

Chapter 2

Solid Fuels

2.1 Introduction

Fuels are conveniently classified as solids, liquids, and gaseous fuels. Solid fuels include peat, wood, and coal and can encompass solid rocket fuels as well as metals. The earliest fuels used by man were nonfossil fuels of wood and oil from plants and fats from animals. The windmill and water wheels were other sources of energy.

Sources of power have changed with the years and will continue to change as shown in Fig. 1.2. In 1992, approximately 7% of the world's power was supplied by hydroelectric plants and the remaining 92.5% from fuels. Natural gas provides 22% of the total power; petroleum, 40%; coal, 25% (of which 7% is derived from hard coal and 18% from the soft coals); and nuclear fuels provide about 7%. But in 2005, approximately 16.6% of the world's power was supplied by hydroelectric plants; 65.9% by thermal power plants; 15.2% by nuclear power plants; and 2.1% by geothermal, solar, and wind power plants. Oil, which has displaced coal as the major fuel, will soon be replaced by natural gas which in turn will be eventually replaced by nuclear energy and environmentally friendly geothermal, solar, and wind power energy.

The origin of coal is not known with certainty. One popular theory claims that coal originated about 250 million years ago as a result of the decay of vegetation primarily from land and swamps and not of marine origin. Bacterial action undoubtedly helped with the reduction process. The first step following the exclusion of oxygen was the formation of peat—a slimy mass of rotting organic matter and debris. Under the pressure of sediments, the peat became dehydrated and hard, forming low-grade coal, called *lignite*. Under further pressure and time, the reactions of condensation and consolidation (50-fold decrease in volume) converted the lignite into a higher grade coal—bituminous coal. A highest grade coal—anthracite—has the highest percentage of carbon. A simplified flow description for coal formation is shown in Fig. 2.1. The three-component ternary phase diagram for the C, H, and O content of the various grades of coal is shown in Fig. 2.2 where comparison is made with cellulose and lignin,¹ the general precursor to coal. The simple weight percentage point of cellulose is indicated by a filled triangle (▲) and the atom percentage is shown as a filled square (■). The bond-equivalent points are meant to account for the bonding (valency) of the elements, namely, 4 for C, 2 for O, and 1 for H. The atom percentage multiplied by the bond factor and normalized (to 100% for all the elements) is called the *bond-equivalent percentage* and is shown as filled circles (●). The values for CH₄, CO₂, and H₂O are also shown in Fig. 2.2 as open circles (○). The direction from cellulose to anthracite shows clearly that the loss of water and oxygen must occur during the coalification process.

¹ Wood consists of about 25% lignin which acts to bind the cellulose fibers together.

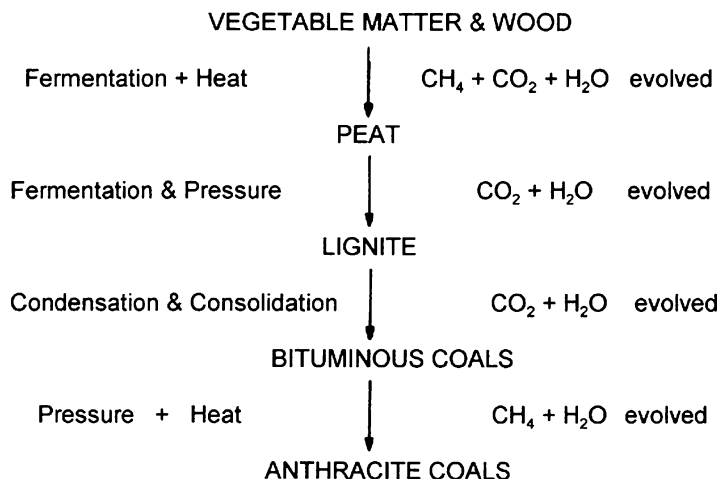


Fig. 2.1 Possible route for the formation of coal from plant matter

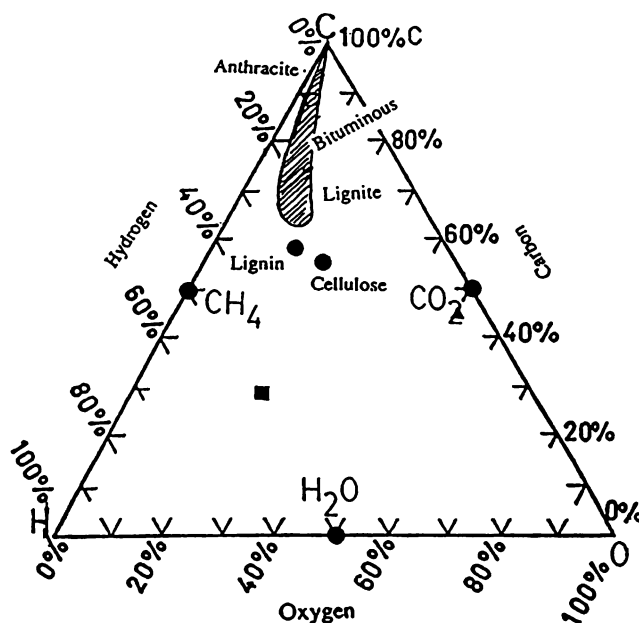


Fig. 2.2 The three-phase ternary bond-equivalent diagram for C-O-H showing the transition from cellulose to anthracite. Cellulose ($\text{C}_6\text{H}_{10}\text{O}_5$) is also shown as \blacktriangle for weight % and as \blacksquare for atom % in the diagram. The other points are bond-equivalent %

Wood was obviously man's first fuel, followed by animal fats and vegetable oil. There is evidence that candles were used during the first Minoan civilization about 3000 B.C. Coal was used by the Chinese about 100 B.C. and the "black stone" was reported to be used by Greek smiths about 250 B.C. The Romans in Great Britain also used coal. Marco Polo describes the mining of "black stone" in his travels 1271–1298 A.D.

Coal is primarily known as a fuel but it is also a valuable chemical. It can be reacted with lime, CaO , at high temperatures (electric arc) to form calcium carbide,

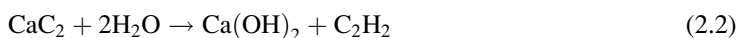
Table 2.1 World coal resources and use in 2006/1996^a

	Recoverable reserves 10 ⁹ t			Uses 10 ⁶ t	
	Hard 2005/1996	Soft 2005/1996	Total 2005/1996	Production 2005/1996	Consumption 2005/1996
Russia	54.1/54	173.1/173	173.1/173	322/331	246.4/284
USA	122.0/122	263/275	263/275	1,162/1,087	1,112.3/1,028
China	68.6/68.6	126.2/126.2	126.2/126.2	2,620.5/1,690	2,584.2/1,532
Germany	0.2/26.4	7.4/73.8	7.4/73.8	220.5/286	269.5/277
Australia	40.9/52.1	84.4/99.6	84.4/99.6	0/276	156.4/135
UK	0.1/1.1	0.2/1.6	0.2/1.6	19.9/62	74.2/78
Canada	3.8/5.0	7.2/9.5	7.2/9.5	72.7/87	65.4/62
Poland	6.6/13.4	8.2/15.8	8.2/15.8	171.1/232	154.8/195
South Africa	54.5/61.0	56.5/61.0	56.5/61.0	275.3/230	207.8/169
India	57.6/80.2	62.3/82.2	62.3/82.2	498.9/352	550.7/342
Rest of the world	65.1/77.5	143.5/170.2	143.5/170.2	1,443.1/922	1,322.1/1,167
Total	473.2/565.3	930.4/1,088.1	930.4/1,088.1	6,806.9/5,625.0	6,743.8/5,269

^aFrom International Energy Annual (2006, 1996)

Hard = anthracite and bituminous; soft = lignite and subbituminous

CaC₂, which when hydrolyzed, forms acetylene (C₂H₂):



Coal is also used to prepare active carbon which is used for the purification of air and water and in numerous industrial processes.

The distribution of coal in the world is given in Table 2.1. The recoverable reserves consist of the coal which can be economically mined with presently known technology and conditions. The proven reserves are the coal known to be present, within +20%, by extensive drilling and experience and are about twice the recoverable reserves. The estimated total world coal resources are about eight times larger and are based on geologically favorable formation within the earth's crust and on previous experience within the countries concerned. It excludes under sea or under ice sites.

Of the world's reserves, the distribution between hard and soft coal is about equal on a global basis. There is enough coal to last the world for 200–1,000 years depending on the rate of usage and the rate of exploration.

Coal in 1947 was at a record high price of \$4.16 per ton at the mine. More than 600 Mt were mined that year in the USA, but already, oil was + beginning to displace it. The old steam engines, which used a ton of coal for every four miles hauling a heavy freight, consumed a quarter of the coal production (125 Mt). By 1960 when the railroad had almost completely converted from coal to diesel, the rail industry used only 2 Mt of coal.

A drop in coal-fired generation in the Organization for Economic Cooperation and Development (OECD) countries is offset by big increases elsewhere, especially China, where 600 gigawatts of new capacity exceeds current capacity of the USA, European Union (EU), and Japan (IEA Outlook 2010). According to the American Worldwide Institute's report (No. 182, Oct. 2010), China is the first world's largest coal user today. China consumed 2.7 billion tons of coal in 2008 or 43% of the world total and in 2.5 times higher than the second largest consumer, the USA.

2.2 Wood and Charcoal

Wood, a renewable source, is not an important industrial fuel today. However, its use continues in some rural areas where it is often supplemented with liquid propane. In some underdeveloped countries, wood is still the principal source of energy. Dry wood contains from 1% to 12% moisture whereas green wood contains from 26% to 50% water. The resinous woods, like pine or cedar, yield about 18.5 MJ/kg of air-dried wood or, allowing for the moisture content, about 21 MJ/kg on a dry weight basis. Hardwoods have a heating value of about 19.4 MJ/kg. The energy available in present forest stocks is estimated to be equivalent to about 270×10^9 t of coal or about 2/3 of the equivalent oil reserves.

Wood-burning fireplaces have become a popular form of heating in the past few years. The normal open hearth fireplace is not an efficient producer of heat since its draft sends most of the hot air up the chimney, creating a partial vacuum pulling cold air into the home. The recent introduction of glass doors to close in the fire and the introduction of outside air to the fire for the combustion process has improved the efficiency of the fireplace, especially with forced air circulation around the fire chamber.

Open fires, however, are a source of pollution since the smoke produced contains large quantities of polynuclear aromatic hydrocarbons such as benzo(a)pyrene, a carcinogen also found in cigarette smoke. In some communities, it has been necessary to restrict the burning of wood because of the resulting air pollution.

2.3 Peat

Peat is formed when dead vegetation is saturated with water which prevents the action of aerobic bacteria. Thus, most of the carbon of the cellulosic matter is retained, and with ageing, peat is formed. It accumulates at an average rate of 0.7 mm/year or worldwide at 210 Mt of carbon. Canada (40%) and Russia (36%) have more than 3/4 of the world's peat land (320 Mha or 150×10^3 Mt of carbon). In Russia, peat deposits occupy about 1/10 of the total country's terrain. It is a spongy watery mass when first obtained from the peat bog. Six tonnes of dry peat yield about 1 t of fuel. A commercial grade of peat contains about 25% water. Air-dried peat has a heating value of about 16.3 MJ/kg. Peat is rich in bitumens, carbohydrates, and humic acids, and as a chemical source, it can yield waxes, paraffins, resins, and oils. Peat also is a source of pharmaceutical and curative preparations as well as a livestock-feed supplement.

Peat is not used in North America as a fuel to any great extent, but in Europe, it has been employed in domestic heating for centuries. Peat is often harvested by massive machinery for industrial use (Fig. 2.3). The machine deposits the cut and macerated peat in long furrows, which are then crosscut into blocks and conveyed to dry storage or dryers. Ireland harvests 4 Mt annually as fuel for generating 20% of the nation's electricity. In Finland, about 3 Mt of peat, with an energy content of 30×10^9 MJ, is used annually. This is about 6% of the total fossil fuel energy used. Peat as a primary fuel was used in 15 power plants in 1983 to generate 950 MW. Peat is also used to generate power for electricity in Russia.

The pyrolysis of peat in the absence of oxygen is being studied in New Zealand, where the oil-wax product is then hydrogenated to form the equivalent to a common crude oil. New Zealand has enough peat to produce 400 Mbbl of oil.

The growth of peatlands consumes CO_2 , and the harvesting of peat and its combustion as a fuel has a twofold adverse effect on the CO_2 balance in our atmosphere, first by releasing CO_2 into the atmosphere and second by removing it as a sink for CO_2 .



Fig. 2.3 This machine cuts and macerates the peat and then sends it along the extended arm which deposits it in rows. The peat is cut into blocks by the discs as the equipment moves forward

2.4 Coal

Coal, the generic term applied to solid fossil fuels, ranges from lignite, which is basically a matured or modified peat, to meta-anthracite, which is more than 98% carbon. The qualities of different coals are classified in different ways either depending on the chemical composition, the heating value, or even the ash content and its fusion temperature. The International Classification of Hard Coals by Type (1956) has been widely accepted. The criteria used include volatile matter and calorific value as well as the swelling and caking properties of the coal. The Economic Commission for Europe has proposed its own classification and codification system. In North America, the common classification of coals is by the ASTM method. The rank classification system² is based on the application and commercial use of coal, namely, in combustion for electric power generation and in the preparation of coke for the metallurgical industry.

2.5 Analysis of Coal

The elemental analysis of coal, i.e., its C, H, O, N, S, and ash residue, may be important to a chemist who wishes to use coal as a chemical or source of carbon, but to an engineer who wants to burn the coal in a heat- or power-generating plant or a coking oven, other parameters are more important—most notably its heat of combustion, moisture level, volatile matter, carbon and sulfur content, as well as the ash. This is called the *proximate analysis* and it is determined as follows:

Moisture content. A sample of coal is ground to pass 20/60 mesh and weighed. It is dried in an oven at 110°C and reweighed. The loss in weight represents the moisture content of the coal.

²The ASTM (American Society for Testing and Materials) has provided detailed definitions (D121-85) and tests (D-388-88) for rank classification.

Table 2.2 Classification of coals by rank^a

Class/group	Fixed carbon, C (%)	Volatile matter, V (%)	Calorific value, ΔH (MJ/kg)
<i>Anthracite</i>			
Meta-anthracite	$98 \leq C$	$V < 2$	
Anthracite	$92 < C < 98$	$2 < V < 8$	
Semianthracite	$86 < C < 92$	$8 < V < 14$	
<i>Bituminous</i>			
Low-volatile bituminous	$78 < C < 86$	$14 < V < 22$	$32.6 < \Delta H$
Medium-volatile bituminous	$69 < C < 78$	$22 < V < 31$	$30.2 < \Delta H < 32.6$
High-volatile A bituminous	$C < 69$	$31 < V$	$26.7 < \Delta H < 30.2$
High-volatile B bituminous			$24.4 < \Delta H < 26.7$
High-volatile C bituminous ^b			
<i>Subbituminous</i>			
Subbituminous A coal			$24.4 < \Delta H < 26.7$
Subbituminous B coal			$22.1 < \Delta H < 24.4$
Subbituminous C coal			$19.3 < \Delta H < 22.1$
<i>Lignitic</i>			
Lignitic A			$14.7 < \Delta H < 19.3$
Lignite B			$\Delta H < 14.7$

^aBased on dry, moisture and mineral free (ash free basis)^bVariable values depending on the agglomerating properties of the coal when freed of volatile matter

Volatile content. The coal sample is heated in an inert atmosphere up to 900°C. The loss in weight varies with the temperature since some of the coal is decomposed into oils and tars which volatilize at various temperatures.

Ash content. A coal sample is heated in a muffle furnace at 900°C in the presence of air to combust the coal leaving the ash residue which is heated to constant weight. If the sample of coal is first freed of volatile matter, then the loss in weight represents the fixed carbon in the coal.

Heat content. This is determined in a bomb calorimeter where a dry sample of coal is burned in an excess of oxygen and the heat evolved is measured. This is often referred to as the caloric value or the heat content of the coal. This includes the combustion of the volatile and tar components as well as the fixed carbon and is therefore related to the actual heat-generating value of the coal. The heat of combustion of pure carbon is 32.8 MJ/kg.

2.6 ASTM Classification

An abbreviated version of the ASTM classification of coal by rank is shown in Table 2.2. The highest rank—meta-anthracite—contains the highest percentage of carbon and the lowest amount of volatile matter. The four classes are divided into 13 groups according to carbon content and heating value. Thus, in the bituminous class, there may be gas coals, coking coals, and steam coals. The proximate and ultimate analysis of typical coals is given in Table 2.3. It is possible to calculate the heat content of coal from its ultimate analysis. From the standard heats of formation of CO₂ (−393.5 kJ/mol), H₂O (−285.8 kJ/mol), and SO₂ (−296.8 kJ/mol), it is possible to derive the formula

$$Q = (1/100)[32.76C + 142.9(H - 0/8) + 9.3S] \quad (2.3)$$

Table 2.3 Proximate and ultimate analysis of five Canadian coals (moisture free)

	BC	NS	NS	Sask	Sask
<i>Proximate analysis</i>					
Volatile carbon	26.1	34.6	35.4	43.5	41.4
Fixed carbon	58.6	49.8	61.7	43.1	46.1
Ash	15.3	15.6	2.9	13.4	12.5
<i>Ultimate analysis</i>					
Carbon	74.4	66.0	84.7	61.1	66.1
Hydrogen	4.3	4.5	5.6	3.6	2.2
Sulfur	0.8	4.9	1.3	1.1	0.6
Nitrogen	1.2	1.4	1.3	1.0	1.3
Ash	15.3	15.6	2.8	13.4	12.5
Oxygen ^a	4.0	7.6	4.3	19.8	17.3
Calorific value ^b (MJ/kg)	28.6	23.8	33.9	17.3	18.3

^aDetermined by difference^bCoal sample as received

where Q is the exothermic heat evolved in the combustion of the coal in units of kJ/g and where C, H, O, and S represent the weight percentage of the element in the coal. Oxygen, which is assumed to be present as H_2O , is normally determined by difference. The assumption concerning oxygen is not too unreasonable since more than half of the oxygen in coal is normally present as OH. If the ash content is significant, then a correction must be made for it. The nitrogen content of coal is usually small and often ignored. Since $\Delta H_s^0(NO_2) = 33.2$ kJ/mol, the added term to the equation would be 2.4 N. Several other formulas have been proposed which are correct for some of the structural aspects of coal.

2.7 Ash

The combustion of coal results in the formation of an ash—the noncombustible component of coal—part of which is carried off with the combustion products as very fine particulate powder called *fly ash*. The heavy ash remaining in the combustion chamber is called *bottom ash* or *boiler slag*. The continuous mining process produces a coal containing about 28% ash. Coal used to generate steam usually has about 15% ash.

The ash is an undesirable component of the coal and is usually reduced during the cleaning process that coal is normally subjected to after being shipped from the mine. This cleaning process removes the rocks, clay, and minerals which invariably mix with the coal.

Some applications such as chain-grate stokers require a minimum of 7–10% ash to protect the metal parts of the furnace. One of the most important characteristics of the bottom ash is its melting point (or fusion temperature) which determines the ease with which it is removed from the furnace. The melting point of these inherent impurities in a coal can be represented by a three-component phase diagram of oxides such as Fe_2O_3 , Al_2O_3 , and SiO_2 or by minerals such as $Al_2O_3 \cdot 2SiO_2$ (clay), SiO_2 (quartz), and MgO . $Al_2O_3 \cdot 2SiO_2$ (feldspar) where lines join the common melting points of the various mixtures. The choice of the components depends on the coal and the impurities in the ash. A high fusion ash melts above $1,316^\circ C$ whereas a low fusion ash melts below $1,093^\circ C$. In some instances, iron oxide or sand (SiO_2) is added to the coal to increase the melting point of the ash so as to favor clinker formation which results in easy removal. Ash with a low fusion temperature can form an undesirable glassy coat of the furnace and grill. In the case where steam is generated, the deposition of this adherent glassy deposit on the fireside of the steel boiler tubes causes the ash to insulate the steel tubes from the heat and thus reduce the efficiency of steam generation.

Table 2.4 Trace element analysis of coal and its various combustion (ash) fractions^a (µg/g)

Element	Symbol	Coal	Bottom ash	Precipitated ^b ash	Bag ^c ash	Stack ^d ash
A. Barium	Ba	150	1,200	1,600	1,540	1,700
Calcium	Ca	4,000	49,000	34,000	21,000	23,000
Cesium	Cs	0.8	10	7	6	8
Magnesium	Mg	420	4,700	5,400	440	4,800
Potassium	K	1,220	16,000	13,000	11,000	13,300
Rubidium	Rb	23	75	160	90	90
Sodium	Na	500	7,100	4,600	3,400	4,000
Strontium	Sr.	120	1,200	1,200	1,000	1,100
B. Aluminum	Al	11,000	100,000	112,000	103,000	103,000
Beryllium	Be	0.9	—	8	10	10
Dysprosium	Dy	1.0	6	10	5	6
Europium	Eu	0.3	3	3	3	3
Hafnium	Hf	0.7	—	9	3	7
Lanthanum	La	5.0	70	60	50	50
Lutetium	Lu	0.2	1	2	0.6	2
Samarium	Sm	1.0	10	12	9	12
Tantalum	Ta	0.3	2	3	1	3
Terbium	Tb	0.3	4	4	0.8	3
Thorium	Th	1.4	20	15	10	12
Uranium	U	0.7	—	9	8	9
Ytterbium	Yb	0.4	4	5	3	4
C. Chromium	Cr	12	160	140	220	370
Cobalt	Co	3	20	40	35	60
Copper	Cu	6	20	84	142	170
Iron	Fe	6,300	140,000	90,000	70,000	70,000
Manganese	Mn	24	360	270	250	510
Nickel	Ni	4	70	35	200	340
Scandium	Sc	3	—	40	20	20
Silver	Ag	2	50	40	7	40
Titanium	Ti	560	5,000	6,500	6,000	6,000
Vanadium	V	20	130	180	240	240
D. Bromine	Br	14	Nil	6	30	12,000
Chlorine	Cl	1,200	Nil	Nil	800	900,000
Fluorine	F	80	—	100	400	33,000
Iodine	I	1	Nil	Nil	Nil	1,300
E. Antimony	Sb	0.5	3	6	11	30
Arsenic	As	12	35	90	230	300
Boron	B	16	—	220	2,000	2,600
Cadmium	Cd	0.3	3	2	4	20
Gallium	Ga	10	30	60	140	140
Lead	Pb	6	70	50	160	200
Mercury	Hg	0.4	0.2	0.5	0.5	500
Selenium	Sc	3	2	14	14	300
Zinc	Zn	27	—	330	380	1,100

^aValues rounded off—average of several coals^bElectrostatic precipitators 99 % efficient^cFilter bags

Table 2.5 Chemical analysis of fly ash (Saskatchewan)

Component	Content (%)	Component	Content (μg/g)
Na (as Na ₂ O)	3.02	As	<1
K (as K ₂ O)	0.48	B	291
Ca (as CaO)	10.87	Cd	2
Mg (as MgO)	1.09	Cr	20
Al (as Al ₂ O ₃)	21.02	Cu	26
Si (as SiO ₂)	57.64	Co	13
Fe (as Fe ₂ O ₃)	2.81	Ga	107
Ti (as TiO ₂)	0.76	Pb	36
P (as P ₂ O ₅)	0.09	Mn	292
S (as SO ₃)	<0.1	Hg	<0.5
		Mo	<50
		Ni	32
		Ag	2.9
		V	72
		Zn	48
		Se	<0.5

Fly ash is usually precipitated by a Cottrell electrostatic precipitator and/or collected in filter bags. The composition of the fly ash usually differs from the bottom ash due to thermal fractionation of the oxides. This is illustrated in Table 2.4 where the composition of the bottom ash is compared with various fractions of the fly ash which is classified into five groups:

- The alkali and alkaline earth metals
- Refractory metals
- Transition metals
- Halogens
- The volatile elements.

As of 2006, about 125 million tons of coal—combustion by-products, including fly ash—were produced in the USA each year, with about 43% of that amount used in commercial applications, according to the American Coal Ash Association website. As of 2005, US coal-fired power plants reported producing 71.1 million tons of fly ash, of which 29.1 million tons were reused in various applications.

In 1995, the US utilities produced 65 Mt/y of fly ash. The 21 coal-fired, thermal-generating plants in Canada produced 16.6 GW consuming 37.8 Mt of coal of which 10% was ash. The fly ash produced was 2.5 Mt. The composition of the fly ashes varies considerably. One particular fly ash from Saskatchewan (see Table 2.5) was recently tested for the extraction and recovery of gallium which can be converted to GaAs. In the near future, GaAs will be replacing silicon as the semiconductor of the electronic industry.

Another potential use of some fly ash is as a source of alumina (Al₂O₃), replacing bauxite which is being exhausted at an ever increasing rate.

2.8 Coal and Its Environment

Though coal is cheap and plentiful, it is a “dirty” fuel which contaminates our environment and contributes to the CO₂ imbalance in our atmosphere as well as oxides of nitrogen from the combustion process. The principal contaminant in coal is sulfur which burns to form sulfur dioxide (SO₂)

which is oxidized to sulfur trioxide (SO_3) in the atmosphere. In the commercial production of sulfuric acid, sulfur (S) is burned to form SO_2 :



The SO_2 can dissolve in water to form sulfurous acid (H_2SO_3). The SO_2 is also catalytically converted to SO_3 using V_2O_5 as a catalyst:



The SO_3 is then treated with water or sulfuric acid solution to form H_2SO_4 .

Similar reactions can occur in the atmosphere with the resulting formation of acid (H_2SO_4) rain which can fall considerable distances from the source. Thus, the acid rain falling in Norway and Sweden primarily originated from coal burning in the Ruhr valley and the UK. Similarly, the acid rain reaching Ontario comes primarily from the US iron and steel centers and industrial Ohio Valley though it is claimed that a large part of the SO_2 is also coming from the nickel smelters in Sudbury, Ontario. A joint US–Canadian study has determined the sources and recommended appropriate solutions to prevent the lakes from becoming too acidic to support aquatic life (fish).

Acid rain is not the only environmental contaminant from coal burning. The average concentration of mercury in coal is about $0.3 \mu\text{g/g}$ (i.e., less than 1 ppm). A 755-MW steam turbine-driven power station burns approximately 7,100 t of coal per day. This corresponds to about 2.5 kg/day of mercury being sent up the stack. With present North America estimates of coal consumption at about 10^{10} t/year, about 3,000 t of mercury is put into the environment. This is about four times the natural source.³

Coal also contains uranium and thorium and their radioactive decay products. Though as much as 98% of the fly ash is precipitated, the 2% remaining escapes up the stack. For a power plant burning 2×10^4 t/day if there is approximately 10% of fly ash, then approximately 40 t/day fly ash escapes up the stack. Measurements have shown that this contains about $500 \mu\text{Ci } ^{226}\text{Ra}$ per day. The fly ash behaves like ordinary smoke and its dispersion follows standard equations. If we assume a wind speed of 1 m/s, a stack of 120 m high will result in a maximum concentration at ground level at 400 m from the stack of $9 \times 10^{-14} \mu\text{Ci } ^{226}\text{Ra}$ per cm^3 air. The maximum permissible concentration (MPC) for ^{226}Ra in air is $10^{-11} \mu\text{Ci}/\text{cm}^3$. Thus, the concentration of ^{226}Ra is two orders of magnitude lower than the MPC, but since fly ash contains other radionuclides (^{230}U , ^{210}Pb , etc.), the long-term effects on those living close to or downwind from coal burning power plants must be carefully monitored.

The use of fly ash in concrete does not solve the disposal problem but only shifts it to another locale. If cement is composed of 30% fly ash, it has been estimated that the radon diffusing out of the concrete (porosity—5%) into a room ($10 \times 10 \times 4$ m) would be about $10^{-9} \mu\text{Ci}/\text{cm}^3$ —100 times lower than the MPC. However, with higher porosity, concrete and lower ventilation rates the margin of safety decreases, and it means that concrete containing fly ash should not be used in structures for habitation though it would be permissible for use in foundations, bridges, and roads.

A recent coal-fired power station located between Los Angeles and Las Vegas has shown that it is possible to burn coal with as much as 3.5% sulfur without contaminating the environment with SO_2 and NO_x . This is done using two existing technologies, coal gasification, and combined cycle generation, i.e., generating electricity simultaneously from turbines running on gas and steam. The plant pulverizes 1,000 t of coal per day, which is converted to synthesis gas by reaction with water and

³ The average concentration of mercury in rock is about $0.1 \mu\text{g/g}$ and since about 10^{10} tone of rock is weathered annually, it is estimated that about 800 tone of Hg is put into the atmosphere each year. This mercury is distributed uniformly around the earth and presents little environmental danger. It is the non-uniform or concentrated dumping of mercury that is dangerous and must be avoided.

oxygen. The ash and minerals fuse and are removed, whereas the H_2S is removed after the gas is cooled by generating steam. Water is then added to the clean gas to reduce NO_x formation upon combustion and more steam is generated to drive the turbines. The cost of power for a 600 MW plant is estimated to be 4–5 cents per kWh.

2.9 Fluidized Bed Combustion

The fluidized bed reactor is about 60 years old, but only in recent years has its application to coal combustion taken on commercial significance. The fluidized bed is the dispersion of a solid, usually in powder form, by a gas, under flow conditions such that the solid takes on the properties of a gas. Such reactors can be designed to operate continuously. Thermal conduction (heat transfer) in such systems can be high, and, as a result, in the case of coal and air, the combustion can occur at much lower temperatures than in the fixed bed system. Thus, the addition of limestone (CaCO_3) or dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) to the fluidized bed system can result in the reduction of oxides of sulfur and oxides of nitrogen.

This is accomplished by the reactions which can occur in the combustion bed:



The lower combustion temperature keeps the equilibrium for the NO_x reaction toward the $\text{O}_2 + \text{N}_2$. See Exercise 18:



This would mean that high sulfur coal could eventually be used in combustion processes without contaminating the environment.

Unfortunately, the effect of increased CO_2 levels in the atmosphere will still contribute to the greenhouse effect. Only the combustion of biomass, H_2 , or renewable energy sources does not enhance the greenhouse effect.

Recent work by the Coal Utilization Research Laboratory in Leatherhead, England, has shown that a slurry of 68% coal in water burned very well in a pressurized fluidized bed reactor. However, much more work remains to be done before such mixtures can be pumped through pipelines and burned directly in specially designed reactors.

2.10 Coke

Coke is produced when a bituminous coal is devolatilized by heating (in the absence of air) to temperatures ranging from 900°C to $1,200^\circ\text{C}$. As the temperature is slowly raised, physical and chemical changes take place. Adsorbed water is lost at temperatures up to 250°C . Some CO and CO_2 are liberated up to 300°C with some pyrogenic water. Above 350°C , the coal becomes plastic and begins to decompose between 500°C and 550°C to form gases and tars. The product at this point is called *semicoke* which still off-gases up to 700°C where the hot coke acts as a catalyst for the decomposition of the volatile products. Above 700°C , the coke is hardened and agglomerated.

The by-product consists of coke-oven gas (55–60% H₂, 20–30% CH₄, 5–8% CO, 2–3% heavy hydrocarbons, 3–5% N₂, and 1–3% CO₂, as well as traces of O₂) having a calorific value of about 17 MJ/m³.

Coal tar is also produced during the coking process. It contains over 300 substances which usually include 5–10% naphthalene, 4–6% phenanthrene, 1–2% carbazole, 0.5–1.5% anthracene, <0.5% phenol, ~1% cresol, and ~1% pyridene compounds and other aromatic hydrocarbons. About 50–60% of the tar consists of high-molecular-weight hydrocarbons.

The principal use of coke is in the blast furnace for steel making, the manufacture of calcium carbide (CaC₂), and other metallurgical processes. The annual world production of coke was about 5.28×10^8 t in 2009 and 4×10^8 t in 1992. The US production of coke has decreased in two times from 22 Mt (2000) to 11.2 Mt (2010) as steel production moved to Asia and the Far East. The coals used for coke production are usually a blend of two or more coals consisting of a high-volatile coal blended with low-volatile coals in a ratio of from 90:10 to 60:40. Such blends increase the rate of coking and produce a better product. The large-sized fused coke (≈ 75 mm) is used in blast furnaces whereas the smaller sized (≈ 20 mm), called *breeze*, is used in boiler-firing, iron ore sintering, electric smelting, and other applications where a purer grade of carbon is required.

The ash content of a metallurgical grade of coke must be less than 10% with a sulfur content <1.5% and a volatile component <1%. The calorific value of such coke is between 31.4 and 33.5 MJ/kg. One tonne of coal normally produces from 650 to 750 kg of coke.

The development of the coal gasification process allows for the removal of contaminants which make the coal a “dirty fuel.” If a new sink for CO₂ can be invented, the need to go fully nuclear could be delayed.

Exercises

1. Discuss the statement “Coal is a dirty fuel.”
2. What is the difference between a primary and secondary fuel?
3. What does charcoal and coke have in common? Compare their properties.
4. Describe a laboratory experiment by which wood could be converted into coal.
5. Explain why the proximate analysis of a coal is useful.
6. Explain why chloride salts should be washed from coal before it is used in combustion processes.
7. Wet coal can be air-dried at room temperature. How does this differ from the moisture content of a coal?
8. Explain why the components in an ash from a coal has a different relative concentration compared to the initial coal.
9. Two recent formulas have been proposed to evaluate the heat of combustion of coals:

$$-\Delta H_c(\text{kJ/g}) = 357.8C + 1135.7H + 59.4N + 111.9S - 84.5O \quad (2.9)$$

Lloyd and Bavenport

$$-\Delta H_c(\text{kJ/g}) = 351C + 116.1H + 62N + 104S - 110O \quad (2.10)$$

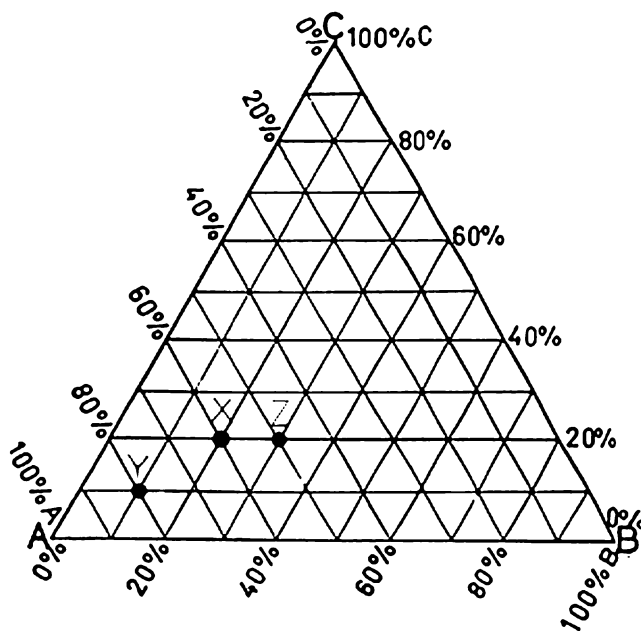
Boie’s formula

Compare the accuracy of these formulas with (2.3) using the data given in Table 2.6.

10. The three-component ternary phase diagram of a bottom ash is shown in Fig. 2.4. (a) How much sand (SiO₂) must be added to each ton of coal (type A) (point x) if the melting temperature of the ash is to be raised from 1,000°C (point x) to 1,200°C (point y)? The ash content of the coal is 10% and the oxides in the ash are graphed as weight %. (b) A second coal (type B) has 15% bottom ash

Table 2.6 Elemental analysis of some solid fuels

	wt. %					$-\Delta H_c$ (kJ/g) measured
	C	H	N	S	O	
<i>Oil shales</i>						
(A) Australia	84.6	11.5	0.56	0.30	3.0	43.7
(B) France	85.1	11.4	1.12	0.32	2.06	43.19
(C) Sweden	85.0	9.0	0.71	1.72	3.6	40.58
<i>Coal</i>						
(D) South Africa	84.3	5.9	2.5	0.70	6.6	35.60
(E) Athabasca tar	82.5	10.0	0.47	4.86	1.7	41.14
<i>Sand</i>						
(F) Syncrude oil						
(a)	87.8	10.1	0.34	0.12	1.6	42.54
(b)	79.2	5.1	1.30	1.30	13.1	32.36

**Fig. 2.4** A = SiO₂, B = Al₂O₃, C = Fe₂O₃. Ash at point X has a melting point of 1,000°C and at point Y the melting point is 1,200°C

with a composition as shown in Fig. 2.4 (point z). What would be the composition of the ash if a blend of the coals was burned A:B of 2:1?

- The proximate analysis of a coal can be determined automatically by thermal gravimetric analysis (TGA). This method involves the automatic recording of the mass of a coal sample while the temperature of the sample is programmed and the atmosphere of the sample controlled. This is illustrated in Fig. 2.5 where the mass of the sample is recorded at 25, 110, and 900°C under the inert atmosphere of nitrogen. Air or oxygen is then introduced while the sample is still at 900°C. (a) Describe the changes which occur at each temperature stage. (b) Determine the proximate analysis of the sample from the results in Fig. 2.5.

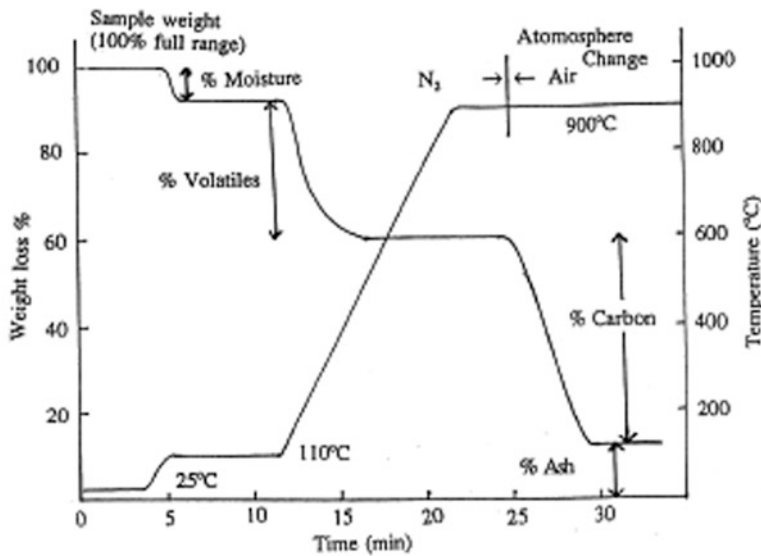


Fig. 2.5 Proximate analysis of a coal by TGA

12. Explain why the elements listed in Table 2.4 are classified into the five specific groups.
13. Explain why the calorific value of the volatile fraction of a coal (per unit mass) is normally greater than that of the fixed carbon of the coal.
14. What is coal gas?
15. Explain why coal is often used as a source of active carbon.
16. Why do some coals have a higher calorific value than pure carbon?
17. Explain why using peat for fuel has an adverse effect on the CO₂ balance of our atmosphere.
18. The equilibrium constant, K_p , for the reaction $N_2 + O_2 = 2NO$ as a function of temperature was determined experimentally to be $\log K_p = a - b/T$ where $a = 1.63$ and $b = 9.452$ (K). Calculate the equilibrium pressure of NO when air is heated to 800, 1,000, and 1,200 K.

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