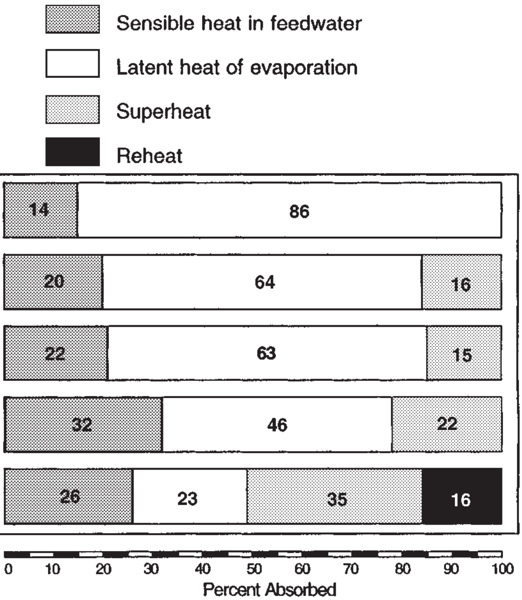


FIG. 27-37 Heat absorption distribution for various types of boilers. (*Adapted from Singer,* Combustion—Fossil Power, *4th ed., Combustion Engineering, Inc., Windsor, Conn., 1991.*)

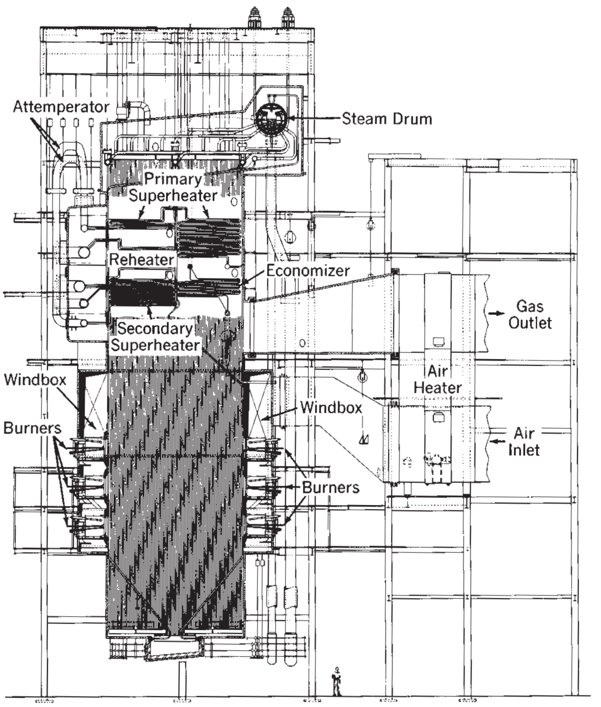


FIG. 27-38 Shop-assembled radiant boiler for natural gas or oil. (*Babcock & Wilcox Co.*)

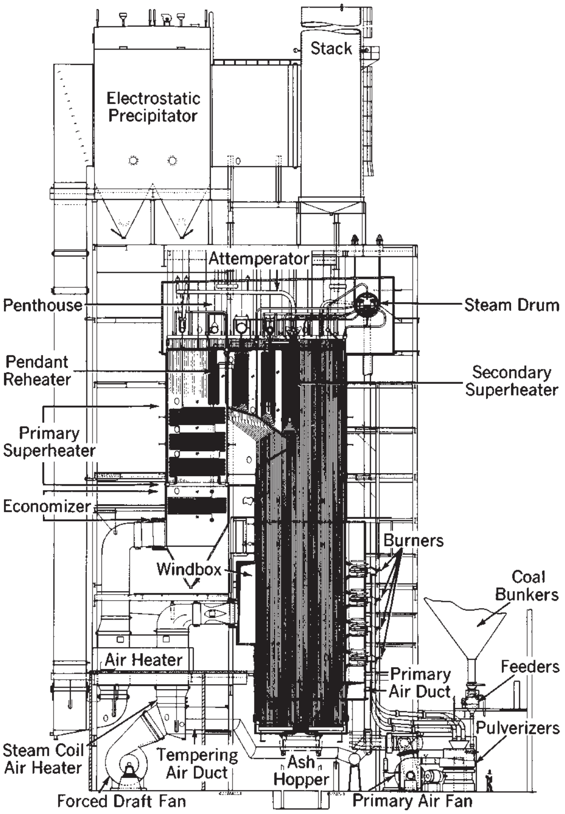


FIG. 27-39 Field-erected radiant boiler for pulverized coal. (*Babcock & Wilcox Co.*)

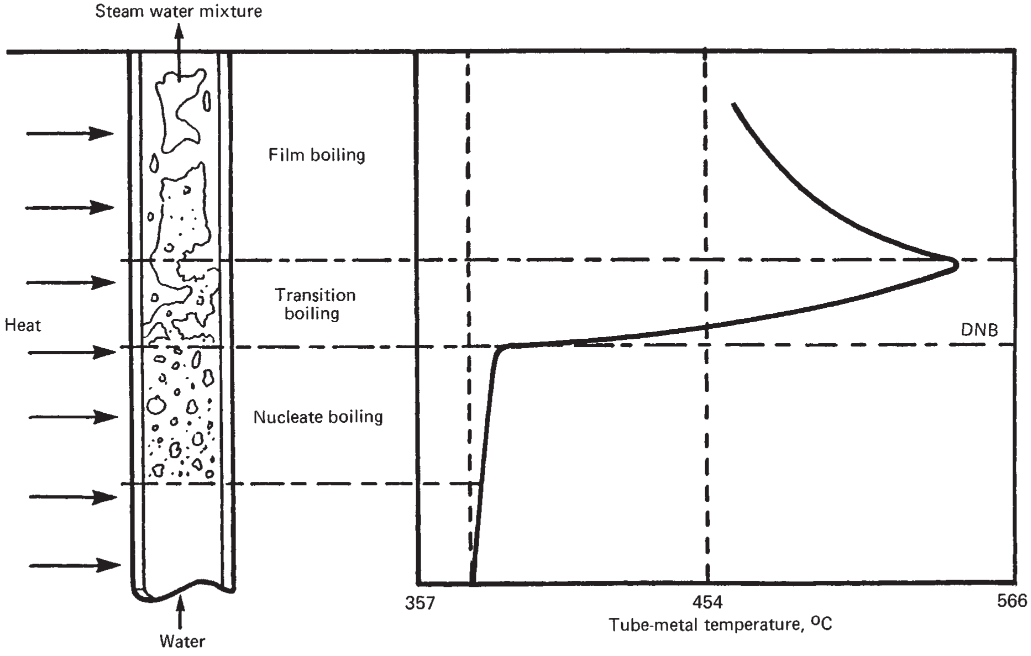


FIG. 27-40 Effect of departure from nucleate boiling (DNB) on tube-metal temperature.

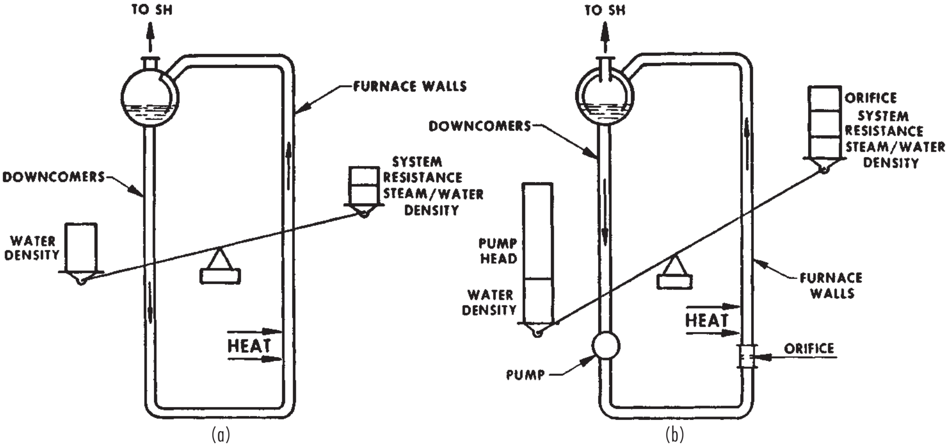


FIG. 27-41 Circulation systems: (*a*) natural circulation; (*b*) pump-assisted circulation.

circulation systems for natural and pump-assisted circulation boilers are illustrated schematically in Fig. 27-41.

Natural circulation in a boiler circulation loop depends only on the difference between the mean density of the fluid (water) in the downcomers and the mean density of the fluid (steam-water mixture) in the heated furnace walls. The actual circulating head is the difference between the total gravity head in the downcomer and the integrated gravity heads in the upcoming legs of the loop containing the heated tubes. The circulating head must balance the sum of the losses due to friction, shock, and acceleration throughout the loop.

In a once-through system, the feedwater entering the unit absorbs heat until it is completely converted to steam. The total mass flow through the waterwall tubes equals the feedwater flow and, during normal operation, the total steam flow. As only steam leaves the boiler, there is no need for a steam drum.

Fuel Characteristics Fuel choice has a major impact on boiler design and sizing. Because of the heat transfer resistance offered by ash deposits in the furnace chamber in a coal-fired boiler, the mean absorbed heat flux is lower than in gas- or oil-fired boilers, so a greater surface area must be provided. Figure 27-42 shows a size comparison between a coal-fired and an oil-fired boiler for the same duty.

In addition, coal characteristics have a major impact on the design and operation of a coal-fired boiler. Coals having a low volatile-matter content usually require higher ignition temperatures and those with less than 12 to 14 percent volatile matter may require supplementary fuel to stabilize ignition. Generally, western U.S. coals are more reactive than others and, consequently, easier to ignite, but because of high moisture content they require higher air temperatures to the mills for drying the coal to achieve proper pulverization. Extremely high-ash coal also may present problems in ignition and stabilization. The ash constituents and the quantity of ash will have a decided influence on sizing the furnace. Accordingly, a thorough review of coal characteristics is needed to establish the effect on the design and operation of a boiler.

Superheaters and Reheaters A superheater raises the temperature of the steam generated above the saturation level. An important function is to minimize moisture in the last stages of a turbine to avoid blade erosion. With continued increase of evaporation temperatures and pressures, however, a point is reached at which the available superheat temperature is insufficient to prevent excessive moisture from forming in the low-pressure turbine stages. This condition is resolved by removing the vapor for reheat at constant pressure in the

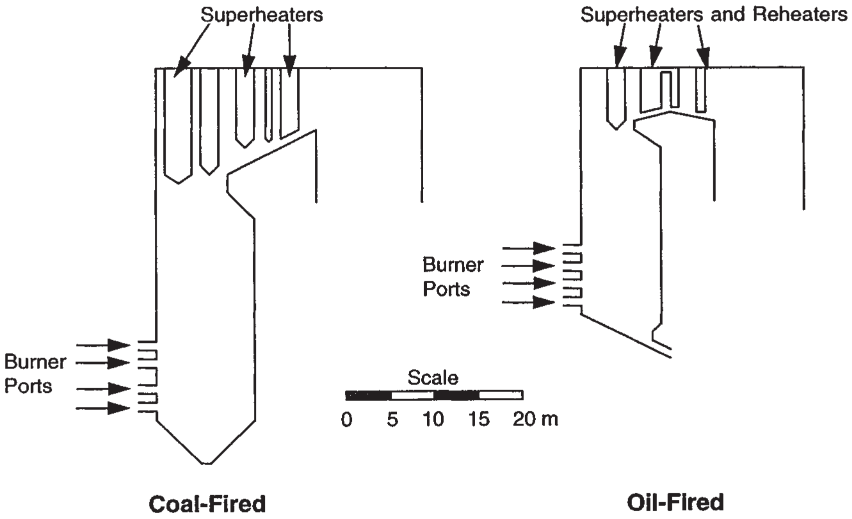


FIG. 27-42 Comparison of the sizes and shapes of typical 500-MW$_e$ coal- and oil-fired boilers. (*Adapted with permission from Lawn,* Principles of Combustion Engineering for Boilers, *Academic Press, London, 1987.*)

boiler and returning it to the turbine for continued expansion to condenser pressure. The thermodynamic cycle using this modification of the Rankine cycle is called the *reheat cycle.*

Economizers Economizers improve boiler efficiency by extracting heat from the discharged flue gases and transferring it to feedwater, which enters the steam generator at a temperature appreciably lower than the saturation-steam temperature.

Industrial Boilers Industrial boilers are steam generators that provide power, steam, or both to an industrial plant, in contrast to a utility boiler in a steam power plant. A common configuration is a stationary water-tube boiler in which some of the steam is generated in a convection-section tube bank (also termed a *boiler bank*). In the original industrial boilers, in fact, almost all of the boiling occurred in that section, but now many industrial steam generators of 180,000 kg/h (397,000 lb/h) and greater capacity are radiant boilers. The boiler steam pressure and temperature and feedwater temperature determine the fraction of total heat absorbed in the boiler bank. For a typical coal-fired boiler producing about 90,000 kg/h (198,000 lb/h):

%, total steam in boiler bank	Boiler pressure		Steam temperature		Feedwater temperature	
	MPa	psia	K	°F	K	°F
45	1.4	200	460	369	389	241
30	4.1	600	672	750	389	241
16	10.3	1500	783	950	450	351
10	12.4	1800	811	1000	450	351

The thicker plate for operation at higher pressures increases the cost of the boiler. As a result, it is normally not economical to use a boiler bank for heat absorption at pressures above 10.7 MPa (1550 psia).

Industrial boilers are employed over a wide range of applications, from large power-generating units with sophisticated control systems, which maximize efficiency, to small low-pressure units for space or process heating, which emphasize simplicity and low capital cost. Although their usual primary function is to provide energy in the form of steam, in some applications steam generation is incidental to a process objective, e.g., a chemical recovery unit in the paper industry, a carbon monoxide boiler in an oil refinery, or a gas-cooling waste-heat boiler in an open-hearth furnace. It is not unusual for an industrial boiler to serve a multiplicity of functions. For example, in a paper-pulp mill, the chemical-recovery boiler is used to convert black liquor into useful chemicals and to generate process steam. At the same plant, a bark-burning unit recovers heat from otherwise wasted material and also generates power.

Industrial boilers burn oil, gas, coal, and a wide range of product and/or waste fuels, some of which are shown in Tables 27-4 and 27-19. Natural gas has become the principal fuel of choice, accounting for approximately two-thirds of all the energy fired in industrial boilers across a wide range of manufacturing industries (Table 27-20). Coal is the second most prevalent fuel, accounting for one-quarter of the energy fired. Waste fuels, however, are increasing in importance.

An excellent brief exposition of industrial boilers is presented as Chapter 8 of *Combustion—Fossil Power,* Singer (ed.), 4th ed., Combustion Engineering, Windsor, Conn., 1991.

Design Criteria Industrial-boiler designs are tailored to the fuels and firing systems involved. Some of the more important design criteria include:

- Furnace heat-release rates, both W/m^3 and W/m^2 of effective projected radiant surface ($Btu/[h\cdot ft^3]$ and $Btu/[h\cdot ft^2]$).
- Heat release on grates
- Flue-gas velocities through tube banks
- Tube spacings

Table 27-21 gives typical values or ranges of these criteria for gas, oil, and coal. The furnace release rates are important, for they establish maximum local absorption rates within safe limits. They also have a bearing on completeness of combustion and therefore on efficiency and particulate emissions. Limiting heat release on grates (in stoker firing) will minimize carbon loss, control smoke, and avoid excessive fly ash.

Limits on flue-gas velocities for gas- or oil-fired industrial boilers

TABLE 27-19 Solid-Waste Fuels Burned in Industrial Boilers

Waste	HHV, kJ/kg*
Bagasse	8374–11,630
Furfural residue	11,630–13,956
Bark	9304–11,630
General wood wastes	10,467–18,608
Coffee grounds	11,397–15,119
Nut hulls	16,282–18,608
Rich hulls	12,095–15,119
Corncobs	18,608–19,306
Rubber scrap	26,749–45,822
Leather	27,912–45,822
Cork scrap	27,912–30,238
Paraffin	39,077
Cellophane plastics	27,912
Polyvinyl chloride	40,705
Vinyl scrap	40,705
Sludges	4652–27,912
Paper wastes	13,695–18,608

*To convert kilojoules per kilogram to British thermal units per pound, multiply by 4.299×10^{-1}.

TABLE 27-20 Fuel Consumption in Boilers in Various Industries

Industry	Annual energy consumption in boilers, PJ/a*			
	Residual oil	Distillate oil	Natural gas	Coal
Aluminum	—	—	2	—
Steel	25	—	66	25
Chemicals	29	6	759	257
Forest products	140	4	381	309
Textiles	12	5	74	32
Fabricated metal	2	1	39	5
Industrial machinery & equipment	3	4	115	12
Transportation equipment	—	2	51	—
Food	25	7	332	151
Petroleum refining	35	2	267	3
TOTAL	27	31	2086	794

SOURCE: *Manufacturing Consumption of Energy,* Energy Information Administration, U.S. Dept. Energy, 1991.

*Within the limit of their probable accuracy, the values of this table are acceptable also for the units of 10^{12} Btu/a. For accurate *conversion,* however, they must be reduced by 5.2 percent.

TABLE 27-21 Typical Design Parameters for Industrial Boilers

Furnace	Heat-release rate, W/m^2* of EPRS†
Natural gas-fired	630,800
Oil-fired	551,900–630,800
Coal: pulverized coal	220,780–378,480
Spreader stoker	252,320–410,020

Stoker, coal-fired	Grate heat-release rate, W/m^2
Continuous-discharge spreader	2,050,000–2,207,800
Dump-grade spreader	1,419,300–1,734,700
Overfeed traveling grate	1,261,000–1,734,700

Flue-gas velocity: type Fuel-fired	Single-pass Boiler, m/s	Baffled	
		Boiler, m/s	Economizer, m/s
Gas or distillate oil	30.5	30.5	30.5
Residual oil	30.5	22.9	30.5
Coal (not lignite)			
Low-ash	19.8–21.3	15.2	15.2–18.3
High-ash	15.2	NA‡	12.2–15.2

*To convert watts per square meter to British thermal units per hour-foot, multiply by 0.317.

†Effective projected radiant surface.

‡Not available.

are usually determined by the need to limit draft loss. For coal firing, design gas velocities are established to minimize fouling and plugging of tube banks in high-temperature zones and erosion in low-temperature zones.

Convection tube spacing is important when the fuel is residual oil or coal, especially coal with low ash-fusion or high ash-fouling tendencies. The amount of the ash and, even more important, the characteristics of the ash must be specified for design.

Natural-circulation and convection boiler banks are the basic design features on which a line of standard industrial boilers has been developed to accommodate the diverse steam, water, and fuel requirements of the industrial market.

Figure 27-43 shows the amount of energy available for power by using a fire-tube boiler, an industrial boiler, and subcritical- and supercritical-pressure boilers. Condensing losses decrease substantially, and regeneration of air and feedwater becomes increasingly important in the most advanced central-station boilers.

The boiler designer must proportion heat-absorbing and heat-recovery surfaces in a way to make the best use of heat released by the fuel. Water walls, superheaters, and reheaters are exposed to convection and radiant heat, whereas convection heat transfer predominates in air preheaters and economizers. The relative amounts of these surfaces vary with the size and operating conditions of the boiler.

Package Boilers In a fire-tube boiler, the hot combustion products flow through tubes immersed in the boiler water, transferring heat to it. In a water-tube boiler, combustion heat is transferred to water flowing through tubes which line the furnace walls and boiler passages. The greater safety of water-tube boilers has long been recognized, and they have generally superseded fire-tube configurations except for small package boiler designs. Fire-tube package boilers range from a few hundred to 18,200 kg/h (40,000 lb/h) steaming capacity. A fire-tube boiler is illustrated in Figs. 27-44 and 27-45. Water-tube package boilers range from a few hundred to 270,000 kg/h (600,000 lb/h) steaming capacity. A water-tube package boiler is illustrated in Fig. 27-46. The majority of water-tube package boilers use natural circulation and are designed for pressurized firing. The most significant advantage of shop-assembled or package boilers is the cost benefit associated with use of standard designs and parts.

Package boilers can be shipped complete with fuel-burning equipment, controls, and boiler trim. It may be necessary to ship the larger units in sections, however, and a shop-assembled boiler with a capacity greater than about 109,000 kg/h (240,000 lb/h) is deliverable only by barge. (For a more detailed discussion of shop-assembled boilers, see Singer, 1991, pp. 8.36–8.42.)

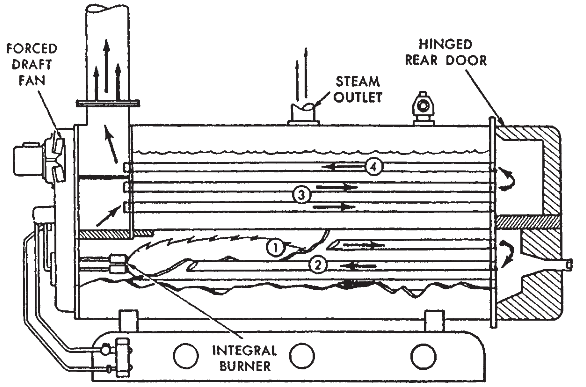


FIG. 27-44 A four-pass packaged fire-tube boiler. Circled numbers indicate passes. (*From Cleaver Brooks, Inc. Reproduced from* Gas Engineer's Handbook, *Industrial Press, New York, 1965, with permission.*)

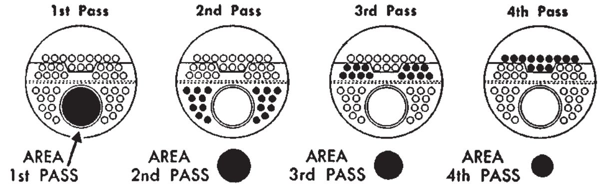


FIG. 27-45 Location and relative size of each of four passes of the flue gas through a fire-tube boiler. (*From Cleaver Brooks, Inc. Reproduced from* Gas Engineer's Handbook, *Industrial Press, New York, 1965, with permission.*)

Fluidized-Bed Boilers As explained in the earlier discussion of coal combustion equipment, the furnace of a fluid-bed boiler has a unique design. The system as a whole, however, consists mainly of standard equipment items, adapted to suit process requirements. The systems for coal and sorbent preparation and feeding, ash removal, and ash disposal are very similar to those found in PC boiler plants, the major difference being that the top size of material used is greater. The water-wall boiler enclosure and convection-pass tubing are also similar to the designs found in PC boilers. In-bed heat-transfer surfaces are arranged similarly to convection-pass tube banks, but the bubbling action subjects them to higher forces and special consideration has to be given to the design of a suitable support structure. A fluidized-bed plant includes particulate removal equipment such as cyclones, multiclones, baghouses, and electrostatic precipitators, all similar to designs found in other solids-handling process plants.

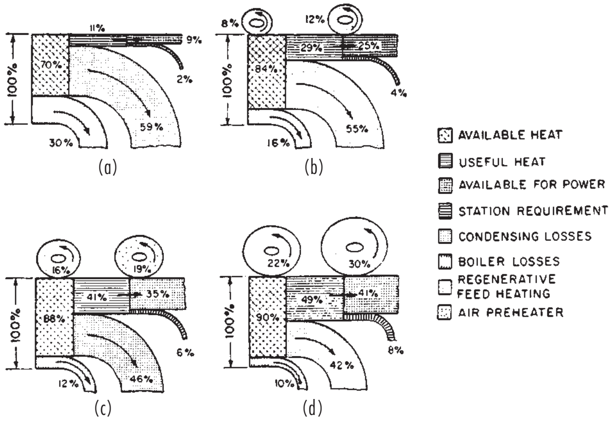


FIG. 27-43 Sankey diagrams for various types of boilers: (*a*) fire-tube boiler; (*b*) industrial boiler; (*c*) subcritical-pressure boiler; (*d*) supercritical-pressure boiler.

Bubbling AFBCs A simplified schematic of a bubbling AFBC is presented in Fig. 27-47. A demonstration plant generating 160 MWe, with a power production intensity[*] of 1.49 MWe/m^2 (1 MWe/16 ft^2), began operation in 1988. Also operating is a 350-MWe unit that employs many of the same design features.

Although subbituminous coal with a top size of 25 mm (1 in) can be fed overbed with good thermal and environmental performance, less reactive bituminous coal must be fed underbed. This requires that the coal be dried and crushed to a top size of 3 mm (⅛ in). A lock-hopper feeder operating at about 0.15 MPa (21 psia) is required to overcome the combined pressure drop across the bed and along the conveying line. A separate lock-hopper system is required to feed the sorbent, also with a top size of 3 mm (⅛ in), but it is introduced into the boiler through the same conveying line. The mixture enters the bed through T nozzles, one per 2 m^2 (22 ft^2) of bed floor area, that divide the flow and distribute it horizontally beneath the tube bank. There is approximately 0.45 m (18 in) between the distributor plate and the bottom of the in-bed tube bank to prevent tube damage by jet impingement from the air and solids feed streams, and to allow access for maintenance. The height of the tube bank itself is around 0.45 m, requiring a normal bed depth of 0.9 m (36 in) to immerse all the tubes completely.

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[*] Power production intensity is the power produced by the boiler per unit area of the plan section of the bed at a stated elevation.

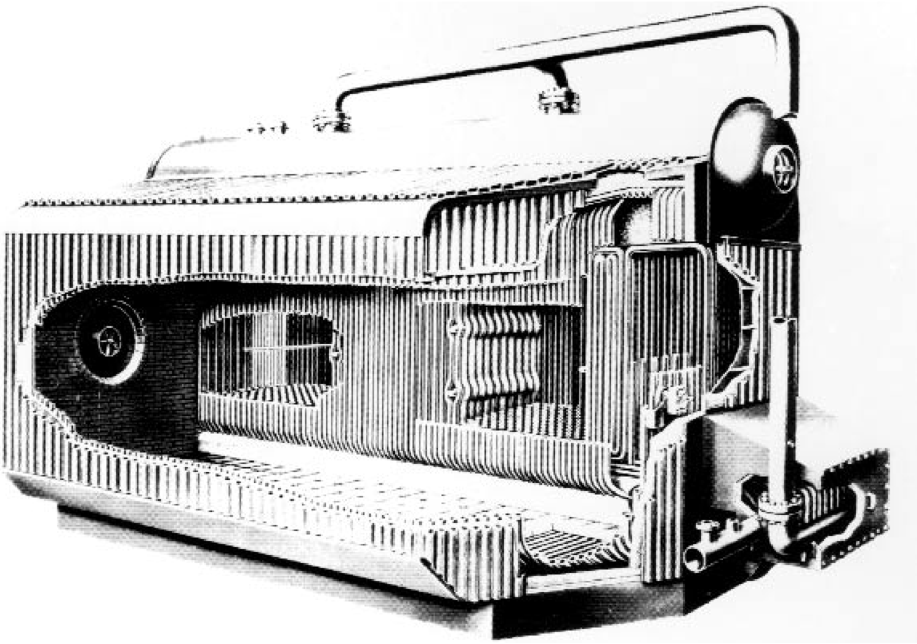

FIG. 27-46 A D-type shop-assembled water-tube boiler. (*Combustion Engineering, Inc.*)

The convection pass cools the flue gas and entrained particulate matter from about 1145 K (1600°F) to below 645 K (700°F). For bituminous coal with a combustion temperature of 1115 K (1550°F), a recycle ratio of 2.5 (mass rate of particulate recycle to coal feed rate) increases combustion efficiency to over 97 percent from around 90 percent without recycle. For a bituminous coal containing 3 percent sulfur, 90 percent sulfur capture is achieved with limestone as sorbent at a calcium-to-sulfur (Ca/S) molar ratio of 2.3 and a recycle ratio of 2.5. A Ca/S molar ratio of over 3.4 is required when there is no recycle. The recycled material also enters the bed through T nozzles, one per 7 m^2 (72 ft^2) of bed floor area. A means of distributing the particulate flow from the multiclones to the feed lines and overcoming the back pressure is required. On the 160-MWe unit, the back pressure is overcome by means of a J-valve.

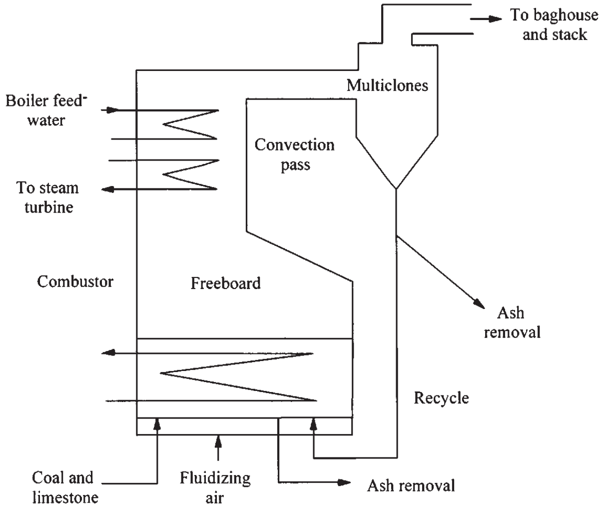

FIG. 27-47 Simplified flow diagram for bubbling AFBC (with underbed feed system).

A typical NO$_x$ level in the combustion gas is around 107 mg/MJ (0.25 lb/10^6 Btu), and the CO level tends to be high (near 86 mg/MJ [0.20 lb/10^6 Btu]). Only one design has used secondary air, and this lowered the NO$_x$ to 86 mg/MJ and the CO to about 43 mg/MJ (0.10 lb/10^6 Btu). NO$_x$ reduction by selective noncatalytic reduction (SNCR) has not been tested in a bubbling AFBC, but without the assistance of secondary air, it may be difficult to distribute the ammonia adequately across the freeboard to achieve the desired effect.

Approximately 85 percent of the heat is released in the bed and the other 15 percent above the bed. Typical heat flux data are tabulated in Table 27-22 for a mean bed temperature of 1115 K (1550°F).

The in-bed heat transfer rate decreases with mean bed particle size. As there is no accurate means of predicting this particle size, even if that of the feedstocks is known, there is a design uncertainty vis-à-vis heat transfer coefficient. If heat exchanger area adjustment has to be made after the boiler is in operation, surface is removed more easily than added. A reasonable design strategy, therefore, is to use an overall coefficient from the lower portion of the range experienced in practice. Then, if the actual coefficient is found to be higher than the design value, the bed temperature needed to maintain the design steam rate will be lower than specified. If the lower bed temperature adversely affects process performance and boiler efficiency, then surface area may need to be removed.

TABLE 27-22 Heat Absorption Distribution in Bubbling AFBCs

	Heat absorption split, %	Heat flux, kW/m^2 (Btu/h·ft^2)
In-bed tubing		
Evaporators	25	147 (46,500)
Superheaters	15	112 (35,500)
Walls	5	134 (42,500)
Freeboard water walls	10	44 (14,000)
Convection pass		
Superheater	20	15 (4,750)
Reheater	15	22 (6,850)
Economizer	10	6.5 (2,050)

Mean bed particle size (thus, the in-bed heat-transfer coefficient) may vary for external reasons such as a change of feedstock supply or a deterioration in crusher performance. This potential source of variation should be considered before any decision to resurface is made.

Circulating AFBCs The circulating AFBC is now more widely used than the bubbling version. A simplified schematic for a design with an external heat exchanger is presented in Fig. 27-48. A 110-MWe demonstration plant had a power production intensity of 1 MWe/m^2 (1 MWe/11 ft^2), almost 50 percent greater than that of a comparable bubbling unit. Circulating AFBC units of 250 MWe are now in service and larger units are being planned.

Circulating AFBCs handle bituminous and subbituminous coals equally well, and their coal preparation and feeding systems are far simpler than those of bubbling versions. The coal is crushed to a top size of 12 mm (½ in), without drying, and fed by gravity into the lower refractory-lined portion of the boiler. The feed points are close to the pressure balance point and so there is little, if any, back pressure; this greatly reduces the sealing requirements. In addition, and sometimes alternatively, the coal can be introduced into the cyclone ash return lines. A minimum of four coal entry points is required to achieve uniform feed distribution in the 110-MWe unit, corresponding to one per 30 m^2 (300 ft^2) of freeboard cross section. High turbulence and the absence of in-bed tubing facilitate adequate mixing of the coal across the combustor. The sorbent is prepared to a top size of 1 mm (0.04 in) and dried so that it can be pneumatically fed to the combustor. Experience showed that no less than eight sorbent feed points were required on the 110-MWe unit (one per 15 m^2 [150 ft^2] of freeboard cross section) to achieve satisfactory performance. Load control is achieved primarily by reducing coal feed rate, with a corresponding reduction in air flow, to lower combustor temperature.

Almost all of the particulate matter leaving the boiler is collected by cyclones and recycled to the base of the unit. The number of cyclones varies in different design concepts, but each cyclone can serve 40 to 60 MWe of generating capacity (in the case of the 110-MWe unit, one recycle point per 60 m^2 (600 ft^2) of freeboard cross section). The collected particulate matter is returned against a backpressure of 0.02 MPa (3 psi), through a J-valve. The recycle ratio can be as high as 40:1, corresponding to a relatively long mean particle residence time and accounting for the high performance of circulating units. For a bituminous coal containing 3 percent sulfur, with limestone sorbent and a combustion temperature of 1115 K (1550°F), the combustion efficiency is 99.0 percent, and 90 percent sulfur retention is attained with a Ca/S molar ratio of 2.2. The NO_x value at this temperature is typically 86 mg/MJ (0.20 lb/MBtu), but it can be reduced to below 43 mg/MJ (0.1 lb/MBtu) by ammonia injected with the secondary air. The corresponding CO level is about 43 mg/MJ.

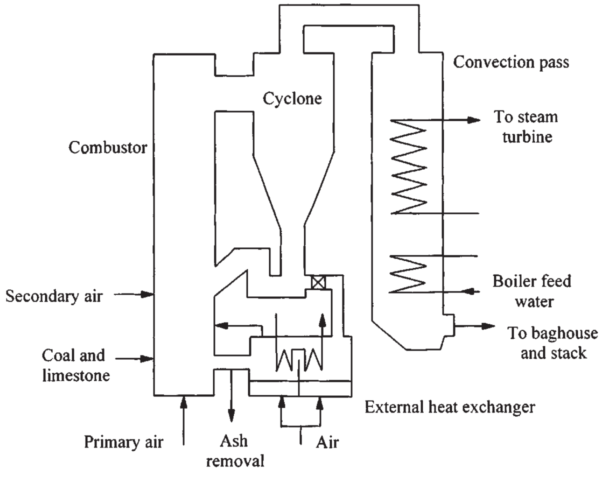

FIG. 27-48 Simplified flow diagram for circulating AFBC (with external heat exchanger).

Bubbling PFBCs Like the AFBC, the bubbling PFBC offers the ability to achieve low SO_2 and NO_x emissions without back-end add-on control equipment. It also offers advantages that the AFBC does not. Pressurized operation results in the boiler being more compact with a reduction in capital cost. Expanding the pressurized flue gas through a gas turbine generator, in combination with a steam turbine generator, increases cycle efficiency and increases power output by up to 25 percent. The lower capital cost and higher efficiency result in a lower cost of electricity.

A PFBC boiler is visually similar to an AFBC boiler. The combustor is made of water-wall tubing, which contains the high-temperature environment, but the whole assembly is placed within a pressure vessel. Unlike an AFBC unit, there is no convection pass, as the flue-gas temperature must be maintained at boiler temperature to maximize energy recovery by the expansion turbine. There is an economizer after the turbine for final heat recovery. A simplified schematic is presented in Fig. 27-49. An 80-MWe demonstration plant, operating at 1.2 MPa (180 psia), began operation in 1989 with a power production intensity of 3 MWe/m^2 (1 MWe/3.5 ft^2). By 1996, five units of this size had been constructed, and a 320-MWe unit is planned to commence operation in 1998.

The boiler, primary and secondary flue-gas cyclones, and ash-cooling circuits are installed within a pressure vessel operating at up to 1.7 MPa (240 psia). Also enclosed are the vessels that store bed material at operating temperature. These facilitate load control by allowing bed level to be raised or lowered rapidly, thus covering or exposing in-bed heat transfer surface and regulating both steam production and gas turbine inlet temperature. Reduced bed level and flue-gas temperature at part load result in some reduction in combustion performance. After leaving the cyclones, which remove over 99 percent of the particulate matter, the flue gas passes down the center of a coaxial pipe to the gas turbine. A custom-designed variable-speed gas turbine is used that is tolerant to the low levels of fine residual particulate matter. The compressed air is delivered to the pressure vessel through the annular portion of the coaxial pipe. This eliminates the need for a refractory-lined pipe and precludes the possibility of refractory passing to the gas turbine and damaging it. A baghouse is used for final particulate matter removal before discharging the flue gas to atmosphere.

Coal is fed as a paste containing 25 wt % water, and sorbent is fed dry by a lock-hopper system with pneumatic conveying. The top size of each feedstock is 3 mm (⅛ in). The latent heat lost evaporating the water fed with the paste is compensated by increased gas turbine power output resulting from the increased flue-gas mass flow rate. For the 80-MWe unit, there are six coal feed points (one per 4.5 m^2 [48 ft^2]) and four sorbent feed points (one per 6.7 m^2 [72 ft^2]), all entering beneath the tube bank along one wall. The bed depth is

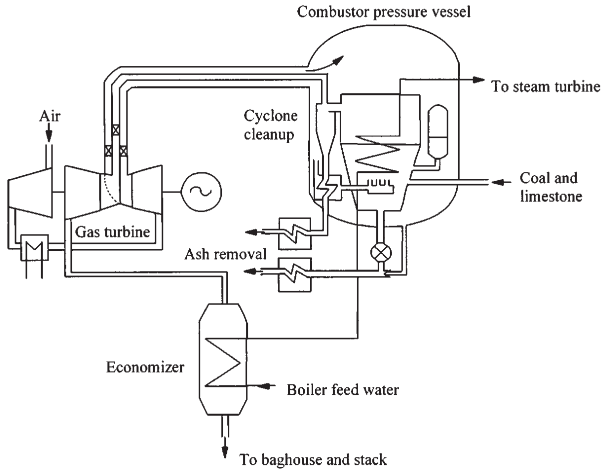

FIG. 27-49 Simplified flow diagram for bubbling PFBC.

about 3.7 m (12 ft) and the tube bank is about 3 m (10 ft) tall. The deep bed increases the in-bed gas residence time to around 4 s compared to less than 0.5 s in a bubbling AFBC unit. For bituminous coal containing 3 percent sulfur, with limestone sorbent and a combustion temperature of 1115 K (1550°F), this residence time allows combustion efficiencies in excess of 99 percent to be achieved without recycle, and 90 percent sulfur capture with a Ca/S molar ratio of 1.9. NO_x values of about 107 mg/MJ (0.25 lb/10^6 Btu) can be reduced to 21 mg/MJ (0.05 lb/10^6 Btu) by SNCR. Although the inherent NO_x level is similar to that achieved in bubbling AFBC units, the CO levels are very much lower, 13 mg/MJ (0.03 lb/10^6 Btu) being attainable.

Over 98 percent of the heat is released in the bed. For similar mean bed temperatures and mean bed particle sizes, the elevated operating pressure results in heat fluxes to the in-bed tubing that are typically 15 to 20 percent greater than in a bubbling AFBC unit.

Circulating PFBC Circulating PFBC technology has been under development only since the late 1980s and is still in the pilot-plant stage. A simplified schematic for a design without an external heat exchanger is presented in Fig. 27-50. An 80-MWe demonstration plant is planned as part of the U.S. Department of Energy Clean Coal Technology Program; operation is likely in 1999.

Compared to bubbling PFBCs, these boilers operate at similar pressures but at higher fluidizing velocities. As a result, the design is more compact, with a projected power production intensity of 10 MWe/m^2 (1 MWe/ft^2), over three times that of the bubbling design. Being more compact implies a pressure vessel of smaller diameter and a plant design adaptable to more modular construction and more shop assembly, with corresponding lower capital cost. Because the boiler is smaller, better distribution of coal and sorbent can be achieved with fewer feed nozzles. Inasmuch as there is no bed level to be maintained, a finer sorbent can be used, allowing it to be more fully utilized. Load control is achieved by cutting back on the air flow while keeping the combustion temperature substantially constant. This maintains high combustion and sulfur-retention performance over the load range and eliminates the need for bed storage vessels. Fewer cyclones are required (one per 80 MWe) and, as the ash collected is recycled, there are no ash coolers. The design uses high-temperature, high-pressure (HTHP) filtration to clean the flue gas prior to its entering the gas turbine. This virtually particulate-free gas allows conventional gas turbines to be used, increasing the selection available, and at the same time eliminates the need for a back-end baghouse.

For a bituminous coal containing 3 percent sulfur with limestone sorbent and a combustion temperature of 1115 K (1550°F), combustion efficiency in excess of 99 percent can be achieved, as can 90 percent sulfur capture with a Ca/S molar ratio of 1.15. The reduced sorbent demand decreases the amount of ash discharged. NO_x values are around 86 mg/MJ (0.20 lb/10^6 Btu) and can be reduced to 21 mg/MJ (0.05 lb/10^6 Btu) by SNCR reactions. As in the case of the bubbling PFBC, the inherent NO_x level is similar to that achieved in circulating AFBC units, but the CO level is very much lower, 13 mg/MJ (0.03 lb/10^6 Btu) being achieved. No heat flux data to the walls are available at present.

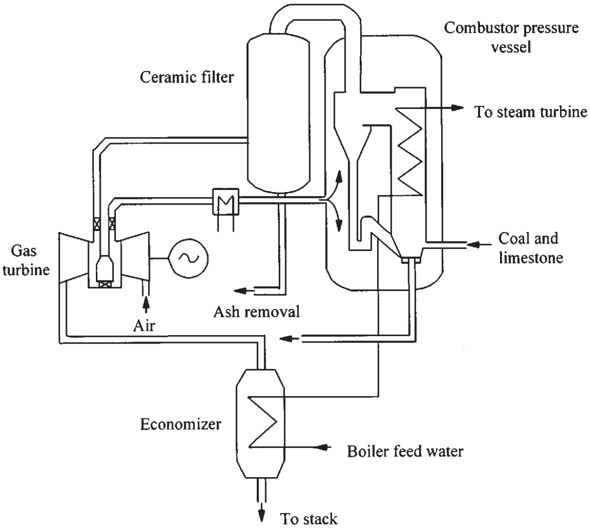

FIG. 27-50 Simplified flow diagram for circulating PFBC.

If all these process and economic advantages are realized, the cost of electricity will be lowered, making circulating PFBC an extremely attractive coal-fired option for power generation.

Advanced PFBC Cycle The latest development in fluidized-bed combustion technology is the concept of an advanced PFBC that generates a fuel gas to feed a high-temperature gas turbine. The efficiency of current combined-cycle plants employing state-of-the-art bubbling or circulating PFBC boilers is limited to about 42 percent (HHV basis) because the maximum permissible combustion gas temperature (therefore, inlet temperature for the gas turbine) is 1145 K (1600°F). At higher bed temperature, the combustor feedstocks can release alkali metal vapor that can lead to fouling and corrosion of the gas turbine blades. Furthermore, the threat of bed ash agglomeration is increased.

The proposed advanced PFBC cycle will permit a turbine inlet gas temperature of over 1535 K (2300°F) by burning a fuel gas produced by pyrolysis of the coal feed. Because the turbine fuel gas must be practically particulate free, it passes through HTHP filters before combustion. The char residue from the pyrolyzer may be burned in a circulating AFBC or PFBC to produce steam for power or heating. The efficiency attainable in an advanced PFBC plant may be as high as 50 percent (HHV basis).

This technology is still in the early pilot stages, the first tests having been conducted in the early 1990s; therefore, insufficient data are available for meaningful comparison with the other PFBC technologies. Nevertheless, it is considered to be potentially the most economic PFBC technology, and development work is continuing with the objective of designing a demonstration plant.

The capital investment for any FBC plant depends upon several factors, including the cost of capital, size of unit, geographic location, and coal type. EPRI has completed several economic evaluations and projects the following costs, in 1994 US dollars, for plants located in Kenosha, Wisconsin, burning Illinois No. 6 bituminous coal containing 4 percent sulfur: 200-MWe circulating AFBC, $1520/kW; 350-MWe bubbling PFBC, $1220/kW; 350-MWe circulating PFBC, $1040/kW; 320-MWe advanced PFBC, $1110/kW. The advanced PFBC has the most potential for cost reduction, and capital investment could be reduced to below $1000/kW.

PROCESS HEATING EQUIPMENT

Many major energy-intensive industries depend on direct-fired or indirect-fired equipment for drying, heating, calcining, melting, or chemical processing. This subsection discusses both direct- and indirect-fired equipment, with the greater emphasis on indirect firing for the process industries.

Direct-Fired Equipment Direct-fired combustion equipment transfers heat by bringing the flame and/or the products of combustion into direct contact with the process stream. Common examples are rotary kilns, open-hearth furnaces, and submerged-combustion evaporators. Table 27-23 gives the average energy consumption rates for various industries and processes that use direct heat. Section 11 of this handbook describes and illustrates rotary dryers, rotary kilns, and hearth furnaces. Forging, heat treating, and metal milling furnaces are discussed by Mawhinney (*Marks' Standard Handbook for Mechanical Engineers*, 9th ed., McGraw-Hill, New York, 1987, pp. 7.47–7.52). Other direct-fired furnaces are described later in this section.

Indirect-Fired Equipment (Fired Heaters) Indirect-fired combustion equipment (fired heaters) transfers heat across either a metallic or refractory wall separating the flame and products of combustion from the process stream. Examples are heat exchangers (dis-

TABLE 27-23 Average Energy Consumption for Various Industries Using Direct Heat

Industry	Product/process	Energy consumption per unit of product	
		GJ/Mg	10^6 Btu/US ton
Paper	Kraft process	20.9	18.0
	Integrated plant/paper*	34.2	29.5
	Integrated plant/paperboard*	18.8	16.2
Glass	Flat glass	17.3	14.9
	Container glass	18.1	15.6
	Pressed/blown	31.6	27.2
Clay/ceramics	Portland cement	4.6	4.0
	Lime	5.5	4.7
	Mineral wool	42.7	36.8
Steel	Blast furnace and steel mills	20.7	17.8
Nonferrous metals	Primary copper	34.2	29.5
	Secondary copper	4.6	4.0
	Primary lead	25.1	21.6
	Secondary lead	0.8	0.7
	Primary zinc	69.6	60.0
	Secondary zinc	5.0	4.3
	Primary aluminum	78.9	68.0
	Secondary aluminum	5.2	4.5

SOURCE: *Manufacturing Consumption of Energy,* Energy Information Administration, U.S. Dept. of Energy, 1991.

*Mixture of direct and indirect firing.

cussed in Sec. 11), steam boilers, fired heaters, muffle furnaces, and melting pots. Steam boilers have been treated earlier in this section, and a subsequent subsection on industrial furnaces will include muffle furnaces.

Fired heaters differ from other indirect-fired processing equipment in that the process stream is heated by passage through a coil or tubebank enclosed in a furnace. Fired heaters are classified by function and by coil design.

Function Berman (*Chem. Eng.* **85**(14): 98–104, June 19, 1978) classifies fired heaters into the following six functional categories, providing descriptions that are abstracted here.

Column reboilers heat and partially vaporize a recirculating stream from a fractionating column. The outlet temperature of a reboiler stream is typically 477 to 546 K (400 to 550°F).

Fractionator-feed preheaters partially vaporize charge stock from an upstream unfired preheater en route to a fractionating column. A typical refinery application: a crude feed to an atmospheric column enters the fired heater as a liquid at 505 K (450°F) and leaves at 644 K (700°F), having become 60 percent vaporized.

Reactor-feed-stream preheaters heat the reactant stream(s) for a high-temperature chemical reaction. The stream may be single-phase/single-component (example: steam being superheated from 644 to 1089 K [700 to 1500°F] for styrene-manufacture reactors); single-phase/multicomponent (example: preheating the feed to a catalytic reformer, a mixture of hydrocarbon vapors and recycle hydrogen, from 700 to 811 K [800 to 1000°F] under pressure as high as 4.1 MPa [600 psia]); or multiphase/multicomponent (example: a mixture of hydrogen gas and liquid hydrocarbon heated from 644 to 727 K [700 to 850°F] at about 20 MPa [3000 psia] before it enters a hydrocracker).

Heat-transfer-fluid heaters maintain the temperature of a circulating liquid heating medium (e.g., a paraffinic hydrocarbon mixture, a Dowtherm, or a molten salt) at a level that may exceed 673 K (750°F).

Viscous-liquid heaters lower the viscosity of very heavy oils to pumpable levels.

Fired reactors contain tubes or coils in which an endothermic reaction within a stream of reactants occurs. Examples include steam/hydrocarbon reformers, catalyst-filled tubes in a combustion chamber; pyrolyzers, coils in which alkanes (from ethane to gas oil) are cracked to olefins; in both types of reactor the temperature is maintained up to 1172 K (1650°F).

Coil Design Indirect-fired equipment is conventionally classified by tube orientation: vertical and horizontal. Although there are many variations of each of these two principal configurations, they all are embraced within seven major types, as follows.

A *simple vertical cylindrical* heater has vertical tubes arrayed along the walls of a combustion chamber fired vertically from the floor. This type of heater does not include a convection section and is inexpensive. It has a small footprint but low efficiency, and it is usually selected for small-duty applications (0.5 to 21 GJ/h [0.5 to 20 10^6 Btu/h]).

Vertical cylindrical; cross-tube convection heaters are similar to the preceding type except for a horizontal convective tube bank above the combustion chamber. The design is economical with a high efficiency and is usually selected for higher-duty applications: 11 to 210 GJ/h (10 to 200 10^6 Btu/h).

The *arbor (wicket)* heater is a substantially vertical design in which the radiant tubes are inverted U's connecting the inlet and outlet terminal manifolds in parallel. An overhead crossflow convection bank is usually included. This type of design is good for heating large gas flows with low pressure drop. Typical duties are 53 to 106 GJ/h (50 to 100 10^6 Btu/h).

In the *vertical-tube single-row double-fired* heater, a single row of vertical tubes is arrayed along the center plane of the radiant section that is fired from both sides. Usually this type of heater has an overhead horizontal convection bank. Although it is the most expensive of the fired heater designs, it provides the most uniform heat transfer to the tubes. Duties are 21 to 132 GJ/h (20 to 125 10^6 Btu/h) per cell (twin-cell designs are not unusual).

Horizontal-tube cabin heaters position the tubes of the radiant-section-coil horizontally along the walls and the slanting roof for the length of the cabin-shaped enclosure. The convection tube bank is placed horizontally above the combustion chamber. It may be fired from the floor, the side walls, or the end walls. As in the case of its vertical cylindrical counterpart, its economical design and high efficiency make it the most popular horizontal-tube heater. Duties are 11 to 105 GJ/h (10 to 100 10^6 Btu).

In the *horizontal-tube box heater with side-mounted convection tube bank,* the radiant-section tubes run horizontally along the walls and the flat roof of the box-shaped heater, but the convection section is placed in a box of its own beside the radiant section. Firing is horizontal from the end walls. The design of this heater results in a relatively expensive unit justified mainly by its ability to burn low-grade high-ash fuel oil. Duties are 53 to 210 GJ/h (50 to 200 10^6 Btu/h).

Vertical cylindrical helical coil heaters are hybrid designs that are classified as vertical heaters, but their in-tube characteristics are like those of horizontal heaters. There is no convection section. In addition to the advantages of simple vertical cylindrical heaters, the helical coil heaters are easy to drain. They are limited to small-duty applications: 5 to 21 GJ/h (5 to 20 10^6 Btu/h).

Schematic elevation sections of a vertical cylindrical, cross-tube convection heater; a horizontal-tube cabin heater; and a vertical cylindrical, helical-coil heater are shown in Fig. 27-51. The seven basic designs and some variations of them are pictured and described in the reference cited above and by R. K. Johnson (*Combustion* **50**(5): 10–16, November 1978).

The design of both radiant and convection sections of fired heaters, along with some equipment descriptions and operating suggestions, are discussed by Berman in *Encyclopedia of Chemical Processing and Design* (McKetta [ed.], vol. 22, Marcel Dekker, 1985, pp. 31–69). He also treats construction materials, mechanical features, and operating points in three other *Chemical Engineering* articles (all in vol. 85 (1978): no. 17, July 31, pp. 87–96; no. 18, August 14, pp. 129–140; and no. 20, Sept. 11, pp. 165–169).

INDUSTRIAL FURNACES

Industrial furnaces serve the manufacturing sector and can be divided into two groups. Boiler furnaces, which are the larger group and are used solely to generate steam, were discussed earlier in the subsection on industrial boilers. Furnaces of the other group are classified as follows: by (1) source of heat (fuel combustion or electricity), (2) func-

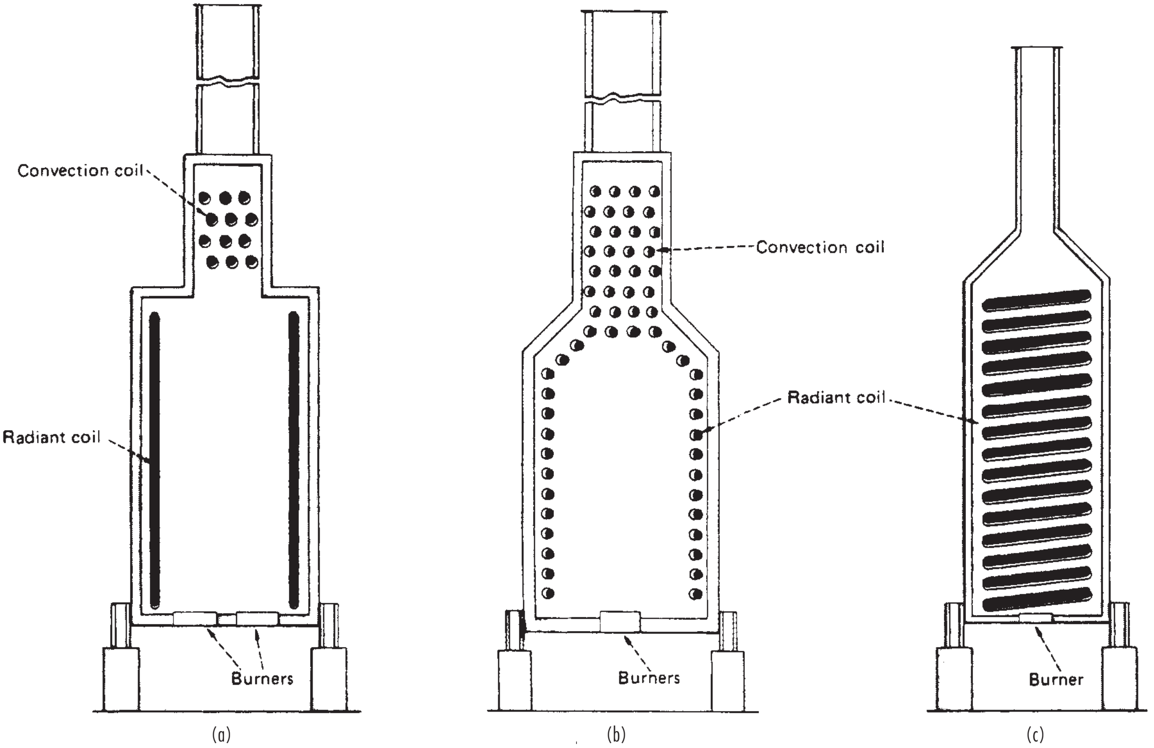

FIG. 27-51 Representative types of fired heaters: (*a*) vertical-tube cylindrical with cross-flow-convection section; (*b*) horizontal-tube cabin; (*c*) vertical cylindrical, helical coil. (*From Berman,* Chem. Eng. ***85:*** *98–104, June 19, 1978.*)

tion (heating without change of phase or with melting), (3) process cycle (batch or continuous), (4) mode of heat application (direct or indirect), and (5) atmosphere in furnace (air, protective, or reactive, including vacuum). Each will be discussed briefly.

Source of Heat Industrial furnaces are either fuel-fired or electric, and the first decision that a prospective furnace user must make is between these two. Although electric furnaces are uniquely suited to a few applications in the chemical industry (manufacture of silicon carbide, calcium carbide, and graphite, for example), their principal use is in the metallurgical and metal-treatment industries. In most cases the choice between electric and fuel-fired is economic or custom-dictated, because most tasks that can be done in one can be done equally well in the other. Except for an occasional passing reference, electric furnaces will not be considered further here. The interested reader will find useful reviews of them in *Kirk-Othmer Encyclopedia of Chemical Technology* (4th ed., vol. 12, articles by Cotchen, Sommer, and Walton, pp. 228–265, Wiley, New York, 1994) and in *Marks' Standard Handbook for Mechanical Engineers* (9th ed., article by Lewis, pp. 7.59–7.68, McGraw-Hill, New York, 1987).

Function and Process Cycle Industrial furnaces are enclosures in which process material is heated, dried, melted, and/or reacted. Melting is considered a special category because of the peculiar difficulties that may be associated with a solid feed, a hot liquid product, and a two-phase mixture in between; it is customary, therefore, to classify furnaces as heating or melting.

Melting Furnaces: The Glass Furnace Most melting furnaces, electric or fuel-fired, are found in the metals-processing industry, but a notable exception is the glass furnace. Like most melting furnaces, a glass furnace requires highly radiative flames to promote heat transfer to the feed charge and employs regenerators to conserve heat from the high-temperature process (greater than 1813 K [2300°F]).

A typical side-port continuous regenerative glass furnace is shown in Fig. 27-52. Side-port furnaces are used in the flat and container glass industries. The burners are mounted on both sides of the furnace and the sides fire alternately. Refractory-lined flues are used to recover the energy of the hot flue gas. The high temperature of the flue gas leaving the furnace heats a mass of refractory material called a *checker.* After the checker has reached the desired temperature, the gas flow is reversed and the firing switches to the other side of the furnace. The combustion air is then heated by the hot checker and can reach 1533 K (2300°F). The cycle of air flow from one checker to the other is reversed approximately every 15 to 30 minutes.

The glass melt is generally 1 to 2 m (3 to 6 ft) deep, the depth being limited by the need for proper heat transfer to the melt. Container glass furnaces are typically 6 to 9 m (20 to 30 ft) wide and 6 to 12 m (20 to 40 ft) long. Flat glass furnaces tend to be longer, typically over 30 m (100 ft), because of the need for complete reaction of the batch ingredients and improved quality (fewer bubbles). They typically have a melting capacity of 450 to 630 Mg/day (500 to 750 US ton/d), compared to a maximum of 540 Mg/day (600 US ton/d) for container and pressed/blown glass furnaces.

Though the stoichiometric chemical energy requirement for glassmaking is only some 2.3 GJ/Mg (2 10^6 Btu/US ton) of glass, the inherently low thermal efficiency of regenerative furnaces means that, in practice, at least 7 GJ/Mg (6 10^6 Btu/US ton) is required. Of this total, some 40 percent goes to batch heating and the required heat of reactions, 30 percent is lost through the furnace structure, and 30 percent is lost through the stack. The smaller furnaces used in pressed/blown glass melting are less efficient, and energy consumption may be as high as 17.4 TJ/Mg (15 10^6 Btu/US ton).

Industrial furnaces may be operated in batch or continuous mode.

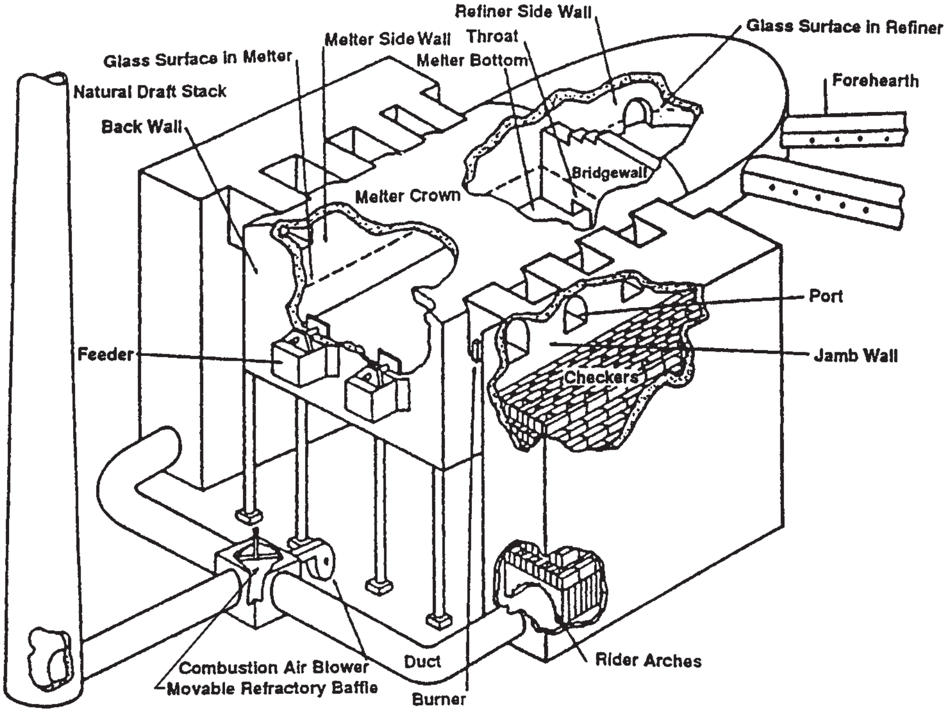

FIG. 27-52 Side-port continuous regenerative glass melting furnace.

Batch Furnaces This type of furnace is employed mainly for the heat treatment of metals and for the drying and calcination of ceramic articles. In the chemical process industry, batch furnaces may be used for the same purposes as batch-tray and truck dryers when the drying or process temperature exceeds 600 K (620°F). They are employed also for small-batch calcinations, thermal decompositions, and other chemical reactions which, on a larger scale, are performed in rotary kilns, hearth furnaces, and shaft furnaces.

Continuous Furnaces These furnaces may be used for the same general purposes as are the batch type, but usually not on small scale. The process material may be carried through the furnace by a moving conveyor (chain, belt, roller), or it may be pushed through on idle rollers, the motion being sustained by an external pusher operating on successively entering cars or trays, each pushing the one ahead along the entire length of the furnace and through the exit flame curtains or doors.

Furnace Atmosphere and Mode of Heating

Direct Heating Industrial furnaces may be directly or indirectly heated, and they may be filled with air or a protective atmosphere, or under a vacuum. Direct heating is accomplished by the hot combustion gases being inside the furnace and therefore in direct contact with the process material. Thus, the material is heated by radiation and convection from the hot gas and by reradiation from the heated refractory walls of the chamber. Three styles of direct firing are illustrated in Fig. 27-53. *Simple direct firing* is used increasingly because of its simplicity and because of improved burners. The *overhead* design allows the roof burners to be so placed as to provide optimum temperature distribution in the chamber. *Underfiring* offers the advantage of the charge's being protected from the flame. The maximum temperature in these direct-heated furnaces is limited to about 1255 K (1800°F) to avoid prohibitively shortened life of the refractories in the furnace.

Indirect Heating If the process material cannot tolerate exposure to the combustion gas or if a vacuum or an atmosphere other than air is needed in the furnace chamber, indirect firing must be employed. This is accomplished in a muffle* furnace or a radiant-tube furnace (tubes carrying the hot combustion gas run through the furnace).

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* A *muffle* is an impenetrable ceramic or metal barrier between the firing chamber and the interior of the furnace. It heats the process charge by radiation and furnace atmosphere convection.

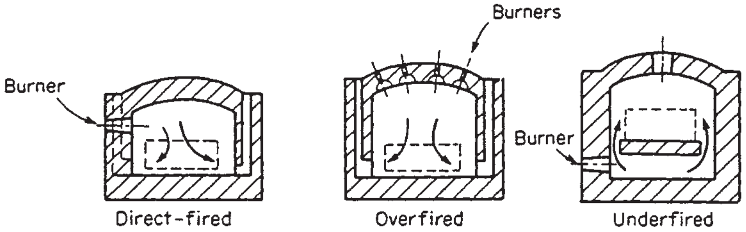

FIG. 27-53 Methods of firing direct-heated furnaces. (*From* Marks' Standard Handbook for Mechanical Engineers, *9th ed., McGraw-Hill, New York, 1987. Reproduced with permission.*)

Atmosphere Protective atmosphere within the furnace chamber may be essential, especially in the heat treatment of metal parts. Mawhinney (in *Marks' Standard Handbook for Mechanical Engineers,* 9th ed., McGraw-Hill, New York, 1987, p. 752) lists pure hydrogen, dissociated ammonia (a hydrogen/nitrogen mixture), and six other protective reducing gases with their compositions (mixtures of hydrogen, nitrogen, carbon monoxide, carbon dioxide, and sometimes methane) that are codified for and by the metals-treatment industry. In general, any other gas or vapor that is compatible with the temperature and the lining material of the furnace can be provided in an indirect-fired furnace, or the furnace can be evacuated.

COGENERATION

Cogeneration is an energy conversion process wherein heat from a fuel is simultaneously converted to useful thermal energy (e.g., process steam) and electric energy. The need for either form can be the primary incentive for cogeneration, but there must be opportunity for economic captive use or sale of the other. In a chemical plant the need for process and other heating steam is likely to be the primary; in a public utility plant, electricity is the usual primary product.

Thus, a cogeneration system is designed from one of two perspectives: it may be sized to meet the process heat and other steam needs of a plant or community of industrial and institutional users, so that the electric power is treated as a by-product which must be either used on site or sold; or it may be sized to meet electric power demand, and the rejected heat used to supply needs at or near the site. The latter approach is the likely one if a utility owns the system; the former if a chemical plant is the owner.

Industrial use of cogeneration leads to small, dispersed electric-power-generation installations—an alternative to complete reliance on large central power plants. Because of the relatively short distances over which thermal energy can be transported, process-heat generation is characteristically an on-site process, with or without cogeneration.

Cogeneration systems will not match the varying power and heat demands at all times for most applications. Thus, an industrial cogeneration system's output frequently must be supplemented by the separate on-site generation of heat or the purchase of utility-supplied electric power. If the on-site electric power demand is relatively low, an alternative option is to match the cogeneration system to the heat load and contract for the sale of excess electricity to the local utility grid.

Fuel saving is the major incentive for cogeneration. Since all heat-engine-based electric power systems reject heat to the environment, that rejected heat can frequently be used to meet all or part of the local thermal energy needs. Using reject heat usually has no effect on the amount of primary fuel used, yet it leads to a saving of all or part of the fuel that would otherwise be used for the thermal-energy process. Heat engines also require a high-temperature thermal input, usually receiving the working fluid directly from a heating source; but in some situations they can obtain the input thermal energy as the rejected heat from a higher-temperature process. In the former case, the cogeneration process employs a heat-engine topping cycle; in the latter case, a bottoming cycle is used.

The choice of fuel for a cogeneration system is determined by the primary heat-engine cycle. Closed-cycle power systems which are externally fired—the steam turbine, the indirectly fired open-cycle gas turbine, and closed-cycle gas turbine systems—can use virtually any fuel that can be burned in a safe and environmentally acceptable manner: coal, municipal solid waste, biomass, and industrial wastes are burnable with closed power systems. Internal combustion engines, on the other hand, including open-cycle gas turbines, are restricted to fuels that have combustion characteristics compatible with the engine type and that yield combustion products clean enough to pass through the engine without damaging it. In addition to natural gas, butane, and the conventional petroleum-derived liquid fuels, refined liquid and gaseous fuels derived from shale, coal, or biomass are in this category. Direct-coal-fired internal combustion engines have been an experimental reality for decades but are not yet a practical reality technologically or economically.

There are at least three broad classes of application for topping-cycle cogeneration systems:

- Utilities or municipal power systems supplying electric power and low-grade heat (e.g., 422 K [300°F]) for local district heating systems
- Large residential, commercial, or institutional complexes requiring space heat, hot water, and electricity
- Large industrial operations with on-site needs for electricity and heat in the form of process steam, direct heat, and/or space heat.

Typical Systems All cogeneration systems involve the operation of a heat engine for the production of mechanical work which, in nearly all cases, is used to drive an electric generator. The commonest heat-engine types appropriate for topping-cycle cogeneration systems are:

- Steam turbines (backpressure and extraction configurations)
- Open-cycle (combustion) gas turbines
- Indirectly fired gas turbines: open cycles and closed cycles
- Diesel engines

Each heat-engine type has unique characteristics, making it better suited for some cogeneration applications than for others. For example, engine types can be characterized by:

- Power-to-heat ratio at design point
- Efficiency at design point
- Capacity range
- Power-to-heat-ratio variability
- Off-design (part-load) efficiency
- Multifuel capability

The major heat-engine types are described in terms of these characteristics in Table 27-24.

TABLE 27-24 Cogeneration Characteristics for Heat Engines

Engine type	Size range, MWe/unit	Efficiency at design point	Part-load efficiency	Multifuel capability	Maximum temperature of recoverable heat, °F (°C)*	Recoverable heat, Btu/kWh†	Typical power-to-heat ratio
Steam turbine							
Extraction-condensing type	30–300	0.25–0.30	Fair	Excellent	200 (93)–600 (315)‡	11,000–35,000	0.1–0.3
Backpressure type	20–200	0.20–0.25	Fair	Excellent	200 (93)–600 (315)‡	17,000–70,000	0.05–0.2
Combustion gas turbines	10–100	0.25–0.30	Poor	Poor	1000 (538)–1200 (649)	3000–11,000	0.3–0.45
Indirectly fired gas turbines							
Open-cycle turbines	10–85	0.25–0.30	Poor	Good	700 (371)–900 (482)	3500–8500	0.4–1.0
Closed-cycle turbines	5–350	0.25–0.30	Excellent	Good	700 (371)–900 (482)	3500–8500	0.4–1.0
Diesel engines	0.05–25	0.35–0.40	Good	Fair to poor	500 (260)–700 (371)	4000–6000	0.6–0.85

*°C + 273 = K

†1 Btu = 1055 J.

‡Saturated steam.

HEAT RECOVERY

REGENERATION

Storage of heat is a temporary operation since perfect thermal insulators are unknown; thus, heat is absorbed in solids or liquids as sensible or latent heat to be released later at designated times and conditions. The collection and release of heat can be achieved in two modes: on a batch basis, as in the checkerbrick regenerator for blast furnaces, or on a continuous basis, as in the Ljungstrom air heater.

Checkerbrick Regenerators Preheating combustion air in open-hearth furnaces, ingot-soaking pits, glass-melting tanks, by-product coke ovens, heat-treating furnaces, and the like has been universally carried out in regenerators constructed of fireclay, chrome, or silica bricks of various shapes. Although many geometric arrangements have been used in practice, the so-called basketweave design has been adopted in most applications.

Blast-Furnace Stoves Blast-furnace stoves are used to preheat the air that is blown into a blast furnace. A typical blast furnace, producing 1500 Mg (1650 US ton) of pig iron per day, will be blown with 47.2 m^3/s (100,000 std ft^3/min) of atmospheric air preheated to temperatures ranging in normal practice from 755 to 922 K (900 to 1200°F). A set of four stoves is usually provided, each consisting of a vertical steel cylinder 7.3 m (24 ft) in diameter, 33 m (108 ft) high, topped with a spherical dome. Characteristic plan and elevation sections of a stove are shown in Fig. 27-54. The interior comprises three regions: in the cylindrical portion, (1) a side combustion chamber, lens-shaped in cross section, bounded by a segment of the stove wall and a mirror-image bridgewall separating it from (2) the chamber of the cylinder that is filled with heat-absorbing checkerbrick, and (3) the capping dome, which constitutes the open passage between the two chambers.

The heat-exchanging surface in each stove is just under 11,500 m^2 (124,000 ft^2). In operation, each stove is carried through a two-step 4-h cycle. In a 3-h *on-gas* step, the checkerbricks in a stove are heated by the combustion of blast-furnace gas. In the alternating *on-wind* 1-h step, they are cooled by the passage of cold air through the stove. At any given time, three stoves are simultaneously on gas, while a single stove is on wind.

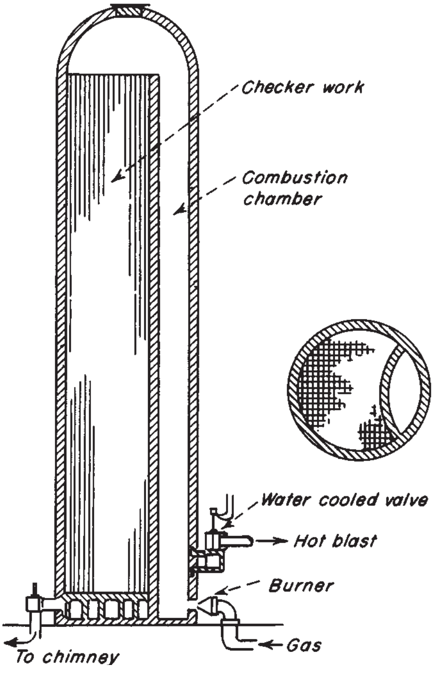

FIG. 27-54 Blast-furnace stove.

At the start of an on-wind step, about one-half of the air, entering at 366 K (200°F), passes through the checkerbricks, the other half being bypassed around the stove through the cold-blast mixer valve. The gas passing through the stove exhausts at 1366 K (2000°F). Mixing this with the unheated air produces a blast temperature of 811 K (1000°F). The temperature of the heated air from the stove falls steadily throughout the on-wind step. The fraction of total air volume bypassed through the mixer valve is continually decreased by progressively closing this valve, its operation being automatically regulated to maintain the exit gas temperature at 811 K. At the end of 1 h of on-wind operation, the cold-blast mixer valve is closed, sending the entire blast through the checkerbricks.

Open-Hearth and Glass-Tank Regenerators These contain checkerbricks that are modified considerably from those used in blast-furnace stoves because of the higher working temperatures, more drastic thermal shock, and dirtier gases encountered. Larger bricks form flue cross sections five times as large as the stove flues, and the percentage of voids in the checkerbricks is 51 percent, in contrast to 32 percent voids in stoves. The vertical height of the flues is limited by the elevation of the furnace above plant level. Short flues from 3 to 4.9 m (10 to 16 ft) are common in contrast to the 26- to 29-m (85- to 95-ft) flue lengths in blast-furnace stoves.

As a result of the larger flues and the restricted surface area per unit of gas passed, regenerators employed with this type of furnace exhibit much lower efficiency than would be realized with smaller flues. In view of the large amount of iron oxide contained in open-hearth exhaust gas and the alkali fume present in glass-tank stack gases, however, smaller checkerbrick dimensions are considered impractical.

Ljungstrom Heaters A familiar continuous regenerative-type air heater is the Ljungstrom heater (Fig. 27-55). The heater assembly consists of a slow-moving rotor embedded between two peripheral housings separated from one another by a central partition. Through one side of the partition a stream of hot gas is being cooled, and, through the other side a stream of cold gas is being heated. Radial and circumferential seals sliding on the rotor limit the leakage between the streams. The rotor is divided into sectors, each of which is tightly packed with metal plates and wires that promote high heat-transfer rates at low pressure drop.

These heaters are available with rotors up to 6 m (20 ft) in diameter. Gas temperatures up to 1255 K (1800°F) can be accommodated. Gas face velocity is usually around 2.5 m/s (500 ft/min). The rotor height depends on service, efficiency, and operating conditions but usually is between 0.2 and 0.91 m (8 and 36 in). Rotors are driven by small motors with rotor speed up to 20 r/min. Heater effectiveness can be as high as 85 to 90 percent heat recovery. Lungstrom-type heaters are used in power-plant boilers and also in the process industries for heat recovery and for air-conditioning and building heating.

Regenerative Burners In these systems a compact heat storage regenerator (containing ceramic balls, for example) is incorporated into the burner. Operating in pairs, one burner fires while the other exhausts: combustion air is preheated in the regenerator of the firing burner and furnace gas gives up heat to the regenerator in the exhausting burner (see Fig. 27-56). Burner operations are switched periodically. Such systems can yield combustion air preheats between 933 K (1220°F) and 1525 K (2282°F) for furnace temperature between 1073 K (1472°F) and 1723 K (2642°F), respectively. Corresponding fuel savings compared to cold-air firing will vary approximately from 30 to 70 percent.

Miscellaneous Systems Many other systems have been proposed for transferring heat regeneratively, including the use of high-temperature liquids and fluidized beds for direct contact with gases, but other problems which limit industrial application are encountered. These systems are covered by methods described in Secs. 11 and 12 of this handbook.

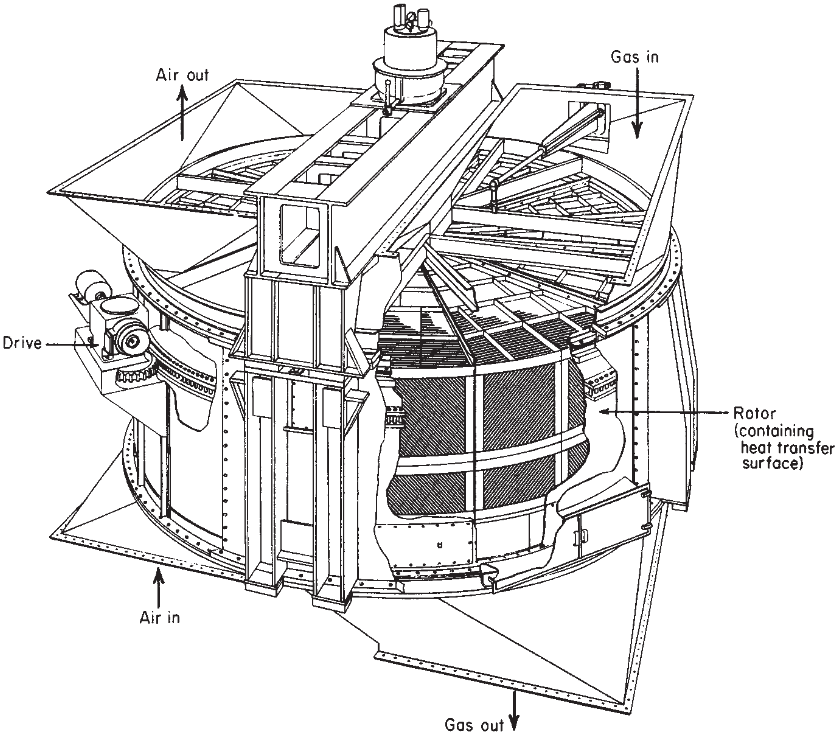

FIG. 27-55 Ljungstrom air heater.

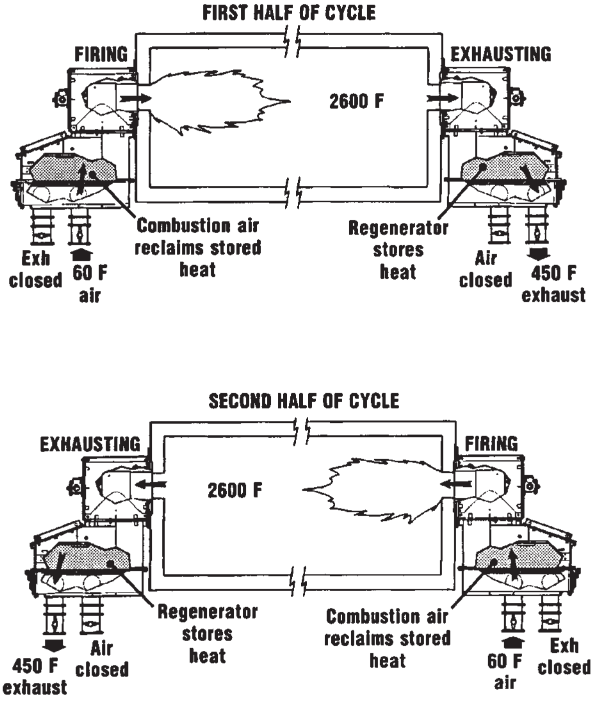

FIG. 27-56 Schematic of a regenerative burner system. (*North American Manufacturing Co.*)

RECUPERATORS

Regenerators are by nature intermittent or cycling devices, although, as set forth previously, the Ljunstrom design avoids interruption of the fluid stream by cycling the heat-retrieval reservoir between the hot and cold fluid streams. Truly continuous counterparts of regenerators exist, however, and they are called *recuperators.*

The simplest configuration for a recuperative heat exchanger is the metallic radiation recuperator (Fig. 27-57). The inner tube carries the hot exhaust gases and the outer tube carries the combustion air. The bulk of the heat transfer from the hot gases to the surface of the inner tube is by radiation, whereas that from the inner tube to the cold combustion air is predominantly by convection.

Shell-and-tube heat exchangers (see Sec. 11) may also be used as recuperators; convective heat transfer dominates in these recuperators. An alternative arrangement for a convective-type recuperator is shown in Fig. 27-58 (the dimpled end of the tube serves to ensure that there is adequate heat transfer from the cool fluid internally and that the tube bottom does not overheat and fail). For applications involving higher temperatures, ceramic recuperators have been developed. These devices can allow operation at up to 1823 K (2822°F) on the gas side and over 1093 K (1508°F) on the air side. Early ceramic recuperators were built of furnace brick and cement, but the repeated thermal cycling caused cracking and rapid deterioration of the recuperator. Later designs have used various approaches to overcome the problems of leakage and cracking, one of which is shown in Fig. 27-59. Silicon carbide tubes carry the combustion air through the waste gas, and flexible seals are used in the air headers. In this manner, the seals are maintained at comparatively low temperatures and the leakage rate can be reduced to a few percent of the total flow.

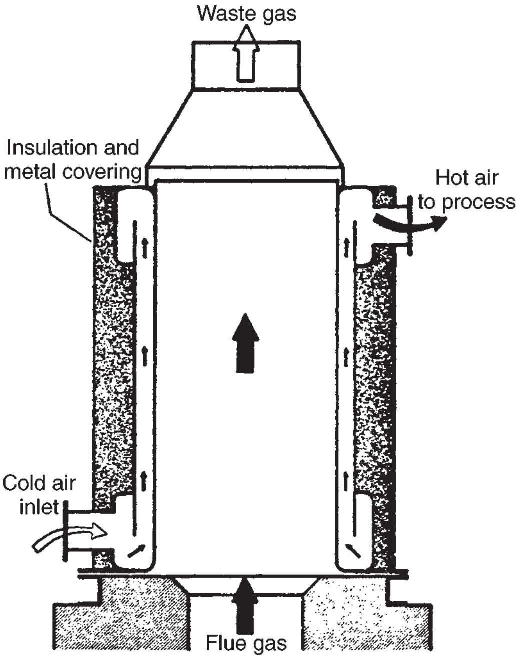

FIG. 27-57 Diagram of a metallic radiation recuperator. (*From Goldstick & Thumann,* Principles of Waste Heat Recovery, *Fairmont Press, Atlanta, 1986.*)

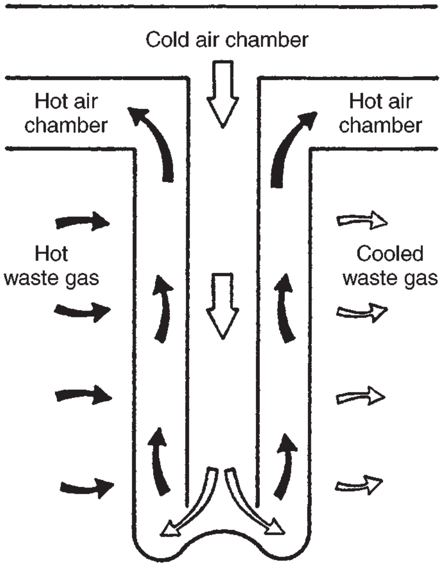

FIG. 27-58 Diagram of a vertical tube-within-tube recuperator. (*From Goldstick & Thumann,* Principles of Waste Heat Recovery, *Fairmont Press, Atlanta, 1986.*)

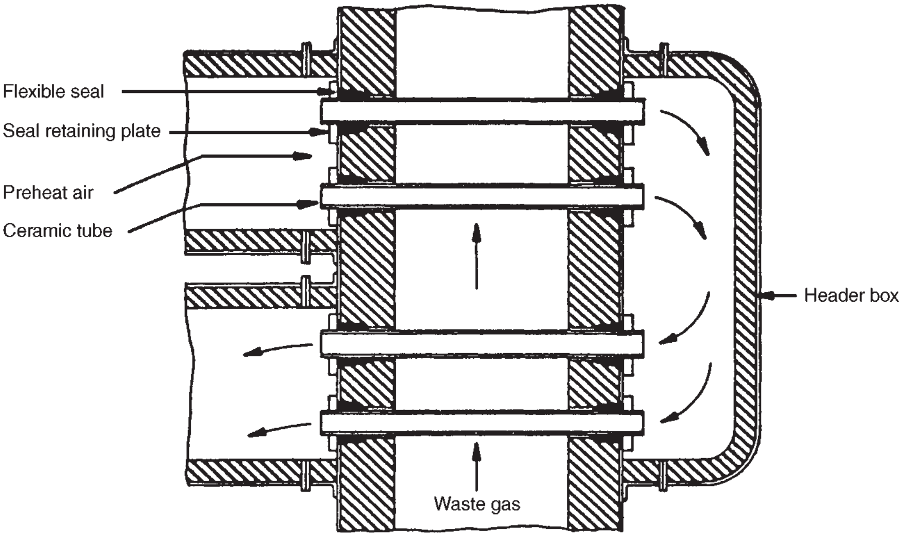

FIG. 27-59 Ceramic recuperator. In this design the seals are maintained at relatively low temperatures, leading to leakage rates of only a few percent. (*From Goldstick & Thumann,* Principles of Waste Heat Recovery, *Fairmont Press, Atlanta, 1986.*)

ELECTROCHEMICAL ENERGY CONVERSION

Electricity has become as indispensable as heat to the functioning of industrialized society. The source of most of the electricity used is the energy of the fuels discussed earlier in this section: liberated by combustion as heat, it drives heat engines which, in turn, drive electrical generators.

In some instances, however, part of the chemical energy bound in relatively high-enthalpy compounds can be converted directly to electricity as these reactants are converted to products of lower enthalpy (galvanic action). A process in the opposite direction also is possible for some systems: an electric current can be absorbed as the increased chemical energy of the higher-enthalpy compounds (electrolytic action). The devices in which electrochemical energy conversion processes occur are called cells.

Galvanic cells in which stored chemicals can be reacted on demand to produce an electric current are termed *primary cells.* The discharging reaction is irreversible and the contents, once exhausted, must be replaced or the cell discarded. Examples are the dry cells that activate small appliances. In some galvanic cells (called *secondary cells*), however, the reaction is reversible: that is, application of an electrical potential across the electrodes in the opposite direction will restore the reactants to their high-enthalpy state. Examples are rechargeable batteries for household appliances, automobiles, and many industrial applications. Electrolytic cells are the reactors upon which the electrochemical process, electroplating, and electrowinning industries are based.

Detailed treatment of the types of cells discussed above is beyond the scope of this handbook. For information about electrolytic cells, interested readers are referred to Fuller, Newman, Grotheer, and King ("Electrochemical Processing," in *Kirk-Othmer Encyclopedia of Chemical Technology,* 4th ed., vol. 9, Wiley, New York, 1994, pp. 111–197) and for primary and secondary cells, to Crompton (*Battery Reference Book,* 2d ed., Butterworth-Heineman, Oxford, U.K., 1995). Another type of cell, however, a galvanic cell to which the reactants of an exothermic reaction are fed continuously, in which they react to liberate part of their enthalpy as electrical energy, and from which the products of the reaction are discharged continuously, is called a *fuel cell.* Fuel cell systems for generating electricity in a variety of applications are being commercialized by a number of companies. The rest of this section is devoted to a discussion of fuel cell technology.

FUEL CELLS

General References: Appleby and Foulkes, *Fuel Cell Handbook,* Kreger Publishing Co., Molabar, Fla., 1993. Hirschenhofer, Staufer, and Engleman, *Fuel Cell Handbook* (Rev. 3), U.S. Dept. of Energy, Morgantown Energy Technology Center, DOE/METC-94/1006, Morgantown, W. Va., 1994. Kinoshita and Cairns, "Fuel Cells," in *Kirk-Othmer Encyclopedia of Chemical Technology,* 4th ed., vol. 11, Wiley, New York, 1994, p. 1098. Liebhafsky and Cairns, *Fuel Cells and Fuel Batteries,* Wiley, New York, 1968. Linden (ed.), *Handbook of Batteries and Fuel Cells,* McGraw-Hill, New York, 1984.

Background Energy conversion in fuel cells is direct and simple when compared to the sequence of chemical and mechanical steps in heat engines. A fuel cell consists of an anode, an electrolyte, and a cathode. On the anode, the fuel is oxidized electrochemically to positively charged ions. On the cathode, oxygen molecules are reduced to oxide or hydroxide ions. The electrolyte serves to transport either the positively charged or negatively charged ions from anode to cathode or cathode to anode. Figure 27-60 is a schematic representation of the reactions in a fuel cell operating on hydrogen and air with a hydrogen-ion-conducting electrolyte. The hydrogen flows over the anode, where the molecules are separated into ions and electrons. The ions migrate through the ionically conducting but electronically insulating electrolyte to the cathode, and the electrons flow through the outer circuit energizing an electric load. The electrons combine eventually with oxygen molecules flowing over the surface of the cathode and hydrogen ions migrating across the electrolyte, forming water, which leaves the fuel cell in the depleted air stream.

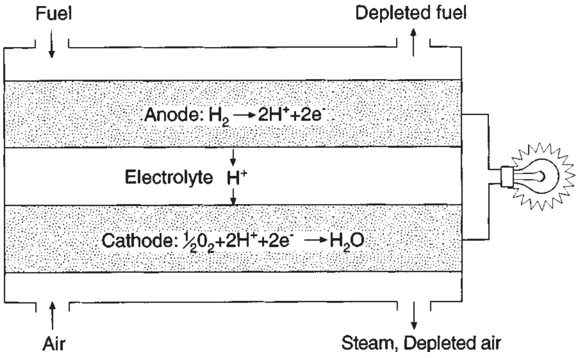

FIG. 27-60 Fuel cell schematic.

A fuel cell has no moving parts. It runs quietly, does not vibrate, and does not generate gaseous pollutants. The idea of the fuel cell is generally credited to Sir William Grove, who lived in the nineteenth century. It took over 100 years for the first practical devices to be built, in the U.S. space program, as the power supply for space capsules and the space shuttle. Commercialization of terrestrial fuel cell systems is beginning only now. Having lower emissions and being more efficient than heat engines, fuel cells may in time become the power source for a broad range of applications, beginning with utility power plants, including civilian and military transportation, and reaching into portable electronic devices.

This slow realization of the concept is due to the very demanding materials requirements for fuel cells. The anodes and cathodes have to be good electronic conductors and must have electrocatalytic properties to facilitate the anodic and cathodic reactions. In addition, the anodes and cathodes must be porous to allow the fuel and oxidant gases to diffuse to the reaction sites, yet they must be mechanically strong enough to support the weight of the fuel cell stacks. The electrolyte must be chemically stable in hydrogen and oxygen, and must have an ionic conductivity of at least 0.1 S/cm. Five classes of electrolytes have been found to meet these requirements: potassium hydroxide, phosphoric acid, perfluorinated sulfonic acid resins, molten carbonates, and oxide-ion-conducting ceramics. Consequently, five types of fuel cell based on these electrolytes have been developed.

Fuel Cell Efficiency The theoretical energy conversion efficiency of a fuel cell $\varepsilon°$ is given by the ratio of the free energy (Gibbs function) of the cell reaction at the cell's operating temperature ΔG_t to the enthalpy of reaction at the standard state $\Delta H°$, both quantities being based on a mole of fuel:

$$\varepsilon° = \frac{\Delta G_t}{\Delta H°} \qquad (27\text{-}50)$$

The enthalpy of reaction is always taken at a temperature of 298 K (77°F), but the product water can be either liquid or gaseous. If it is liquid, the efficiency is based on the higher heating value (HHV), but if the product is gaseous, the efficiency is based on the lower heating value (LHV). If the fuel cell runs on hydrogen and oxygen at 373 K (212°F), the theoretical conversion efficiency is 91 percent LHV or 83 percent HHV. The theoretical efficiency of fuel cells as given in Eq. (27-50) is equivalent to the Carnot efficiency of heat engines with the working medium absorbing heat at the flame temperature of the fuel and rejecting it at 298 K. Owing to materials and engineering limitations, heat engines cannot operate at the Carnot limit. Fuel cells can run at efficiencies near the theoretical values but only at low power density (power produced per unit of active fuel cell area). At higher power densities, the efficiency of fuel cells is constrained by electrical resistances within the bulk and at the interfaces of the materials, and by gas diffusion losses.

TABLE 27-25 Thermodynamic Values for $H_2 + \frac{1}{2}O_2 = H_2O$ (g)

Temperature, K	Enthalpy of reaction ($\Delta H°$), kJ/mol	Free energy of reaction ($\Delta G°$), kJ/mol	Equilibrium cell potential ($E°$), V
300	−241.8	−228.4	1.18
500	−243.9	−219.2	1.14
700	−245.6	−208.8	1.06
900	−247.3	−197.9	1.03
1100	−248.5	−187.0	0.97
1300	−249.4	−175.7	0.91

When no net current is flowing, the equilibrium potential of the fuel cell is given by the Nernst equation:

$$E° = \frac{-\Delta G_t}{nF} \qquad (27\text{-}51)$$

where $E°$ is the electrochemical equilibrium potential, V; n is the number of electrons transferred in the cell reaction (equivalents), and F is the Faraday constant. If the units of ΔG_t are J/mol, F has the value 96,487 C/mol·equiv. The potential depends on the chemical species of the fuel and the operating temperature. For hydrogen and oxygen, variation of the equilibrium cell potential with temperature is shown in Table 27-25.

When current is flowing, the actual cell operating potential is given by:

$$E = E° - (a_{\text{an}} + a_{\text{ca}}) - (b_{\text{an}} + b_{\text{ca}}) \frac{RT}{nF} \ln i - Ai \qquad (27\text{-}52)$$

where a and b are characteristic constants for the electrochemical reactions at the electrode materials; the subscripts an and ca refer to the anode and the cathode, respectively; R is the gas constant; T is the cell temperature; A is the area-specific resistance of the fuel cell; and i is the current density (current flow per unit of active fuel cell area) in the cell.

Graphs of operating potential versus current density are called *polarization curves*, which reflect the degree of perfection that any particular fuel cell technology has attained. High cell operating potentials are the result of many years of materials optimization. Actual polarization curves will be shown below for several types of fuel cell.

The actual efficiency of an operating fuel cell is given by:

$$\varepsilon = \frac{-nFE}{\Delta H°} U_f \qquad (27\text{-}53)$$

where U_f is the electrochemical fuel utilization (amount of fuel converted divided by amount fed to the cell). For pure hydrogen the fuel utilization can be 1.0, but for gas mixtures it is often 0.85. Equations (27-52) and (27-53) show that the efficiency of fuel cells is not constant, but depends on the current density. The more power that is drawn, the lower the efficiency.

When the fuel gas is not pure hydrogen and air is used instead of pure oxygen, additional adjustment to the calculated cell potential becomes necessary. Since the reactants in the two gas streams practically become depleted between the inlet and exit of the fuel cell, the cell potential is decreased by a term representing the log mean fugacities, and the operating cell efficiency becomes:

$$\varepsilon_{fc} = \frac{nFU_f}{\Delta H°}\left[E° - \sum a - \sum b \frac{RT}{nF} \ln i - A\,i\right] - \frac{RTU_f}{\Delta H°}\left[\nu_f \ln(\text{log mean } \hat{f}_f) + \nu_{\text{ox}} \ln(\text{log mean } \hat{f}_{\text{ox}})\right] \qquad (27\text{-}54)$$

The quantities ν_f and ν_{ox} are the stoichiometric coefficients for the fuel cell reaction, and $\hat{f}_f$ and $\hat{f}_{\text{ox}}$ are the fugacities of fuel and oxygen in their respective streams.

Further, as the current density of the fuel cell increases, a point is inevitably reached where the transport of reactants to or products from the surface of the electrode becomes limited by diffusion. A *concentration polarization* is established at the electrode, which diminishes the cell operating potential. The magnitude of this effect depends on many design and operating variables, and its value must be obtained empirically.

Design Principles An individual fuel cell will generate an electrical potential of about 1 V or less, as discussed above, and a current that is proportional to the external load demand. For practical applications, the voltage of an individual fuel cell is obviously too small, and cells are therefore stacked up as shown in Fig. 27-61. Anode/electrolyte/cathode assemblies are electrically connected in series by inserting a bipolar plate between the cathode of one cell and the anode of the next. The bipolar plate must be impervious to the fuel

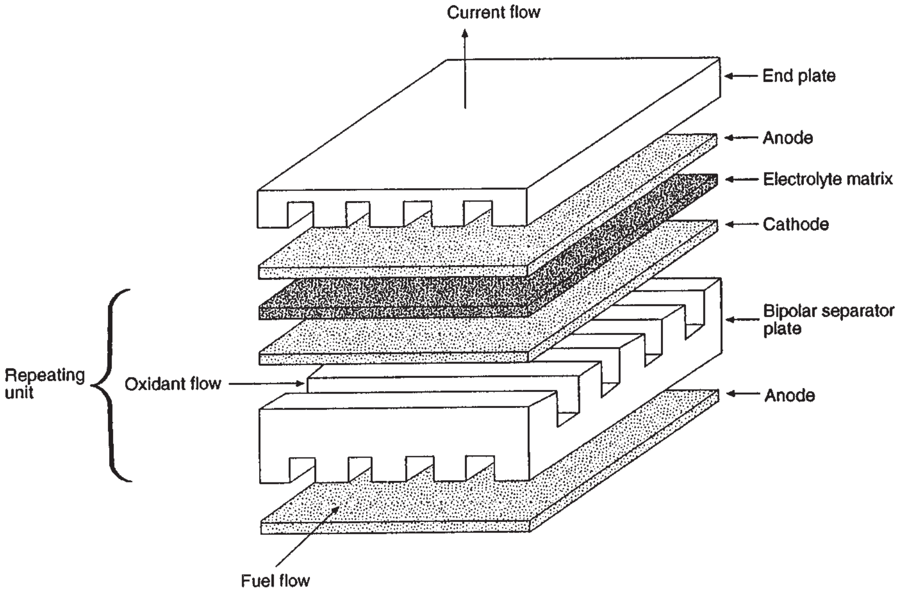

FIG. 27-61 Stacking of individual fuel cells.

and oxidant gases, chemically stable under reducing and oxidizing conditions, and an excellent electronic conductor. In addition, it is often used to distribute the gases to the anode and cathode surfaces through flow channels cut or molded into it.

The number of fuel cells that are stacked is determined by the desired electrical potential. For 110-V systems it can be about 200 cells. Since a typical fuel cell is about 5 mm (0.2 in) thick, a 200-cell stack assembly (including the end hardware that keeps the unit under compression) is about 2 m (6 ft) tall. The reactant and product gas streams are supplied and removed from the stack by external or internal manifolding. Externally manifolded stacks have shallow trays on each of the four sides to supply the fuel and air and to remove the depleted gases and reaction products. The manifolds are mechanically clamped to the stacks and sealed at the edges. These manifold seals must be gastight, electrically insulating, and able to tolerate thermal expansion mismatches between the stack and the manifold materials as well as dimensional changes due to aging.

Alternatively, reactant and product gases can be distributed to and removed from individual cells through internal pipes in a design analogous to that of filter presses. Care must be exercised to assure an even flow distribution between the entry and exit cells. The seals in internally manifolded stacks are generally not subject to electrical, thermal, and mechanical stresses, but are more numerous than in externally manifolded stacks.

Because fuel cells generate an amount of excess heat consistent with their thermodynamic efficiency, they must be cooled. In low-temperature fuel cells, the cooling medium is generally water or oil, which flows through cooling plates interspaced throughout the stack. In high-temperature cells, heat is removed by the reactant air stream and also by the endothermic fuel reforming reactions in the stack.

Types of Fuel Cells The five major types of fuel cell are listed in Table 27-26. Each has unique chemical features. The *alkaline fuel cell* (AFC) has high power density and has proven itself as a reliable power source in the U.S. space program, but the alkaline electrolyte reacts with carbon dioxide, which is present in reformed hydrocarbon fuels and air. The *polymer electrolyte fuel cell* (PEFC) and the *phosphoric acid fuel cell* (PAFC) are compatible with carbon dioxide, but both are sensitive to carbon monoxide (PEFC much more so than PAFC), which is adsorbed onto the platinum catalyst and renders it inactive. Therefore, these three types of fuel cell require pure hydrogen as fuel; and if the hydrogen has been obtained by reforming a fuel such as natural gas, the hydrogen-rich fuel stream must be purified before being introduced into the fuel cell. The *molten carbonate fuel cell* (MCFC) and the *solid oxide fuel cell* (SOFC) can tolerate carbon monoxide and can operate on hydrocarbon fuels with minimal fuel processing, but they operate at elevated temperatures.

The operating temperature also affects the fuel cell operating potential. A high operating temperature accelerates reaction rates but lowers the thermodynamic equilibrium potential. These effects balance one another, and, in practice, the operating point of any fuel cell is usually between 0.7 and 0.8 V. The cell reactions for the five types of fuel cell are summarized in Table 27-27. It is important to note that in cells with acidic electrolytes (PAFC and PEFC) the product water evolves on the air electrode, but in the alkaline ones (AFC, MCFC, and SOFC) it is generated on the fuel electrode. This has consequences for the processing of hydrocarbon fuels, as discussed later.

Following is a summary of the materials, operating characteristics, and mode of construction for each type of fuel cell.

Alkaline Fuel Cell The electrolyte for NASA's space shuttle orbiter fuel cell is 35 percent potassium hydroxide. The cell operates between 353 and 363 K (176 and 194°F) at 0.4 MPa (59 psia) on hydrogen and oxygen. The electrodes contain platinum-palladium and platinum-gold alloy powder catalysts bonded with polytetrafluoroethylene (PTFE) latex and supported on gold-plated nickel screens for current collection and gas distribution. A variety of materials, including asbestos and potassium titanate, are used to form a microporous separator that retains the electrolyte between the electrodes. The cell structural materials, bipolar plates, and external housing are usually nickel, plated to resist corrosion. The complete orbiter fuel cell power plant is shown in Fig. 27-62.

Typical polarization curves for alkaline fuel cells are shown in Fig. 27-63. It is apparent that the alkaline fuel cell can operate at about 0.9 V and 500 mA/cm^2 current density. This corresponds to an energy conversion efficiency of about 60 percent HHV. The space shuttle orbiter power module consists of three separate units, each measuring 0.35 by 0.38 by 1 m (14 by 15 by 40 in), weighing 119 kg (262 lb), and generating 15 kW of power. The power density is about 100 W/L and the specific power, 100 W/kg.

Polymer Electrolyte Fuel Cell The PEFC, also known as the *proton-exchange-membrane fuel cell* (PEMFC), is of much interest because it is capable of high power density and it can deliver about 40 percent of its nominal power at room temperature. These features have made the PEFC a candidate to replace internal combustion engines in transportation applications, and prototype passenger cars with fuel cell power sources have been developed. Methanol, ethanol, hydrogen, natural gas, dimethyl ether, and common transportation fuels such as gasoline are being considered as fuel. All but hydrogen require a reforming step to provide hydrogen for the fuel cell. The

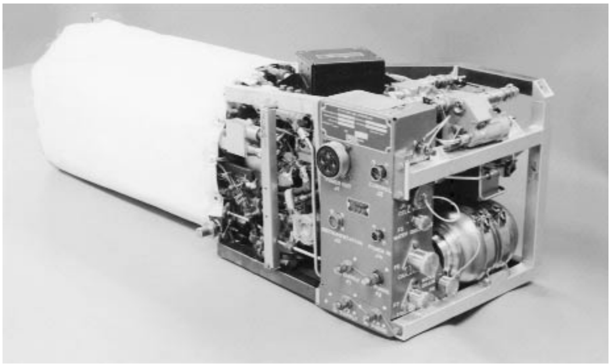

FIG. 27-62 Orbiter power plant. (*International Fuel Cells.*)

TABLE 27-26 Fuel Cell Characteristics

Type of fuel cell	Electrolyte	Operating temperature K	Operating temperature °C	Coolant medium
Alkaline	KOH	363	90	Water
Polymer	$CF_3(CF_2)_nOCF_2SO_3^-$	353	80	Water
Phosphoric acid	H_3PO_4	473	200	Steam/water
Molten carbonate	Li_2CO_3-K_2CO_3	923	650	Air
Solid oxide	$Zr_{0.92}\ Y_{0.08}0_{1.96}$	1273	1000	Air

TABLE 27-27 Fuel Cell Reaction Electrochemistry

Type of fuel cell	Conducting ion	Anode reaction	Cathode reaction
Alkaline	OH^-	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$
Polymer	H^+	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Phosphoric acid	H^+	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Molten carbonate	CO_3^{2-}	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$
Solid oxide	O^{2-}	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$	$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$

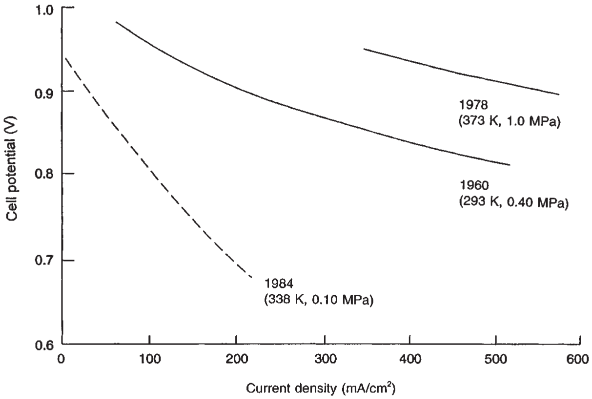

FIG. 27-63 Polarization curves for alkaline fuel cells.

motivation for this development effort is the virtual elimination of both on-road emissions from automobiles and the range limitations associated with battery-powered electric automobiles.

The electrolyte is a perfluorosulfonic acid ionomer, commercially available under the trade name of Nafion™. It is in the form of a membrane about 0.17 mm (0.007 in) thick, and the electrodes are bonded directly onto the surface. The electrodes contain very finely divided platinum or platinum alloys supported on carbon powder or fibers. The bipolar plates are made of graphite or metal.

Typical platinum catalyst loadings needed to support the anodic and cathodic reactions are currently 1 to 2 mg/cm^2 of active cell area. Owing to the cost of platinum, substantial efforts have been made to reduce the catalyst loading, and some fuel cells have operated at a catalyst loading of 0.25 mg/cm^2.

To be ionically conducting, the fluorocarbon ionomer must be "wet": under equilibrium conditions, it will contain about 20 percent water. The operating temperature of the fuel cell must be less than 373 K (212°F), therefore, to prevent the membrane from drying out.

Being acidic, fluorocarbon ionomers can tolerate carbon dioxide in the fuel and air streams; PEFCs, therefore, are compatible with hydrocarbon fuels. However, the platinum catalysts on the fuel and air electrodes are extremely sensitive to carbon monoxide: only a few parts per million are acceptable. Catalysts that are tolerant to carbon monoxide are being explored. Typical polarization curves for PEFCs are shown in Fig. 27-64.

A schematic diagram of a methanol-fueled PEFC system is shown in Fig. 27-65. A methanol reformer (to convert CH_3OH to H_2 and CO_2 as the principal products), a water-gas shift reactor (to convert most of the coproduct CO to CO_2, and to provide additional H_2), and a preferential oxidizer (to reduce the residual CO to 10 ppm) are included in the system.

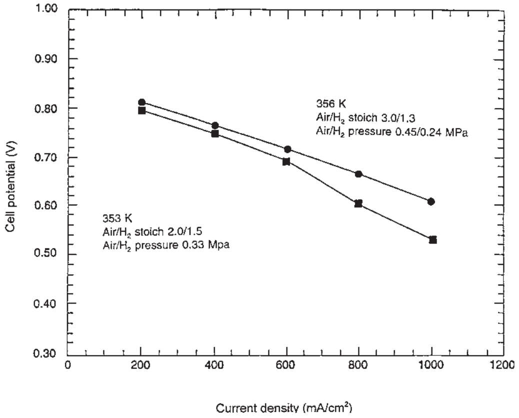

FIG. 27-64 Polarization curves for PEFC stacks.

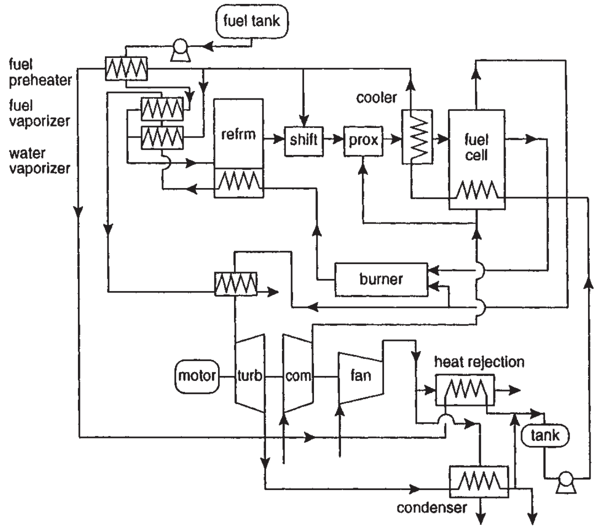

FIG. 27-65 Methanol-fueled PEFC system schematic.

Polymer electrolyte fuel cells can be obtained from several developers. These fuel cells deliver about 5 kW of power and measure 30 by 30 by 70 cm (12 × 12 × 28 in.). For the large production volume anticipated if the automotive industry were to adopt the PEFC, a system cost of less than $100/kW may be reached eventually.

Phosphoric Acid Fuel Cell This type of fuel cell was developed in response to the industry's desire to expand the natural-gas market. The electrolyte is 93 to 98 percent phosphoric acid contained in a matrix of silicon carbide. The electrodes consist of finely divided platinum or platinum alloys supported on carbon black and bonded with PTFE latex. The latter provides enough hydrophobicity to the electrodes to prevent flooding of the structure by the electrolyte. The carbon support of the air electrode is specially formulated for oxidation resistance at 473 K (392°F) in air and positive potentials.

The bipolar plate material of the PAFC is graphite. A portion of it has a carefully controlled porosity that serves as a reservoir for phosphoric acid and provides flow channels for distribution of the fuel and oxidant. The plates are electronically conductive but impervious to gas crossover.

In a typical PAFC system, methane passes through a reformer with steam from the coolant loop of the water-cooled fuel cell. Heat for the reforming reaction is generated by combusting the depleted fuel. The reformed natural gas contains typically 60 percent H_2, 20 percent CO, and 20 percent H_2O. Because the platinum catalyst in the PAFC can tolerate only about 0.5 percent CO, this fuel mixture is passed through a water gas shift reactor before being fed to the fuel cell.

PAFC systems are commercially available from the ONSI Corporation as 200-kW stationary power sources operating on natural gas. The stack cross section is 1 m^2 (10.8 ft^2). It is about 2.5 m (8.2 ft) tall and rated for a 40,000-h life. It is cooled with water/steam in a closed loop with secondary heat exchangers. The photograph of a unit is shown in Fig. 27-66. These systems are intended for on-site power and heat generation for hospitals, hotels, and small businesses. Another application, however, is as "dispersed" 5- to 10-MW power plants in metropolitan areas. Such units would be located at electric utility distribution centers, bypassing the high-voltage transmission system. The market entry price of the system is $3000/kW. As production volumes increase, the price is projected to decline to $1000 to 1500/kW.

Molten Carbonate Fuel Cell The electrolyte in the MCFC is a

FIG. 27-66 PC-25™ commercial 200-kW PAFC generator. (*International Fuel Cells.*)

mixture of lithium/potassium or lithium/sodium carbonates, retained in a ceramic matrix of lithium aluminate. The carbonate salts melt at about 773 K (932°F), allowing the cell to be operated in the 873 to 973 K (1112 to 1292°F) range. Platinum is no longer needed as an electrocatalyst because the reactions are fast at these temperatures. The anode in MCFCs is porous nickel metal with a few percent of chromium or aluminum to improve the mechanical properties. The cathode material is lithium-doped nickel oxide.

The bipolar plates are made from either Type 310 or Type 316 stainless steel, which is coated on the fuel side with nickel and aluminized in the seal area around the edge of the plates. Both internally and externally manifolded stacks have been developed.

In MCFCs, the hydrogen fuel is generated from such common fuels as natural gas or liquid hydrocarbons by steam reforming; the fuel processing function can be integrated into the fuel cell stack because the operating temperature permits reforming using the waste heat. An added complexity in MCFCs is the need to recycle carbon dioxide from the anode side to the cathode side to maintain the desired electrolyte composition. (At the cathode, carbon dioxide reacts with incoming electrons and oxygen in air to regenerate the carbonate ions that are consumed at the anode.) The simplest way is to burn the depleted fuel and mix it with the incoming air. This works well but dilutes the oxygen with the steam generated in the fuel cell. A steam condenser and recuperative heat exchanger can be added to eliminate the steam, but at increased cost.

The fuel cell must be cooled with either water or air, and the heat can be converted to electricity in a bottoming cycle. The dc electrical output of the stack is usually converted to ac and stepped up or down in voltage, depending on the application. Analogous to PAFCs, MCFC stacks are about 1 m^2 (10.8 ft^2) in plan area and quite tall. A stack generates 200 to 300 kW. Market entry is expected in 1999.

Solid Oxide Fuel Cell In SOFCs the electrolyte is a ceramic oxide ion conductor, such as yttrium-doped zirconium oxide. The conductivity of this material is 0.1 S/cm at 1273 K (1832°F); it decreases to 0.01 S/cm at 1073 K (1472°F), and by another order of magnitude at 773 K (932°F). Because the resistive losses need to be kept below about 50 mV, the operating temperature of the SOFC depends on the thickness of the electrolyte. For a thickness of 100 μm or more, the operating temperature is 1273 K (1832°F), but fuel cells with thin electrolytes can operate between 973 and 1073 K (1292 and 1472°F).

The anode material in SOFCs is a cermet (metal/ceramic composite material) of 30 to 40 percent nickel in zirconia, and the cathode is lanthanum manganite doped with calcium oxide or strontium oxide. Both of these materials are porous and mixed ionic/electronic conductors. The bipolar separator typically is doped lanthanum chromite, but a metal can be used in cells operating below 1073 K (1472°F). The bipolar plate materials are dense and electronically conductive.

Typical polarization curves for SOFCs are shown in Fig. 27-67. As discussed earlier, the open-circuit potential of SOFCs is less than 1 V because of the high temperature, but the reaction overpotentials are

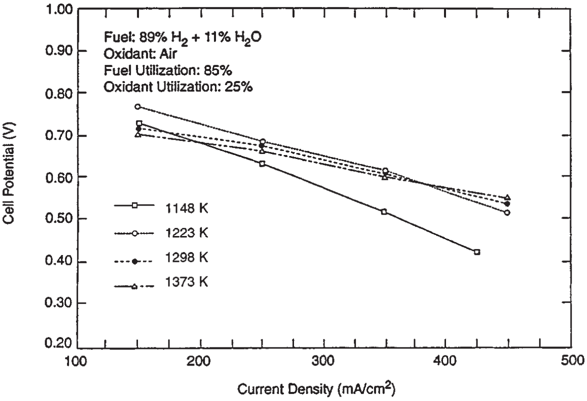

FIG. 27-67 Polarization curves at different temperatures for 50-cm active length thin-wall SOFCs.

small, yielding almost linear curves with slopes corresponding to the resistance of the components.

SOFCs can have a planar geometry similar to PEFCs, but the leading technology is tubular, as shown in Fig. 27-68. The advantage of the tubular arrangement is the absence of high-temperature seals.

Like MCFCs, SOFCs can integrate fuel reforming within the fuel cell stack. A prereformer converts a substantial amount of the natural gas using waste heat from the fuel cell. Compounds containing sulfur (e.g., thiophene, which is commonly added to natural gas as an odorant) must be removed before the reformer. Typically, a hydrodesulfurizer combined with a zinc oxide absorber is used.

The desulfurized natural gas is mixed with the recycled depleted fuel stream containing steam formed in the fuel cell. About 75 percent of the methane is converted to hydrogen and carbon monoxide in the prereformer. The hydrogen-rich fuel is then passed over the fuel cell anode, where 85 percent is converted to electricity. The balance is burned with depleted air in the combustion zone.

The hot combustion gas preheats the fresh air and the prereformer, and can be used further to generate steam. The system is cooled with 200 to 300 percent excess air. A 25-kW SOFC generator system is shown in Fig. 27-69.

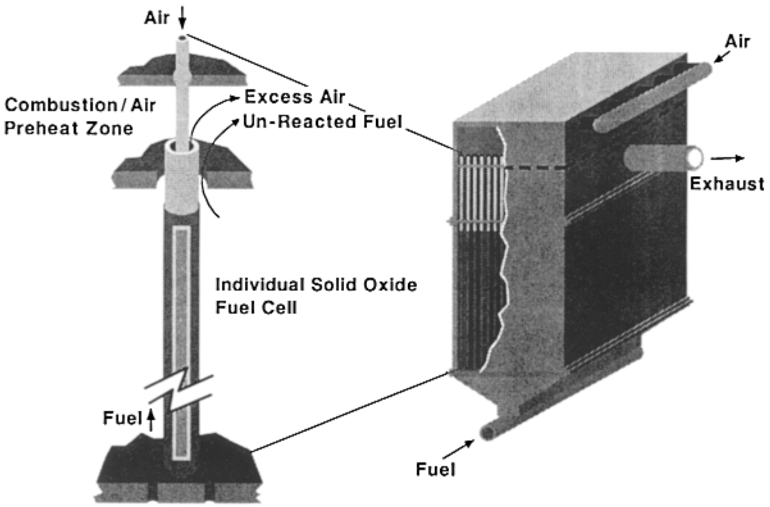

FIG. 27-68 Configuration of the tubular SOFC. (*Courtesy of Westinghouse Electric Corporation.*)

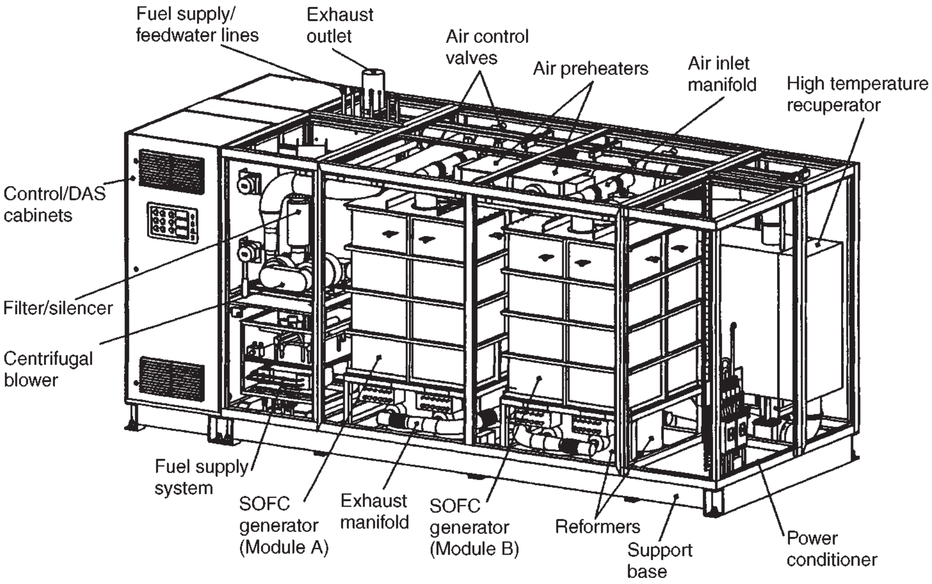

FIG. 27-69 SOFC 25-kW system package. (*Courtesy of Westinghouse Electric Corporation.*)