

SECTION 24

Energy Resources,  
Conversion,  
and Utilization

# PERRY'S CHEMICAL ENGINEERS' HANDBOOK

8TH EDITION



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# Energy Resources, Conversion, and Utilization\*

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## Nomenclature and Units

Symbol	Definition	SI units	U.S. Customary System units	Acronym	Definition
$A$	Area specific resistance	$\Omega/\text{m}^2$	$\Omega/\text{ft}^2$	AFBC	atmospheric fluidized bed combustion
$c$	Heat capacity	$\text{J}/(\text{kg}\cdot\text{K})$	$\text{Btu}/(\text{lb}\cdot^\circ\text{F})$	AFC	alkaline fuel cell
$E$	Activation energy	$\text{J}/\text{mol}$	$\text{Btu}/\text{lb mol}$	AGC-21	Advanced Gas Conversion Process
$E$	Electrical potential	$\text{V}$	$\text{V}$	BGL	British Gas and Lurgi process
$f$	Fugacity	$\text{kPa}$	$\text{psia}$	COE	cost of electricity
$F$	Faraday constant	$\text{C}/\text{mol}$	$\text{C}/\text{lb mol}$	COED	Char Oil Energy Development Process
$\Delta G$	Free energy of reaction	$\text{J}/\text{mol}$	$\text{Btu}/\text{lb mol}$	DOE	U.S. Department of Energy
$\Delta H$	Heat of reaction	$\text{J}/\text{mol}$	$\text{Btu}/\text{lb mol}$	EDS	Exxon Donor Solvent Process
$i$	Current density	$\text{A}/\text{m}^2$	$\text{A}/\text{ft}^2$	FBC	fluidized bed combustion
$k$	Rate constant	$\text{g}/(\text{h}\cdot\text{cm}^3)$	$\text{lb}/(\text{h}\cdot\text{ft}^3)$	HAO	hydrogenated anthracene oil
$K$	Latent heat of vaporization	$\text{kJ}/\text{kg}$	$\text{Btu}/\text{lb}$	HPO	hydrogenated phenanthrene oil
$P$	Pressure	$\text{kPa}$	$\text{psia}$	HRI	Hydrocarbon Research, Inc.
$Q$	Heating value	$\text{kJ}/\text{kg}$	$\text{Btu}/\text{lb}$	HTI	Hydrocarbon Technologies, Inc.
$R$	Gas constant	$\text{J}/\text{mol}\cdot\text{K}$	$\text{Btu}/\text{lb mol}\cdot^\circ\text{R}$	IGCC	integrated gasification combined-cycle
$s$	Relative density	Dimensionless	Dimensionless	KRW	Kellogg-Rust-Westinghouse process
$T$	Temperature	$\text{K}$	$^\circ\text{F}$	MCFC	molten carbonate fuel cell
$U$	Fuel utilization	percent	percent	MTG	methanol-to-gasoline process
$V$	Molar gas volume	$\text{m}^3/\text{mol}$	$\text{ft}^3/\text{lb mol}$	OTFT	once-through Fischer-Tropsch process
$Z$	Compressibility factor	Dimensionless	Dimensionless	PAFC	phosphoric acid fuel cell
Greek Symbol				PC	pulverized coal
$\epsilon$	Energy conversion efficiency	Percent	Percent	PEFC	polymer electrolyte fuel cell
Acronyms and Unit Prefixes				PFBC	pressurized fluidized bed combustion
Symbol	Name	Value		Quad	$10^{15}$ Btu
E	Exa	$10^{18}$		SASOL	South African operation of synthetic fuels plants
G	Giga	$10^9$		SMDS	Shell Middle Distillate Synthesis Process
K	Kilo	$10^3$		SNG	synthetic natural gas
M	Mega	$10^6$		SOFC	solid oxide fuel cell
P	Peta	$10^{15}$		SRC	solvent-refined coal
T	Tera	$10^{12}$			
Z	Zetta	$10^{21}$			

## INTRODUCTION

**GENERAL REFERENCES:** Loftness, *Energy Handbook*, 2d ed., Van Nostrand Reinhold, New York, 1984. Energy Information Administration, *Emissions of Greenhouse Gases in the United States 2003*, U.S. Dept. of Energy, DOE/EIA-0573 (2004). 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, 1993. Turner, *Energy Management Handbook* 5th ed., The Fairmont Press, Lilburn, Ga., 2004. *National Energy Policy*, National Energy Policy Development Group, Washington, May 2001.

*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*, 7th ed., Sec. 27, has been updated and condensed. Recent improvements in materials and manufacturing methods have brought fuel cells closer to being economic for stationary and transportation power generation, but additional advances are required for broad adoption.

## 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	Discovered conventionally reservoired	Total estimated resource
Coal	6.48	12.5	96.2
Petroleum	0.16	0.5	1.2
Natural gas	0.21	0.4	1.6

\*ZJ = 10<sup>21</sup> J. (To convert to 10<sup>18</sup> 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 <sup>6</sup> Btu/US ton
Lignite and subbituminous coal	23.2 MJ/kg	20 × 10 <sup>6</sup> Btu/US ton
Crude oil	38.5 MJ/L	5.8 × 10 <sup>6</sup> Btu/bbl
Natural-gas liquids	25.2 MJ/L	3.8 × 10 <sup>6</sup> Btu/bbl
Natural gas	38.4 MJ/m <sup>3</sup>	1032 Btu/ft <sup>3</sup>

1 bbl = 42 US gal = 159 L = 0.159 m<sup>3</sup>

## 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. *Annual Book of ASTM Standards*, sec. 5, ASTM International, West Conshohocken, Pa., 2004. *Methods of Analyzing and Testing Coal and Coke*, U.S. Bureau of Mines Bulletin, 638, 1967.

**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 24-1 shows the classification system described in ASTM D 388-99 (2004) (ASTM International, op. cit.). 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 specified weight or if the button swells or has a porous cell structure.

The Parr formulas, Eqs. (24-1) to (24-3), are used for classifying coals according to rank. The Parr formulas are employed in litigation cases.

$$F' = \frac{100(F - 0.15S)}{100 - (M + 1.08A + 0.55S)} \quad (24-1)$$

TABLE 24-1 Classification of Coals by Rank\*

Class/group	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)†				Agglomerating character
					MJ/kg		Btu/lb		
	Equal or greater than	Less than	Greater than	Equal or less than	Equal or greater than	Less than	Equal or greater than	Less than	
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	

Adapted, with permission, from D388-99, Standard Classification of Coals by Rank; copyright ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

\*This classification does not apply to certain coals, as discussed in source.

†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.

$$V' = 100 - F' \quad (24-2)$$

$$Q' = \frac{100(Q - 50S)}{100 - (M + 1.08A + 0.55S)} \quad (24-3)$$

where  $M$ ,  $F$ ,  $A$ , and  $S$  are weight percentages, on a moist basis, of moisture, fixed carbon, ash, and sulfur, 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** 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 a 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 coal from a given deposit is remarkably constant when calculated on this basis.

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** [ASTM D 3172-89 (2002), ASTM International, op. cit.] 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 calcite. The **ultimate analysis** [ASTM D 3176-89 (2002), ASTM International, op. cit.] is the determination by prescribed methods of the ash, carbon, hydrogen, nitrogen, sulfur, and (by difference) oxygen. Other, minor constituent elements are also sometimes determined, most notably chlorine.

The **heating value**, or **calorific value**, expressed as kJ/kg (Btu/lb), 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 (ASTM D 5865-04, ASTM International, op. cit.). 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)  $Q_h$ . And  $Q_h$  in Btu/lb ( $\times 2.326 = \text{kJ/kg}$ ) on a dry basis can be approximated by a formula developed by the Institute of Gas Technology:

$$Q_h = 146.58C + 568.78H + 29.4S - 6.58A - 51.53(O + N) \quad (24-4)$$

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 heating value when the water is not condensed is called the **low heating value** (LHV)  $Q_l$  and is obtained from

$$Q_l = Q_h - K \cdot W \quad (24-5)$$

where  $W$  = weight of water in the combustion products/weight of fuel burned. The factor  $K$  is the latent heat of vaporization at the partial pressure of the vapor in the gas, which, at 20°C, is 2395 kJ/kg (1030 Btu/lb) of water. Thus,

$$Q_l = Q_h - \%H \cdot 214 \quad \text{kJ/kg} \quad (24-6)$$

$$Q_l = Q_h - \%H \cdot 92.04 \quad \text{Btu/lb} \quad (24-7)$$

where  $\%H$  = weight percent hydrogen in the coal and all values are on an as-determined (including moisture) basis.

**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 major forms: as organic sulfur (20 to 80 percent of the sulfur), which is a part of the coal substance; as pyrite ( $\text{FeS}_2$ ); and as sulfate (<5 percent of the sulfur in unoxidized coals). Organic sulfur is chemically bound to the coal substance, and severe treatment is necessary to break the chemical bonds to remove the sulfur. There is no existing economical method that will remove organic sulfur. 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 (as of 1997) recoverable U.S. coal reserves of all ranks, by sulfur content and major producing region, are shown in Table 24-2. The values in the table are in units of  $10^9$  metric tonnes (Pg) as reported in *U.S. Coal Reserves: 1997 Update*, DOE/EIA-0529(97). 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).

**Mercury** Impending regulations limiting the emission of mercury from coal-fired furnaces have created great interest in knowing the concentration of mercury in various coals, determining the fate of mercury during combustion, and developing methods to control mercury emissions to the atmosphere. Most commercially produced U.S. coals have mercury contents of about 0.05 to 0.2 mg/kg, dry basis, although numerous individual coals fall outside that range. Depending on the specific coal properties, furnace conditions, and type and configuration of pollution control devices with which the furnace is equipped, less than 10 percent or more than 90 percent of the coal mercury will be emitted to the atmosphere with the flue gas. The chemical form of the vaporous mercury in the flue gas, whether elemental or ionic, is important, because ionic mercury is easier to capture with available technology than is elemental mercury. The chemical form is apparently influenced by the chlorine content of the coal: coals with higher chlorine contents (0.05 percent and higher) tend to produce mainly ionic mercury in their flue gases, and thus the mercury emissions from these coals are more easily controlled.

**Coal-Ash Characteristics and Composition** When coal is to be burned, used in steel making, or gasified, it is often important to know the ash fusibility, or the temperatures at which formed pyramids of ash attain certain defined stages of fusing in either a mildly reducing or an oxidizing atmosphere; these temperatures are known as the initial deformation, softening, hemispherical, and fluid temperatures. The procedure for determining the fusibility of coal ash is prescribed by ASTM D 1857-04 (ASTM International, op. cit.). The ash fusibility temperatures are most often used as indicators of the tendency of the ash to form sintered or fused masses, which can impede gas flow through a grate and impair heat flow through furnace heat-transfer surfaces, or as indicators of 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).

**TABLE 24-2 Estimate of Recoverable U.S. Coal Reserves by Sulfur Ranges and Regions (Pg)**

	Low sulfur*	Medium sulfur*	High sulfur*	Total
Appalachia	10.6	18.4	21.1	50.2
Interior	0.7	9.1	52.6	62.4
West	79.6	49.5	8.0	137.1
U.S. total	90.9	77.0	81.7	249.6

\*Sulfur content ranges defined in units of kg S/kg (lb S/MBtu) as follows: low sulfur, < 0.29 (< 0.60); medium sulfur, 0.29 to 0.80 (0.61 to 1.67); high sulfur, > 0.80 (> 1.67).



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

SiO <sub>2</sub>	20–60
Al <sub>2</sub> O <sub>3</sub>	10–35
Fe <sub>2</sub> O <sub>3</sub>	5–35
CaO	1–20
MgO	0.3–4
TiO <sub>2</sub>	0.5–2.5
P <sub>2</sub> O <sub>5</sub>	0.01–1
Na <sub>2</sub> O and K <sub>2</sub> O	1–4
SO <sub>3</sub>	0.1–12

Knowledge of the composition of coal ash is useful for estimating and predicting the fouling and corrosion of heat-exchange surfaces in pulverized-coal-fired furnaces and in coke making. Multiple correlations for ash composition and ash fusibility are discussed in *Coal Conversion Systems Technical Data Book* (part IA, U.S. Dept. of Energy, 1984). The slag viscosity-temperature relationship provided in that reference for completely melted slag is

$$\text{Log viscosity} = \frac{10^7 M}{(T - 150)^2 + C} \quad (24-8)$$

where viscosity is in poise ( $\times 0.1 = \text{Pa}\cdot\text{s}$ ),  $M = 0.00835(\text{SiO}_2) + 0.00601(\text{Al}_2\text{O}_3) - 0.109$ ,  $C = 0.0415(\text{SiO}_2) + 0.0192(\text{Al}_2\text{O}_3) + 0.0276$  (equivalent  $\text{Fe}_2\text{O}_3$ ) +  $0.0160(\text{CaO}) - 3.92$ , and  $T = \text{temperature, K}$ .

The oxides in parentheses are the weight percentages of these oxides when  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}$  are normalized to 100 percent.

**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 720–91 (2004) (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 409–02, 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. 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 <sup>3</sup>	lb/ft <sup>3</sup>
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 dropping a sample of coal onto a steel plate in a specified manner and comparing the size distribution before and after the test, as in ASTM D 440–86 (2002) (ASTM International, op. cit.). A complementary property, *friability*, is the tendency of coal to break during repeated handling, and it is determined by the standard tumbler test, as in ASTM D 441–86 (2002) (ASTM International, op. cit.).

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*), the process by which a coke is manufactured (e.g., vertical slot oven coke), or the end use (e.g., blast furnace coke). The carbonization of coal into coke involves a complex set of physical and chemical changes. Some of the physical changes 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.) Essentially all coal-derived coke produced in the United States is high-temperature coke for metallurgical applications; its production comprises nearly 5 percent of the total bituminous coal consumed in the United States. About 90 percent of this type of coke is made in slot-type by-product recovery ovens, and the rest is made in heat recovery ovens. Blast furnaces use about 90 percent of the production, the rest going mainly to foundries and gas plants. The ranges of chemical and physical properties of metallurgical coke used in the United States are given in Table 24-3. Blast furnaces use about 90 percent of the production, the rest going mainly to foundries and gas plants.

The typical by-product yields per U.S. 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<sup>3</sup>); 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 must meet specifications not required of blast furnace coke. The volatile matter should not exceed 1.0 percent, the sulfur should not exceed 0.7 percent, the ash should not exceed 8.0 percent, and the size should exceed 100 mm (4 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.

**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

**TABLE 24-3 Chemical and Physical Properties of Metallurgical Cokes Used in the United States**

Property	Range of values
Volatile matter	0.5–1.0%, dry basis
Ash content	8–12%, dry basis
Sulfur content	0.6–1.0%, dry basis
Stability factor	55–65
Hardness factor	60–68
Strength after reaction	55–65
Apparent specific gravity (water = 1.0)	0.8–0.99

TABLE 24-4 Waste Fuel Analysis

Type of waste	Heating value, Btu/lb	Percentage composition by weight					Density, lb/ft <sup>3</sup>
		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.

755 to 811 K (900 to 1000°F) and spraying it into a large vertical cylinder where cracking and polymerization reactions occur. 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. Petroleum coke contains many of the impurities from its feedstock; thus, the sulfur content is usually high, and appreciable quantities of vanadium 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 <sup>3</sup>	1.28–1.42	1.5–1.6

Most petroleum coke is used for fuel, but some premium delayed coke known as “needle coke” is used to make anodes for the aluminum industry. That coke is first calcined to less than 0.5 percent volatiles at 1300 to 1400°C before it is used to make anodes.

### Other Solid Fuels

**Coal Char** Coal char is, generically, the nonagglomerated, nonfusible residue from the thermal treatment of coal; however, it is more specifically the solid residue from low- or medium-temperature carbonization processes. Char is used as a fuel or a carbon source. Chars have compositions intermediate between those of coal and coke: the volatile matter, sulfur content, and heating values of the chars are lower, and the ash content is higher, than those of the original coal.

**Peat** Peat is partially decomposed plant matter that has accumulated in a water-saturated environment. It is the precursor of coal but is not classified as coal. Peat is used extensively as a fuel primarily in Ireland and the former Soviet Union, but in the United States, its main use is in horticulture and agriculture. 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 27.9 to 30.2 MJ/kg (12,000 to 13,000 Btu/lb).

**Solid Wastes and Biomass** The generation of large quantities of solid wastes is a significant feature of affluent societies. In the United

States in 2001 the rate was about 2 kg (4.4 lb) per capita per day, or nearly 208 Tg (229 M short tons) per year. Table 24-4 shows that the composition of miscellaneous refuse is fairly uniform, but size and moisture variations cause major difficulties in efficient, economical disposal. The fuel value of municipal solid wastes is usually sufficient to enable self-supporting combustion, leaving only the incombustible residue and reducing by 90 percent the volume of waste consigned to landfill. The heat released by the combustion of waste can be recovered and utilized, although this is not always economically feasible.

Wood, wood scraps, bark, and wood product plant waste streams are major elements of biomass, industrial, and municipal solid waste fuels. In 1991, about 1.7 EJ ( $1.6 \times 10^{15}$  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). Tire-derived fuel (TDF), which is produced by shredding and processing waste tires and which has a heating value of 30.2 to 37.2 MJ/kg (13,000 to 16,000 Btu/lb), is an important fuel for use in cement kilns and as a supplement to coal in steam raising.

### LIQUID FUELS

**Liquid Petroleum Fuels** The discussion here focuses on burner fuels rather than transportation fuels. There is overlap, particularly for fuels in the distillate or “gas oil” range. Other factors such as the Tier II gasoline specifications, the ultralow-sulfur diesel specifications, and the gradual reduction in crude quality impact refining and blending practices for burner 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, and boiling ranges are given in Table 24-5.

**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 24-5 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 4814-03 and D 910-03), diesel fuels (D 975-03), and aviation and gas-turbine fuels (D 1655-03 and D 2880-03).

TABLE 24-5 Detailed Requirements for Fuel Oils<sup>a</sup>

Property	ASTM Test Method <sup>b</sup>	No. 1 Low Sulfur <sup>c</sup>	No. 1 <sup>c</sup>	No. 2 Low Sulfur <sup>c</sup>	No. 2 <sup>c</sup>	Grade No. 4 (Light) <sup>c</sup>	No. 4	No. 5 (Light)	No. 5 (Heavy)	No. 6
Flash point, °C, min	D 93—Proc. A D 93—Proc. B	38 —	38 —	38 —	38 —	38 —	— 55	— 55	— 55	— 60
Water and sediment, % vol, max	D 2709 D 95 + D 473	0.05 —	0.05 —	0.05 —	0.05 —	— (0.50) <sup>d</sup>	— (0.50) <sup>d</sup>	— (1.00) <sup>d</sup>	— (1.00) <sup>d</sup>	— (2.00) <sup>d</sup>
Distillation temperature, °C	D 86	—	—	—	—	—	—	—	—	—
10% volume recovered, max		215	215	—	—	—	—	—	—	—
90% volume recovered, min		—	—	282	282	—	—	—	—	—
90% volume recovered, max		288	288	338	338	—	—	—	—	—
Kinematic viscosity at 40°C, mm <sup>2</sup> /s	D 445	—	—	—	—	—	—	—	—	—
min		1.3	1.3	1.9	1.9	1.9	>5.5	—	—	—
max		2.1	2.1	3.4	3.4	5.5	24.0 <sup>e</sup>	—	—	—
Kinematic viscosity at 100°C, mm <sup>2</sup> /s	D 445	—	—	—	—	—	—	5.0	9.0	15.0
min		—	—	—	—	—	—	8.9 <sup>e</sup>	14.9 <sup>e</sup>	50.0 <sup>e</sup>
max		—	—	—	—	—	—	—	—	—
Ramsbottom carbon residue on 10% distillation residue, % mass, max	D 524	0.15	0.15	0.35	0.35	—	—	—	—	—
Ash, % mass, max	D 482	—	—	—	—	0.05	0.10	0.15	0.15	—
Sulfur, % mass max <sup>f</sup>	D 129 D 2622	— 0.05	— 0.50	— 0.05	— 0.50	—	—	—	—	—
Copper strip corrosion rating, max, 3 h at 50°C	D 130	No. 3	No. 3	No. 3	No. 3	—	—	—	—	—
Density at 15°C, kg/m <sup>3</sup>	D 1298	—	—	—	—	>876 <sup>g</sup>	—	—	—	—
min		850	850	876	876	—	—	—	—	—
max		—	—	—	—	—	—	—	—	—
Pour point, °C, max <sup>h</sup>	D 97	-18	-18	-6	-6	-6	-6	—	—	<sup>i</sup>

Adapted, with permission, from D396-06, Standard Specification for Fuel Oils; copyright ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

<sup>a</sup> 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.

<sup>b</sup> The test methods indicated are the approved referee methods. Other acceptable methods are indicated in Sections 2 and 5.1 of ASTM D 396.

<sup>c</sup> Under U.S. regulations, Grades No. 1, No. 1 Low Sulfur, No. 2, No. 2 Low Sulfur, and No. 4 (Light) are required by 40 CFR Part 80 to contain a sufficient amount of the dye Solvent Red 164 so its presence is visually apparent. At or beyond terminal storage tanks, they are required by 26 CFR Part 48 to contain the dye Solvent Red 164 at a concentration spectrally equivalent to 3.9 lb per thousand barrels of the solid dye standard Solvent Red 26.

<sup>d</sup> 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 0.50 mass percent, and a deduction in quantity shall be made for all water and sediment in excess of 1.0 mass percent.

<sup>e</sup> 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.

<sup>f</sup> Other sulfur limits may apply in selected areas in the United States and in other countries.

<sup>g</sup> This limit ensures a minimum heating value and also prevents misrepresentation and misapplication of this product as Grade No. 2.

<sup>h</sup> 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<sup>2</sup>/s and the minimum 90% recovered temperature shall be waived.

<sup>i</sup> 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.

ASTM D 4057-95 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.

Foreign specifications are generally available from the American National Standards Institute, New York; United States federal specifications, at Naval Publications and Forms, Philadelphia. The International Association for Stability, Handling and Use of Liquid Fuels maintains a web site, [www.iash.net](http://www.iash.net), with extensive references to fuel standards.

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 were described by ASTM D 2069, Standard Specification for Marine Fuels, which was withdrawn in 2003. Specifications under ASTM D-396 or foreign specifications may be substituted as appropriate.

**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 4740-02, will detect sludge in pilot blends. Tests employing centrifuges, filtration (D 4870-99), 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 24-6.

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:

$$H = 26 - 15s \quad (24-9)$$

TABLE 24-6 Typical Ultimate Analyses of Petroleum Fuels

Composition, %	No. 1 fuel oil (41.5° API)	No. 2 fuel oil (33° API)	No. 4 fuel oil (23.2° API)	Low sulfur, No. 6 F.O. (12.6° API)	High sulfur, No. 6 (15.5° API)
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.

where  $H$  = percent hydrogen and  $s$  = relative density at 15°C (with respect to water), also referred to as specific gravity.

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. 24-1):

$$\text{Degrees API} = \frac{141.5}{s} - 131.5 \quad (24-10)$$

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).

Heat of combustion can be estimated within 1 percent from the relative density of the fuel by using Fig. 24-1. 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 24-5.) 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<sup>2</sup>/s (0.054 ft<sup>2</sup>/s) at 298 K (77°F) to about 700 mm<sup>2</sup>/s (0.0075 ft<sup>2</sup>/s) and 50 mm<sup>2</sup>/s (0.000538 ft<sup>2</sup>/s) on heating to 323 K (122°F) and 373 K (212°F), respectively. Viscosity of 1000 mm<sup>2</sup>/s or less is required for manageable pumping. Proper boiler atomization requires a viscosity between 15 and 65 mm<sup>2</sup>/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:

$$c = \frac{1.685 + (0.039 \times ^\circ\text{C})}{\sqrt{s}} \quad (24-11)$$

$$c' = \frac{0.388 + (0.00045 \times ^\circ\text{F})}{\sqrt{s}} \quad (24-12)$$

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. 24-2. 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<sup>2</sup>][°F/in]).

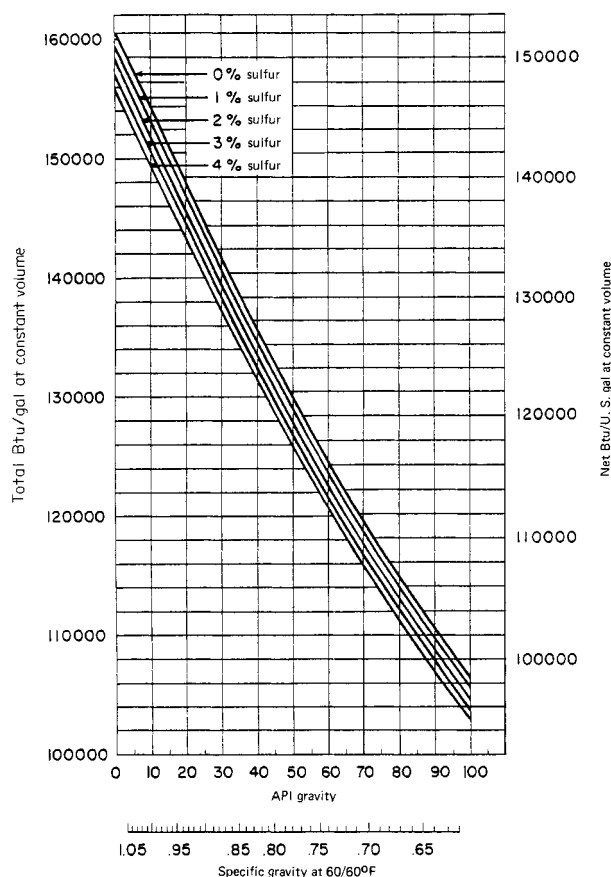


FIG. 24-1 Heat of combustion of petroleum fuels. To convert Btu/U.S. gal to kJ/m<sup>3</sup>, multiply by 278.7.

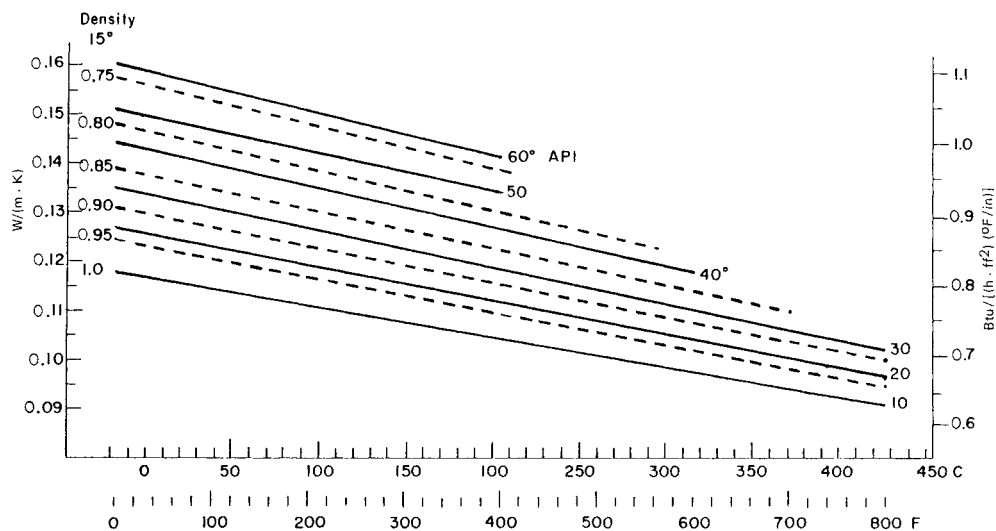


FIG. 24-2 Thermal conductivity of petroleum liquids. The solid lines refer to density expressed as degrees API; the broken lines refer to relative density at 288 K (15°C). ( $K = [^{\circ}\text{F} + 459.7]/1.8$ )

**Commercial Considerations** Fuels are sold in gallons and in multiples of the 42-gal barrel (0.159 m<sup>3</sup>) in the United States, while a weight basis is used in other parts of the world. Transactions exceeding about 20 to 40 m<sup>3</sup> (5000 to 10,000 U.S. 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 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*, 2003 (published by the National Fire Protection Association, Quincy, Ma.), liquid petroleum fuels are placed in Class I through Class III B based on their flash point, boiling point, and vapor pressure.

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 either are strip-mined and extracted with hot water or employ steam-assisted gravity drainage (SAGD) for in situ recovery of heavy oil (bitumen). The bitumen is processed into naphtha, kerosene, and gasoline fractions (which are hydrotreated), in addition to gas (which is recovered). Current production of syncrude from Canadian tar sands is about 113,000 T/d (790,000 B/d) with expected increases to about 190,000 T/d (1.7 MB/d) by 2010.

**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 partial combustion 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 with significant pretreatment or by incorporating upgrading units into the refinery.

**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 24-7 shows representative data for liquid fuels from tar sands, oil shale, and coal.

### GASEOUS FUELS

**RESERVE AND PRODUCTION INFORMATION:** DOE/EIA-0216(2003), November 2004; U.S. Crude Oil, Natural Gas, and Natural Gas Liquids Reserves: 2003 Annual Report, Table 2, Table 8, Table 12; *Annual Energy Review 2003*, DOE/EIA-0364, September 2004; *Natural Gas Annual 2003*, DOE/EIA-0131(03), December 2004, Table 9.

**Natural Gas** Natural gas is a combustible gas that occurs in porous rock of the earth's crust and is often found with accumulations of crude oil or coal. Natural gas termed *dry* has less than 0.013 dm<sup>3</sup>/m<sup>3</sup> (0.1 gal/1000 ft<sup>3</sup>) of gasoline. Above this amount, it is termed *wet*.

Proven reserves of conventionally reservoired natural gas in the United States total about 5.35 Tm<sup>3</sup> (189 Tft<sup>3</sup>). An additional 0.53 Tm<sup>3</sup> (18.7 Tft<sup>3</sup>) of proven reserves are in coal bed methane deposits. Production in 2003 was about 0.54 Tm<sup>3</sup> (19.1 Tft<sup>3</sup>), over 75 percent

TABLE 24-7 Characteristics of Typical Nonpetroleum Fuels

	Conventional coal-tar fuels from retorting <sup>a</sup>		Typical coal-derived fuels with different levels of hydrogenation <sup>b</sup>				Synthetic crude oils, by hydrogenation	
	CTF 50	CTF 400	Minimal	Mild	Mild <sup>c</sup>	Severe	Oil shale	Tar sands <sup>d</sup>
Distillation range, °C			175–280	280–500	160–415	175–400	125–495	
Density, kg/m <sup>3</sup> , 15°C	1.018	1.234	0.974	1.072	0.964	0.9607	0.914	0.864
lb U.S. gal, 60°F	8.5	10.3	8.1	8.9	8.0	8.0	7.6	7.2
Viscosity, mm <sup>2</sup> /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	87.1
Hydrogen	7.9	5.4	9.1	7.5	9.7	10.1	11.1	12.69
Oxygen	3.6	2.4	3.6–4.3	1.4–1.8	2.4	0.3	0.5	0.04
Nitrogen	0.9	1.4	0.9–1.1	1.2–1.4	0.6	0.04	0.09	0.07
Sulfur	0.2	0.7	<0.2	0.4–0.5	0.07	0.004	0.04	0.10
Ash <sup>e</sup>	Trace	0.15	<0.001	<sup>f</sup>				
C/H ratio, weight	11.0	16.5	9.4	11.9	9.1	8.9	8.0	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						

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

<sup>b</sup>Properties depend on distillation range, as shown, and to a lesser extent on coal source.

<sup>c</sup>Using recycle-solvent process.

<sup>d</sup>Tar sands, although a form of petroleum, are included in this table for comparison.

<sup>e</sup>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

<sup>f</sup>Inherent ash is “trace” or “<0.1%,” although entrainment in distillation has given values as high as 0.03 to 0.1%.

from nonassociated gas wells. Conventional proven reserves have declined about 0.03 Tm<sup>3</sup> (0.9 Tft<sup>3</sup>) per year from 1977 through 2003. Net gas imports in 2003 were 0.09 Tm<sup>3</sup> (3.3 Tft<sup>3</sup>), about 15 percent of consumption. Imports as LNG were 0.4 Tft<sup>3</sup>, about 2 percent of gas consumption.

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

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 24-8 shows the range of compositions in large cities in the United States.

TABLE 24-8 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 <sub>2</sub>	0	1.1
N <sub>2</sub>	0.31	2.47
He	0.01	0.06
Heating value	38.15(1024)	40.72(1093)
MJ/m <sup>3</sup> (Btu/ft <sup>3</sup> )		
Specific gravity	0.586	0.641
Ref.: Air at 288 K (60°F)		

\*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).

Commodity natural gas is substantially free of sulfur compounds; the terms *sweet* and *sour* are used to denote the absence or presence of H<sub>2</sub>S. 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<sub>2</sub>S and total sulfur compounds seldom exceed 0.023 and 0.46 g/m<sup>3</sup> (1.0 and 20.0 gr/100 std ft<sup>3</sup>), respectively. The majority of pipeline companies responding to a 1994 survey limited H<sub>2</sub>S to less than 0.007 g/m<sup>3</sup> (0.3 gr/100 std ft<sup>3</sup>), but a slightly smaller number continued specifying 0.023 g/m<sup>3</sup>, in accord with an American Gas Association 1971 recommendation.

**Supercompressibility of Natural Gas** All gases deviate from the simple gas laws to a varying extent. This deviation is called *supercompressibility* and must be taken into account in gas measurement, particularly at high line pressure. For example, since natural gas is more compressible under high pressure at ordinary temperatures than is called for by Boyle's law, gas purchased at an elevated pressure gives a greater volume when the pressure is reduced than it would if the gas were ideal.

The supercompressibility factor may be expressed as

$$Z = (RT/PV)^{1/2} \quad (24-13)$$

where  $Z$  = supercompressibility factor;  $R$  = universal gas constant, 8.314 kPa·m<sup>3</sup>/(kmol·K);  $T$  = gas temperature, K;  $P$  = gas pressure, kPa;  $V$  = molar gas volume, m<sup>3</sup>/kmol.

For determining supercompressibility 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 m<sup>3</sup> (1 ft<sup>3</sup>) of liquid methane at 111 K (–260°F) equals about 18 m<sup>3</sup> (630 ft<sup>3</sup>) of gaseous methane. One cubic meter (264 U.S. gal) weighs 412 kg (910 lb) at 109 K (–263°F). The heating value is about 24 GJ/m<sup>3</sup> (86,000 Btu/U.S. gal). The heat of vaporization of LNG at 0.1 MPa is 232 MJ/m<sup>3</sup> of liquid. On a product gas basis, the heat required is about 0.3 kJ/m<sup>3</sup> (10 Btu/std ft<sup>3</sup>) of gas produced.

LNG is actively traded in international commerce. In 2003 LNG was about 13 percent of gas imports to the United States but only 2 percent of gas consumption. The Energy Information Administration (EIA) projects (Annual Energy Outlook 2004) that gas imports will grow to 5.5 Tft<sup>3</sup> in 2010 and to 7.2 Tft<sup>3</sup> in 2025, with nearly all the increased volume being LNG.

Specialized ships are used to transport LNG. Receiving terminals have storage tankage and reevaporization facilities. Several new terminals have been proposed, but none has advanced to construction at this writing.

**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 refining of petroleum, 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, to a small extent, by the electrolysis of water.

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<sup>3</sup> (90 to 1100 Btu/ft<sup>3</sup>). 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<sup>3</sup> (100 gr/100 ft<sup>3</sup>) 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 both geographically and temporally. Oil and gas markets have been highly volatile in recent years while steam coal markets have not. Much combustion equipment is designed for a specific fuel, limiting the potential for fuel switching to take advantage of price trends. The costs given in Table 24-9 are U.S. averages not necessarily applicable to a specific location; they do provide fuel cost trends.

**TABLE 24-9 Time-Price Relationships for Fossil Fuels**

Year	Bituminous coal, \$/Mg (\$/U.S. ton)	Wellhead natural gas, \$/1000 m <sup>3</sup> (\$/1000 scf)	Crude oil, domestic first purchase price, \$/m <sup>3</sup> (\$/bbl)
1975	21.81 (19.79)	15.54 (0.44)	48.24 (7.67)
1985	33.93 (30.78)	88.64 (2.51)	151.52 (24.09)
1995	28.17 (25.56)	54.74 (1.55)	91.96 (14.62)
2000	26.51 (24.05)	129.96 (3.68)	168.06 (26.72)
2003	29.29 (26.57)	175.87 (4.98)	173.35 (27.56)

SOURCE: *Annual Energy Review* 2003, DOE/EIA-0384, September 2004, Tables 7.8, 6.7, and 5.18, respectively.

### 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 than solid fuels, technologies have been, and continue to be, developed to economically convert coal into liquid and gaseous fuels.

Bodley, Vyas, and Talwalker (*Clean Fuels from Coal Symposium II*, Institute of Gas Technology, Chicago, 1975) presented the chart in Fig. 24-3, 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., Elliott (ed.), 1981. *Coal Gasification Guidebook: Status, Applications, and Technologies*, Electric Power Research Institute, EPRI TR-102034, Palo Alto, Calif., 1993. *Riegel's Handbook of Industrial Chemistry*, 10th ed., Kent (ed.), Chap. 17, 2003. *Gasification* by Higman and van der Burgt, Elsevier, 2003. "The Case for Gasification" by Stiegel and Ramezan, EM, Dec. 2004, pp. 27-33.

**Background** The advantages of gaseous fuels have resulted in an increased demand for gas and led to the invention of advanced processes for coal gasification. Converting coal to combustible gas has been practiced commercially since the early 19th century. Chapter 17 of *Riegel's Handbook of Industrial Chemistry*, 10th ed., provides a good summary of the early history of coal gasification. Coal-derived gas was distributed in urban areas of the United States for residential and commercial uses until its displacement by lower-cost natural gas, starting in the 1940s. At about that time, development of oxygen-based gasification processes was initiated. An early elevated-pressure gasification process, developed by Lurgi Kohle u Mineralöltechnik GmbH, is still in use. The compositions of gases produced by this and a number of more recent gasification processes are listed in Table 24-10.

**Theoretical Considerations** The chemistry of coal gasification can be approximated by assuming coal is only carbon and considering the most important reactions involved (see Table 24-11). Reaction (24-14), the combustion of carbon with oxygen, which can be assumed to go to completion, is highly exothermic and supplies most of the thermal energy for the other gasification reactions. The oxygen used in the gasifier may come from direct feeding of air or may be high-purity oxygen from an air separation unit. Endothermic reactions (24-16) and (24-17), which represent the conversion of carbon to combustible gases, are driven by the heat energy supplied by reaction (24-14).

Hydrogen and carbon monoxide produced by the gasification reaction react with each other and with carbon. The hydrogenation of carbon to produce methane, reaction (24-15), is exothermic and contributes heat energy. Similarly, methanation of CO, reaction (24-19), can also contribute heat energy. These reactions are affected by the water-gas-shift reaction (24-18), the equilibrium of which controls the extent of reactions (24-16) and (24-17).

Several authors have shown [cf. Gumz, *Gas Producers and Blast Furnaces*, Wiley, New York, 1950; Elliott and von Fredersdorff, *Chemistry of Coal Utilization*, 2d suppl. vol., Lowry (ed.), Wiley, New

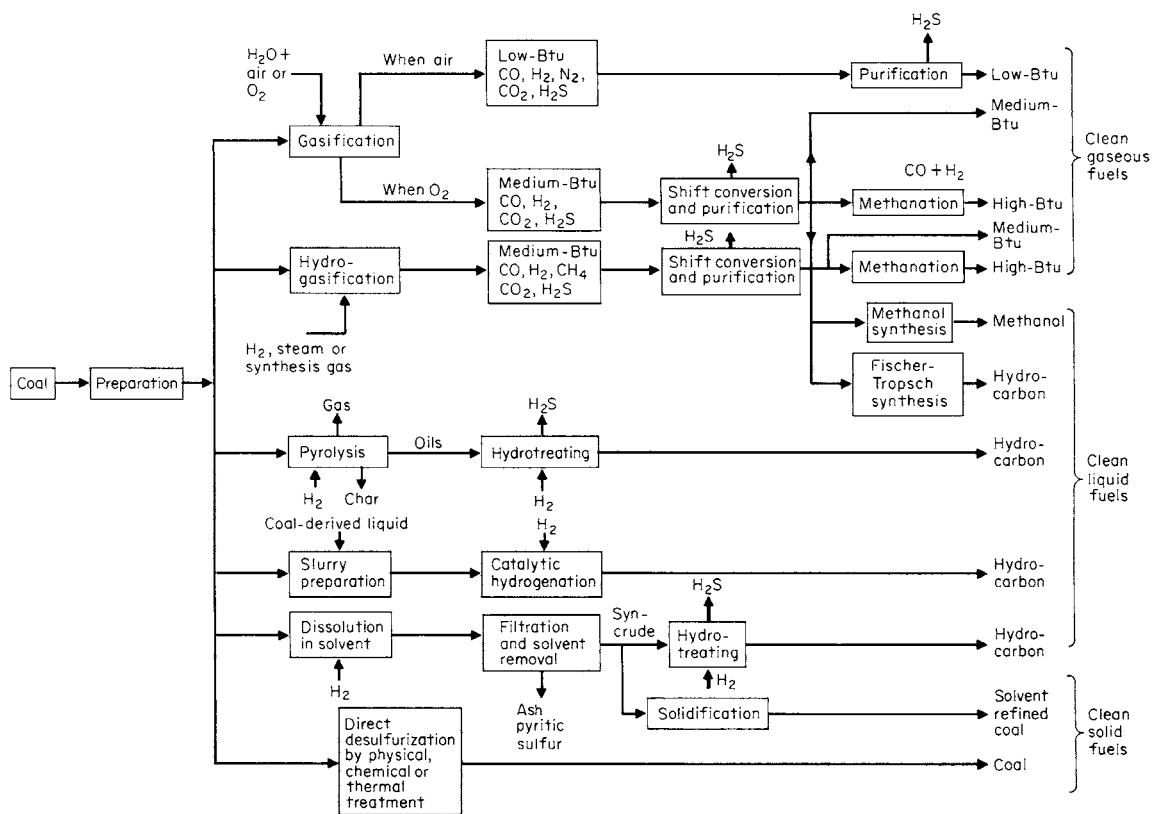


FIG. 24-3 The production of clean fuels from coal. (Based on W. Bodle, K. Vyas, and A. Talwalker; Clean Fuels from Coal Symposium II, Institute of Gas Technology, Chicago, 1975.)

York, 1963] that there are three fundamental gasification reactions: the Boudouard reaction (24-17), the heterogeneous water-gas-shift reaction (24-18), and the hydrogasification reaction (24-15). The equilibrium constants for these reactions are sufficient to calculate equi-

librium for all the reactions listed. Unfortunately, it is not possible to calculate accurate gas composition by using reactions (24-14) to (24-19). One reason is that not all reactions may be in equilibrium. Another reason is that other reactions are taking place. Since gasifica-

TABLE 24-10 Coal-Derived Gas Compositions

Gasifier technology	Sasol/Lurgi <sup>a</sup>	Texaco/GE Energy <sup>†</sup>	BGL <sup>‡</sup>	E-Gas/ConocoPhillips	Shell/Uhde <sup>§</sup>
Type of bed	Moving	Entrained	Moving	Entrained	Entrained
Coal feed form	Dry coal	Coal slurry	Dry coal	Coal slurry	Dry coal
Coal type	Illinois No. 6	Illinois No. 6	Illinois No. 6	Illinois No. 6	Illinois No. 5
Oxidant	Oxygen	Oxygen	Oxygen	Oxygen	Oxygen
Pressure, MPa (psia)	0.101 (14.7)	4.22 (612)	2.82 (409)	2.86 (415)	2.46 (357)
Ash form	Slag	Slag	Slag	Slag	Slag
Composition, vol %					
H <sub>2</sub>	52.2	30.3	26.4	33.5	26.7
CO	29.5	39.6	45.8	44.9	63.1
CO <sub>2</sub>	5.6	10.8	2.9	16.0	1.5
CH <sub>4</sub>	4.4	0.1	3.8	1.8	0.03
Other hydrocarbons	0.3	—	0.2	—	—
H <sub>2</sub> S	0.9	1.0	1.0	1.0	1.3
COS	0.04	0.02	0.1	0.1	0.1
N <sub>2</sub> + Ar	1.5	1.6	3.3	2.5	5.2
H <sub>2</sub> O	5.1	16.5	16.3	—	2.0
NH <sub>3</sub> + HCN	0.5	0.1	0.2	0.2	0.02
HCl	—	0.02	0.03	0.03	0.03
H <sub>2</sub> S : COS	20 : 1	42 : 1	11 : 1	10 : 1	9 : 1

<sup>a</sup>Rath, "Status of Gasification Demonstration Plants," *Proc. 2d Annu. Fuel Cells Contract Review Mtg.*, DOE/METC-9090/6112, p. 91.

<sup>†</sup>Coal Gasification Guidebook: Status, Applications, and Technologies, Electric Power Research Institute, EPRI TR-102034, 1993, p. 5-28.

<sup>‡</sup>Ibid., p. 5-58.

<sup>§</sup>Ibid., p. 5-48.



TABLE 24-11 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	(24-14)
$C + 2H_2 \rightarrow CH_4$	+74,900	Hydrogasification	(24-15)
$C + H_2O \rightarrow CO + H_2$	-175,440	Steam-carbon	(24-16)
$C + CO_2 \rightarrow 2CO$	-172,580	Boudouard	(24-17)
Gas-phase reaction			
$CO + H_2O \rightarrow H_2 + CO_2$	+2,853	Water-gas shift	(24-18)
$CO + 3H_2 \rightarrow CH_4 + H_2O$	+250,340	Methanation	(24-19)
Pyrolysis and hydropyrolysis			
$CH_x$	$\left(1 - \frac{x}{4}\right)C + \left(\frac{x}{4}\right)CH_4$	Pyrolysis	(24-20)
$CH_x + m H_2$	$\left[1 - \left(\frac{x+2m}{4}\right)\right]C + \left(\frac{x+2m}{4}\right)CH_4$	Hydropyrolysis	(24-21)

tion of coal always involves elevated temperatures, thermal decomposition (pyrolysis) takes place as coal enters the gasification zone of the reactor. Reaction (24-20) treats coal as a hydrocarbon and postulates its thermal disintegration to produce carbon (coke) and methane. Reaction (24-21) illustrates the stoichiometry of hydrogasifying part of the carbon to produce methane.

These reactions can be used to estimate the effect of changes in operating parameters on gas composition. As temperature increases, endothermic reactions are favored over exothermic reactions. Methane production will decrease, and CO production will be favored as reactions are shifted in the direction in which heat absorption takes place. An increase in pressure favors reactions in which the number of moles of products is less than the number of moles of reactants. At higher pressure, production of  $CO_2$  and  $CH_4$  will be favored.

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, and other gases formed by combustion and pyrolysis. The assumption made in Table 24-11 that the solid reactant is carbon is probably close to correct, but the type of char formed affects the kinetics of gas-solid reactions. The overall reaction is probably rate-controlled below 1273 K (1832°F). Above this temperature, pore diffusion has an overriding effect, and at very high temperatures surface-film diffusion probably controls. For many gasification processes, the reactivity of the char is quite important and can depend on feed coal characteristics, the method of heating, the 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, the particle is heated through several distinct thermal zones. In the initial heat-up zone, coal carbonization or devolatilization dominates. In the successively hotter zones, char devolatilization, char gasification, and fixed carbon combustion are the dominant processes. About 17 percent of total gas production occurs during coal devolatilization, and about 23 percent is produced during char devolatilization. The balance is produced during char gasification and combustion.

**Gasifier Types and Characteristics** The three main types of gasifier reactors, moving bed, fluidized bed, and entrained bed, as shown in Fig. 24-4, are all in commercial use. The moving bed is sometimes referred to as a "fixed" bed, because the coal bed is kept at a constant height. These gasifiers can differ in many ways: size, type of coal fed, feed and product flow rates, residence time, and reaction temperature. Gas compositions from the gasifiers discussed below are listed in Table 24-10.

**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 which case the coal bed rests on a rotating grate which allows the dry ash to fall through for removal. To reduce steam usage, a slagging bottom gasifier was developed by British Gas and Lurgi (BGL) in which the ash is allowed to melt and drain off through a slag tap. This gasifier has over twice the capacity per unit of cross-section

area of the dry-bottom gasifier. The BGL technology is offered commercially by Allied Syngas and Advantica.

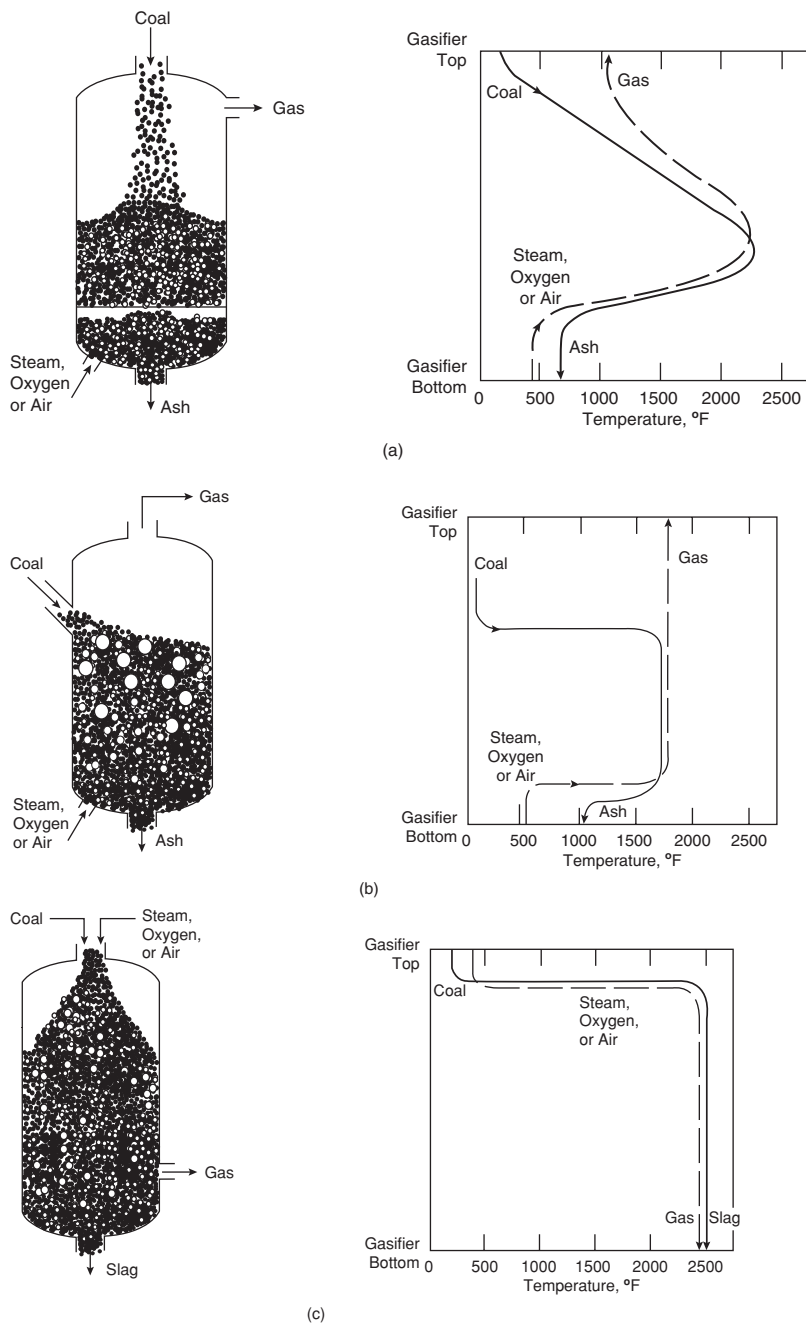
**Fluidized bed** The problem of coal agglomeration is eliminated by a fluidized-bed gasifier developed by GTI. The U-Gas gasification process uses an agglomerating-ash fluidized-bed gasifier in which crushed limestone can be injected with the coal for sulfur capture. Char and ash that exit the gasifier with the product gas are recycled to the hot agglomerating and jetting zone, where temperatures are high enough to pyrolyze fresh coal introduced at that point, 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. The agglomerating fluid-bed gasifier can be blown by either air or oxygen. 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 capacity.

**Entrained bed** The primary example of an oxygen-blown, dry-feed, entrained-flow gasifier is the Shell gasifier. An advantage of Shell coal gasification technology is its ability to process a range of coals, with a wide variety of coals (from brown coal to anthracite) having 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. Uhde and Shell are marketing this technology.

Two slurry-fed, entrained-flow gasifiers are the Texaco gasifier (now owned by GE) and the E-Gas gasifier (now owned by ConocoPhillips). The Texaco gasifier is similar to the Shell gasifier, except that the coal is fed as a slurry. Reactor exit gas is cooled either by direct water injection or by a radiative cooler directly below the reactor. The E-Gas gasifier differs from other systems in that it uses a two-stage reactor. The bulk of the feed slurry and all the oxygen are sent to the first (horizontal) stage, where the coal is gasified. Hot gas flows into the second (vertical) stage, where the remainder of the coal slurry is injected. Hot fuel gas is cooled in a fire-tube boiler fuel gas cooler.

**Gasification-Based Liquid Fuels and Chemicals** Liquid fuels and chemicals from gasification-based synthesis gas are described in the coal liquefaction section following this section. While the downstream areas of power system and indirect liquefaction plants will differ markedly, the gasification sections will be quite similar and are described in this section.

**Gasification-Based Power Systems** An important driving force for coal gasification process development is the environmental superiority of gasification-based power generation systems, generally referred to as integrated gasification combined-cycle (IGCC) power production (Fig. 24-5). Coal is crushed prior to being fed to a reactor, where it is gasified through contact with steam and air or oxygen. Partial oxidation produces the high-temperature [1033 to 2255 K



**FIG. 24-4** Gasifier types and temperature profiles: (a) fixed bed (dry ash); (b) fluidized bed; (c) entrained flow. (This figure was published in N. Holt and S. Alpert, "Integrated Gasification Combined-Cycle Power," vol. 7, pp. 897–905, in *Encyclopedia of Physical Science and Technology*, 3d ed. Copyright Elsevier, 2002.)

(1400 to 3600°F), depending on the type of gasifier] reducing environment necessary for gasification. The product fuel gas passes through heat recovery and cleanup, where particulates (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 electric power generation.

All three basic gasifier types could be incorporated into IGCC plant designs, although to date only entrained-flow gasifiers have actually been deployed. With each gasifier type, the oxidant can be air or oxygen, and the coal can be fed dry or in a slurry. The composition of the fuel gas, as well as its pressure and temperature, is determined by the design of the gasifier and the gas cleanup system.

There are several features of IGCC power systems that contribute to their improved thermal efficiency and environmental superiority compared to a conventional pulverized-coal fired power plant. First, the

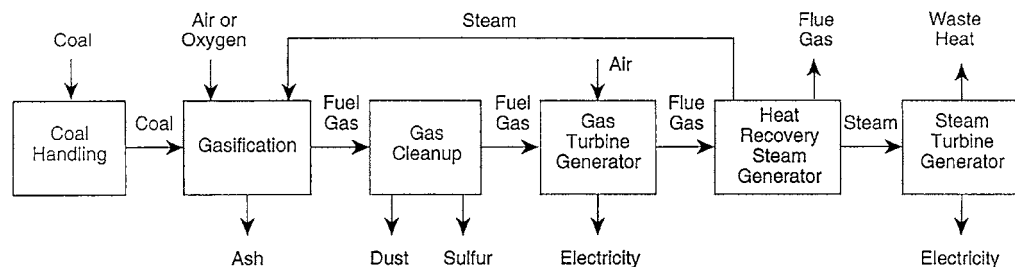


FIG. 24-5 Integrated gasification combined-cycle block diagram.

mass flow rate of gas from a gasifier is about one-fourth that from a combustor, because the gasifier is oxygen-blown and operates substoichiometrically, while the combustor is air-blown and operates with excess air. Because of the elevated operating pressure and the lack of nitrogen dilution, the volumetric gas flow to the sulfur removal system is actually only 0.5 percent to 1 percent of the volumetric flow to the flue gas desulfurization unit; this lowers the capital cost of the gas cleanup system.

Furthermore, the sulfur in coal-derived fuel gas is mainly present as hydrogen sulfide, which is much more easily recovered than the sulfur dioxide in flue gas. Not only can hydrogen sulfide 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 flue gas, but also neither lime nor limestone is required. Nitrogen in the coal is largely converted to nitrogen gas or ammonia, which is easily removed by water washing, thus reducing nitrogen oxide emissions when the fuel gas is burned. Carbon dioxide can also be scrubbed from the fuel gas, and if even further reductions in carbon emissions are required, the carbon monoxide in the fuel gas can be converted to hydrogen and carbon dioxide before  $\text{CO}_2$  removal. Finally, it has been estimated that the cost of mercury removal from an IGCC system would be only about one-tenth the cost for a conventional power plant.

Another advantage is that the IGCC system generates electricity by both combustion (Brayton cycle) and steam (Rankine cycle) turbines. The inclusion of the Brayton topping cycle improves efficiency compared to a conventional power plant's Rankine cycle-only generating system. Typically, about two-thirds of the power generated comes from the Brayton cycle and one-third from the Rankine cycle.

**Current Status** There have been substantial advancements in the development of gasification-based power systems during the last two decades. Programs are in place in the United States to support demonstration projects and for conducting research to improve efficiency, cost effectiveness, and environmental performance of IGCC power generation. Two areas of research that are likely to produce significant improvements in coal gasification technology are air separation (oxygen production) and fuel gas cleanup (removal of sulfur, mercury, particulates, and other pollutants).

Gasification technology is being widely used throughout the world. A study conducted in 2004 indicated that there were 156 gasification projects worldwide. Total capacity of the projects in operation was 45,000 MW (thermal) with another 25,000 MW (thermal) in various stages of development. As discussed later, in addition to producing fuel gas for power production, synthesis gas production by gasification is the first step in the indirect liquefaction of coal. Furthermore, gasification of carbonaceous, hydrogen-containing fuels is an effective method of thermal hydrogen production and is considered to be a key technology in the transition to a hydrogen economy. Therefore, the possibility exists for the coproduction of electric power and liquid fuels while sequestering carbon dioxide. Such an option could allow a gasifier in an IGCC system to operate at full capacity at all times, producing fuel gas at times of peak power demand and a mix of fuel gas and synthesis gas at other times.

In 2005, there were four coal-based IGCC power plants in operation in the world: Tampa Electric in Polk County, Florida, based on a Texaco (now GE) gasifier; Wabash repowering project in Indiana, based on E-Gas (now ConocoPhillips E-Gas); and Buggenum in The Netherlands and Puertollano in Spain, both based on Shell gasifiers (N.A.H. Holt, "IGCC Technology—Status, Opportunities, and Issues," *EM*, Dec. 2004, pp. 18–26).

**Cost of Gasification-Based Power Systems** Comparing power options is complicated by the many different parameters that must be considered in making a cost determination: coal cost; coal properties, including sulfur and moisture contents; ambient temperature; degree of process integration; gas turbine model; and gas cleanup method. These, and many other factors, have a significant impact on cost.

While comparison of absolute costs among different power systems is difficult, the costs of the component units are usually within given ranges. For an oxygen-blown IGCC power system, the breakdown of the capital cost for the four component units is: air separation plant, 10 to 15 percent; gasifier including gas cleanup, 30 to 40 percent; combined-cycle power unit, 40 to 45 percent; and balance of plant, 5 to 10 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.

One of the main challenges to the development and deployment of IGCC power plants has been that the capital cost was significantly higher than that of a natural-gas-fired generating unit, thereby negating the fuel cost savings. However, if natural gas prices remain substantially above \$4.75/GJ (\$5.00/10<sup>6</sup> Btu), that should no longer be the case. Moreover, capital costs of IGCC power plants are likely to decline considerably as more of these facilities are built, standard designs are developed, and economies of scale are realized.

## Coal Liquefaction

**GENERAL REFERENCES:** *Riegel's Handbook of Industrial Chemistry*, 10th ed., Kent (ed.), Ch. 17 Coal Technology, Kluwer Academic/Plenum Publishers, New York, 2003. *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. 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, Cinquigrane, and Srivastava, "Iron-Based Catalyst for Slurry-Phase Fischer-Tropsch Process: Technology Review," *Fuel Processing Technology*, **30**, 83–151 (1992). Wender, "Reactions of Synthesis Gas," *Fuel Processing Technology*, **48**, 189–297 (1996).

**Background** Coal liquefaction denotes the process of converting solid coal to a liquid fuel. The primary objective of any coal liquefaction process is to increase the hydrogen-to-carbon molar ratio. For a typical bituminous coal, this ratio is about 0.8, while for light petroleum it is about 1.8. A secondary objective is to remove sulfur, nitrogen, oxygen, and ash so as to produce a nearly pure hydrocarbon. There are several ways to accomplish liquefaction: (1) pyrolysis, (2) direct hydrogenation of the coal at elevated temperature and pressure, (3) hydrogenation of coal slurried in a solvent, and (4) gasification of coal to produce synthesis gas (a mixture of hydrogen and carbon monoxide, also referred to as syngas) followed by the use of Fischer-Tropsch (F-T) chemistry to produce liquid products. The first three of these approaches are generally referred to as direct liquefaction, in that the coal is directly converted to a liquid. The fourth approach is termed indirect liquefaction, because the coal is first converted to an intermediate product.

**Pyrolysis** In pyrolysis, coal is heated in the absence of oxygen to drive off volatile components, leaving behind a solid residue enriched in carbon and known as char or coke. Most coal pyrolysis operations are for the purpose of producing metallurgical coke, with the liquids

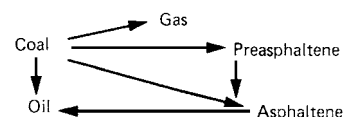
produced being considered only as a by-product. However, some small-scale work has been done to maximize liquids production by heating the coal at carefully controlled conditions of temperature vs. time, usually in several stages. Although capable of producing a significant liquid yield, this approach has two major drawbacks. First, the liquids produced are of low quality and require significant upgrading to convert them to salable products. Second, a large fraction of the original heating value of the coal remains in the char, which must be profitably marketed to make the pyrolysis process economically feasible. Two processes that reached a high state of development were the COED process developed by FMC Corporation, which used a series of fluidized beds operating at successively higher temperatures, and the TOSCOAL process, which used a horizontal rotating kiln.

**Direct Hydrogenation** In direct hydrogenation, pulverized coal is contacted with hydrogen at carefully controlled conditions of temperature and pressure. The hydrogen reacts with the coal, converting it to gaseous and liquid products. In some cases the coal is impregnated with a catalyst before being introduced into the reactor. Again, small-scale experiments have been successfully conducted. However, the major difficulty with this approach is scale-up to commercial size. Significant technical problems exist in feeding a large volume of powdered coal (powdered coal is necessary to provide a large surface area for reaction) into a reactor at high pressure, heating it to the desired temperature, and then quenching the products.

**Direct Liquefaction of Coal** Figure 24-6 presents a simplified process flow diagram of a typical direct coal liquefaction plant using coal slurry hydrogenation. Coal is ground and slurried with a process-derived solvent, mixed with a hydrogen-rich gas stream, preheated, and sent to a one- or two-stage liquefaction reactor system. In the reactor(s), the organic fraction of the coal dissolves in the solvent, and the dissolved fragments react with hydrogen to form liquid and gaseous products. Sulfur in the coal is converted to hydrogen sulfide,

nitrogen is converted to ammonia, and oxygen is converted to water. The reactor products go to vapor/liquid separation. The gas is cleaned and, after removal of a purge stream to prevent buildup of inerts, mixed with fresh hydrogen and recycled. The liquid is sent to fractionation for recovery of distillates. Heavy gas-oil is recycled as process solvent, and vacuum bottoms are gasified for hydrogen production. Ash from the gasifier is sent to disposal. Heavy direct liquefaction products contain polynuclear aromatics and are potentially carcinogenic. However, this problem can be avoided by recycling to extinction all material boiling above the desired product endpoint.

**Direct Liquefaction Kinetics** Hydrogenation of coal in a slurry is a complex process, the mechanism of which is not fully understood. It is generally believed that coal first decomposes in the solvent to form free radicals which are then stabilized by extraction of hydrogen from hydroaromatic solvent molecules, such as tetralin. If the solvent does not possess sufficient hydrogen transfer capability, the free radicals can recombine (undergo retrograde reactions) to form heavy, nonliquid molecules. A greatly simplified model of the liquefaction process is shown below.



Many factors affect the rate and extent of coal liquefaction, including temperature, hydrogen partial pressure, residence time, coal type and analysis, solvent properties, solvent-to-coal ratio, ash composition, and the presence or absence of a catalyst. Many kinetic expressions have appeared in the literature, but since they are generally specific to a particular process, they will not be listed here. In general, liquefaction is

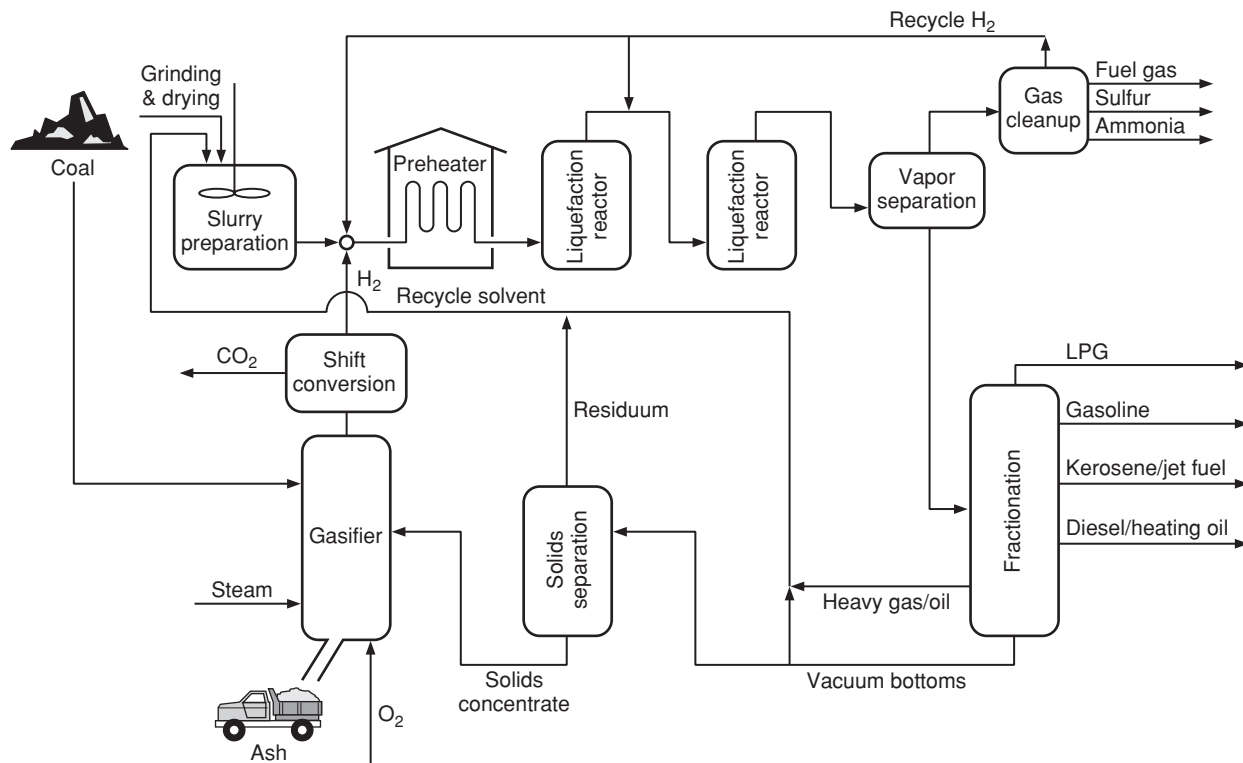


FIG. 24-6 Direct liquefaction of coal.

promoted by increasing the temperature, hydrogen partial pressure, and residence time. However, if the temperature is too high, gas yield is increased and coking can occur. Solvent-to-coal ratio is important. If the ratio is too low, there will be insufficient hydrogen transfer activity; on the other hand, if the ratio is high, a larger reactor will be necessary to provide the required residence time. Typical operating conditions are:

Temperature	670–730 K (750–850°F)
Pressure	10.3–20.7 MPa (1500–3000 psia)
Residence time	0.5 h
Solvent-to-coal ratio	1.5–2 kg/kg (1.5–2 lb/lb)

For the most highly developed processes, maf coal conversion can be as high as 90 to 95 % with a C<sub>4</sub>+ distillate yield of 60 to 75 wt % and a hydrogen consumption of 5 to 7 wt %. When an external catalyst is used, it is typically some combination of cobalt, nickel, and molybdenum on a solid acid support, such as silica alumina. In slurry hydrogenation processes, catalyst life is typically fairly short because of the large number of potential catalyst poisons present in the system.

Several variations of the slurry hydrogenation process, depicted in Fig. 24-6 and discussed below, were tested at pilot-plant scale. Table 24-12 presents typical operating conditions and yields for these processes.

The *SRC-I process*, developed by the Pittsburg & Midway Coal Mining Co. in the early 1960s, was not really a liquefaction process; rather, it was designed to produce a solid fuel for utility applications. Only enough liquid was produced to keep the process in solvent balance. The bottoms product was subjected to filtration or solvent extraction to remove ash and then solidified to produce a low-ash, low-sulfur substitute for coal. However, the value of the product was not high enough to make this process economically viable.

The *SRC-II process*, developed by Gulf Oil Corp., was an improved version of the SRC-I process, designed to produce more valuable liquid products, rather than a solid. The major difference between SRC-II and the typical process described above was the recycle of a portion of the fractionator bottoms to the slurry feed tank. This increased the ash content of the reactor feed. This ash, particularly the iron pyrites in the ash, acted as a catalyst and improved product yield and quality.

The *Exxon Donor Solvent (EDS) Process*, developed by the Exxon Research and Engineering Co., differed from the typical process in that, before being recycled, the solvent was hydrogenated in a fixed-bed reactor using a hydrotreating catalyst, such as cobalt or nickel molybdate. Exxon found that use of this hydrogen donor solvent with carefully controlled properties improved process performance. Exxon developed a solvent index, based on solvent properties, which correlated with solvent effectiveness.

The *H-Coal Process*, based on H-Oil technology, was developed by Hydrocarbon Research, Inc. (HRI). The heart of the process was a three-phase, ebullated-bed reactor in which catalyst pellets were fluidized by the upward flow of slurry and gas through the reactor. The reactor contained an internal tube for recirculating the reaction mixture to the bottom of the catalyst bed. Catalyst activity in the reactor was maintained by the withdrawal of small quantities of spent catalyst and the addition of fresh catalyst. The addition of a catalyst to the reactor is the main feature which distinguishes the H-Coal Process from the typical process.

*Two-stage liquefaction* is an advanced process concept that provides higher yields of better quality products by carrying out the coal solution and the hydrogenation/hydrocracking steps in separate reactors whose conditions are optimized for the reaction that is occurring. Either or both reactors may be catalytic. Slurry catalysts have been tested, in addition to the more conventional supported catalysts, as a means of simplifying reactor design and removing process constraints. The U.S. Department of Energy and its private sector collaborators, Hydrocarbon Technologies, Inc., and others, have advanced the development of the two-stage direct liquefaction process to commercialization status during the last two decades. Coal-derived product quality has been improved dramatically (less than 50 ppm nitrogen content, for example) through the addition of in-line fixed-bed hydrotreating of the product stream.

In *coal-oil coprocessing*, coal is slurried in petroleum residuum rather than in recycle solvent, and both the coal and petroleum components are converted to high-quality fuels in the slurry reactor. This variation offers the potential for significant cost reduction by eliminating or

**TABLE 24-12 Direct Liquefaction Process Conditions and Product Yields**

Developer Process Coal type Operating conditions	Gulf <sup>a</sup> SRC-I Kentucky 9 & 14	Gulf SRC-II Illinois No. 6	Exxon EDS Illinois No. 6	HRI H-Coal Illinois No. 6	SCS, <sup>b</sup> EPRI, Amoco Two-stage Illinois No. 6	HTI Two-stage Illinois No. 6
Nominal reactor residence time, h	0.5	0.97	0.67			
Coal space velocity per stage, kg/(h·m <sup>3</sup> ) (lb/(h·ft <sup>3</sup> ))				530 (33.1)	825 <sup>c</sup> (51.7)	310 (19.4)
Temperature, K (°F)	724 (842)	730 (855)	722 (840)	726 (847)	700 (800)	692 (787)
Total pressure, MPa (psia)	10.3 (1500)	13.4 (1950)	10.3 (1500)			19.2 (2790)
H <sub>2</sub> 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					1.5 × 10 <sup>-3</sup> (3.0)	2.3 × 10 <sup>-3</sup> (4.5)
Product yields, wt % maf coal						
H <sub>2</sub>	-2.4	-5.0	-4.3	-5.9	-6.0	-7.2
H <sub>2</sub> O	—	—	12.2 <sup>d</sup>	8.3	9.7	9.8
H <sub>2</sub> S, CO <sub>2</sub> , NH <sub>3</sub>	—	9.6	4.2 <sup>e</sup>	5.0	5.2	5.2
C <sub>1</sub> -C <sub>3</sub>	3.7 <sup>f</sup>	13.9 <sup>f</sup>	7.3	11.3	6.5	5.6
C <sub>4</sub> + distillate	13.5 <sup>g</sup>	46.8 <sup>g</sup>	38.8	53.1	65.6	73.3
Bottoms <sup>h</sup>	68.4	30.7	41.8	28.2	19.0	13.3
Unreacted coal <sup>i</sup>	5.4	4.6	—	6.4	7.0	5.0
Distillate end point, K (°F)	727 (850)	727 (850)	911 (1180)	797 (975)	797 (975)	524 (975)

<sup>a</sup> In partnership with Pittsburg & Midway Coal Mining Co.

<sup>b</sup> Southern Company Services, Inc., prime contractor for Wilsonville Facility.

<sup>c</sup> Coal space velocity is based on settled catalyst volume.

<sup>d</sup> CO<sub>2</sub> is included.

<sup>e</sup> CO<sub>2</sub> is excluded.

<sup>f</sup> C<sub>4</sub> is included.

<sup>g</sup> C<sub>4</sub> is excluded.

<sup>h</sup> Unreacted coal is included.

<sup>i</sup> "Unreacted coal" is actually insoluble organic matter remaining after reaction.

reducing recycle streams. More importantly, fresh hydrogen requirements are reduced, because the petroleum feedstock has a higher initial hydrogen content than coal. As a result, plant capital investment is reduced substantially. Other carbonaceous materials, such as municipal waste, plastics, cellulose, and used motor oils, might also serve as cofeedstocks with coal in this technology.

**Commercial Operations** The world's only commercial-scale direct coal liquefaction plant, located in the Inner Mongolia Autonomous Region of China, was dedicated in 2004. The plant is scheduled to begin production in 2007. The first train of the first phase of the Shenhua Direct Coal Liquefaction Plant will liquefy 2,100,000 Mg/a (2,315,000 ton/yr) of coal from the Shangwan Mine in the Shenhua coal field of Inner Mongolia. The plant will use a combination of technologies developed in the United States, Japan, and Germany with modifications and enhancements developed in China. The first train will use a two-stage reactor system and include an in-line hydrotreater and produce 591,900 Mg/a (652,460 ton/yr) of diesel; 174,500 Mg/a (192,350 ton/yr) of naphtha; 70,500 Mg/a (77,710 ton/yr) of LPG; and 8300 Mg/a (9150 ton/yr) of ammonia. When completed, the plant will include 10 trains producing approximately 10,000,000 Mg/a (11,000,000 ton/yr) of oil products.

Unlike the processes described above, *indirect liquefaction* is not limited to coal but may be performed using any carbonaceous feed, such as natural gas, petroleum residues, petroleum coke, coal, and biomass. Figure 24-7 presents a simplified process flow diagram for a typical indirect liquefaction process using coal as the feedstock. The syngas is produced in a gasifier (see the description of coal gasifiers earlier in this section), which partially combusts the coal or other feed at high temperature [1500 to 1750 K (2200 to 2700°F)] and moderate pressure [2 to 4 MPa (300 to 600 psia)] with a mixture of oxygen (or air) and steam. In addition to H<sub>2</sub> and CO, the raw synthesis gas contains other constituents, such as CO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, N<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub>, as well as particulates and, with some gasifiers, tars.

The syngas leaving the gasifier is cooled and passed through particulate removal equipment. Following this, depending on the requirements of the syngas conversion process, it may be necessary to adjust the H<sub>2</sub>/CO ratio. Modern high-efficiency gasifiers typically produce syngas with a H<sub>2</sub>/CO molar ratio between 0.45 and 0.7, which is lower than the stoichiometric ratio of about 2 for F-T synthesis or methanol production. Some F-T catalysts, particularly iron catalysts, possess water-gas shift conversion activity and permit operation with a low H<sub>2</sub>/CO ratio [see reaction (24-25)]. Others, such as cobalt catalysts, possess little shift activity and require adjustment of the H<sub>2</sub>/CO ratio before the syngas enters the synthesis reactor.

After shift conversion (if required), acid gases (CO<sub>2</sub> and H<sub>2</sub>S) are scrubbed from the synthesis gas. A guard chamber is sometimes used to remove the last traces of H<sub>2</sub>S, since F-T catalysts are generally very sensitive to sulfur poisoning. 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 1.5 to 6.1 MPa (220 to 880 psia). Products, whose composition depends on operating conditions, the catalyst employed, and the reactor design, include saturated hydrocarbons (mainly straight chain paraffins from methane through *n*-C<sub>30</sub> and higher), oxygenates (methanol, higher alcohols, ethers), and 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 formation:

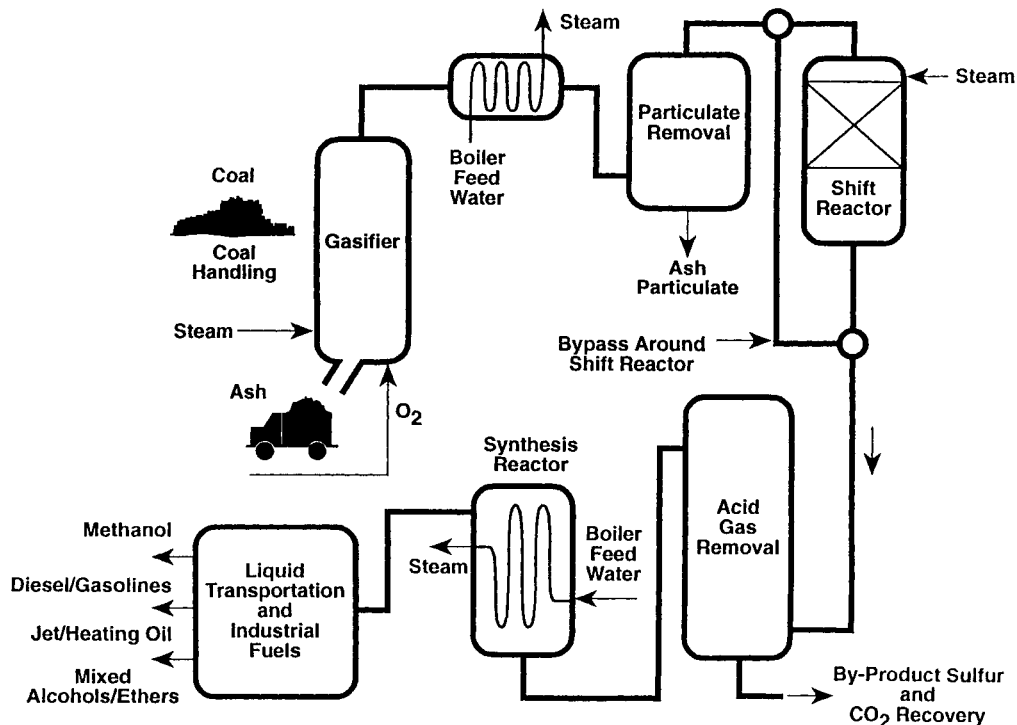
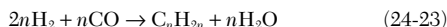


FIG. 24-7 Indirect liquefaction of coal.

Olefins formation:

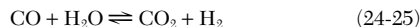


Alcohols formation:



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

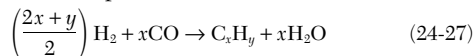
Water-gas shift:



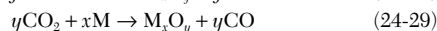
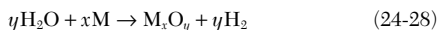
Boudouard disproportionation:



Surface carbonaceous deposition:



Catalyst oxidation-reduction:



Bulk carbide formation:



where M represents a catalytic metal atom.

The production of hydrocarbons using traditional F-T catalysts is governed by chain growth (polymerization) kinetics. The theoretical equation describing the distribution of hydrocarbon products, commonly referred to as the Anderson-Schulz-Flory (ASF) equation, is

$$\log \frac{W_n}{n} = n \log \alpha + \log \frac{(1-\alpha)^2}{\alpha} \quad (24-31)$$

where  $W_n$  is the weight fraction of products with carbon number  $n$ , and  $\alpha$  is the chain growth probability, i.e., the probability that a carbon chain on the catalyst surface will grow by adding another carbon atom rather than desorb from the catalyst surface and terminate. In deriving Eq. (24-31),  $\alpha$  is assumed to be independent of chain length. However,  $\alpha$  is dependent on temperature, pressure,  $\text{H}_2/\text{CO}$  ratio, and catalyst composition. As  $\alpha$  increases, the average carbon number of the product also increases. When  $\alpha$  equals 0, methane is the only product formed. As  $\alpha$  approaches 1, the product becomes predominantly wax. In practice,  $\alpha$  is not really independent of chain length. Methane production, particularly with cobalt catalysts, is typically higher than predicted; and  $\text{C}_2$  yield is often lower. Some investigators have found a significant deviation from the ASF distribution for higher-carbon-number products and have proposed a dual alpha mechanism to explain their results.

Figure 24-8 provides a graphical representation of Eq. 24-32 showing the weight fraction of various products as a function of  $\alpha$ . This figure shows that there is a particular  $\alpha$  that will maximize the yield of any desired product, such as gasoline or diesel fuel. Based on the ASF equation, the weight fraction of material between carbon numbers  $m$  and  $n$  inclusive is given by

$$W_{mn} = m\alpha^{m-1} - (m-1)\alpha^m - (n+1)\alpha^n + n\alpha^{n+1} \quad (24-32)$$

The  $\alpha$  to maximize the yield of the carbon number range from  $m$  to  $n$  is given by

$$\alpha_{\text{opt}} = \left( \frac{m^2 - m}{n^2 + n} \right)^{1/(n-m+1)} \quad (24-33)$$

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

**F-T Catalysts** The patent literature is replete with recipes for the production of F-T catalysts, with most formulations being based on iron, cobalt, or ruthenium, typically with the addition of some promoter(s). Nickel is sometimes listed as a F-T catalyst, but nickel has too much hydrogenation activity and produces mainly methane. In practice, because of the cost of ruthenium, commercial plants use either cobalt-based or iron-based catalysts. Cobalt is usually deposited on a refractory oxide support, such as alumina, silica, titania, or zirconia. Iron is typically not supported and may be prepared by precipitation.

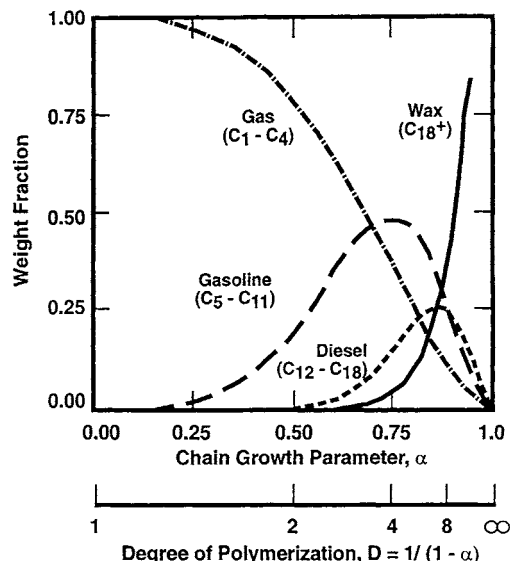
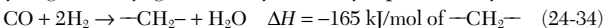


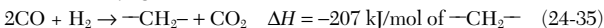
FIG. 24-8 Product yield in Fischer-Tropsch synthesis.

Of the large number of promoters listed in patents, rhenium or one of the noble metals may be used to promote cobalt, and iron is often promoted with potassium.

**Reactor Design** The F-T reaction is highly exothermic and, for hydrogen-rich syngas, can be symbolically represented by



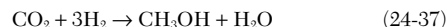
For CO-rich syngas, the overall reaction is



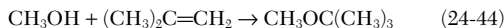
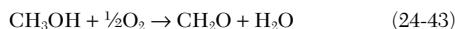
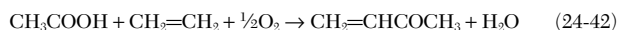
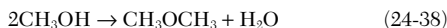
Because of the high heat release, adequate heat removal from the reactor is critical. High temperatures result in high yields of methane as well as coking and sintering of the catalyst. Three types of reactors (tubular fixed bed, fluidized bed, and slurry) provide good temperature control, and all three 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. Fluid bed reactors are limited to the production of products that are volatile at reactor operating conditions. Nonvolatile products accumulate on the catalyst and destroy its fluidizing properties.

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

**Chemicals from Syngas** A wide range of products can be produced from syngas. These include such chemicals as methanol, ethanol, isobutanol, dimethyl ether, dimethyl carbonate, and many other chemicals. Typical methanol-producing reactions are

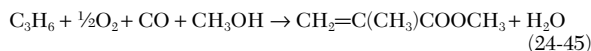


Once methanol is produced, it can be converted to an extensive range of materials. The following reactions illustrate some of the chemicals of major importance that can be made from methanol. Among these are dimethyl ether, acetic acid, methyl acetate, acetic anhydride, vinyl acetate, formaldehyde, and methyl tertiarybutyl ether (MTBE).



Reaction (24-38) can occur in parallel with the methanol-producing reactions, thereby overcoming the equilibrium limitation on methanol formation. Higher alcohols can also be formed, as illustrated by reaction (24-24), which can generate either linear or branched alcohols, depending on the catalyst used and the operating conditions. The production of methyl acetate, reaction (24-40), from synthesis gas is currently being practiced commercially. Following methanol synthesis, one-half of the methanol is reacted with carbon monoxide to form acetic acid, which is reacted with the rest of the methanol to form methyl acetate.

Methyl acrylate and methyl methacrylate, which are critical to the production of polyesters, plastics, latexes, and synthetic lubricants, can also be produced. For example, methyl methacrylate can be produced from propylene and methanol:



**Commercial Operations** 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 employed both fixed-bed (Arge) and entrained-bed (Synthol) reactors. The fixed-bed reactors have been converted to natural gas, and the Synthol reactors have been replaced by advanced fixed-fluidized bed reactors. Two additional plants that employ dry-ash Lurgi Mark IV coal gasifiers and entrained-bed (Synthol) reactors for synthesis gas conversion were constructed with start-ups in 1980 and 1983. In addition to producing a significant fraction of South Africa's transportation fuel requirements, these plants produce more than 120 other products from coal.

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 F-T and oxygenate synthesis. SASOL commissioned a 5-m-diameter slurry reactor in 1993, which doubled the wax capacity of the SASOL I facility. The development work on slurry reactors shows that they have several advantages over competing reactor designs: (1) excellent heat-transfer capability resulting in nearly 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 slurry reactors, effective separation of catalyst from the products can be difficult but is crucial to successful operation.

The United States has two commercial facilities that convert coal to fuels or chemicals via a syngas intermediate. The Great Plains Synfuels

Plant, located in Beulah, N. Dak., and operated by Dakota Gasification Company (DGC), produces synthetic natural gas (SNG) from North Dakota lignite. Fourteen Lurgi dry-ash gasifiers in the plant convert approximately 15,400 Mg/d (17,000 U.S. ton/day) of lignite into syngas which is methanated to about  $4.7 \times 10^6 \text{ N}\cdot\text{m}^3$  ( $166 \times 10^6 \text{ std ft}^3$ ) of pipeline-quality gas. 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, a wide assortment of other products are produced and sold (anhydrous ammonia, ammonium sulfate, phenol, cresylic acid, naphtha, krypton and xenon gases, liquid nitrogen, and carbon dioxide).

Eastman Chemical Company has operated a coal-to-methanol plant in Kingsport, Tenn., since 1983. Two Texaco gasifiers (one is a backup) process 34 Mg/h (37 U.S. ton/h) of coal to synthesis gas. Using ICI methanol technology, the synthesis gas is converted to methanol, which is an intermediate in the production of methyl acetate and acetic acid. The plant produces about 225,000 Mg/a (250,000 U.S. ton/yr) of acetic anhydride. As part of the DOE Clean Coal Technology Program, Air Products and Chemicals, Inc., and Eastman Chemical Company constructed and operated a 9.8 Mg/h (260 U.S. ton/d) slurry-phase reactor for the conversion of synthesis gas to methanol.

Despite the success of SASOL, most of the commercial interest in Fischer-Tropsch synthesis technology is based on natural gas, as this represents a way to bring remote gas deposits to market using conventional tankers. In 1985, Mobil commercialized its Methanol-to-Gasoline (MTG) technology in New Zealand, natural gas being the feedstock. This fixed-bed process converted synthesis gas to 4000 Mg/d (4400 U.S. ton/day) of methanol; the methanol could then be converted to 2290 m<sup>3</sup>/d (14,400 bbl/d) of gasoline. Owing to economic factors, the plant was used primarily for the production of methanol; it has been shut down due to an insufficient gas supply.

Shell Gas B.V. constructed a 1987 m<sup>3</sup>/d (12,500 bbl/d) F-T plant in Malaysia that started operations in 1994. The Shell Middle Distillate Synthesis (SMDS) process uses natural gas as the feedstock to fixed-bed reactors containing cobalt-based catalyst. The heavy hydrocarbons from the F-T 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 with no sulfur.

The largest F-T facility based on natural gas is the Moss gas 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<sup>3</sup>/d (45,000 bbl/d).

In addition to these commercial facilities, several companies have smaller-scale demonstration facilities, generally with capacities of a few hundred barrels per day of liquid products. For example, Exxon Research and Engineering Company 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<sup>3</sup>/d (200 bbl/d).

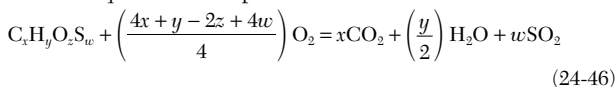
## HEAT GENERATION

**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





$x$ ,  $y$ ,  $z$ , and  $w$  being the number of atoms of carbon, hydrogen, oxygen, and sulfur, respectively, in the fuel. For example, 1 mol of methane ( $\text{CH}_4$ ) 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:

$$24.45 \left( \frac{C}{12} + \frac{H}{4} - \frac{O}{32} + \frac{S}{32} \right) = m^3 \text{O}_2 / \text{kg fuel} \quad (24-47)$$

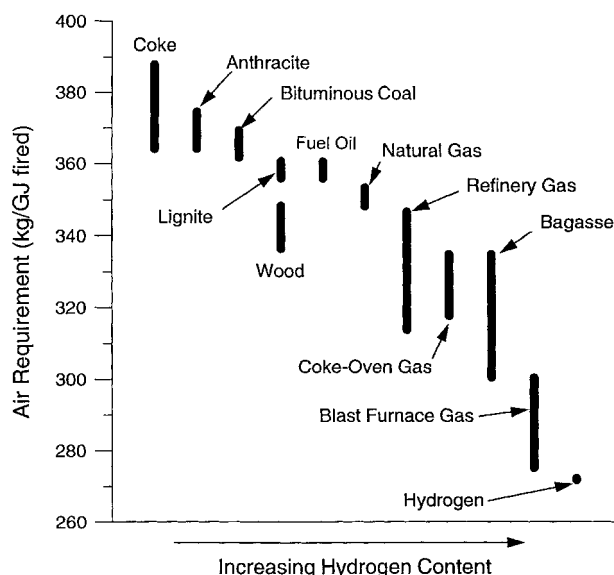
where  $C$ ,  $H$ ,  $O$ , and  $S$  are the decimal weights of these elements in 1 kg of fuel. (To convert to  $\text{ft}^3$  per lb of fuel, multiply by 16.02.) The mass of oxygen (in kg) required can be obtained by multiplying the volume by 1.31. The volume of theoretical air can be obtained by using a coefficient of 116.4 in Eq. (24-47) in place of 24.45.

Figure 24-9 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. (24-5). If the ultimate analysis is known, Eq. (24-4) can be used to determine HHV.

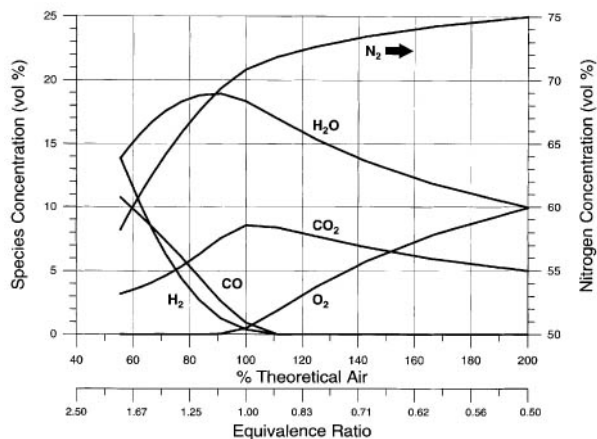
**Excess Air for Combustion** More than the theoretical amount of air is necessary in practice to achieve complete combustion. This excess air is expressed as a percentage of the theoretical air amount. The *equivalence ratio* is defined as the ratio of the actual fuel-air ratio to the stoichiometric 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 24-10 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 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).



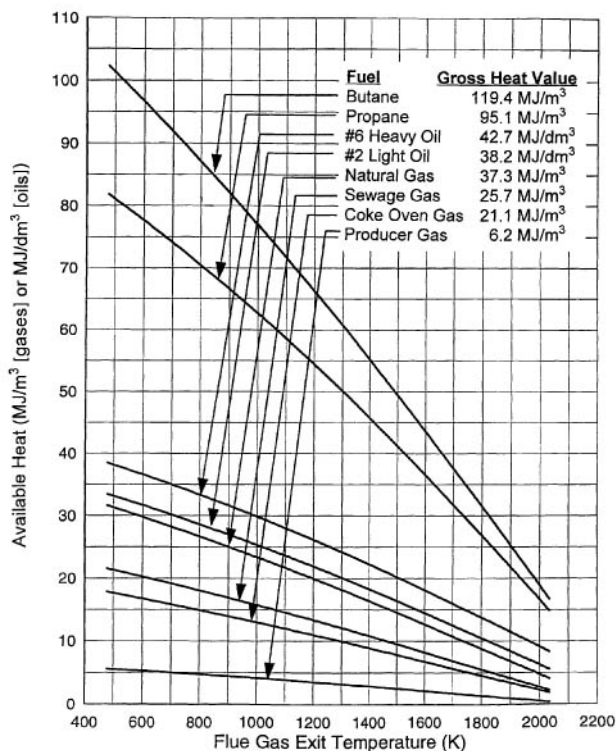
**FIG. 24-9** Combustion air requirements for various fuels at zero excess air. To convert from kg air/GJ fired to lb air/10<sup>6</sup> Btu fired, multiply by 2.090.



**FIG. 24-10** Effect of fuel-air ratio on flue-gas composition for a typical U.S. natural gas containing 93.9%  $\text{CH}_4$ , 3.2%  $\text{C}_2\text{H}_6$ , 0.7%  $\text{C}_3\text{H}_8$ , 0.4%  $\text{C}_4\text{H}_{10}$ , 1.5%  $\text{N}_2$  and 1.1%  $\text{CO}_2$  by volume.

**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 24-11 shows the *available heat* in the products of combustion for various common fuels. The available heat is the total heat



**FIG. 24-11** 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<sup>3</sup> to Btu/ft<sup>3</sup>, multiply by 26.84. To convert from MJ/dm<sup>3</sup> to Btu/gal, multiply by 3585.

TABLE 24-13 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 <sub>2</sub>	lower	upper	in air	in O <sub>2</sub>	
Acetylene, C <sub>2</sub> H <sub>2</sub>	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 <sub>4</sub> H <sub>10</sub>	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 <sub>2</sub> H <sub>4</sub>	745/882	2222/3540	—	3.0	12.5	0.48/1.56	—	98
Gasoline	553/536	—	—	1.4	7.6	—	—	—
Hydrogen, H <sub>2</sub>	845/1062	2318/4010	3247/5385	4.0	74.2	2.83/9.3	—	57
Hydrogen sulfide, H <sub>2</sub> S	565/558	—	—	4.3	45.5	—	—	—
Mapp gas, (allene) C <sub>3</sub> H <sub>4</sub>	728/850	—	3200/5301	3.4	10.8	—	4.69/15.4	—
Methane, CH <sub>4</sub>	905/1170	2191/3484	—	5.0	15.0	0.45/1.48	4.50/14.76	90
Methanol, CH <sub>3</sub> OH	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 <sub>3</sub> H <sub>8</sub>	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 <sub>3</sub> H <sub>6</sub>	—	—	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.

released during combustion minus the flue-gas heat loss (including the heat of vaporization of any water formed in the POC).

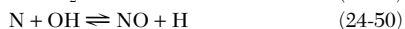
**Flammability Limits** There are both upper (or rich) and lower (or lean) limits of flammability of fuel-air or fuel-oxygen mixtures. Outside these limits, a self-sustaining flame cannot form. Flammability limits for common fuels are listed in Table 24-13.

**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 24-13.

**Pollutant Formation and Control in Flames** Key combustion-generated air pollutants include nitrogen oxides (NO<sub>x</sub>), sulfur oxides (principally SO<sub>2</sub>), particulate matter, carbon monoxide, and unburned hydrocarbons.

**Nitrogen Oxides** Three reaction paths, each having unique characteristics (see Fig. 24-12), are responsible for the formation of NO<sub>x</sub> during combustion processes: (1) *thermal* NO<sub>x</sub>, which is formed by the combination of atmospheric nitrogen and oxygen at high temperatures; (2) *fuel* NO<sub>x</sub>, which is formed from the oxidation of fuel-bound nitrogen; and (3) *prompt* NO<sub>x</sub>, which is formed by the reaction of fuel-derived hydrocarbon fragments with atmospheric nitrogen. (NO<sub>x</sub> is used to refer to NO + NO<sub>2</sub>. NO is the primary form in combustion products [typically 95 percent of total NO<sub>x</sub>]. NO is subsequently oxidized to NO<sub>2</sub> in the atmosphere.)

**Thermal NO<sub>x</sub>** The formation of thermal NO<sub>x</sub> is described by the Zeldovich mechanism:



The first of these reactions is the rate-limiting step. Assuming that O and O<sub>2</sub> are in partial equilibrium, the NO formation rate can be expressed as follows:

$$\frac{d[\text{NO}]}{dt} = A[\text{N}_2][\text{O}_2]^{1/2} \exp\left(\frac{-E}{RT}\right) \quad (24-51)$$

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

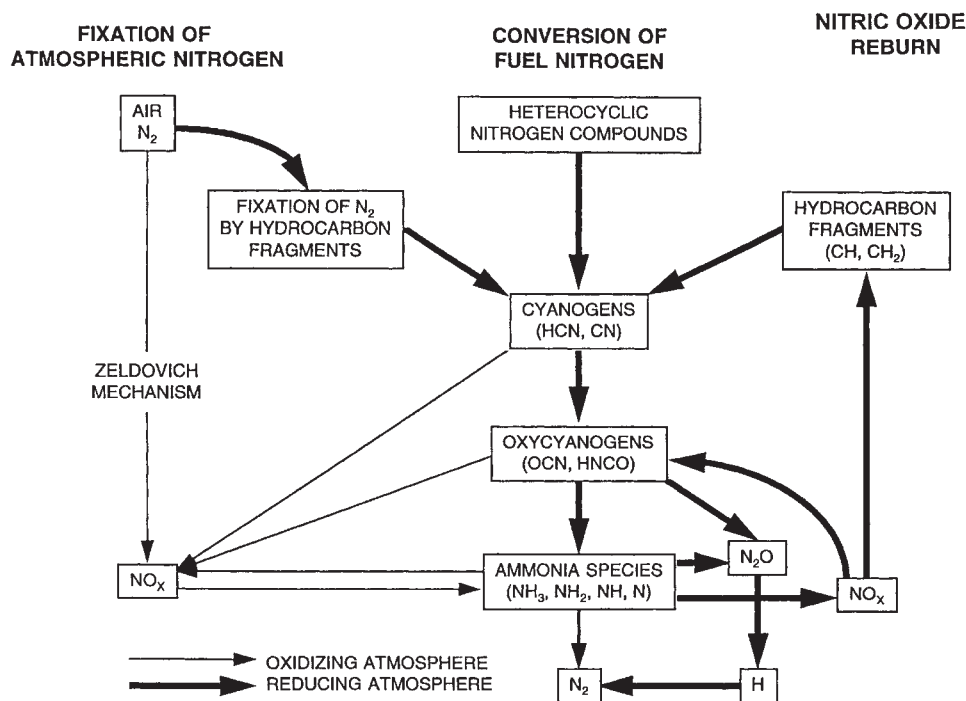
**Fuel NO<sub>x</sub>** Fuel-bound nitrogen (FBN) is the major source of NO<sub>x</sub> emissions from combustion of nitrogen-bearing fuels such as heavy oils, coal, and coke. Under the reducing conditions surrounding the burning droplet or particle, the FBN is converted to fixed nitrogen species such as HCN and NH<sub>3</sub>. 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<sub>x</sub>, 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<sub>x</sub>** Hydrocarbon fragments (such as C, CH, CH<sub>2</sub>) may react with atmospheric nitrogen under fuel-rich conditions to yield fixed nitrogen species such as NH, HCN, H<sub>2</sub>CN, 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<sub>x</sub>. Its control is important only when attempting to reach the lowest possible emissions.

**NO<sub>x</sub> emission control** It is preferable to minimize NO<sub>x</sub> 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. 24-13, are air staging, fuel staging, flue-gas recirculation, and lean premixing.

**Air staging** Staging the introduction of combustion air can control NO<sub>x</sub> 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<sub>x</sub>. 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<sub>x</sub>. 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<sub>x</sub> 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<sub>x</sub> emissions when burning gaseous fuels. The first combustion stage is very lean, resulting in low thermal and prompt NO<sub>x</sub>. 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<sub>x</sub> reduction through reburning



**FIG. 24-12** Nitrogen oxide formation pathways in combustion.

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<sub>x</sub> 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<sub>x</sub>. Recirculated flue gas is a diluent that reduces flame temperatures. External and internal recirculation paths have been applied: internal 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<sub>x</sub> 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  $\text{NO}_x$  emissions can be achieved by pre-mixing 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  $\text{NO}_x$ . However, achieving such low emissions requires operating near the lean stability limit. This is an attractive  $\text{NO}_x$  control approach for gas turbines, where operation at high excess air does not incur an efficiency penalty. In this application,  $\text{NO}_x$  emissions have been reduced by 75 to 95 percent.

**Sulfur Oxides** Sulfur occurs in fuels as inorganic minerals (primarily pyrite,  $\text{FeS}_2$ ), 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 pyrolyzed during the volatilization phase of oil and coal combustion and react in the gas phase to form predominantly  $\text{SO}_2$  and some  $\text{SO}_3$ . 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  $\text{SO}_2$  is further oxidized to  $\text{SO}_3$ , 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<sub>2</sub> 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

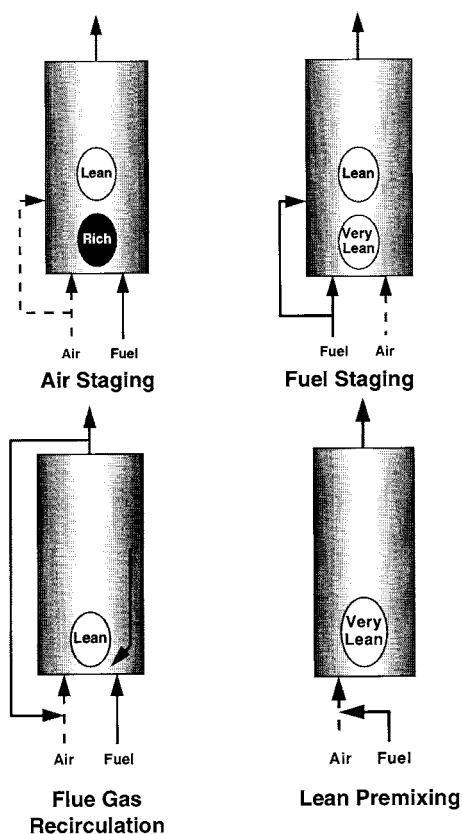


FIG. 24-13 Combustion modifications for  $\text{NO}_x$  control.

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  $\mu\text{m}$ ), 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  $\text{CO}_2$ . 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  $\text{CO}_2$  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  $\text{H}_2$ ,  $\text{CH}_4$ , CO,  $\text{CO}_2$ , and  $\text{C}_2$ - $\text{C}_4$  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

\*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.

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  $4.4 \text{ MW/m}^2$  ( $1.4 \times 10^6 \text{ Btu/[h}\cdot\text{ft}^2]$ ) for severely slagging coals to  $6.6 \text{ MW/m}^2$  ( $2.1 \times 10^6 \text{ Btu/[h}\cdot\text{ft}^2]$ ) for low-slagging fuels.

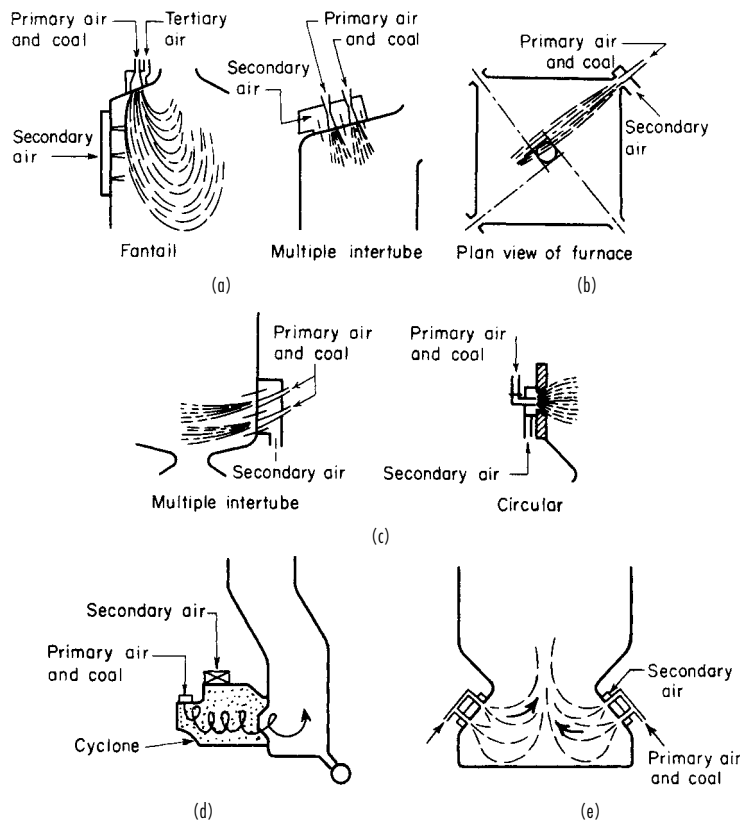
The various burner and furnace configurations for PC firing are shown schematically in Fig. 24-14. The U-shaped flame, designated as *fantail vertical firing* (Fig. 24-14a), was developed initially for pulverized coal before the advent of water-cooled furnace walls. Because a large percentage of the 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. 24-14, 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  $31 \text{ m/s}$  ( $100 \text{ ft/s}$ ).

In *tangential firing* (Fig. 24-14b), 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  $30^\circ$ , enabling the operator to selectively utilize in-furnace heat-absorbing surfaces, especially the superheater.

The circular burner shown in Fig. 24-15 is widely used in horizontally fired furnaces and is capable of firing coal, oil, or gas in capacities as high as  $174 \text{ GJ/h}$  ( $1.65 \times 10^8 \text{ Btu/h}$ ). 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- $\text{NO}_x$  burners* are designed to delay and control the mixing of coal and air in the main combustion zone. A typical low- $\text{NO}_x$  air-staged burner is illustrated in Fig. 24-16. This combustion approach can reduce  $\text{NO}_x$  emissions from coal burning by 40 to 50 percent. Because of the reduced flame temperature and delayed mixing in a low- $\text{NO}_x$  burner, unburned carbon emissions may increase in some applications and for some coals. *Overfire air* is another technique for



**FIG. 24-14** Burner and furnace configurations for pulverized-coal firing: (a) vertical firing; (b) tangential firing; (c) horizontal firing; (d) cyclone firing; (e) opposed-inclined firing.

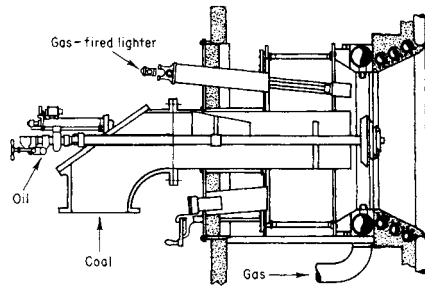


FIG. 24-15 Circular burner for pulverized coal, oil, or gas. (From Marks' Standard Handbook for Mechanical Engineers, 8th ed., McGraw-Hill, New York, 1978.)

staging the combustion air to control  $\text{NO}_x$  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  $\text{NO}_x$  emissions by 20 to 30 percent. *Reburn* is a  $\text{NO}_x$  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  $\sim 1.15$ ), under which conditions a portion (50 to 60 percent) of the  $\text{NO}_x$  is converted to molecular nitrogen.

**Pulverizers** The pulverizer is the heart of any solid-fuel suspension-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. 24-17. Capacity can also be seriously reduced by excessive moisture in the coal, but it can be restored by

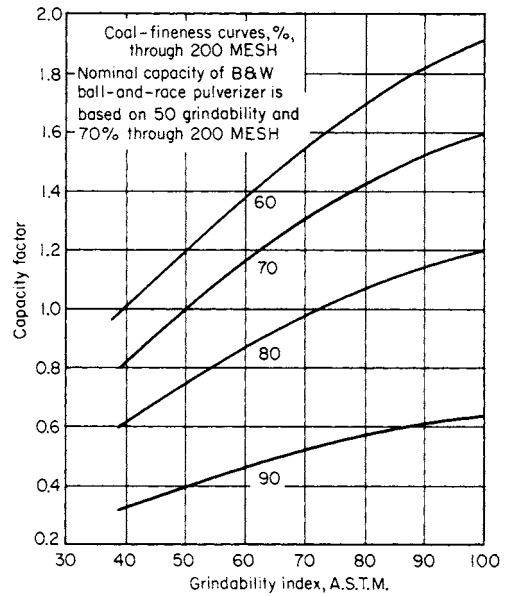


FIG. 24-17 Variation of pulverizer capacity with the grindability of the coal and the fineness to which the coal is ground. (Babcock & Wilcox Co.)

increasing the temperature of the primary air. Figure 24-18 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  $74 \mu\text{m}$ .

**Cyclone Furnaces** In *cyclone firing* (Fig. 24-14d) 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

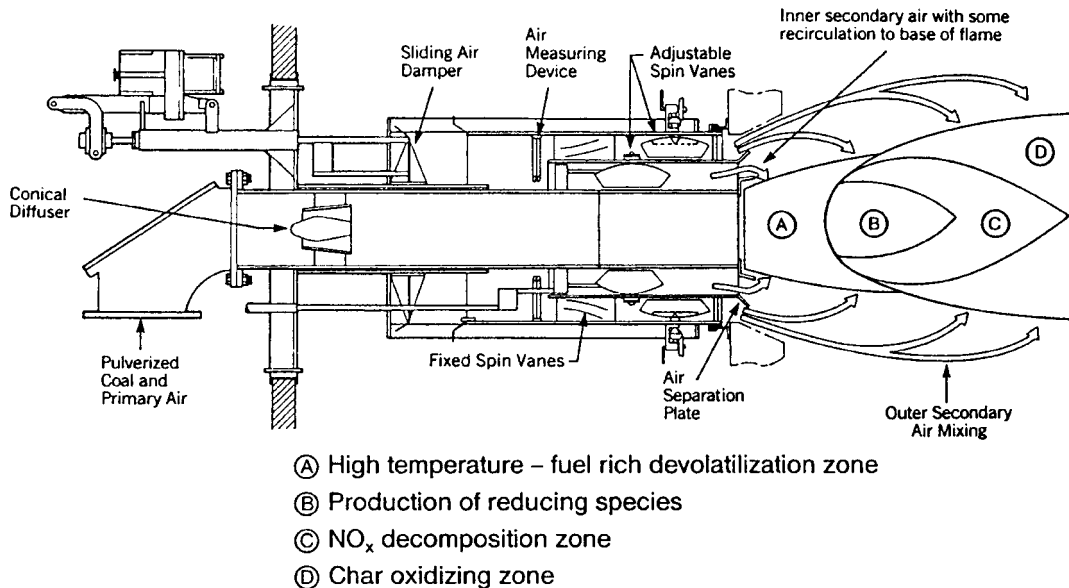
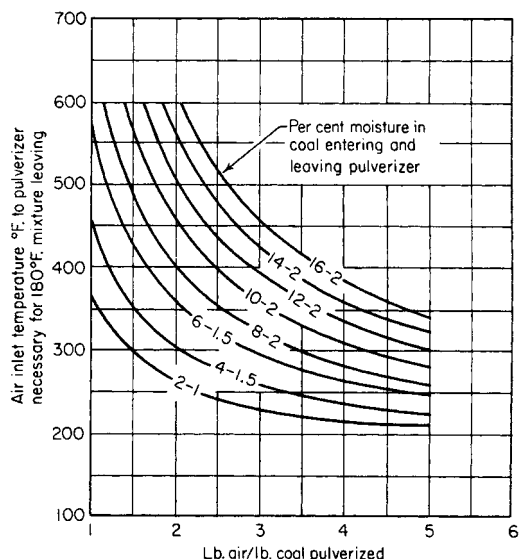


FIG. 24-16 Low- $\text{NO}_x$  pulverized coal burner. (Babcock & Wilcox Co.)

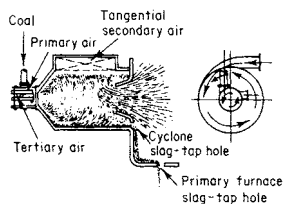


**FIG. 24-18** Effect of moisture in coal on pulverizer capacity. Sufficient drying can be accomplished to restore capacity if air temperatures are high enough.  $[K = (°F + 459.7)/1.8]$  (Combustion Engineer, *Combustion Engineering Inc.*, New York, 1966.)

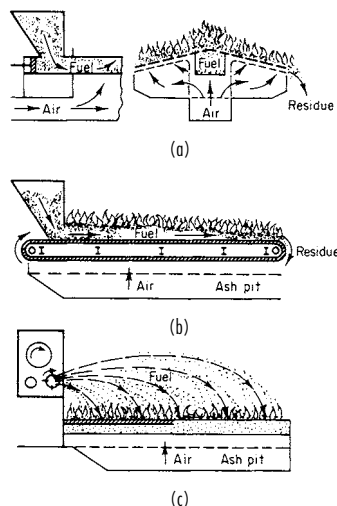
coarser ones are thrown centrifugally to the chamber wall, where most of them are captured in a sticky wall coating of molten slag. The secondary air, admitted tangentially along the top of the cyclone furnace, sweeps the slag-captured particles and completes their combustion. A typical firing rate is about  $18.6 \text{ GJ}/(\text{h}\cdot\text{m}^3)$  ( $500,000 \text{ Btu}/(\text{h}\cdot\text{ft}^3)$ ). The slag drains continuously into the boiler furnace and thence into a quenching tank. Figure 24-19 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. 24-20.

**Underfeed Firing** Both fuel and air have the same relative 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 ( $\frac{3}{4}$  to 2 in) and no more than 50 percent through a 6-mm ( $\frac{1}{4}$ -in) screen. Overfire air or steam jets are frequently used in the bridgwall at the end of the stoker to promote turbulence.



**FIG. 24-19** Cyclone furnace. (From Marks' Standard Handbook for Mechanical Engineers, 9th ed., McGraw-Hill, New York, 1987.)



**FIG. 24-20** Basic types of mechanical stokers: (a) underfeed; (b) crossfeed; (c) overfeed (spreader stoker).

In the *multiple-retort stoker*, rams feed coal to the top of sloping grates between banks of tuyeres. Auxiliary small sloping rams perform 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 ( $\frac{1}{4}$ -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. 24-20c). 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 ( $\frac{3}{4}$ -in) nut and slack with not more than 30 percent less than 6.4 mm ( $\frac{1}{4}$  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 Sec. 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, or spent sorbent (limestone or dolomite) if in-bed sulfur capture is included in the design. The fluidizing action promotes good solids mixing and gas-solids contacting that allow high combustion efficiency to be achieved at temperatures significantly lower than those of a pulverized coal (PC) 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<sub>x</sub> formation. This latter benefit, in conjunction with in-bed sulfur capture capability, constitutes one of the great advantages of fluidized-bed combustion: in situ pollution control. Having this control built into the furnace reduces the extent of back-end clean up required for a given emissions standard.

There are two types of FBC unit being sold commercially, *bubbling* and *circulating*, both operating at atmospheric pressure. Typical superficial fluidizing velocities are as follows.

Bubbling FBC 1.5 to 2.7 m/s (5 to 9 ft/s)

Circulating FBC 3.7 to 7.3 m/s (12 to 24 ft/s)

Pressurized FBC (PFBC) designs, bubbling and circulating, have been under development since the 1970s, but all work has now been curtailed. Work on an advanced PFBC design, incorporating partial coal gasification and char combustion, has also been curtailed. Several commercial bubbling PFBC units were built in the 1990s, covering the range 80 to 340 MWe. However, no new PFBC plants have been

announced since 1996, and consequently the technology is dropped from this edition of the Handbook.

**Bubbling Beds** A large proportion of the noncombustible feedstock—sand, ash, or sorbent-derived material—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, resulting in the rapid vertical mixing of the bed material that promotes even temperatures and good gas-solids contacting.

Early bubbling FBC units were designed to burn coal, and the heat released was removed by heat transfer to in-bed tubes and/or to the water-wall tubes used to enclose the furnace. These surfaces experienced high rates of metal loss through the combined effects of erosion and abrasion. Protective measures such as plasma-sprayed coatings and metal fins to disrupt the solids flow pattern were used. These were effective for only short periods before requiring replacement, and so maintenance requirements were high.

The two largest bubbling-bed FBC units built, 160 and 350 MWe, entered into service in the late 1980s burning bituminous coal. However, for coal applications, the overall performance of circulating fluidized-bed units has proved superior, and bubbling-bed designs of this size are no longer marketed. The bubbling technology is now mainly used for burning high-moisture biomass fuels for which in-bed heat-transfer surfaces are not required. These units are usually designed for generating capacities below 120 MWe, and typical fuels include wood wastes, paper mill and sewage sludges, and peat.

The boilers are of water-wall construction with the walls in the bed region lined with refractory to protect against erosion and abrasion damage. The heat released in the bed is removed from the flue gas by the exposed water walls and by convection pass tubing set in the gas path after the boiler. The coal boilers included multiclones to collect elutriated carbon and recycle it back to the boiler to increase combustion efficiency. However, because biomass is more reactive, recycle is not required.

To accommodate the wide variations in fuel moisture content while maintaining close bed temperature control, two control strategies are used.

- Operate the bed substoichiometrically so that bed temperature varies with the fluidizing air (primary combustion air). There is an equal and opposite change in the air fed above the bed (secondary combustion air) to complete the combustion process, the total air remaining constant. As the fuel moisture increases, the primary air-flow rate increases, increasing the fluidizing velocity and releasing more heat in the bed to evaporate the additional water and keep the bed temperature constant. The bed operates less substoichiometrically, and in-bed combustion efficiency increases. At the same time the secondary air is reduced, and as there is less above-bed combustion, the upper furnace temperature falls. The control action is reversed when the fuel moisture content decreases. The split of primary to secondary airflow ranges from above 80:20 for high-moisture fuels to below 50:50 for low-moisture fuels.
- The above strategy results in variations in fluidizing velocity that might produce poor fluidization at some operating conditions with a resulting reduction in combustion efficiency. To maintain fluidizing velocity constant, recirculated flue gas is mixed with the primary combustion air to lower its oxygen content while keeping the combined fluidization gas flow rate constant. Air may be fed above the bed to complete combustion, but this is controlled independently of the air passing to the bed. As the fuel moisture increases, less flue gas is recirculated, the oxygen content of the primary combustion air and in-bed combustion both increase, and secondary air decreases. The control action is reversed when the fuel moisture content decreases.

**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. 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 circulating-bed design is the leading FBC technology and is the only design currently offered at sizes above 120 MWe. Units as large as 320 MWe have been built incorporating subcritical steam conditions with reheat and supercritical designs of up to 600 MWe are available. The fuels used in these designs are coals or opportunity fuels such as petroleum coke, although one 240-MWe unit is designed to operate solely on biomass. Circulating FBC boilers as small as 25 MWe have been built to fire either coal or biomass. However, as the size gets smaller, the circulating FBC becomes less competitive for biomass firing, and as indicated earlier, the bubbling FBC design is favored for this application.

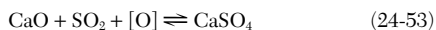
The heat released in the furnace is removed from the flue gas by the exposed upper water-wall tubes. As the units increase in size, more heat-transfer surface is required than is provided by the walls. Surface can be added by wrapping horizontal tubing over the walls of the upper furnace, or by added 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. The potential for erosion or abrasion of the tubes in this bed is low as the recirculating solids are mostly less than 500  $\mu\text{m}$  and are well fluidized at velocities of only around 0.6 m/s [2 ft/s].

The combustion air is introduced at two levels, 60 to 70 percent being introduced through the distributor and 30 to 40 percent above the bed. This staged entry results in the lower reaches operating substoichiometrically, which helps to reduce  $\text{NO}_x$  emissions but tends to reduce the fluidizing velocity at the base of the combustor. To compensate for this and to increase solids mixing by increasing the local gas velocity, the portion of the combustor below the secondary air entry points is tapered.

**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. This increase in operating flexibility increases the capital cost, offsetting at least partially the economic benefits of reduced fuel pricing.

**Sulfur Emissions** Sulfur present in a fuel is released as  $\text{SO}_2$ , 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  $\text{CaSO}_4$  and  $\text{CaO}$ , with small amounts of  $\text{CaCO}_3$ .



The sulfation reaction has an optimum at a mean bed temperature of around 1116 K (1550°F). Units are usually designed to operate at this

temperature, but changes in operating conditions to achieve power output and accommodate changes in fuel composition often result in the plant operating at above or below the optimum temperature. To compensate for the ensuing reduction in sulfur capture, more sorbent is fed to the bed.

Emissions standards are becoming increasingly more stringent, and environmental permits for recent CFB projects have required sulfur capture efficiencies greater than 98 percent. Achieving this with only in-bed sulfur capture requires Ca/S molar ratios as high as 3 (3 mol of calcium in the sorbent for each mole of sulfur in the coal). For a 3 percent sulfur coal and a sorbent with 38 percent calcium, the sorbent-to-coal weight ratio is 0.3. To reduce the sorbent demand for the same sulfur capture efficiency, a back-end dry scrubber is used to remove additional  $\text{SO}_2$  from the flue gas. This has been demonstrated to lower the Ca/S molar ratio to 1.9, a sorbent-to-coal weight ratio of 0.19. For a coal with 12 percent ash, this 37 percent reduction in sorbent feed rate reduces the amount of ash sent to disposal by 17 percent. This reduction in solids handling requirements improves process economics primarily by lowering the operating costs of the plant. The capital cost remains roughly the same, the cost of the dry scrubber being mainly offset by the reduction in solids handling equipment.

The sorbent used in the dry scrubber can be either lime or reactivated ash captured by the baghouse. The baghouse ash contains unreacted sorbent particles with a surface coating of calcium sulfate that prevents  $\text{SO}_2$  reaching the  $\text{CaO}$  at their core. Hydrating these solids causes the material to swell and crack, thus exposing the unreacted  $\text{CaO}$ , which when recycled back to the boiler is available to react with additional  $\text{SO}_2$ . As lime is more expensive than limestone, using the baghouse ash is the preferred approach. It also eliminates the need to provide separate handling facilities for lime.

**Nitrogen Oxide Emissions** FBC units achieve excellent combustion and sulfur emission performance at relatively modest combustion temperatures in the range of 1060 to 1172 K [1450 to 1650°F]. At these temperatures no atmospheric nitrogen is converted to  $\text{NO}_x$ . The prime variables influencing  $\text{NO}_x$  formation are excess air, mean bed temperature, nitrogen content of the fuel, and Ca/S molar ratio. With respect to the latter, high sorbent feed rates increase the free lime content, and this catalyzes  $\text{NO}_2$  formation. Typical  $\text{NO}_x$  emissions, consisting of around 90 percent  $\text{NO}$  and 10 percent  $\text{NO}_2$ , are in the range 86 to 129 mg/MJ [0.2 to 0.3 lb/MBtu]. These values have been reduced to as low as 21 mg/MJ [0.05 lb/MBtu] by injecting ammonia into the boiler freeboard to promote selective noncatalytic reduction (SNCR) reactions. This is a less costly approach than the selective catalytic reduction (SCR) units required for PC plants.

Because the operating temperature is lower, FBC units release more  $\text{N}_2\text{O}$  than do PC units. Nitrous oxide is a greenhouse gas that absorbs 270 times more heat per molecule than carbon dioxide and as such is likely to come under increased scrutiny in the future. The emissions at full load from coal-fired units are around 65 mg/MJ [0.15 lb/MBtu], but these increase as load is reduced and furnace temperature falls. Measurements from biomass-fired FBCs have not been made. Combustion processes do not contribute greatly to current U.S.  $\text{N}_2\text{O}$  emissions; agriculture and motor vehicles account for 86 percent of the total.

**Particulate Emissions** To meet environmental regulations, FBC boilers use a back-end particulate collector, such as a baghouse or an electrostatic precipitator (ESP). Compared to PC units, because of its sulfur sorbent content, the ash from a circulating CFB has higher resistivity and is finer because the flue gas path contains cyclones. Both factors result in a reduction in ESP collection efficiency, although lowering the gas velocity and providing additional collection fields can compensate for this albeit at increased capital cost. Bubbling FBC designs fired on biomass do not normally feed sulfur sorbents and do not include dust collectors in the flue gas path. For these applications suitably designed ESPs are often included. In general, however, baghouses are the preferred particulate collection devices.

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.

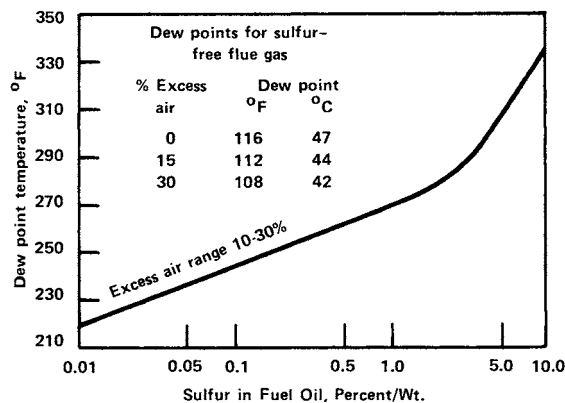
**Mercury Emissions** The U.S. Environmental Protection Agency (EPA) has proposed new rules that require power plants to reduce their mercury emissions by 70 percent by 2018. Tests on operating fluidized beds show that inherent mercury capture from the flue gas for bituminous coals is over 90 percent, but for lignites capture is closer to 50 percent. The reasons for this difference are not fully understood but could be explained by the higher reactivity of lignite resulting in lower unburned carbon carryover. Carbon is known to adsorb elemental and ionic mercury, and a low carbon content will result in reduced mercury capture. The combustion efficiency for less reactive bituminous coal is lower, resulting in more carbon carryover and possibly accounting for the higher mercury capture. Recent tests have shown that halide-impregnated activated carbons injected into flue gas streams can capture over 90 percent of the mercury present. So the low inherent mercury capture associated with lignite can be compensated for by activated carbon injection ahead of the dust collection device used.

## COMBUSTION OF LIQUID FUELS

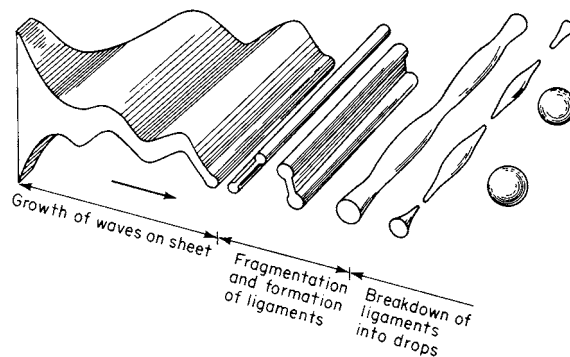
Oil is typically burned as a suspension of droplets generated by atomizing the fuel. As the droplets pass from the atomizer into the flame zone, they are heated both by radiation from the flame and by convection from the hot gases that surround them, and the lighter fuel components vaporize. The vapors 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 24-6).  $\text{SO}_2$  is the principal product of sulfur combustion with stoichiometric or leaner fuel-air mixtures, but with the excess air customarily used for satisfactory combustion,  $\text{SO}_3$  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 24-21 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 24-22 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. 24-23), 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



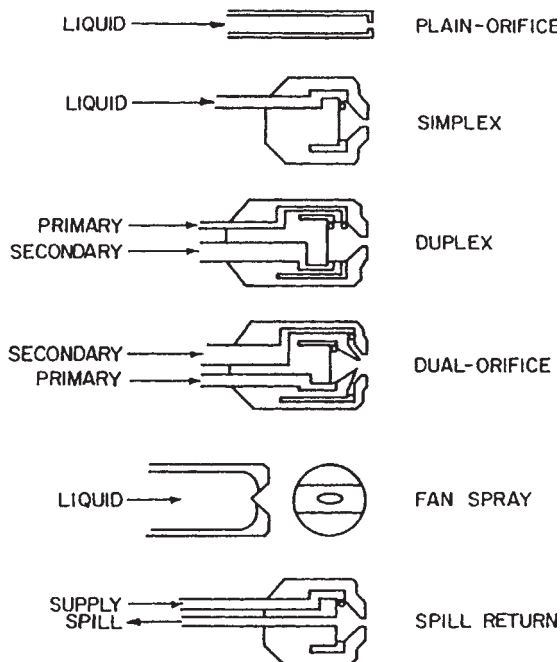
**FIG. 24-21** Maximum flue-gas dew point versus percent of sulfur in typical oil fuels. ( $K = [^{\circ}\text{F} + 459.7]/1.8$ )



**FIG. 24-22** Idealized process of drop formation by breakup of a liquid sheet. (After Dombrowski and Johns, *Chem. Eng. Sci.* 18:203, 1963.)

(steam or air) assists in the atomization process. Low oil viscosity (less than  $15 \text{ mm}^2/\text{s}$ ) 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 ( $212^{\circ}\text{F}$ ) for No. 6 oil to 623 K ( $480^{\circ}\text{F}$ ) for vacuum bottoms.

**Pressure Atomizers** The commonest type of pressure atomizer is the swirl-type (Fig. 24-24). 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



**FIG. 24-23a** Common types of atomizers: pressure atomizers. (From Lefebvre, *Atomization and Sprays*, Hemisphere, New York, 1989. Reproduced with permission. All rights reserved.)

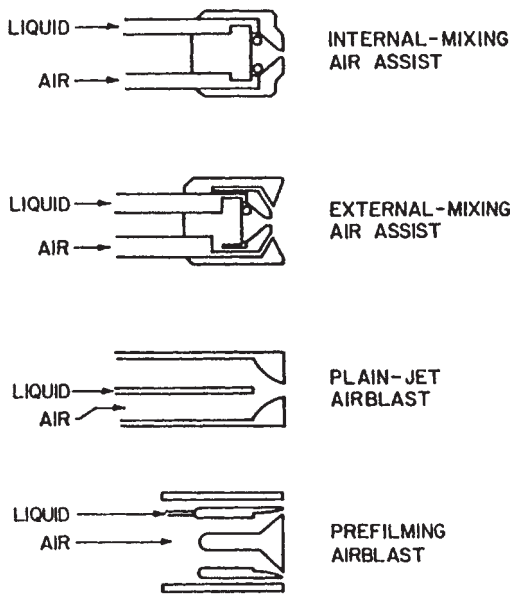


FIG. 24-23b Common types of atomizers: twin-fluid atomizers. (From Lefebvre, *Atomization and Sprays*, Hemisphere, New York, 1989. Reproduced with permission. All rights reserved.)

turndown ratio is approximately 4:1. Pressure atomization is most effective for lighter fuel oils.

**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. 24-25), 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  $\mu\text{m}$  and a top size of about 100  $\mu\text{m}$  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. 24-26, and Fig. 24-27 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.

Many oil burners are designed as combination gas/oil burners. An example of a modern low- $\text{NO}_x$  oil/gas forced-draft burner is shown in Fig. 24-28. 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. 24-29.

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).

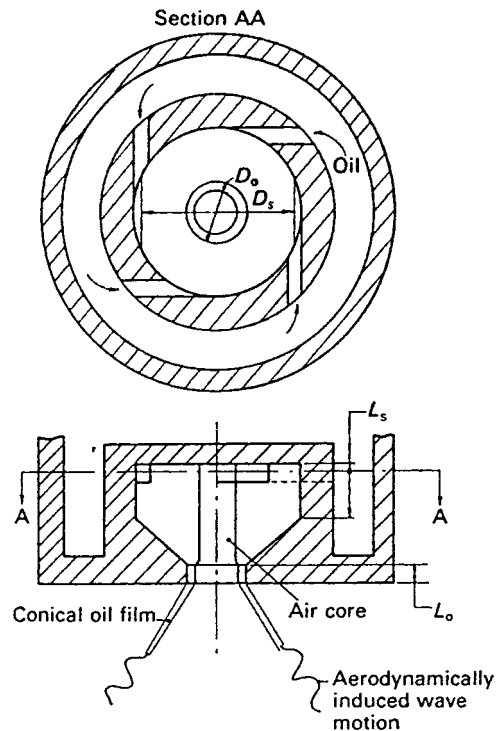


FIG. 24-24 Swirl pressure-jet atomizer. (From Lefebvre, *Atomization and Sprays*, Hemisphere, New York, 1989. Reproduced with permission. All rights reserved.)

## 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  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ . 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  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Soot and carbon black are formed if insufficient oxygen is present or if the combustion process is arrested before completion.

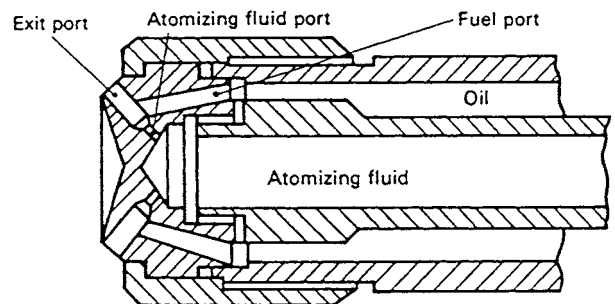
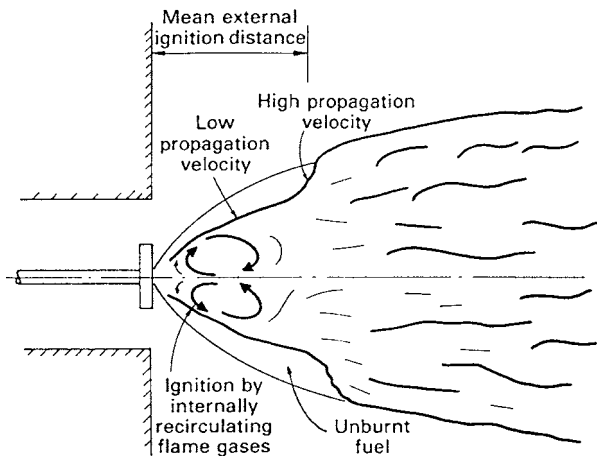


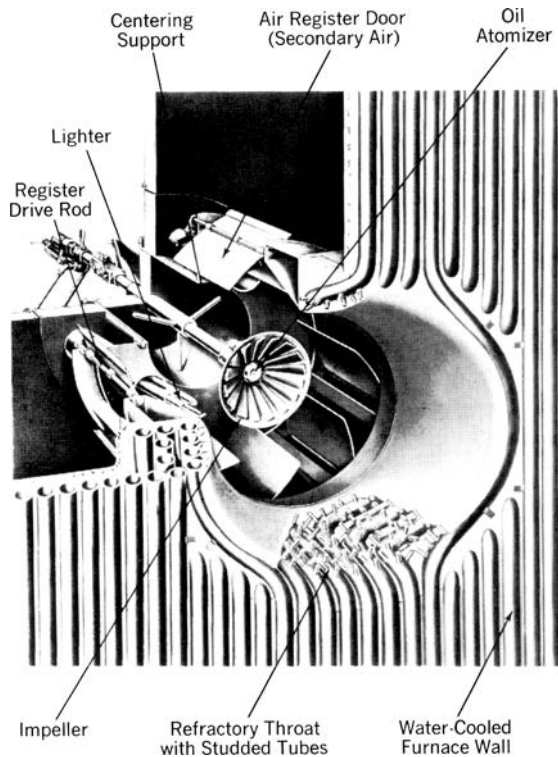
FIG. 24-25 Y-jet twin-fluid atomizer. (From Lefebvre, *Atomization and Sprays*, Hemisphere, New York, 1989. Reproduced with permission. All rights reserved.)



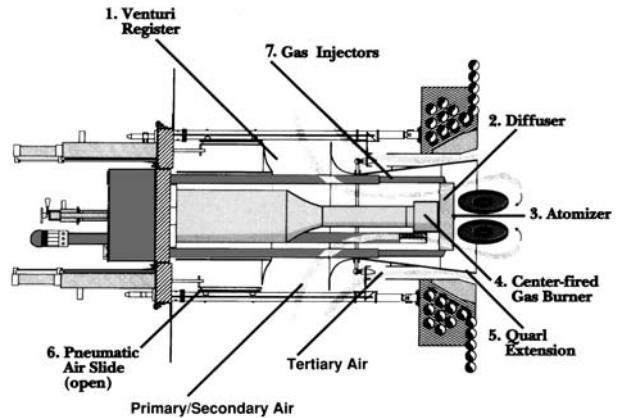
**FIG. 24-26** Structure of typical oil flame. (From *Lawn, Principles of Combustion Engineering for Boilers*, Academic Press, London, 1987. Reprinted with permission.)

**Gas Burners** Gas burners may be classified as premixed or non-premixed. Many types of flame stabilizer are employed in gas burners. Bluff body, swirl, and combinations thereof are the predominant stabilization mechanisms.

**Fully Premixed Burners** A fully premixed burner includes a section for completely mixing the fuel and air upstream of the burner.



**FIG. 24-27** Circular register burner with water-cooled throat for oil firing. (Babcock & Wilcox Co.)



**FIG. 24-28** Low-NO<sub>x</sub> combination oil/gas forced-draft boiler burner. (Todd Combustion, Inc.)

The burner proper consists essentially of a flame holder. 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<sub>x</sub> 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. 24-30 and 24-31.

**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. 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<sub>x</sub> emissions. Gas burners that achieve such staging are available.

**Air-staged burners** Low-NO<sub>x</sub> air-staged burners for firing gas (or oil) are shown in Fig. 24-28. A high-performance, low-NO<sub>x</sub> burner for high-temperature furnaces is shown in Fig. 24-32. In this design, both air-staging and external flue-gas recirculation are used to achieve extremely low levels of NO<sub>x</sub> 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<sub>x</sub> control because gaseous fuels typically contain little or no fixed nitrogen. Figure 24-33 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<sub>x</sub> control. NO<sub>x</sub> reductions of 80 to 90 percent have been achieved by staging fuel combustion.

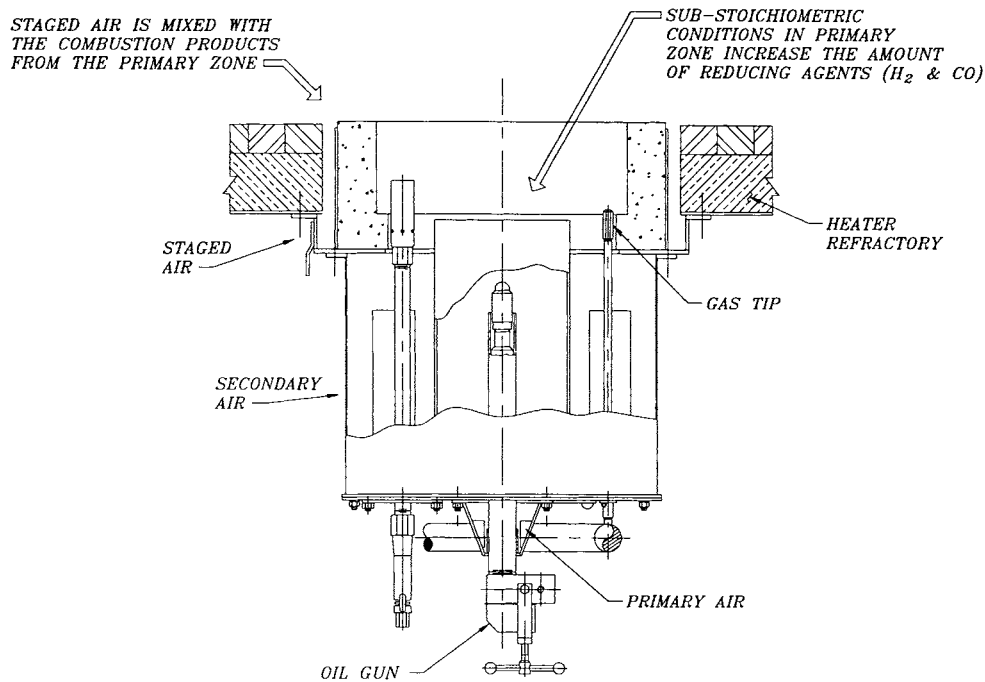


FIG. 24-29 Air-staged natural-draft combination oil/gas burner. (Callidus Technologies, Inc.)

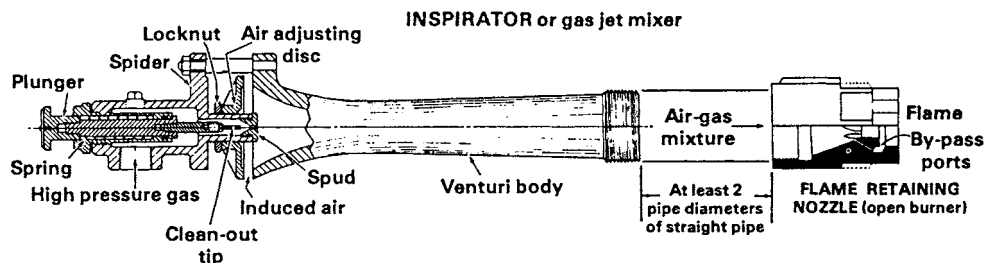


FIG. 24-30 Inspirator (gas-jet) mixer feeding a large port premix nozzle of the flame retention type. High-velocity gas emerging from the spud entrains and mixes with air induced in proportion to the gas flow. The mixture velocity is reduced and pressure is recovered in the venturi section. (From North American Combustion Handbook, 3d ed., North American Manufacturing Company, Cleveland, 1996.)

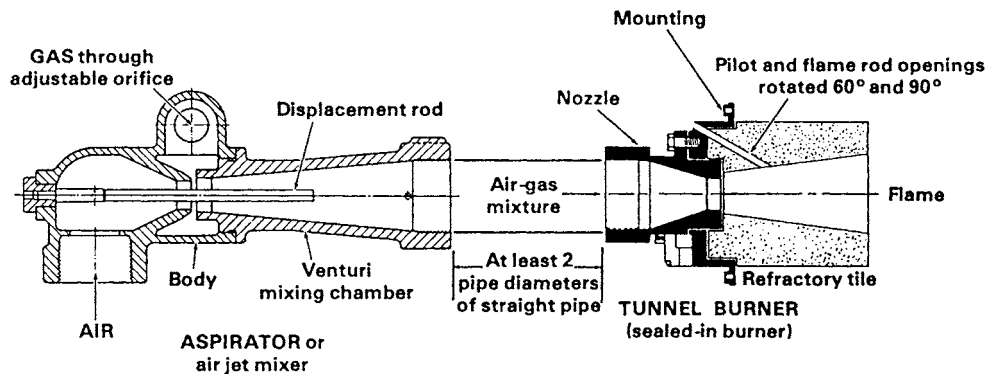
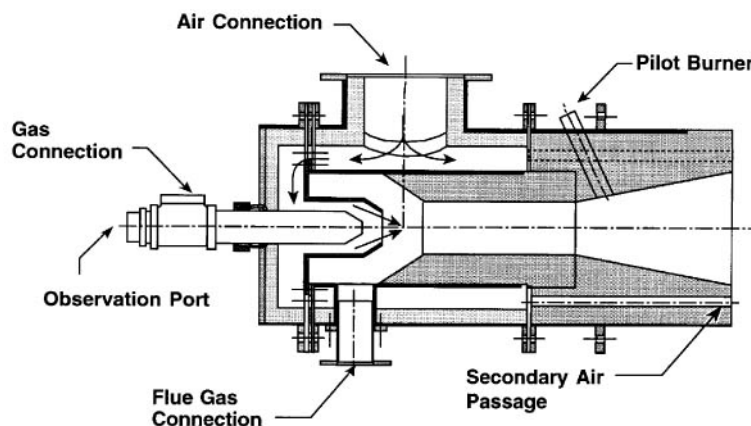
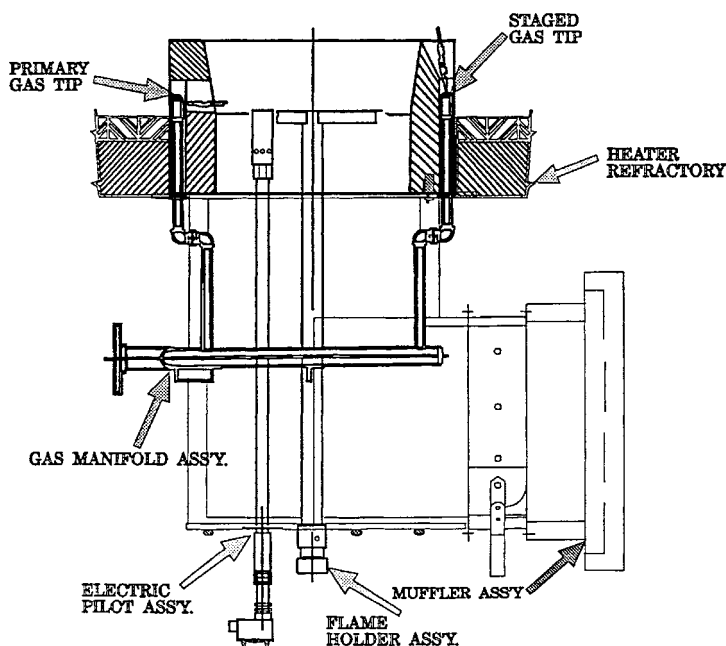


FIG. 24-31 Aspirator (air-jet) mixer feeding a sealed-in large port premix tunnel burner. Blower air enters at lower left. Gas from an atmospheric regulator is pulled into the air stream from the annular space around the venturi throat in proportion to the air flow. (From North American Combustion Handbook, 3d ed., North American Manufacturing Company, Cleveland, 1996.)



**FIG. 24-32** Low- $\text{NO}_x$  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. 24-33** Low- $\text{NO}_x$  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 24-34 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).

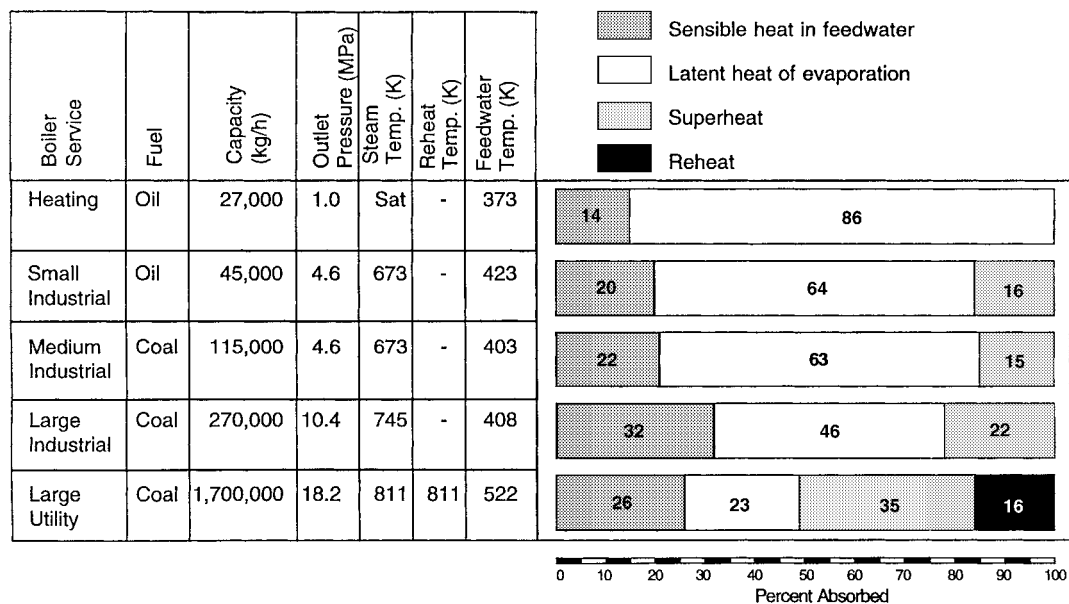


FIG. 24-34 Heat absorption distribution for various types of boilers. (Adapted from Singer, Combustion—Fossil Power, 4th ed., Combustion Engineering, Inc., Windsor, Conn., 1991.)

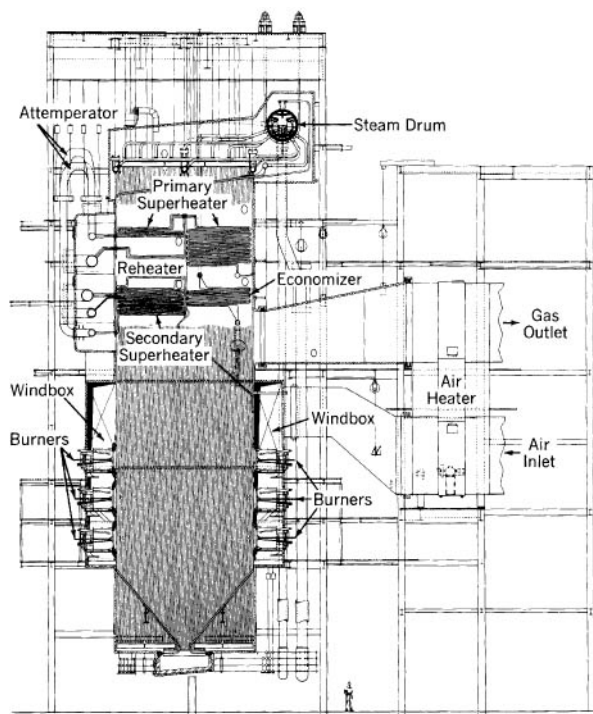


FIG. 24-35 Shop-assembled radiant boiler for natural gas or oil. (Babcock & Wilcox Co.)

These units are designed for operation at pressures up to 11.4 MPa (1650 psia) and 783 K (950°F). Figure 24-35 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. 24-36.

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



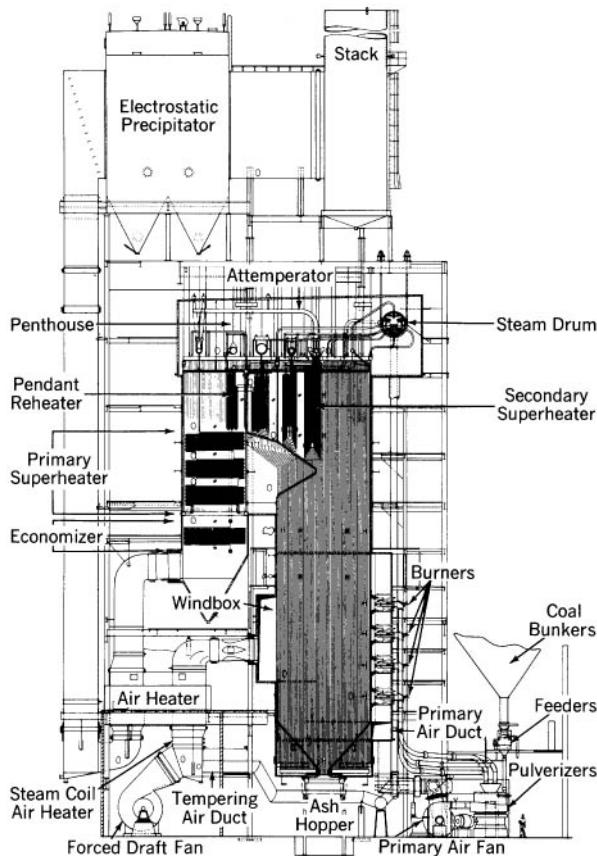


FIG. 24-36 Field-erected radiant boiler for pulverized coal. (Babcock & Wilcox Co.)

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.

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.

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.

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 for 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 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,



TABLE 24-14 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
Corncocks	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  $4.299 \times 10^{-1}$ .

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 24-4 and 24-14. Natural gas has become the principal fuel of choice, accounting for approximately 80 percent of all the energy fired in industrial boilers across a range of manufacturing industries (Table 24-15). Coal is the second most prevalent fuel, accounting for about 15 percent 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  $\text{W/m}^3$  and  $\text{W/m}^2$  of effective projected radiant surface ( $\text{Btu}/[\text{h}\cdot\text{ft}^3]$  and  $\text{Btu}/[\text{h}\cdot\text{ft}^2]$ )
- Heat release on grates
- Flue-gas velocities through tube banks
- Tube spacings

TABLE 24-16 Typical Design Parameters for Industrial Boilers

Furnace		Heat-release rate, $\text{W/m}^2$ 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, $\text{W/m}^2$	
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		Baffled	
Fuel-fired	Single-pass Boiler, m/s	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.

Table 24-16 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 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 24-37 shows the amount of energy available for power by using a fire-tube boiler, an industrial boiler, and subcritical- and

TABLE 24-15 Fuel Consumption in Boilers in Various Industries

Industry	Annual energy consumption (PJ/a)				
	Total	Residual fuel oil	Distillate fuel oil	Natural gas	Coal
Chemicals	539	—	—	451	88
Food	323	8	6	237	72
Paper	212	29	2	143	38
Petroleum and coal products	169	6	2	159	2
Transportation equipment	56	—	1	48	7
Plastics and rubber products	54	5	1	48	—
Primary metals	40	—	—	40	—
Beverage and tobacco products	34	—	—	29	5
Computer and electronic products	29	1	1	27	—
Wood products	18	1	1	15	1
Textile mills	15	—	1	—	14
Total	1,489	50	15	1,197	227

SOURCE: 2002 *Manufacturing Energy Consumption Survey*, Energy Information Administration, U.S. Dept. of Energy.

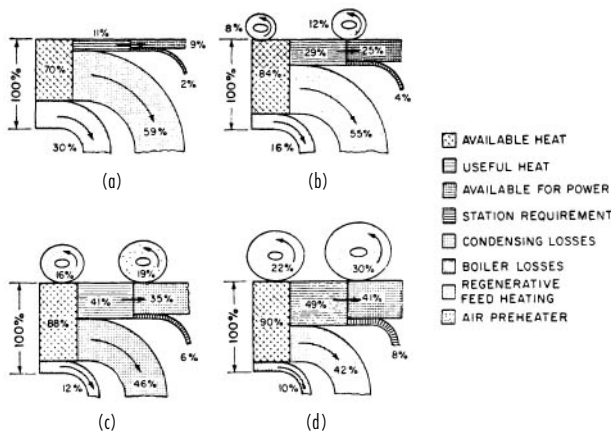


FIG. 24-37 Sankey diagrams for various types of boilers: (a) fire-tube boiler; (b) industrial boiler; (c) subcritical-pressure boiler; (d) supercritical-pressure boiler.

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. 24-38 and 24-39. 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. 24-40. The majority of water-tube package boilers use natural circulation and are designed for pressurized firing. The most

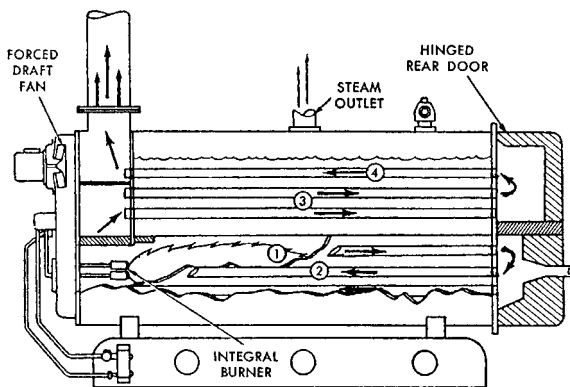


FIG. 24-38 A four-pass packaged fire-tube boiler. Circled numbers indicate passes. (From Cleaver Brooks, Inc. Reproduced from Gas Engineer's Handbook, Industrial Press, New York, 1965, with permission.)

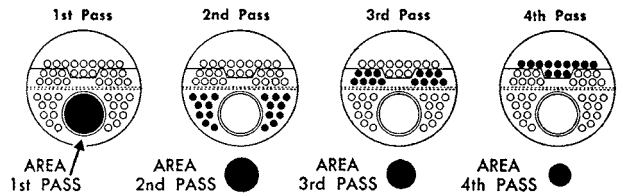


FIG. 24-39 Location and relative size of each of four passes of the flue gas through a fire-tube boiler. (From Cleaver Brooks, Inc. Reproduced from Gas Engineer's Handbook, Industrial Press, New York, 1965, with permission.)

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.)

**Fluidized-Bed Boilers** Although the furnace of a fluid-bed boiler has a unique design, the system as a whole consists mainly of standard equipment items adapted to suit process requirements. The systems for feedstock preparation and feeding (biomass, coal, sorbent, and sand), ash removal, and ash disposal are very similar to those found in PC boiler plants, the main difference being that the top size of the material being handled is greater. The water-wall boiler enclosure and convection pass tubing are also similar to the designs found in PC boilers. The fluidized-bed plant includes particulate removal equipment such as cyclones, baghouses, and ESPs, with designs similar to those found in other solids-handling process plants.

**Bubbling FBCs** A simplified schematic of a bubbling FBC plant is presented in Fig. 24-41. This design is used primarily for burning biomass, although coal may be cofired to maintain heat release rates when feeding high-moisture feedstocks such as sludges.

The biomass is fed overbed through multiple feed chutes using air jets to help distribute the fuel over the surface of the bed. Variable-speed screw conveyors are usually used to meter the fuel feed rate and control steam output. Feedstocks such as bark and waste wood are chipped to a top size of 25 mm (1 in) to ensure complete combustion. The bed usually consists of sand around 1 m (3 ft) deep. This serves to retain the fuel in the furnace, extending its in-furnace residence time and increasing combustion efficiency. It also provides a heat sink to help maintain bed temperature during periods of fluctuating fuel moisture content.

Biomass fuels, especially forestry products and waste wood, can contain oversized material such as rocks and other debris. If this material is allowed to accumulate, the quality of fluidization deteriorates, resulting in poor fuel mixing and reduced combustion efficiency. To avoid this mal-operation, units typically employ an open-bottom floor design that allows easy solids removal while still ensuring even distribution of the fluidizing air. The fluidizing air (primary combustion air) is fed into large bore pipes extending across the width of the furnace and enters the boiler through a series of nozzles set in the pipes. The pipes are spaced to allow material to drain from all areas of the bed.

The bed temperature control strategies discussed earlier in this section result in the bed operating substoichiometrically. This helps lower the formation of  $\text{NO}_x$  but increases the amount of CO formed and the amount of unburned fuel leaving the bed. To complete the combustion process, secondary air is introduced through multiple ports above the bed with the upper furnace height designed to achieve 2- to 3-s flue gas residence time. The velocity of the secondary air should be sufficient to penetrate across the furnace and facilitate thorough mixing with the flue gas leaving the surface of the bed. Although the unburned carbon leaving the furnace is low, the CO is still relatively high at 43 to 128 mg/MJ (0.10 to 0.25 lb/MBtu), which may be a problem in nonattainment areas.

Ammonia injected into the upper furnace is used to promote SNCR reactions to reduce  $\text{NO}_x$  emissions. The optimum temperature for

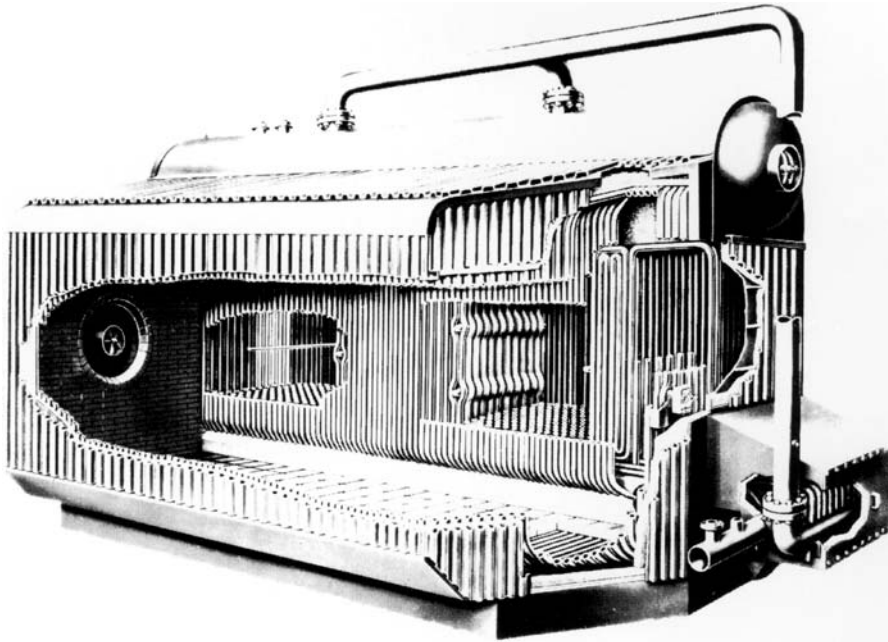


FIG. 24-40 A D-type shop-assembled water-tube boiler. (Combustion Engineering, Inc.)

these reactions is around  $830^{\circ}\text{C}$  ( $1520^{\circ}\text{F}$ ), but the upper furnace temperature varies depending upon the extent of secondary combustion air usage. To ensure that the ammonia enters into a region at the optimum temperature, multiple levels of injection ports are provided.

**Circulating FBCs** The circulating FBC is the more widely deployed than the bubbling-bed design and at far larger sizes. A simplified schematic for a design with an external heat exchanger is presented in Fig. 24-42. As of 2005 there were over 20 units in the range of 200 to 320 MWe worldwide, and a similar number were in the planning stages.

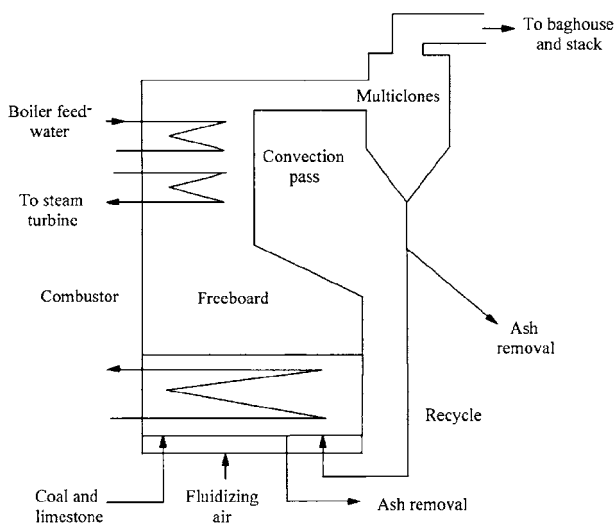


FIG. 24-41 Simplified flow diagram for bubbling AFBC (with underbed feed system).

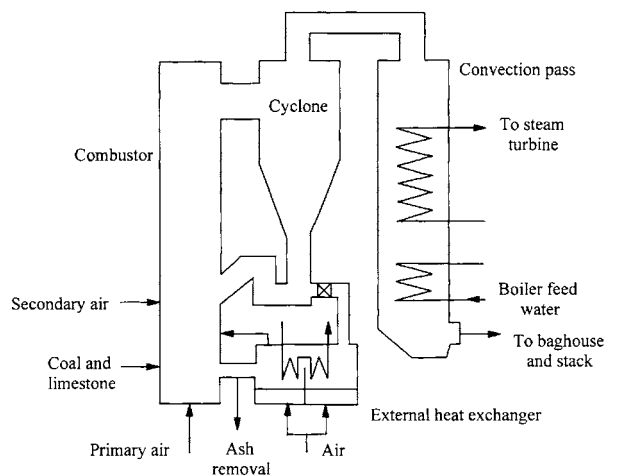


FIG. 24-42 Simplified flow diagram for circulating AFBC (with external heat exchanger).

The most widely used fuels are low-grade coals with high ash and moisture contents, making them unsuitable for use in PC plants. The coal is crushed to a top size of 12 mm (1/2 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 the low backpressure greatly reduces the sealing requirements. In some designs the coal is also introduced into the cyclone ash return lines. The larger units average a feed point for every  $23 \text{ m}^2$  ( $250 \text{ ft}^2$ ) of freeboard cross section. The highly turbulent bed facilitates good 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 also using one feed point for every  $23 \text{ m}^2$  ( $250 \text{ ft}^2$ ) of freeboard cross section. Load control

is achieved primarily by reducing the coal feed rate, with a corresponding reduction in airflow, to reduce the heat release rate. As the heat-transfer area remains unchanged, the furnace temperature falls.

Almost all 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 for the larger units one cyclone is provided for 100 to 130 MWe of generating capacity, providing one recycle point for 210 to 290 m<sup>2</sup> (720 to 950 ft<sup>2</sup>) 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 bituminous coal combustion, efficiency is close to 99 percent, but like the biomass-fired bubbling beds, CO levels are relatively high at around 43 mg/MJ (0.1 lb/MBtu).

## 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 24-17 gives the average energy consumption rates for various industries and processes that use direct heat. Section 12 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 (discussed 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.

**TABLE 24-17 Average Energy Consumption for Various Industries Using Direct Heat**

Industry	Product/process	Energy consumption per unit of product	
		GJ/Mg	10 <sup>6</sup> 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.

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<sup>6</sup> 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<sup>6</sup> 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<sup>6</sup> 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<sup>6</sup> 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<sup>6</sup> 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. 24-43. 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

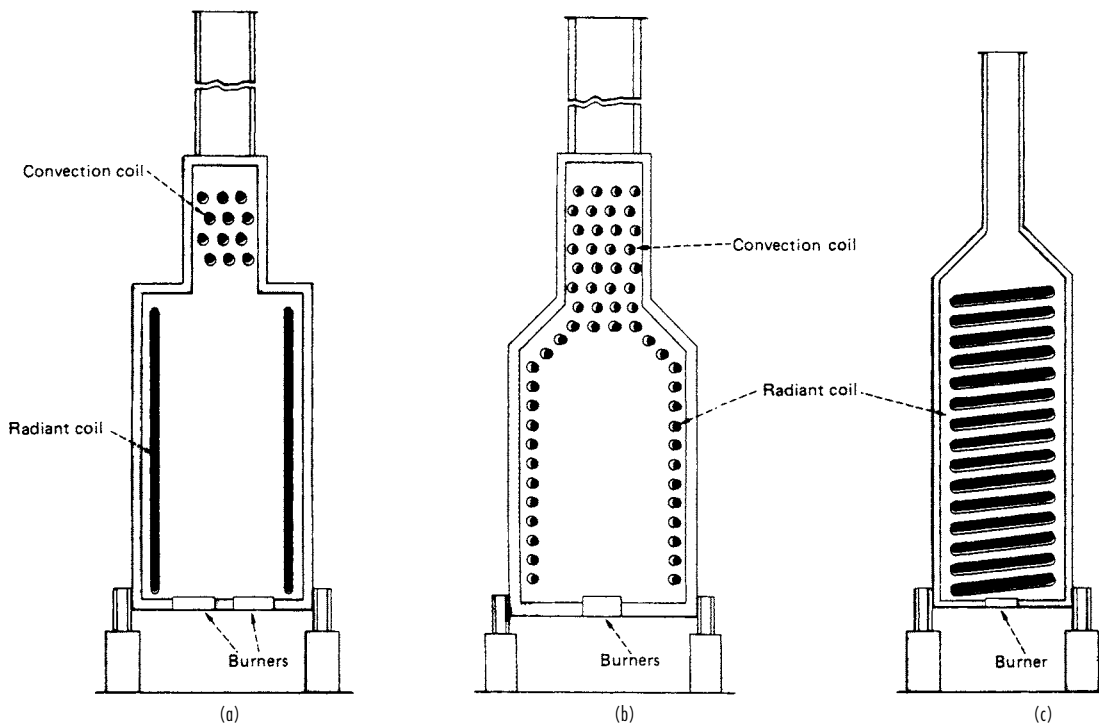
Industrial furnaces serve the manufacturing sector and can be divided into two groups. Boiler furnaces, which are the larger group and are used solely to generate steam, were discussed earlier in the subsection

on industrial boilers. Furnaces of the other group are classified as follows: by (1) source of heat (fuel combustion or electricity), (2) function (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)].



**FIG. 24-43** 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.)

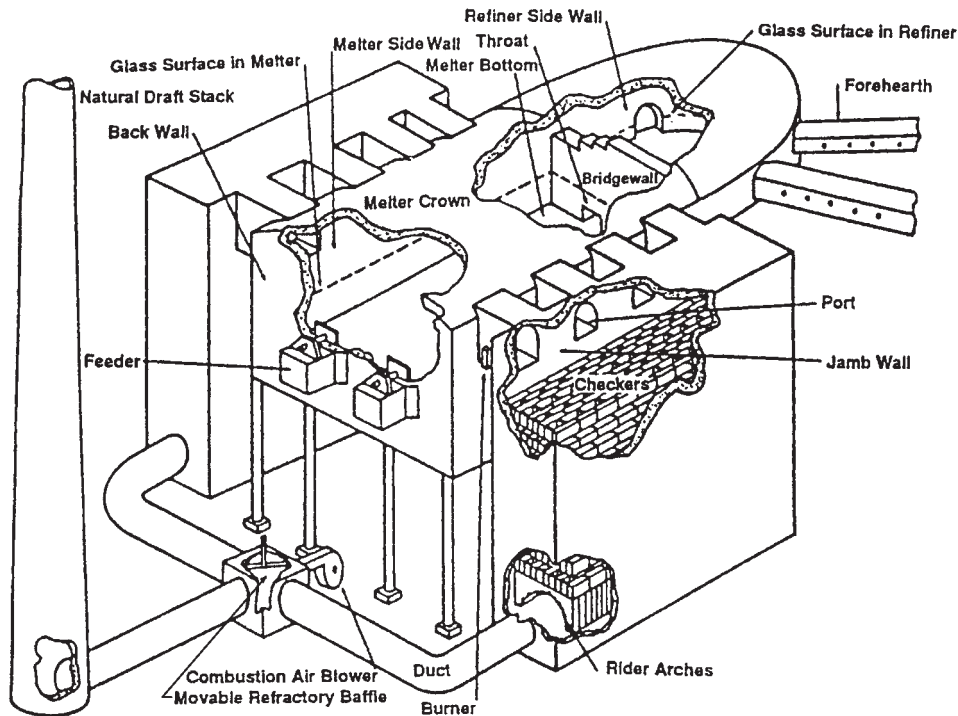


FIG. 24-44 Side-port continuous regenerative glass melting furnace.

A typical side-port continuous regenerative glass furnace is shown in Fig. 24-44. 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 airflow from one checker to the other is reversed approximately every 15 to 30 min.

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 U.S. ton/d), compared to a maximum of 540 Mg/day (600 U.S. ton/d) for container and pressed/blown glass furnaces.

Though the stoichiometric chemical energy requirement for glass-making is only some 2.3 GJ/Mg ( $2 \cdot 10^6$  Btu/U.S. ton) of glass, the inherently low thermal efficiency of regenerative furnaces means that, in practice, at least 7 GJ/Mg ( $6 \cdot 10^6$  Btu/U.S. 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 ( $15 \cdot 10^6$  Btu/U.S. ton).

Industrial furnaces may be operated in batch or continuous mode.

**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. 24-45. *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<sup>a</sup> furnace or a radiant-tube furnace (tubes carrying the hot combustion gas run through the furnace).

<sup>a</sup>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.

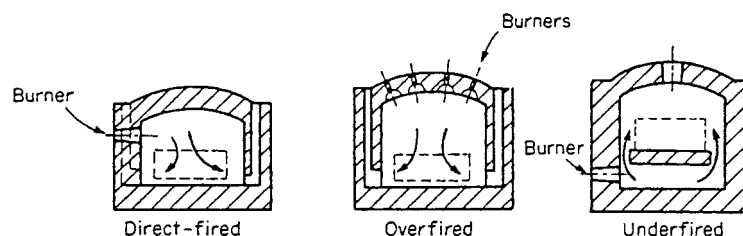


FIG. 24-45 Methods of firing direct-heated furnaces. (From Marks' Standard Handbook for Mechanical Engineers, 9th ed., McGraw-Hill, New York, 1987. Reproduced with permission.)

**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

TABLE 24-18 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.

- 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 24-18.

## 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-Heinemann, 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:** W. Vielstich, A. Lamm, H. A. Gasteiger, eds., *Handbook of Fuel Cells*, John Wiley & Sons, 2003. *Fuel Cell Handbook* (Rev. 7), U.S. Department of Energy, DOE/NETL-2004/1206. Appleby and Foulkes, *Fuel Cell Handbook*, Kreger Publishing Co., Molabar, Fla., 1993. 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 ions from anode to cathode or the negatively charged ions from cathode to anode. Figure 24-46 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.

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 has only recently begun. 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

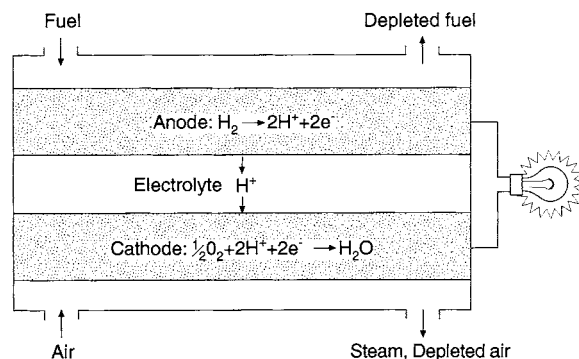


FIG. 24-46 Fuel cell schematic.



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  $\epsilon^\circ$  is given by the ratio of the free energy (Gibbs function) of the cell reaction at the cell's operating temperature  $\Delta G_t$  to the enthalpy of reaction at the standard state  $\Delta H^\circ$ , both quantities being based on a mole of fuel:

$$\epsilon^\circ = \frac{\Delta G_t}{\Delta H^\circ} \quad (24-54)$$

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. (24-54) 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.

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

$$E^\circ = \frac{-\Delta G_t}{nF} \quad (24-55)$$

where  $E^\circ$  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  $\Delta G_t$  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 24-19.

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

$$E = E^\circ - (a_{an} + a_{ca}) - (b_{an} + b_{ca}) \frac{RT}{nF} \ln i - Ai \quad (24-56)$$

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:

$$\epsilon = \frac{-nFE}{\Delta H^\circ} U_f \quad (24-57)$$

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 (24-56) and (24-57) 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

$$\epsilon_{fc} = \frac{nFU_f}{\Delta H^\circ} \left[ E^\circ - \sum a - \sum b \frac{RT}{nF} \ln i - Ai \right] - \frac{RTU_f}{\Delta H^\circ} [v_f \ln(\log \text{ mean } \hat{f}_f) + v_{ox} \ln(\log \text{ mean } \hat{f}_{ox})] \quad (24-58)$$

The quantities  $v_f$  and  $v_{ox}$  are the stoichiometric coefficients for the fuel cell reaction, and  $\hat{f}_f$  and  $\hat{f}_{ox}$  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. 24-47. 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 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.

**TABLE 24-19 Thermodynamic Values for  $H_2 + \frac{1}{2}O_2 = H_2O$  (g)**

Temperature, K	Enthalpy of reaction ( $\Delta H^\circ$ ), kJ/mol	Free energy of reaction ( $\Delta G^\circ$ ), kJ/mol	Equilibrium cell potential ( $E^\circ$ ), 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

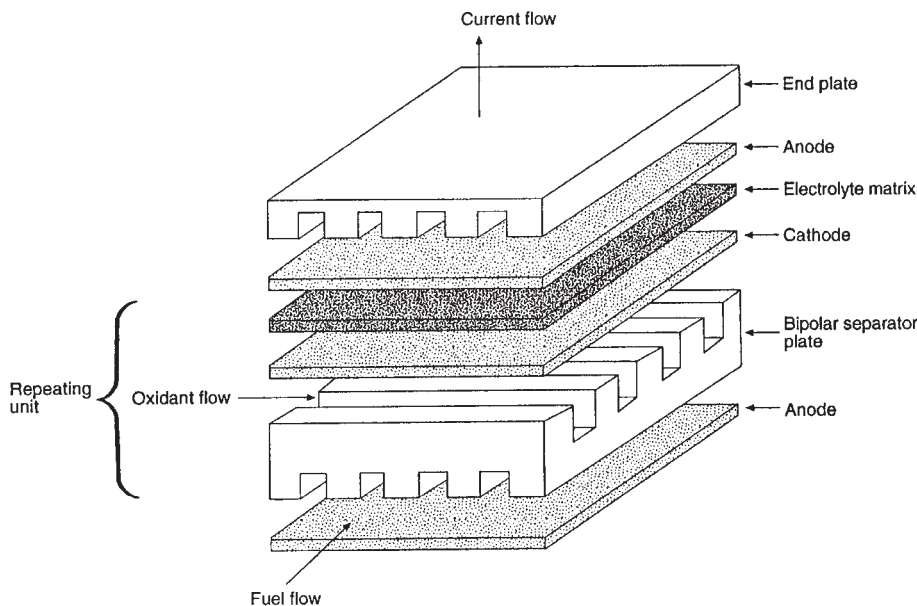


FIG. 24-47 Stacking of individual fuel cells.

**Types of Fuel Cells** The five major types of fuel cell are listed in Table 24-20. 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 tolerant of 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 carbon dioxide 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 in more than one way. 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 24-21. 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 system design. Whenever water needs to be recovered for generating hydrogen from hydrocarbon fuels, a condenser is required in PAFC and PEFC systems. In others, the depleted fuel can be recycled.

TABLE 24-20 Fuel Cell Characteristics

Type of fuel cell	Electrolyte	Operating temperature		Coolant medium
		K	°C	
Alkaline	KOH	363	90	Water
Polymer	$\text{CF}_3(\text{CF}_2)_n\text{OCF}_2\text{SO}_3^-$	353	80	Water
Phosphoric acid	$\text{H}_3\text{PO}_4$	473	200	Steam/water
Molten carbonate	$\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$	923	650	Air
Solid oxide	$\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}$	1273	1000	Air

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 micro-porous 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. 24-48.

Typical polarization curves for alkaline fuel cells are shown in Fig. 24-49. It is apparent that the alkaline fuel cell can operate at about 0.9 V and 500 mA/cm<sup>2</sup> current density. This corresponds to an energy

TABLE 24-21 Fuel Cell Reaction Electrochemistry

Type of fuel cell	Conducting ion	Anode reaction	Cathode reaction
Alkaline	$\text{OH}^-$	$\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$	$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$
Polymer	$\text{H}^+$	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$
Phosphoric acid	$\text{H}^+$	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$
Molten carbonate	$\text{CO}_3^{2-}$	$\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$	$\frac{1}{2}\text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$
Solid oxide	$\text{O}^{2-}$	$\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$	$\frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$

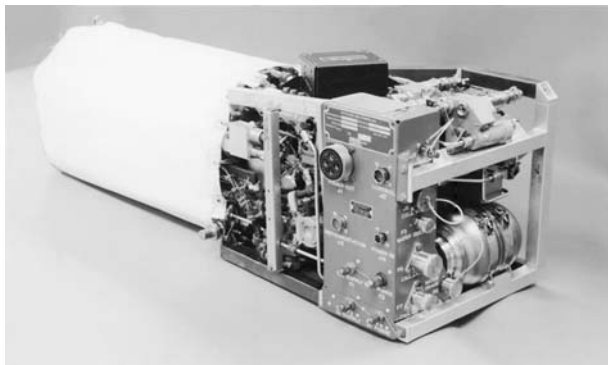


FIG. 24-48 Orbiter power plant. (International Fuel Cells.)

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 great interest for transportation applications 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 automobiles. Methanol, ethanol, hydrogen, natural gas, dimethyl ether, and common transportation fuels such as gasoline are being considered as fuel, but hydrogen is currently preferred. The motivation for developing fuel-cell-powered vehicles is a dramatic reduction in environmentally harmful emissions and high fuel economy.

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-filled polymer or metal.

Typical platinum catalyst loadings needed to support the anodic and cathodic reactions are currently 0.2 to 0.5 mg/cm<sup>2</sup> of active cell area. Owing to the cost of platinum, substantial efforts have been made to reduce the catalyst loading.

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

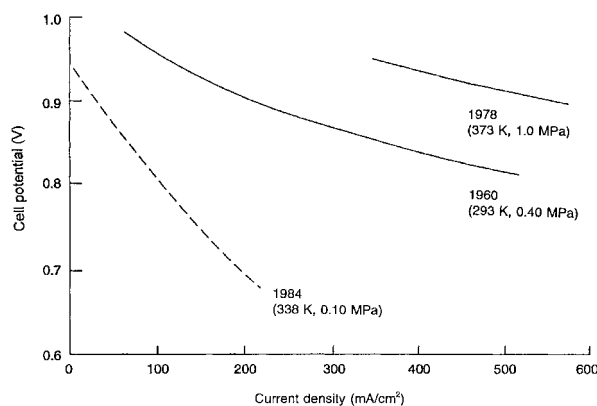


FIG. 24-49 Polarization curves for alkaline fuel cells.

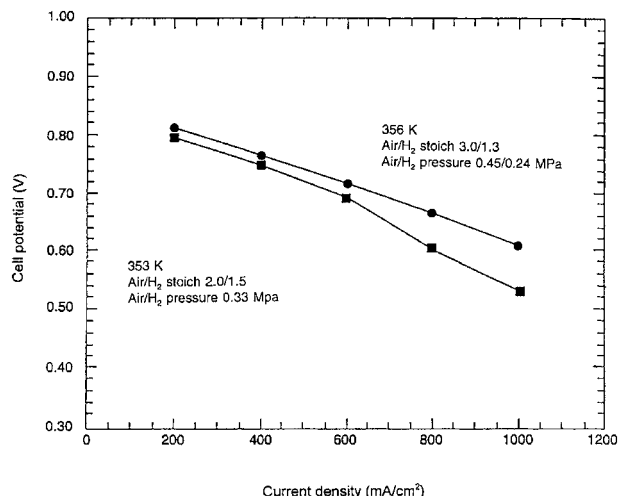


FIG. 24-50 Polarization curves for PEFC stacks.

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 more tolerant to carbon monoxide are being explored. Typical polarization curves for PEFCs are shown in Fig. 24-50.

As mentioned, the primary motivation for the PEFC development was the anticipated applicability in transportation. However, the economics of stationary use are more forgiving, and commercialization of the technology will likely begin as grid-independent power supplies. Figure 24-51 shows a 5-kW PEFC system operating on natural gas.



FIG. 24-51 Natural gas-fueled 5-kW PEFC system. (Courtesy of Plug Power.)

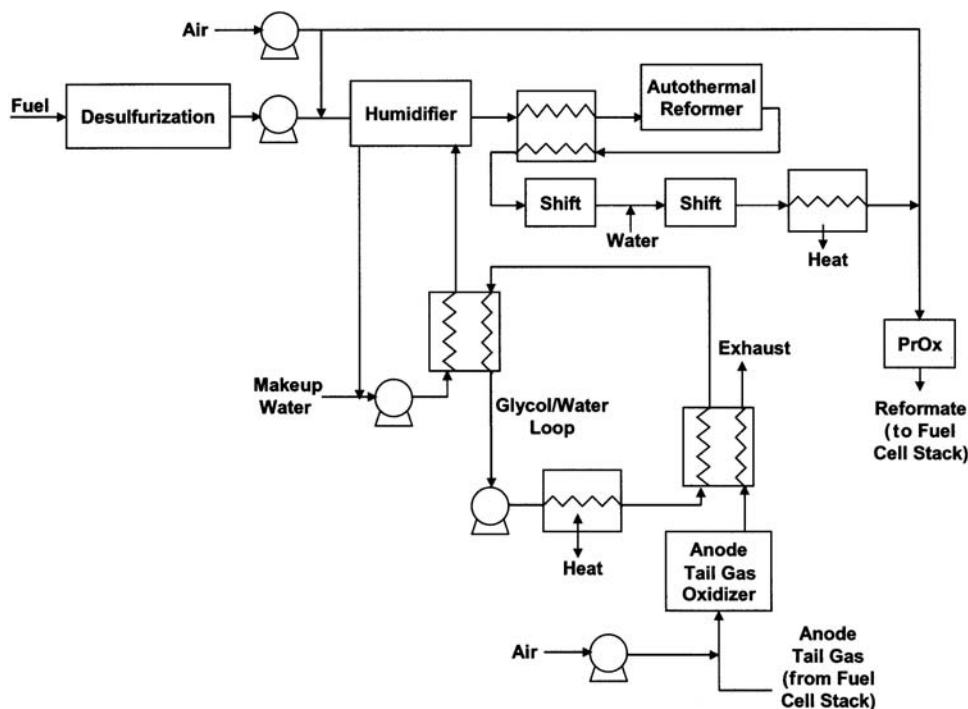


FIG. 24-52 System diagram for reformer-based PEFC system.

The fuel cell stack is visible in the center as a black box, and the fuel processing train is seen on the left. The smaller box on the right contains the power conditioning equipment. Figure 24-52 shows the system diagram for the unit. Natural gas is desulfurized and then mixed with air and steam before entering the autothermal reformer that converts the methane to a mixture of hydrogen, carbon monoxide, and carbon dioxide. Typically this reaction occurs over a catalyst at about 973 K [700°C]. To decrease the carbon monoxide content of this gas, it is cooled to about 623 K [350°C] and reacted with additional water in the so-called shift reactors. Because of the sensitivity of the anode catalyst to carbon monoxide, a preferential oxidation of the remaining carbon monoxide is done before the hydrogen-rich gas is fed to the fuel cell.

About 70 percent of the hydrogen is converted to electricity in the fuel cell stack, and the tail gas is then burned to generate heat which is transferred via a glycol/water loop to the steam generator. The same loop passes through the cooling plates or the fuel cell to remove heat.

A particular version of the PEFC is the **direct methanol fuel cell** (DMFC). As the name implies, an aqueous solution of methanol is used as fuel instead of the hydrogen-rich gas, eliminating the need for reformers and shift reactors. The major challenge for the DMFC is the “crossover” of methanol from the anode compartment into the cathode compartment through the membrane that poisons the electrodes by CO. Consequently, the cell potentials and hence the system efficiencies are still low. Nevertheless, the DMFC offers the prospect of replacing batteries in consumer electronics and has attracted the interest of this industry.

**Phosphoric Acid Fuel Cell** In this type of fuel cell, 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.

PAFC systems are commercially available from UTC Power as 200-kW stationary power sources operating on natural gas. The stack cross section is 1 m<sup>2</sup> (10.8 ft<sup>2</sup>). 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. Fuel processing is similar to that in a PEFC system, but a preferential oxidizer is not needed. These systems are intended for on-site power and heat generation for hospitals, hotels, and small businesses.

**Molten Carbonate Fuel Cell** The electrolyte in the MCFC is a 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.

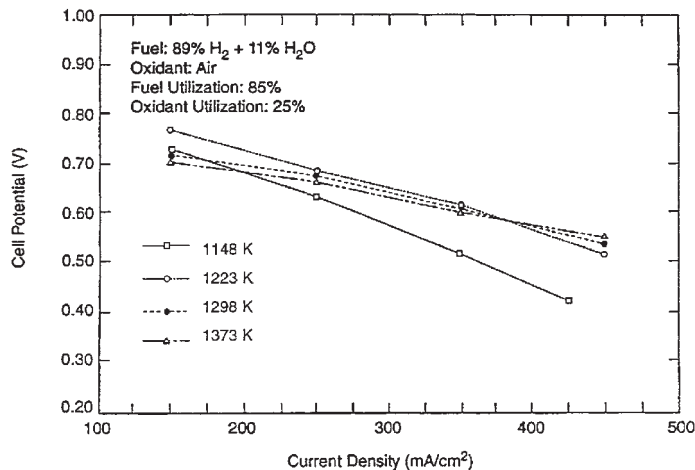


FIG. 24-53 Polarization curves at different temperatures for 50-cm active length thin-wall SOFCs.

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  $1 \text{ m}^2$  ( $10.8 \text{ ft}^2$ ) in plan area and quite tall. A stack generates 200 to 300 kW.

**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  $0.1 \text{ S/cm}$  at  $1273 \text{ K}$  ( $1832^\circ\text{F}$ ); it decreases to  $0.01 \text{ S/cm}$  at  $1073 \text{ K}$  ( $1472^\circ\text{F}$ ), and by another order of magnitude at  $773 \text{ K}$  ( $932^\circ\text{F}$ ). Because the resistive losses need to be kept below about  $50 \text{ mV}$ , the operating temperature of the SOFC depends on the thickness of the electrolyte. For a thickness of  $100 \text{ }\mu\text{m}$  or more, the operating temperature is  $1273 \text{ K}$  ( $1832^\circ\text{F}$ ) but fuel cells with thin electrolytes can operate between  $973$  and  $1073 \text{ K}$  ( $1292$  and  $1472^\circ\text{F}$ ).

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  $1073 \text{ K}$  ( $1472^\circ\text{F}$ ). The bipolar plate materials are dense and electronically conductive.

Typical polarization curves for SOFCs are shown in Fig. 24-53. As discussed earlier, the open-circuit potential of SOFCs is less than  $1 \text{ V}$  because of the high temperature, but the reaction overpotentials are 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. 24-54. 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)

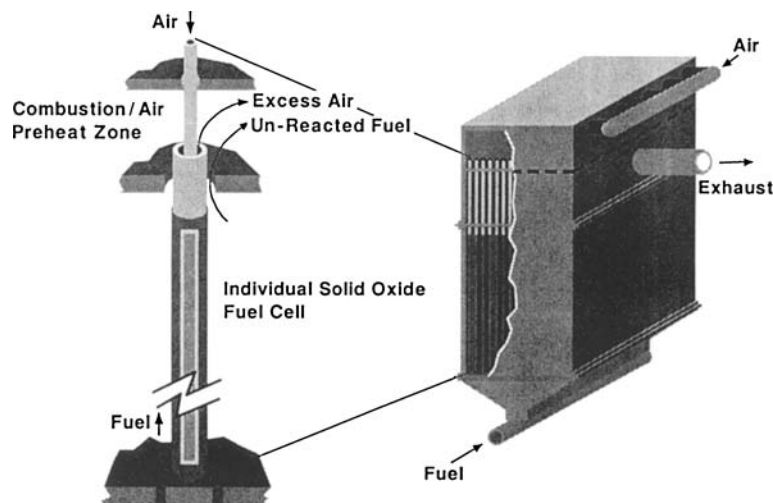


FIG. 24-54 Configuration of the tubular SOFC. (Courtesy of Westinghouse Electric Corporation.)

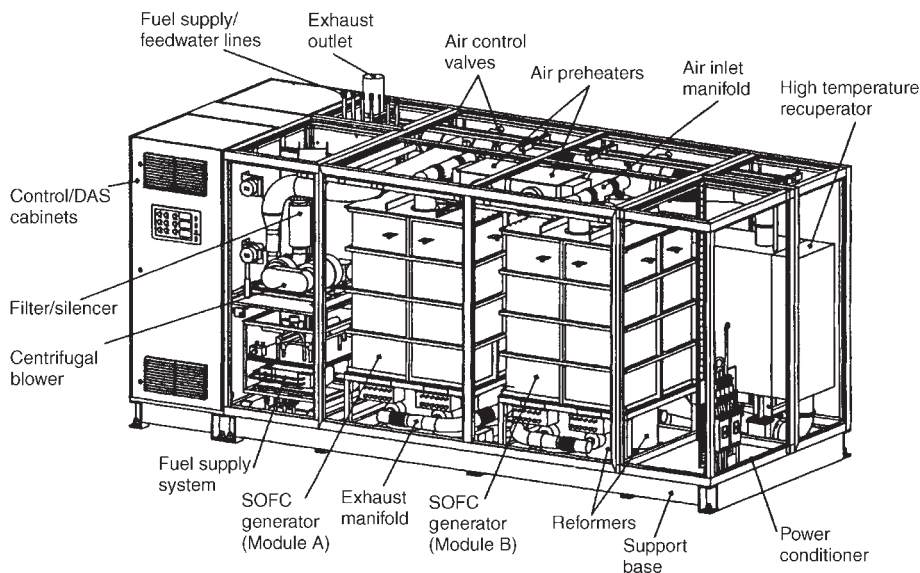


FIG. 24-55 SOFC 25-kW system package. (Courtesy of Westinghouse Electric Corporation.)

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. 24-55.

## ENERGY RECOVERY

Most processing energy enters and then leaves the process as energy, separate from the product. The energy enters as electricity, steam, fossil fuels, etc. and then leaves, released to the environment as heat, through "coolers," hot combustion flue gases, waste heat, etc. Recovering heat to be used elsewhere in the process is important to increase process efficiency and minimize cost. Minimizing the total annualized costs for this flow of energy through the process is a complex engineering task in itself, separate from classic process design. Since these costs include the costs for getting energy into and out of the process, they should be evaluated together, as elements integrated within a larger system. Such a holistic system evaluation impacts how the overall project will be designed (utilities supply, reaction and separations design, pinch analyses, 3D process layout, plot plan, etc.). Therefore, evaluation and selection of the process energy technology system should be performed at the start of the project design cycle, during **technology selection VIP** (see the subsection "Value-Improving Practices" in Sec. 9), when the **potential to influence project costs exists at its maximum value**.

Following the 1970s energy crisis, enhanced technology systems have been developed which can **significantly reduce the annualized costs for process energy**. Several of these technologies are presented below, because they are broadly applicable, have a rapid payback, and can make a significant reduction in overall annualized energy costs. Wet surface air coolers (WSACs), an evaporative cooling technology, are presented in Sec. 12.

### ECONOMIZERS

**GENERAL REFERENCES:** "Latest Advances in the Understanding of Acid Dew-point Corrosion: Corrosion and Stress Corrosion Cracking in Combustion Gas

Condensates," W.M.M. Huijbregts and R.G.I. Leferink, *Anti-Corrosion Methods and Materials*, vol. 51, no. 3, 2004, pp. 173-188 (<http://www.hbscc.nl/>); "Get Acid Dew Points of Flue Gas," A.G. Okkes, *Hydrocarbon Processing*, July 1987, pp. 53-55; Lahtvee, T., Schaus, O., *Study of Materials to Resist Corrosion in Condensing Gas-Fired Furnaces*, Final Report to Gas Research Institute, GRI-80/0133, February, 1982; Ball, D., et al., *Condensing Heat Exchanger Systems for Oil-Fired Residential/Commercial Furnaces and Boilers: Phase I and II*, US DOE BNL-51617, 1982; Razgaitis, R., et al., *Condensing Heat Exchanger Systems for Residential/Commercial Furnaces: Phase III*, US DOE BNL-51770, 1984; Razgaitis, R., et al., *Condensing Heat Exchanger Systems for Residential/Commercial Furnaces and Boilers: Phase IV*, BNL-51943, 1985; Butcher, T.A., Park, N., and Litzke, W., "Condensing Economizers: Thermal Performance and Particulate Removal Efficiencies," in *ASME Two Phase Flow and Heat Transfer, HTD*, vol. 197, 1992 (for U.S. DOE reports see: <http://www.osti.gov/energycitations>).

Economizers improve boiler thermal efficiency by recovering heat from the combustion flue gases exhausted from the steam boiler section. The recovered heat is used to heat colder streams (heat sinks), before ultimate discharge of the waste gas to atmosphere. This recovered heat displaces the need to burn additional fuel to heat these same streams.

Normally, after being heated, these streams are used in the boiler area (deaerator feedwater, cold return condensate, boiler feedwater, RO feedwater) or in the combustion chamber (air preheat). However, economizers can be used to recover and supply heat elsewhere, such as hot process water or hot utility water, especially as used in the food processing and pulp/paper industries. Additionally, recovered flue gas waste heat can be used indirectly; i.e., remote process streams can be heated locally with hot steam condensate, and then the cooled return steam condensate can be reheated in the flue gas economizer. An



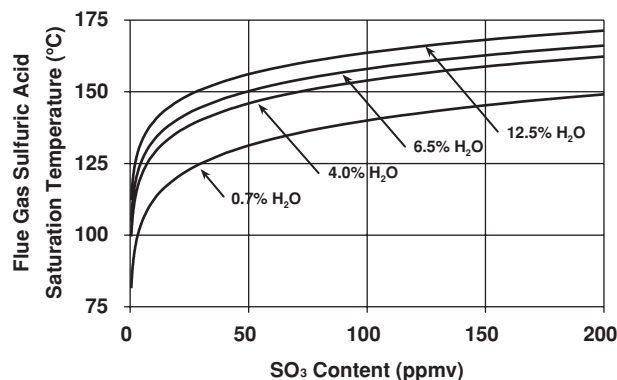


FIG. 24-56 Calculated sulfuric acid dew points, as a function of  $\text{SO}_3$  content, for various flue gas water vapor concentrations. (Courtesy W. M. M. Huijbregts, 2004.)

extension of these concepts is provided by the application of using hot water to vaporize LNG: hot-water-based liquid is used to vaporize the process stream [LNG: stored near 122 K ( $-151^\circ\text{C}$ ), returning near 273 K ( $0^\circ\text{C}$ )] to the hot water heater. Before entering the hot water heater, the cooled stream recovers flue gas waste heat in a condensing economizer.

**Acid Dew Point** For fossil fuels, the acid dew point temperature is that temperature at which the actual mixed acid vapor pressure equals the mixed acid vapor saturation pressure. The mixed acid dew point can be approximated by the sulfuric acid dew point (Fig. 24-56). It can be described as a function of the  $\text{SO}_3$  and water content of the flue gas (Huijbregts). These concentrations result from the sulfur, hydrogen, and free water content of the fuel; the relative humidity of the air; and the amount of excess air used. Using the equation of Verhoff, where  $T$  is degrees K and  $P$  is mm Hg (see Okkes, A.G.):

$$T_{\text{dew}}(\text{SO}_3) = 1000 / [2.276 - 0.0294 \ln(P_{\text{H}_2\text{O}}) - 0.0858 \ln(P_{\text{SO}_3}) + 0.0062 \ln(P_{\text{H}_2\text{O}} P_{\text{SO}_3})] \quad (24-59)$$

The corrosiveness of flue gas condensate is further complicated by the presence of other components ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ , etc.). The sources of these components can be either the fuel or the combustion air (salt, ammonia, Freon, chlorine, chlorinated VOCs, etc.), usually producing a more corrosive condensate.

**Water Dew Point** For flue gas, the water dew point is that temperature at which the actual water vapor pressure equals the water saturation vapor pressure. Cooling the flue gas below this temperature will result in the formation of liquid water [or ice, below 273 K ( $0^\circ\text{C}$ )]. For example, burning natural gas with 3 percent excess oxygen (15 percent excess air), the flue gas water dew point would be (Fig. 24-57)  $\sim 330$  K ( $56.7^\circ\text{C}$ ).

**Boiler Thermal Efficiency** Traditionally, boiler thermal efficiency is calculated  $Q_{\text{OUT}}/Q_{\text{IN}}$ , where  $Q_{\text{IN}}$  is the LHV (lower heating value) of the fuel. A rule of thumb for economizers is that boiler efficiency increases by  $\sim 1$  percent for every  $22^\circ\text{C}$  ( $40^\circ\text{F}$ ) drop in temperature of the dry flue gas. These two statements do not reveal the considerable quantity of **additional heat**, available to be recovered through **condensation of the water vapor** in the flue gas, which is lost to atmosphere with hot flue gas. Based on fuel HHV (higher heating value), the total latent heat loss can be substantial: an additional 9.6 percent (natural gas), 8.0 percent (propane), 6.5 percent (heating oil).

**Conventional Economizers** Conventional economizers can be constructed from relatively inexpensive materials, such as low-alloy carbon steels, if they will be operated dry on the gas side, with flue gas side metal temperatures above the acid dew point. This practice is done to protect the economizer from corrosion, caused by the acidic flue gas condensate. Conventional economizers can also be con-

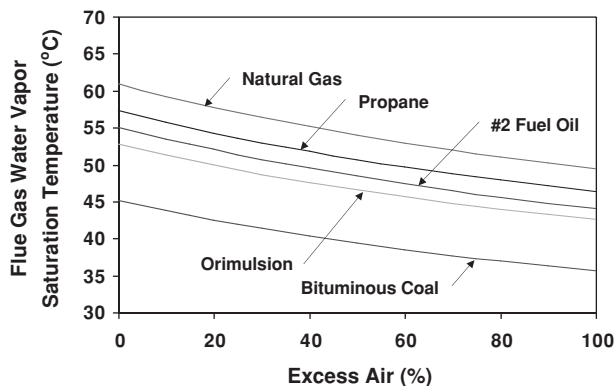


FIG. 24-57 Calculated flue gas water vapor dew points, for different fuel types, as a function of excess air [Orimulsion (28.3% water), Pittsburgh Seam 8 (5% water)]. (Courtesy T. A. Butcher, US DOE; [www.bnl.gov](http://www.bnl.gov).)

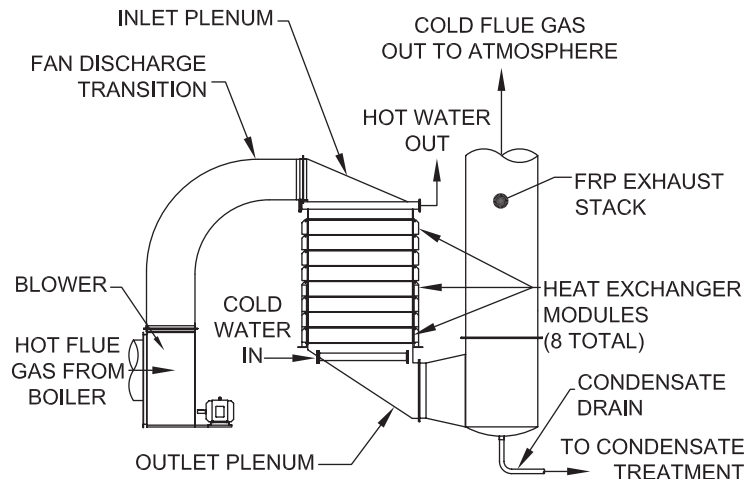
structed from more expensive materials, and can be operated below the acid dew point, but above the water dew point. This practice permits greater heat recovery, but with a generally lower payback. A compromise practice for operation below the acid dew point is to use less expensive but less corrosion-resistant materials, accepting an accelerated rate of corrosion, and periodically replacing the damaged heat-transfer surfaces when needed. Nevertheless, when high-sulfur fuel is burned (oil, coal, etc.), typically the water inlet feed to a conventional economizer is preheated to a temperature above the anticipated acid dew point.

**Condensing Economizers** Flue gas condensing waste heat economizers are designed to operate **below the flue gas water dew point**. This temperature can range from about 316 K ( $43^\circ\text{C}$ ) to 333 K ( $60^\circ\text{C}$ ), depending on the amount of hydrogen and water in the fuel, the amount of excess combustion air used, and the humidity of the air. [Higher flue gas water dew points can be encountered for other industrial applications, such as product driers, fryers (food processing), waste water incinerators, etc.] Such economizers recover **flue gas sensible heat** as well as **water vapor latent heat** from the hot flue gas. Fuel consumption is reduced in proportion to the efficiency increase.

Condensing economizers are constructed from inexpensive, but durable, corrosion-resistant materials. Extensive materials testing has been performed for operation in this service, including for coal combustion (Lahtvee, Ball, Razgaitis, and Butcher). The metallurgy for the tube-side liquid is determined by the liquid chemistry requirements (usually water-based liquid): 304 stainless steel is typical.

For gas-side materials, one available technology employs Teflon-covered metal tubing and Teflon tube sheets. This technology is often operated across both the acid and water dew points, and can accept inlet gas temperatures to 533 K ( $260^\circ\text{C}$ ). Typical applications may achieve a cold-end  $\Delta T$  below  $45^\circ\text{C}$  ( $80^\circ\text{F}$ ), improve the boiler thermal efficiency by  $\sim 10$  percent (LHV basis), and have a simple payback of 2 to 3 years, based on **fuel avoidance** (Figs. 24-58 and 24-59).

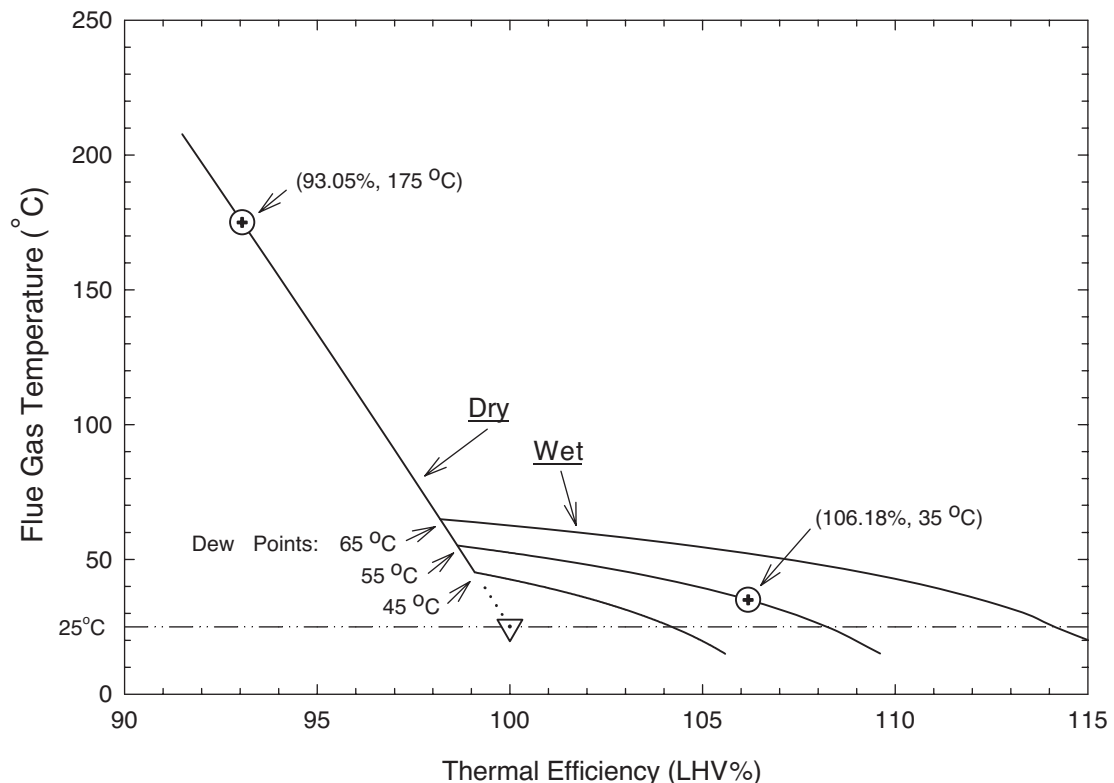
A second technology employs metallic finned tubing, extruded over the water tubing. Aluminum 1000 series fins are preferred, for heat-transfer reasons in natural gas applications, but stainless steel (or other material) fins are used for higher temperatures and/or more corrosive flue gas. This second technology both is less expensive and has better heat transfer (per  $\text{ft}^2$ ). Consequently, for the same payback the cold-end approach can be lower, and the water outlet temperature and the boiler efficiency improvement higher. Flue gas condensate from combustion of natural gas typically has a pH of  $\sim 4.3$ , and aluminum fins are suitable. For more acidic (or erosive) flue gas conditions, other metallurgy (Incoloy® 825 and Hastelloy®), or a Hersite or equivalent coating, may be used to prevent corrosion damage (Fig. 24-60).



**FIG. 24-58** Standard equipment arrangement, flue gas condensing economizer waste heat recovery system (flow: left to right). The ID fan draws hot flue gas from the boiler, propelling it into the top of the condensing economizer. (Courtesy CHX Condensing Heat Exchanger Co.; [www.chxheat.com](http://www.chxheat.com).)

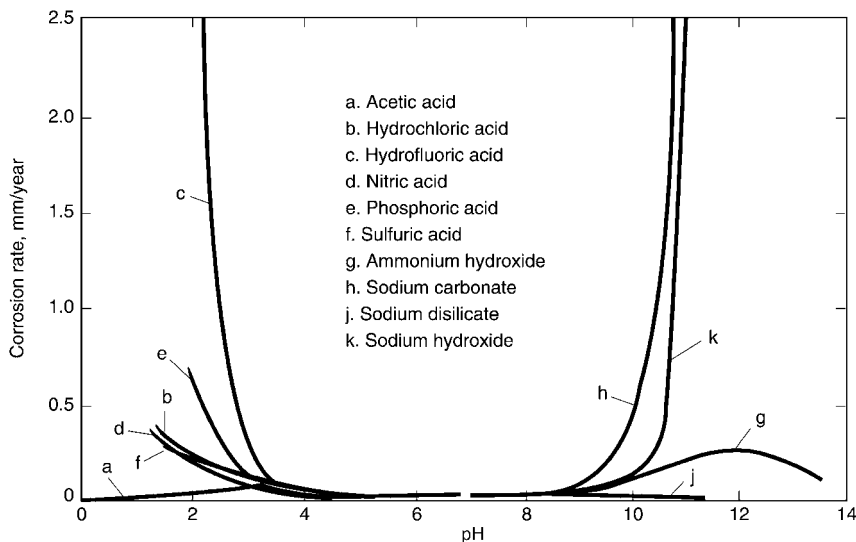
Flue gas condensate at different temperatures, compositions and relative corrosivity condenses and exists at different positions within the condensing economizer. These positions are not fixed in space or time, but move back and forth, in response to changing load conditions

in either stream. Condensing economizers are typically equipped with water spray nozzles for periodic washdown of the flue gas side, to be used (infrequently) for natural gas combustion, but more frequently for services having heavier pollutant loading, such as oil, coal, etc. Over



**FIG. 24-59** Characteristic curves for boiler thermal efficiency as a function of flue gas effluent temperature and flue gas water dew points. Based on the LHV of a fuel, and stoichiometric reaction, 100 percent efficiency would be achieved if sufficient combustion heat were recovered and removed, so that the temperature of the effluent flue gas was reduced to 25°C. For a flue gas with a 55°C dew point, recovering additional heat via condensation by cooling from 175 to 35°C (as shown) would increase the overall efficiency by more than 13 percent. (Courtesy Combustion & Energy Systems, Ltd.; [www.condexenergy.com](http://www.condexenergy.com).)





**FIG. 24-60** Effect of corrosion on 1100-H14 aluminum alloy by various chemical solutions. Observe the minimal corrosion in the pH range from 4.0 to 9.0. The low corrosion rates in acetic acid, nitric acid, and ammonium hydroxide demonstrate that the nature of the individual ions in solution is more important than the degree of acidity or alkalinity. (With permission from ASM International; [www.asminternational.org](http://www.asminternational.org). Courtesy of Combustion & Energy Systems, Ltd.; [www.condexenergy.com](http://www.condexenergy.com).)

200 such heat exchangers have been installed, some in service for more than 20 years (2005). This technology is suitable for heat recovery applications of any magnitude.

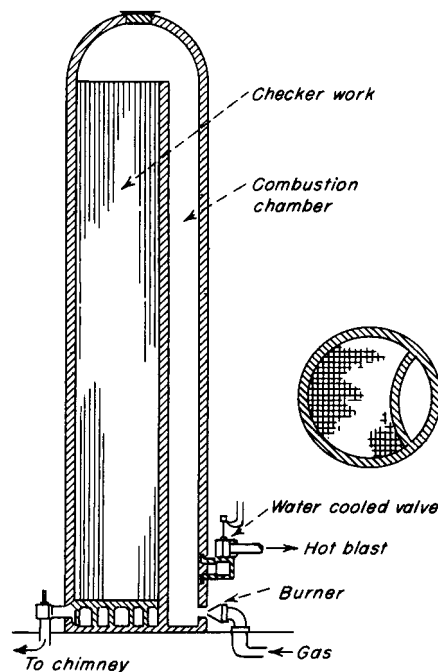
Several **environmental benefits** are gained through employment of this condensing technology. Burning less fuel proportionally reduces **collateral combustion emissions** ( $\text{NO}_x$ ,  $\text{SO}_x$ ,  $\text{CO}$ ,  $\text{CO}_2$  and particulates, including  $\text{PM}_{2.5}$ ). Additionally, **flue gas pollutant removal** occurs in the condensing economizer, as has been extensively investigated, characterized, and modeled by the U.S. DOE (Butcher et al.) including applications burning coal and Orimulsion. Typically, the condensate will contain most (by mass, >90 percent) of the highly dissociated inorganic matter ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{NH}_3$ , salts, etc.) and the **larger-diameter particulates** (>10  $\mu\text{m}$ ) and a lower but substantial fraction (>60 percent) of the **smaller-diameter particulates** (<5  $\mu\text{m}$ ). Such gross pollutant removal can be a cost effective first stage for a traditional air pollution control system, by reducing the volume of the flue gas to be treated (water content and temperature) as well as reducing the concentration of the pollutants in the flue gas to be treated downstream. Unlike spray quenching, such indirect quench-cooling segregates the flue gas pollutants from the cooling system fluid, generating a much smaller, concentrated waste water stream for subsequent waste treatment. Although pollutant removal percentages are high, they are functions of the specific real-time mass- and heat-transfer conditions within the economizer. Condensate treatment from boiler economizers normally is neutralization, often using the boiler blowdown, and release to the sewer and sewage treatment.

## REGENERATORS

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 U.S. ton) of pig iron per day, will be blown with 47.2  $\text{m}^3/\text{s}$  (100,000 std  $\text{ft}^3/\text{min}$ ) 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. 24-61. The interior comprises three regions: in the cylindrical portion, (1) a side combustion chamber,



**FIG. 24-61** Blast-furnace stove.

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  $11,500 \text{ m}^2$  ( $124,000 \text{ ft}^2$ ). 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.

At the start of an on-wind step, about one-half of the air, entering at  $366 \text{ K}$  ( $200^\circ\text{F}$ ), 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  $1366 \text{ K}$  ( $2000^\circ\text{F}$ ). Mixing this with the unheated air produces a blast temperature of  $811 \text{ K}$  ( $1000^\circ\text{F}$ ). 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  $811 \text{ K}$ . 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. 24-62). 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  $1255 \text{ K}$  ( $1800^\circ\text{F}$ ) can be accommodated. Gas face velocity is usually around  $2.5 \text{ m/s}$  ( $500 \text{ ft/min}$ ). The rotor height depends on service, efficiency, and operating conditions but usually is between 0.2 and  $0.91 \text{ m}$  (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. Ljungstrom-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. 24-63). Burner operations are switched periodically. Such systems can yield combustion air preheats between  $933 \text{ K}$  ( $1220^\circ\text{F}$ ) and  $1525 \text{ K}$  ( $2282^\circ\text{F}$ ) for furnace temperature between  $1073 \text{ K}$  ( $1472^\circ\text{F}$ ) and  $1723 \text{ K}$  ( $2642^\circ\text{F}$ ), respectively.

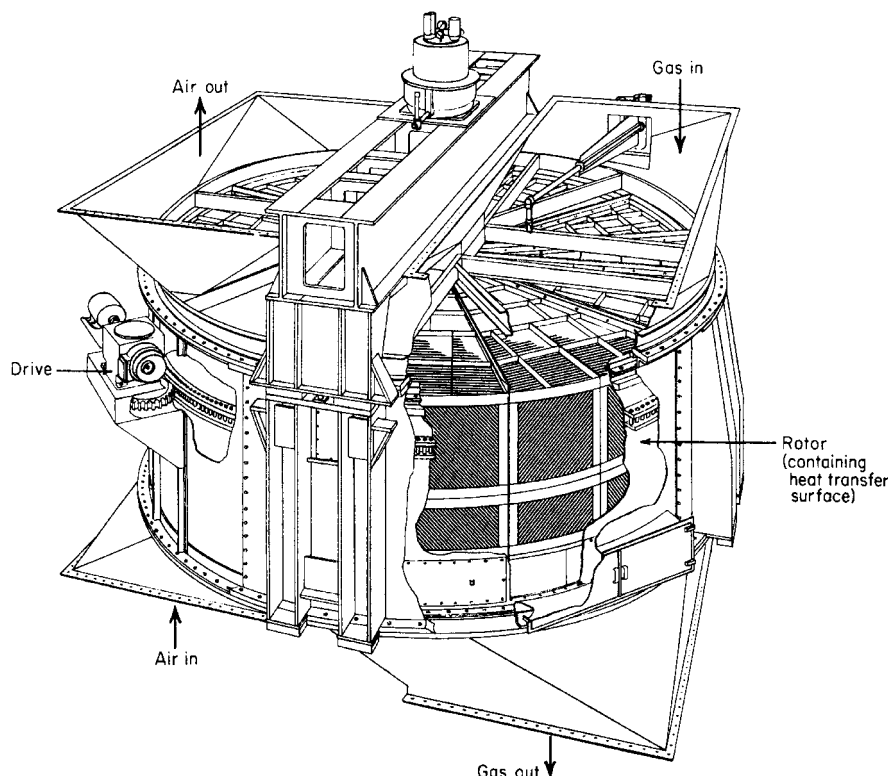


FIG. 24-62 Ljungstrom air heater.

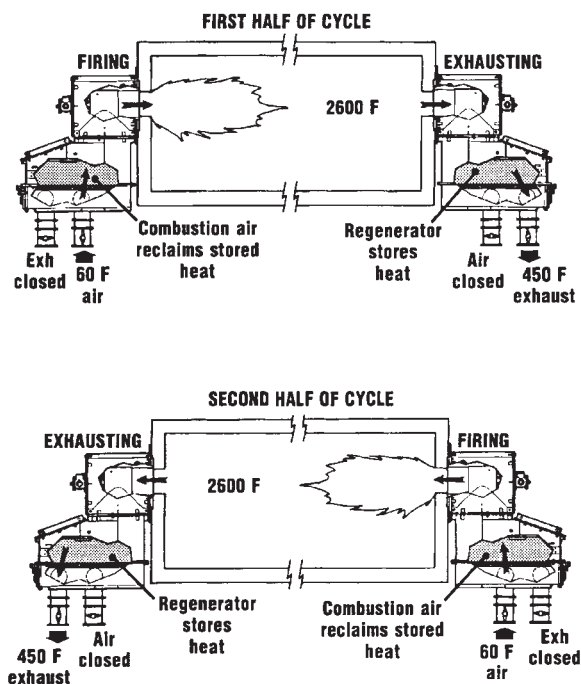


FIG. 24-63 Schematic of a regenerative burner system. (North American Manufacturing Co.)

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.

## RECUPERATORS

Regenerators are by nature intermittent or cycling devices, although, as set forth previously, the Ljungström 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. An inner tube carries the hot exhaust gases and an 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. 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. In one configuration, for example, 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.

## TURBINE INLET (AIR) COOLING

**GENERAL REFERENCES:** See "Bibliography" at <http://www.turbineinletcooling.org/resources>.

Turbine inlet cooling (TIC) can increase gas turbine (GT) power output on a hot day by 10 to 30 percent, while improving (reducing) the turbine heat rate (kJ/kW<sub>e</sub>) by as much as 5 percent. By increasing the air compressor inlet air density, turbine inlet air cooling is the most cost-effective method for increasing turbine gross power output, for fixed-altitude GTs.

GTs are "constant-volume machines," such that a fixed-speed GT air compressor section draws a nearly constant volumetric flow of inlet air, independent of ambient air conditions. Air density drops with increased altitude (reduced barometric pressure), increased ambient temperature, and, to a lesser degree, increased water content (specific humidity).

Increasing the air density increases the GT inlet air mass flow. For a given stoichiometric fuel-to-air-ratio and a given combustion temperature, increased air mass flow allows increased fuel flow, resulting in increased GT power output. Additionally, compressor efficiency increases with decreased air temperatures, resulting in less parasitic compressor shaft work consumed and greater net turbine power output. Therefore, TIC increases net incremental power output faster than incremental fuel consumption, resulting in improved overall fuel efficiency (reduced heat rate); see Fig. 24-64.

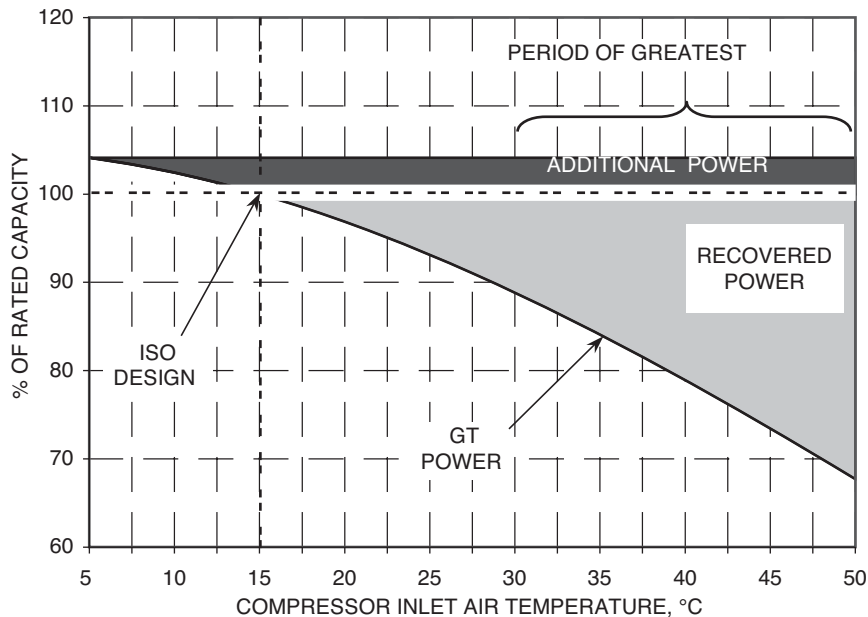
**Evaporative Technologies** These TIC technologies cool the inlet air by vaporizing water in direct contact with the inlet air, using the latent heat of vaporization of water. These technologies either spray water directly into the airstream as a fog or mist or evaporate the water from fixed wetted media placed in the airstream.

Performance of these technologies is typically an 85 percent approach to the ambient wet-bulb temperature ( $T_{WB}$ ) from the ambient dry-bulb temperature ( $T_{DB}$ ), limited to a 3°F approach to the ambient  $T_{WB}$ . For locations with high  $T_{DB}$  and low  $T_{WB}$ , the cooling benefit can be significant. For locations with humid conditions, the relative cooling achievable by evaporative technologies can be very limited. Additionally, on a given day, the relative changes in hourly  $T_{DB}$  and  $T_{WB}$  will result in variable GT peak power output.

Evaporative TIC technologies have the minimum installed and operating costs. The operating electric parasitic load is generally considered insignificant. Water chemistry management is crucial to prevent maintenance problems caused by dissolved or suspended matter in the water, fouling either the evaporation media or the turbines themselves.

**Refrigeration Technologies** These TIC technologies indirectly cool the inlet air, typically using either chilled water or a vaporizing refrigerant, in a finned coil heat exchanger placed in the incoming airstream. Refrigeration technologies can achieve and maintain much lower air compressor inlet temperatures, largely independent of changing ambient conditions (Fig. 24-65). Best design practices (ice formation / consequent GT damage) have restricted the OEM recommended minimum inlet air cooling temperatures to the 5° to 10°C [41° to 50°F] range. Refrigeration can be supplied by either absorption or mechanical chillers. Absorption chillers employ either LiBr or ammonia absorption. Electrically driven centrifugal packaged chiller systems, using chilled water as a secondary refrigerant, account for the majority of refrigeration machine types. R-123, R-134a, and R-717 are the most common refrigerants offered by vendors. Several installations have used direct refrigeration through R-22 or ammonia (R-717) vaporization in the TIC air coil, with refrigerant condensation in a wet surface air cooler (WSAC) or an air-cooled condenser. Site-specific sources of cooling (the heat sink), such as LNG vaporization, have also been used. The water condensate generated by cooling inlet air below the ambient dew point can be employed as makeup water for a cooling tower or a WSAC.

While refrigeration technologies can provide a near-constant GT inlet air temperature, and thus a nearly constant GT power output, refrigeration TIC systems are significantly more expensive than evaporative systems. However, the incremental net power output from the refrigeration system, when measured on a unit cost basis (\$ per kW<sub>e</sub>),



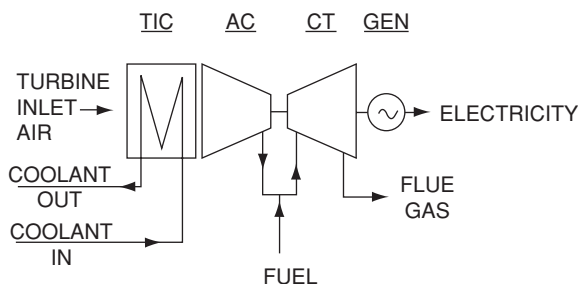
**FIG. 24-64** Effect of inlet air ambient temperature on the power output of a typical GT. If ambient air at 95°F (35°C) were cooled to 50°F (10°C), the gross GT power output would be increased by approximately 22 percent, and the gross heat rate improved by 3.7 percent. Operated at its ISO conditions [15°C (59°F) at sea level], GT rated performance is 100 percent. (*Turbine Air Systems*; [www.tas.com](http://www.tas.com).)

costs much less than the unit cost of the GT itself, thereby decreasing the overall unit cost of the GT plant. Refrigeration technologies require a significant energy input to operate. In the case of electric-driven chillers, the parasitic electric load can consume 10 percent to 15 percent of the GT gross incremental increase in power. Therefore, the net overall plant incremental output, after allowance for the refrigeration system parasitic load, is used for evaluating the economics of these systems.

**Thermal Energy Storage (TES)** A TES system consists of an insulated cold storage tank and a chiller, generating ice or chilled water, which is accumulated in the tank. A TES system is typically installed when TIC is required for only a limited number of operating hours per day. The **principal TES benefit** is that the *net* electrical peak output of the power plant is maximized, by shifting the parasitic electric power loss (chiller power demand) from the period of peak demand (midday) to the off-peak hours (night). A **second benefit** is a reduced overall capital cost for a smaller chiller (usually half-sized) because the smaller chiller is operated either continuously (partial storage) or over a nighttime period (full storage). A **third benefit** is

the reduced operating costs, stemming from the ability to use lower-value off-peak power for the chilling load. A **fourth benefit** is that the chiller will typically perform better during the nighttime off-peak period, due to lower ambient temperatures, reducing the energy required for refrigerant compression. A **fifth benefit** is the ability to increase or decrease generation capacity in a short time period, when called upon, to stabilize the transmission system or grid the plant is tied into. However, a TES site footprint may be larger, to include the TES storage tank.

**Summary** Evaporative technologies have the lowest capital and operating costs, but their benefit is limited by ambient conditions. They are most effective where the peak  $T_{WB}$  is lowest, especially at times of peak demand, as are found in hot, arid regions. Refrigeration technologies can achieve and maintain constant lower temperatures, independent of ambient conditions. However, they have higher initial capital and operating costs. Although refrigeration technologies are favored for use in warm, humid regions, where both the peak daytime  $T_{WB}$  and air conditioning demand are highest, they have been selected and installed in more northern temperate latitudes (Canada) and arid climates as well. TES and other hybrids, which combine various technologies, are used to minimize the overall annualized costs for TIC systems. The unit costs for TIC technologies are substantially lower than are the unit costs for new GTs. Therefore, the installation of a new TIC technology to an existing GT system may offer the lowest-cost choice for increasing the output capability of that older system. For new installations, the inclusion of an optimal TIC technology with the new GT should result in minimizing the annualized cost for output power. Typical unit costs for TIC options range from \$25 (evaporative) to \$200 (refrigeration) per  $kW_e$  of incremental power output, vs. \$300 to \$500 per  $kW_e$  for a new single cycle GT. Selection of the most suitable TIC option for any given application (new or retrofit) requires a careful evaluation of (1) the local power requirements and revenues for power generation, (2) the local meteorological conditions, and (3) the capabilities and costs of different TIC technology options, offered by the various TIC vendors (see [www.turbineinletcooling.org](http://www.turbineinletcooling.org)).



**FIG. 24-65** Mechanical refrigeration TIC systems utilizing chilled water for cooling turbine inlet air, and cooling towers to reject the waste heat into the environment, account for the majority of refrigeration TIC systems sold.

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