

1

HISTORY AND TERMINOLOGY

1.1 INTRODUCTION

Coal is an organic sedimentary rock that contains varying amounts of carbon, hydrogen, nitrogen, oxygen, and sulfur as well as trace amounts of other elements, including mineral matter, as well as methane which is found within the pore systems of the coal (ASTM D121; Speight, 2013a). It is a solid, brittle, combustible, carbonaceous rock formed by the decomposition and alteration of vegetation by compaction, temperature, and pressure and varies in color from brown to black and is usually stratified as a *coal seam*. The source of the vegetative precursors to coal is a variety of ancient plant forms as well as ancient woody precursors. The plant precursors that eventually formed coal were deposited as dead and decaying carbonaceous materials that were compacted, hardened, chemically altered, and metamorphosed by the pressure (in some cases accompanied by heat) of overlying sediments over geologic time (Table 1.1). When the plants died, the biomass was deposited in anaerobic, aquatic environments where the low oxygen level prevented the reduction of the biomass and release of carbon dioxide.¹

¹The standard method (ASTM D121) forms the basis for coal standards in which the technical terms used in the standards for coal and coke are defined. In addition, the standards includes terms related to the sampling of coal and coke under conditions required for most commercial and technical purposes related to coal and coke as well as the bias and related statistical testing terms. Also included are (1) the description of coal, both visually in the field and microscopically in the laboratory, and (2) the chemical and physical analyses of coal and coke involved in the classification of coal.

TABLE 1.1 The Geologic Timescale

Era	Period	Epoch	Approximate Duration (Millions of Years)	Approximate Number of Years Ago (Millions of Years)
Cenozoic	Quaternary	Holocene	10,000 years ago to the present	
		Pleistocene	2	0.01
	Tertiary	Pliocene	11	2
		Miocene	12	13
		Oligocene	11	25
		Eocene	22	36
		Paleocene	71	58
Mesozoic	Cretaceous	71	65	
	Jurassic	54	136	
	Triassic	35	190	
Paleozoic	Permian	55	225	
	Carboniferous	65	280	
	Devonian	60	345	
	Silurian	20	405	
	Ordovician	75	425	
	Cambrian	100	500	
Precambrian		3380	600	

Evidence of the types of plants that contributed to carboniferous deposits can occasionally be found in the coal as fossil imprints as well as in the shale and sandstone sediments that overlie coal deposits.

Coal sediments (*coal beds*, *coal seams*) can range from fractions of an inch to hundreds of feet in thickness and are found in all geologic periods from Silurian through Quaternary, but the earliest commercially important coals are found in rocks of Mississippian age (Carboniferous in Europe). Coal is generally formed in either a fluvial environment or in a basin that is open to marine incursions and consists of more than 50% w/w (typically more than 70% v/v) carbonaceous material (organic material containing carbon, hydrogen, and other elements as well as inherent moisture, which is a moisture that occurs within the coal).

1.2 DEFINITIONS AND TERMINOLOGY

Simply and by definition, coal is an organic rock. In addition, coal is also defined as a black or dark-brown combustible mineral substance consisting of carbonized vegetable matter, used as a fuel.

It is customary (especially through this text) to use the word *coal* in the singular form but the word is, in reality, applicable to materials having a rather wide range of properties – this is similar to the use of the word *petroleum* (or *crude oil*), which encompassed a variety of materials from low-boiling (light) conventional crude oil to

the thicker viscous high-boiling heavy oil (Speight, 2014). In terms of coal, one sample might be a wet, easily crumbling brown material looking like partially decayed wood (Lignite) while another would be a very hard, glossy black, lustrous material (anthracite). In addition, the heating value (Chapter 8) of these samples would range from about 5000 to about 15,000 BTU/lb. Thus, the use of the word *coal* in this text implies either a single family member of a uniquely defined material as well as a family of natural-occurring family of organic rocks having both similarities and differences within the members of that family.

The name *coal* is thought to be derived from the Old English *col* that was a type of charcoal at the time. Generally, coal was not mined to any large extent during the early Middle Ages (prior to 1000 AD) but there are written records of coal being mined after 1000 AD. Moreover, coal is, in some areas, referred to as *sea-coal* as it is occasionally found washed up on beaches, especially those in the north east area of England. However, the rapidly expanding use of coal throughout the nineteenth century and the early part of the twentieth century has seen a phenomenal increase in coal use. This increased popularity has made it necessary to devise acceptable methods for coal analysis with the goal of correlating fuel composition and properties with behavior (Vorres, 1993; Speight, 2013a).

In the modern system of terminology, coal is subdivided into various types that are the result of geological processes pressure to the dead precursors over time and under suitable conditions (which are difficult to define), it is transformed successively into: (1) lignite, (2) sub-bituminous coal, (3) bituminous coal, and (4) anthracite (Speight, 2013a,b).

Lignite (sometimes referred to as *brown coal*) is the lowest rank of coal and used almost exclusively as fuel for electric power generation. *Sub-bituminous coal*, which has properties that range from similar properties of lignite to those of bituminous coal, is used primarily as fuel for steam-electric power generation (Speight, 2013b) and is an important source (through pyrolytic decomposition) of low-boiling aromatic hydrocarbons for the chemicals industry (Speight, 2013a). *Bituminous coal* is a dense black sedimentary rock that often has well-defined bands of bright and dull material; it is used primarily as fuel in steam-electric power generation, with substantial quantities used for heat and power applications in manufacturing and to make coke. *Anthracite* (black coal, hard coal, stone coal, blind coal, black diamond, and crow coal) is a hard, glossy black coal and is the most metamorphosed type of coal (the highest rank of the coal series) in which the carbon content is between 92.1% and 98%. Anthracite does not emit tar or other hydrocarbonaceous vapor when heated below the point of ignition – it ignites with difficulty and burns with a short, blue, and smokeless flame. Finally, although not an official definition in the sense of the four previous definitions, *steam coal* is the name given to a grade of coal that has properties between those of bituminous coal and anthracite and which was once widely used as a fuel for steam locomotives. With respect to this specialized use, it is sometimes known as *sea coal* in the United States.

Peat is considered by some observers/scientists/engineers to be a precursor of coal and to be a type of coal but the lack of any obvious resemblance to any other four coal types presented earlier tends to negate such inclusion into the coal sequence.

It was during the Industrial Revolution in the eighteenth and nineteenth century the demand for coal surged. The great improvement of the steam engine by James Watt, patented in 1769, was largely responsible for the growth in coal use. The history of coal mining and use is inextricably linked with that of the Industrial Revolution – iron and steel production, rail transportation, and steamships. Coal was also used to produce gas for gas lights in many cities, which was called *town gas*. This process of coal gasification witnessed the growth in gas lights across metropolitan areas at the beginning of the nineteenth century, particularly in London. The use of coal gas in street lighting was eventually replaced with the emergence of the modern electric era. With the development of electric power in the nineteenth century, the future of coal use became closely tied to electricity generation. The first practical coal-fired electric generating station, developed by Thomas Edison, went into operation in New York City in 1882, supplying electricity for household lights.

Steam coal, also known as thermal coal, is used in power stations to generate electricity (Speight, 2013a, 2013b). The earliest conventional coal-fired power stations used lump coal, which was burnt on a grate in boilers to raise steam. Currently, the coal is first milled to a fine powder, which increases the surface area and allows it to burn more quickly. In these pulverized coal (PC) combustion systems, the powdered coal is blown into the combustion chamber of a boiler where it is burnt at high temperature. The hot gases and heat energy produced converts water – in tubes lining the boiler – into steam.

As a result of the surge in coal use during the decades of the nineteenth and twentieth century, the use of coal increased and it was during this time that coal properties were not consistent and that certain types of coal were available – the adage *coal was not coal was not coal* gained wide acceptance and several types of coal existed. Thus, coal is now classified as various types and each type has distinctly different properties from the other types. In fact, each country has a varied system of nomenclature to describe the various types of coal and it is only through measurement of the analytical properties that any relationship can be made between the various names (Table 1.2). However, the terminology is not always standard and whether or not a standard terminology will ever be accepted remains to be seen. But understanding the analytical chemistry and analytical properties of coal is an essential aspect in international trade.

1.3 PRECURSORS OF COAL

Coal formation began during the Carboniferous Period, which is known as the *first coal age* and major coal deposits were formed in every geological period since the Upper Carboniferous Period, 270–350 million years ago (Table 1.1).

Layers of plant debris – such as lignin, were deposited in wet or swampy regions under conditions of limited exposure to air and complete decay as the debris accumulated, thereby resulting in the formation of peat. As the peat became buried by sediment, it was subjected to higher temperatures and pressures resulting in chemical and physical changes that, over time, formed coal. Cycles of plant debris accumulation and deposition were followed by diagenetic

TABLE 1.2 Variations in the English and German Systems of Coal Nomenclature

German Classification ^a	English (UK) Designation	Volatiles (% w/w)	Carbon (% w/w)	Hydrogen (% w/w)	Oxygen (% w/w)	Sulfur (% w/w)	Heat Content (Btu/lb) ^b
Braunkohle	Lignite (brown coal)	45–65	60–75	6.0–5.8	34–17	0.5–3.0	<12,250
Flammkohle	Flame coal	40–45	75–82	6.0–5.8	>9.8	ca. 1.0	<14,150
Gasflammkohle	Gas flame coal	35–40	82–85	5.8–5.6	9.8–7.3	ca. 1.0	<14,600
Gaskohle	Gas coal	28–35	85–87.5	5.6–5.0	7.3–4.5	ca. 1.0	<15,030
Fettkohle	Fat coal	19–28	87.5–89.5	5.0–4.5	4.5–3.2	ca. 1.0	<15,200
Esskohle	Forge coal	14–19	89.5–90.5	4.5–4.0	3.2–2.8	ca. 1.0	<15,200
Magerkohle	Non-baking coal	10–14	90.5–91.5	4.0–3.75	2.8–3.5	ca. 1.0	15,200
Anthrazit (Steinkohle)	Anthracite	7–12	>91.5	<3.75	<2.5	ca. 1.0	<15,175

^aWhile Braunkohle (brown coal) has the approximate properties of US lignite, the next six grades in the table (Flammkohle, Gasflammkohle, Gaskohle, Fettkohle, Esskohle, and Magerkohle) represent a step-by-step transition from sub-bituminous coal to bituminous coal (US classification, ASTM D388) while the last class (Anthrazit) is approximately equivalent to anthracite, but more inclusive (US anthracite has <6% volatiles).

^bRounded to the nearest 10 units; 1 kJ/kg = 0.4299 Btu/lb.

(i.e., biological) and tectonic (i.e., geological) actions, and, depending on the extent of temperature, time, and forces exerted, the different ranks of coal formed – this concept is not new and came into being during the latter part of the eighteenth century.

Indeed, in order to emphasize the complexity of coal and the complexity of the coal-forming processes, a note regarding some of the potential precursors is worthy of consideration. However, there is also the cautious assumption that there are little, if any, differences (natural selection notwithstanding) between the natural product chemicals known now and those in existence at the time of deposition of the coal beds. Perhaps a reasonable assumption, but it is fraught with uncertainties.

Thus, the makeup of the organic portion of plants consists of carbohydrates, lignin, and proteins, as well as other polymers (Table 1.3). Indeed, it is these higher polymers that are often considered as contributors to the organic substance of coal. But, of course, the relative amount of each of these constituents varies greatly with the particular species of plant; as well as the relative stage of growth of the plant. Furthermore, recognition of the fact that each of the aforementioned compound types is a very broad classification (and does not make any attempt to include individual molecular types) indicates the general complexity of the original plant debris. It is only this fact (probably more than any other single contribution) that determines the complexity of the final *coal molecule*.

Nevertheless, it is possible (in an attempt to simplify an already complex situation) to acknowledge some generalities; the lignin content of plants may fall within the range of 10–35% w/w while in woody material the lignin may be within the narrower range of 25–30% w/w (all of these approximations are given as percentages of the dry weight of the plant material). In fact, the protein content of grasses has been assigned to fall within the range of 15–20% w/w while woody materials contain little, if any, protein constituents; the cellulose (carbohydrate) content of grasses falls in the range of 20–55% w/w (all of these approximate ranges are given as percentages of the dry weight of the plant material).

TABLE 1.3 Examples of the Types of Macromolecules in Plants

Natural Polymer ^a	Plant Tissue	Structures Present
Carbohydrates	Cell	Mono- and polysaccharides
Cellulose	Wood, other tissues	Mono- and polysaccharides
Cutin	Leafs, stems	Hydroxy acids
Hemicellulose	Wood, other tissues	Mono- and polysaccharides
Lignin	Wood	Alkyl phenols
Lipids	Seeds	Fats, steroids, phospholipids
Phospholipids	Seeds	Glycerol, fatty acids
Proteins	Various	Amino acids, polypeptides
Sporopollenin	Spores, pollen	Polymeric carotenoids
Waxes	Cuticles, surface structure	Long-chain hydrocarbons

^aListed in alphabetical order.

Thus, from these broad generalities alone, plant debris is complex and the original plant debris that formed the precursors to coal may have been even more complex (depending on location and the circumstances leading to the deposition. Giving consideration to (1) the different chemical precursors of coal (as presented subsequently), (2) the varied geological environment, (3) the maturation conditions, and (4) the variation of coal analysis within a seam, the rationale for an average structure of coal defeats itself. The complexity of the original precursors includes: various carbohydrates and polysaccharides, a variety of proteins, vegetable oils, fats, waxes (including lower molecular weight hydrocarbons), as well as plant resins, tannins, alkaloids, porphyrins, and the inorganic mineral) constituents of plants. On this note, it is necessary to point out that mineral matter in coal is often classified as inherent mineral matter or as extraneous mineral matter (Chapter 4). The inherent mineral matter is the inorganic material that originated as part of the plant material that formed the organic debris in the source bed. On the other hand, extraneous mineral matter is the inorganic material that was brought into the coal-forming deposit by various means from external sources.

1.4 COAL-FORMING PROCESSES

The *coalification process* (*coal-forming process*) is, simply defined, the progressive change in the plant debris as it becomes transformed from peat to lignite and then through the higher ranks of coal to anthracite (Francis, 1961; Speight, 2013a). In the peat swamp, as dead plant matter accumulates, aerobic bacteria rapidly oxidize cellulose and other components producing methane (CH_4), carbon dioxide and ammonia (from the nitrogen-containing components). The resulting decomposed material compacts about 50% and is largely composed of lignin, a complex, 3-dimensional polymer rich in aromatic (benzene) rings. These bacteria quickly use up the available oxygen and die ending the first stage of the process. Anaerobic bacteria take over the decomposition process and they produce acids as metabolic waste products. When the pH of the medium is sufficient ($\text{pH} \approx 4$), these bacteria die. The product at this stage is a gel-like material called *Gytta* (sometime referred to as *proto-coal*). When the *Gytta* is buried to a depth of 2000–3000 ft, the temperature is approximately 100°C (212°F) at which water and other volatiles are driven off. Furthermore, as part of the coalification process, it is usually *assumed* that a regular (or at least a near-regular) progression exists from lignite to anthracite and that the progression is consecutive (Figure 1.1) but concurrency (i.e., simultaneous formation of different coal types) must also be considered a possibility and may even be the norm under certain conditions and in a variety of locales. In summary, *consecutiveness* is not proven, although it is often claimed.

Whereas the degree of coalification generally determines the rank of the coal, the process is not a series of regular, or straightforward, chemical changes. Indeed, complexity is the norm insofar as the metamorphosis of the plant debris relies not only on geological time but also on other physical factors, such as temperature and pressure. Thus, the occurrence of a multitude of different and complex, chemical reactions

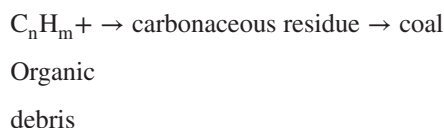
Component	-----Composition, % w/w-----			-----Physical effects---		-----Chemical effects-----	
	Carbon	Hydrogen	Oxygen	Increasing pressure	Increasing temperature	Oxygen elimination	Increasing aromatization
Wood	48-50	6-8	42-46	↓	↓	↓	↓
Peat	48-50	49-52	33-35				
Lignite	68-72	5-6	24-26				
Subbituminous coal	74-76	5-6	18-22				
Bituminous coal	84-86	5-6	8-12				
Anthracite	92-95	3-4	1-3				

*Some observers have raised the possibility that the process is not sequential but that each coal is a by-product of the process.

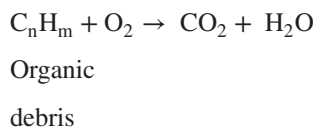
Figure 1.1 Schematic representation of the coalification process.

(no matter how simple they appear on paper or how simply they occur in laboratory simulations) is inherent in the coalification process.

Thus, the theories about the formation of coal require that the original plant debris eliminate hydrogen and oxygen either occasionally or continuously under the prevailing conditions, ultimately leading to a product containing approximately 90% carbon (i.e., anthracite). In order for this maturation to proceed, chemical principles require that oxidation reactions be completely inhibited; that is, the chemistry proceeds according to carbonaceous residue coal organic debris but not according to:



Rather than:



The formation of coal under the slow conditions generally referred to as geological time may, nevertheless, be regarded as occurring in the absence of oxygen, thereby promoting the formation of highly carbonaceous molecules through losses of oxygen and hydrogen from the original organic molecules (Figure 1.1).

1.5 HETEROATOMS IN COAL

The type of analytical characterization that is performed in order to determine the properties of coal are used to predict its technological behavior. Typically, there are

two characteristics that influence the use of coal: its composition and its rank. Coal composition is in turn represented by: (1) type (nature of the organic components) and (2) grade, which is determined by the amount of mineral matter in the coal (or, in other words, by the dilution of the organic matrix by mineral matter).

At this point, it is pertinent to discuss the heteroatom species in coal (the non-hydrocarbon species in coal, i.e., nitrogen-, oxygen-, and sulfur-containing species) insofar as these species can arise from the plant precursors as well as from external sources such as might occur during the maturation process. These species (presented subsequently in alphabetical order rather than by effects) are also influential in determining the extent of atmospheric emissions that often have an adverse effect (and draw adverse comments) on the use of coal as an energy source (Speight, 2013a,b).

1.5.1 Nitrogen

Nitrogen is typically found in coal in the 0.5–1.5% range by weight. As with oxygen, a number of different types of nitrogen-C containing compounds have been isolated from coal-derived liquids (Speight, 2013a). Examples of these include aniline derivatives, pyridine derivatives, quinoline derivatives, iso-quinoline derivatives, carbazole derivatives, and indole derivatives, which carry alkyl and aryl substituents (Schweighardt et al., 1977; Palmer et al., 1992; Baxby et al., 1994; Palmer et al., 1994).

Nitrogen has been the least studied of the principal elements in coal but, except in rare cases, the nitrogen present in coal is bound into the organic carbonaceous part. Fragmentary information is available concerning the nitrogen-containing compounds present in coal, but they do appear to be stable and are thought to be primarily heterocyclic. The original source of nitrogen in coal may have been both plant and animal protein. Plant alkaloids, chlorophyll, and other porphyrins contain nitrogen in cyclic structures stable enough to have withstood changes during the coalification process and thus to have contributed to the nitrogen content of coal. The amount of nitrogen in coal appears to be only weakly correlated with coal rank (Davidson, 1994).

A wide variety of aromatic nitrogen compounds is found in the coals; no evidence of saturated amines was found. Pyrrole derivatives, pyridine derivatives, pyridine derivatives, and aromatic amine derivatives are found in coal; of these, pyrrole structures are the most prevalent. Pyridine nitrogen is prevalent in all except low-rank coals – the low pyridine content in low-rank (high-oxygen) coals correlates with a high content of pyridone derivatives. This observation suggests that, with increasing maturation of coal, the pyridone loses its oxygen and is transformed into pyridine.

The emissions of nitrogen oxides from coal combustion may bear a relationship to the nitrogen types in the coal, although much the nitrogen may remain in the char (Hindmarsh et al., 1994; Wang et al., 1994), (analogous to nitrogen remaining in petroleum coke (Speight, 2014)). However, the influence of coal properties on nitrogen

oxide (NO_x) emission levels is not well defined. It is clear that several factors influence NO_x formation, the roles and interaction of such factors as nitrogen partitioning (between the volatiles and chars), nitrogen functionality, coal rank, coal nitrogen content and volatile content in the formation of NO_x . However, it has been demonstrated repeatedly that the selection of coals on the basis of coal nitrogen content is an inappropriate and ineffective means of restricting NO_x emissions. The selection of coals should be the sole preserve of the generating utility that has the best understanding of the influence of their combustion plant design and operation on the level of NO_x emissions. Furthermore, the continued use of coal nitrogen as a controlling specification for coal supplies to an expanding utility market will not only fail to limit NO_x emission levels but will also result in the limitation on the development of new coal resources.

Thus, it can be assumed that the amount of nitrogen in the coal and the way in which it is bound into the coal structure affects the amount and distribution of nitrogen oxide emissions. The proportion of the coal sulfur volatilized on partial gasification could be related to the coal substance gasified, using one equation for all the coals. For coal nitrogen, however, a single equation can describe the data from both pyrolysis and partial gasification (Middleton et al., 1997).

The suggestion that the nitrogen functionality exerts an indirect effect, possibly related to rank, is a reasonable explanation but has not been fully proven by application of analytical techniques.

1.5.2 Oxygen

The inclusion of oxygen in both the organic and inorganic portions of coal presumably arises from a variety of plant sources, although there is also the strong possibility that oxygen inclusion occurs during the maturation by contact of the precursors with aerial oxygen and with the oxygenated waters that percolate through the detrital deposits. The oxygen content of coal ranges from a high of 20–30% by weight for a lignite to a low of around 1.5–2.5% by weight for an anthracite.

In the organic portion of coal, oxygen is present in hydroxyl ($-\text{OH}$), usually phenol groups, carboxyl groups (CO_2H), methoxyl groups ($-\text{OCH}_3$), and carbonyl groups ($=\text{C}=\text{O}$). In low-rank coal, the hydroxyl oxygen averages about 6–9%, while high-rank coals contain less than one percent. The percentages of oxygen in carbonyl, methoxyl, and carboxyl groups average from a few percent in low rank and brown coal to almost no measurable value in high-rank coal. The inorganic materials in coal that contain oxygen are the various forms of moisture, silicates, carbonates, oxides, and sulfates. The silicates are primarily aluminum silicates found in the shale-like portions. Most of the carbonate is calcium carbonate (CaCO_3), the oxides are mainly iron oxides (FeO and Fe_2O_3), and the sulfates are calcium and iron (CaSO_4 and FeSO_4).

The oxygen content of a given coal is normally determined by difference:

$$\% \text{ oxygen} = 100 - (\% \text{C} + \% \text{H} + \% \text{N} + \% \text{S} + \% \text{ash}) \text{ (all calculated on a dry basis)}$$

1.5.3 Sulfur

Sulfur is an important consideration in coal utilization and, hence, there is a considerable amount of published work relating to the development of methods to improve the efficiency of the techniques as well as improve the accuracy and precision of the sulfur determination. The sulfur content of coal is quite variable, typically in the range of 0.5–5.0% w/w – this includes both inorganic and organic sulfur. Inorganic sulfur is present mainly in the form of iron pyrite. Sulfur contained in the precursor proteins and amino acids may be a source of sulfur in coal but hydrogen sulfide and pyrite are quite capable of reacting with the coal precursors to produce sulfur constituents as found in coal (Baruah and Upreti, 1994; Speight, 2013a).

The inclusion of sulfur in coal is largely unknown and has been presumed to arise from the sulfur-containing plant constituents such as protein and oils although there are other means by which sulfur might be included into the coal (Casagrande, 1987; Palmer et al., 1992; 1994). The predominant mode of sulfur incorporation into coal varies with the nature of the coal.

Sulfur is present in coal in three forms, either as (1) organically bound sulfur, (2) inorganic sulfur (pyrite or marcasite, FeS_2), and (3) inorganic sulfates (ASTM D2492; ISO 157) (Wawrzynkiewicz and Sablik, 2002; Speight, 2013a,b and references cited therein). The amount of organic sulfur is usually <3% w/w of the coal, although exceptionally high amounts of sulfur (up to 11%) have been recorded. Sulfates (mainly calcium sulfate, CaSO_4 , and iron sulfate, FeSO_4) rarely exceed 0.1% except in highly weathered or oxidized samples of coal. Pyrite and marcasite (the two common crystal forms of FeS_2) are difficult to distinguish from one another and are often (incorrectly) designated simply as pyrite.

Free sulfur as such does not occur in coal to any significant extent. The amount of the sulfur-containing materials in coal varies considerably, especially for coals from different seams. In addition, pyrite is not uniformly distributed in coal and can occur as layers or slabs or may be disseminated throughout the organic material as very fine crystals. The content of sulfates, mainly gypsum ($\text{CaSO}_4 \cdot 7\text{H}_2\text{O}$) and ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), rarely exceeds trace amounts (i.e., <0.1%) except in highly weathered or oxidized coals.

When coal is mined, fresh sulfur-bearing minerals in the coal and rocks are exposed to air and water. The resulting chemical reactions produce sulfuric acid and precipitates. The acid water flowing from coal mines, if not treated, can damage life forms in the receiving streams. The iron and sulfate precipitates often discolor stream beds with yellow and orange stains. In a similar manner, when burned, sulfur escaping in the flue gases can combine with water in the atmosphere to produce acidic precipitation (*acid rain*). For the same reasons, burning high-sulfur coal can be corrosive to the metal equipment used in a power plant.

Organic sulfur can represent >50% of the total sulfur found in some coals can arise from the interaction of peat-type precursors with hydrogen sulfide to produce organic sulfur (Casagrande, 1987). On the other hand, there are several lines of evidence (Chou, 1990), which lead to the conclusion that sulfur in plant material is the

principal source of sulfur in low-sulfur coal whereas in medium- and high-sulfur coals, seawater is also a predominant source of sulfur (Chou, 1990).

The most abundant sulfur functional types found in coal are believed to be derivatives of the thiophene ring system. Other important sulfur types are aryl sulfides, alkyl sulfides, and acyclic sulfides. It should, however, be kept in mind that most of the information on sulfur compounds has been obtained by the analysis of small molecules obtained upon the decomposition of the coal matrix and the more drastic degradation techniques are very likely to alter the chemical structure of the sulfur compounds originally present in the coal matrix.

1.5.4 Other Elements

A variety of other elements also occur in coal but their presence and amounts are strictly dependent upon the coal source (Speight, 2013a).

Chlorine occurs in coal (and is believed to be a factor not only in fouling problems but also in corrosion problems. The chlorine content of coal is normally low, usually only a few tenths of a percent or less. It occurs predominantly as sodium, potassium, and calcium chlorides, with magnesium and iron chlorides present in some coals. There is evidence that chlorine may also be combined with the organic matter in coal.

Mercury has been identified as a very dangerous environmental contaminant, largely by reason of the process of concentration in the food chain. Thus, the presence of mercury in coal is an extremely sensitive issue. The possible emission of mercury that may be found in coal is an environmental concern. In addition, mercury can go through a series of chemical transformations that convert elemental mercury (itself a toxin) to a highly toxic form (Tewalt et al., 2001). The most toxic form of mercury is methyl-mercury, an organic form created by a complex bacterial conversion of inorganic mercury, which enters and accumulates within the food chain, particularly in aquatic organisms such as fish and birds, causing various diseases in animals and humans. The creation of methyl-mercury in ecosystems is a function of mercury availability, bacterial population, nutrient load, acidity and oxidizing conditions, sediment load, and sedimentation rates. Methyl-mercury in coal is known to be associated with iron (Fe), copper (Cu), and sulfur (S). In particular, it is often associated with sulfur in both pyrite and marcasite (FeS_2); where it is found in the form of a solid solution and in association with the mineral sphalerite (ZnS). In the coal combustion process, mercury is released mainly as elemental mercury, since the thermodynamic equilibrium favors this state at coal combustion temperatures. In the combustion zone, mercury is vaporized from the coal as elemental mercury (Hg). As the flue gas temperature decreases, elemental mercury is oxidized to form mercuric oxide (HgO), as well as mercuric chloride (HgCl_2), and mercurous chloride (Hg_2Cl_2), subject to the presence of chlorine in the system.

Most coals contain small amounts of *mineral carbonates* made up primarily of calcium carbonate and to a lesser extent ferrous and other metal carbonates. Some coals contain a comparatively large amount of the inorganic carbonates and the determination of carbon dioxide content is required in estimating the mineral matter content of

these high-carbonate coals. Indeed, it is necessary to have a knowledge of the carbonate content of coal in order to correct the carbon figure and since, without resorting to very elaborate analyses, it would be impossible to express the carbonate content as definite quantities of calcium carbonate, magnesium carbonate, etc., it is customary, and sufficient for all analytical purposes, to express it simply in terms of carbon dioxide.

Arsenic and *selenium* occur in coal to the extent of several parts per million and, on combustion of the coal a varying quantity of these elements are released or retained in the ash, depending largely on the conditions under which the combustion takes place and on the nature of the coal ash.

1.6 PHYSICAL STRUCTURE

The behavior of coal during processing is determined by its physicochemical composition and structure. The examination of the physical and chemical structure of coal has been hampered by the inability to find techniques that measure any meaningful properties of such large complex structures. Most attacks on the problem have been by means of breaking down the structure into smaller, more tractable pieces, examining these and making inferences about the original structure. With many types of coal, the severity of the treatment needed to rupture the molecules raises doubts as to the validity of the method. It is claimed with some justification (but still with considerable doubt) that brown coal, which is geologically younger, may bear more resemblance to the molecules of classical organic chemistry.

Structurally, coal is a complex system in which organic material dominates, typically representing 85–95% w/w of a dry coal (Speight, 2013a). These organic materials occur in various different petrographic types (macerals), which reflect the nature of the precursor plant material. Various inorganic materials, particularly aluminosilicates and pyrites (especially in high-sulfur coals), comprise 5–15% of the coal. A third structural element, and perhaps its most distinctive feature when compared to other solid fossil fuel sources like petroleum and oil shale, is an extensive network of pores. These pores provides coal a high surface area ($>100\text{ m}^2/\text{g}$) for bituminous coal, sub-bituminous coal, and lignite and an appreciable volume of pore space, allowing access to a significant fraction of the organic material.

Briefly, the maceral *vitrinite* is the most common component of coal and is derived from the same biogenic precursors as coals, namely land plants and humic peats. Vitrinite forms during diagenesis by the thermal alteration of lignin and cellulose in plant cell walls. It is therefore common in sedimentary rocks that are rich in organic matter, such as shale formations and marls with a terrigenous origin. In fact, vitrinite reflectance (Chapter 7) to establish rank of bituminous coals has the following advantages: (1) steady increase of vitrinite reflectance with rank, (2) independence from composition or homogeneity of the reflectance measurement, (3) independence of sample size, and (4) minimal effects of oxidation. Carbonate minerals, evaporite minerals, and sandstone minerals have very low vitrinite content.

There is a much more important aspect of coal composition that must be considered. For example, chemical constituents represent the molecular structure of coal but the form in which these chemical constituents eventually become incorporated into the coal matrix must also be given due consideration. Thus, in terms of the chemical origin of coal, certain plant tissues contain chemical constituents of markedly similar molecular structures but there must be some attempt to recognize that incorporation into the coal precursor of a particular plant tissue (or a large part of the tissue of that particular plant) can also occur. While the maturation process may cause chemical changes to the individual chemical constituents of the tissue, this same maturation process(es) may also cause physical changes to the tissue (in to) that may cause it to appear as a recognizable entity in the coal (ASTM D2793; ASTM D2796; ASTM D2797; ASTM D2799).

There has, however, been a tendency to depart from these types of investigations over the last four decades and to concentrate on the so-called molecular structure of coal in the hope that elucidation of this elusive entity will assist in the understanding of the technological behavior of coal. Fortunately, there has been a surge of interest within the last decade in the physical macrostructure of coal with special emphasis on the relation of the petrographic properties of coal to its technological behavior. Indeed, equating technological behavior of coal (or, for that matter, any feedstock) with a definite entity should warrant far more attention than the attempts to equate technological behavior with a hypothetical (albeit, unknown) molecular structure.

1.7 PETROLOGY AND PETROGRAPHY

1.7.1 Petrology

Coal petrology, which dates back to the beginning of the twentieth century, is the fundamental discipline that deals with the origin, occurrence, physical and chemical properties, and utilization of coal (Bustin et al., 1983; Taylor et al., 1998; Belkin et al., 2009). Thus, coal petrology is the study of the organic and inorganic constituents of coal and their transformation via metamorphism. Coal petrology is applied to the studies of the depositional environments of coals, correlation of coals for geological studies, and the investigation of coals for their industrial utilization. Traditionally, the latter has been dominated by the use of coal petrology in the optimization of coal blends for the production of metallurgical coke, but can also include the use of petrology in evaluating coals for beneficiation (coal preparation for downstream utilization) and combustion. Therefore, coal petrology has a strong influence on the types of analytical methods that are applied to coal.

In addition to its chemical properties, the efficient use of a coal also requires a knowledge of its physical properties, such as its density (which is dependent on a combination of rank and mineral matter content), hardness, and grindability (both related to coal composition and rank). Other properties include its abrasion index (derived mainly from coarse-grained quartz) and the particle size distribution. Float-sink testing may also be included with the analysis process. This involves

separating the (crushed) coal into different density fractions as a basis for assessing its response to coal preparation processes. Float-sink techniques may also be used to provide a coal sample that represents the expected end product of a preparation plant, in order to assess the quality of the coal that will actually be sold or used rather than the in-situ or run-of-mine material represented by an untreated (raw) coal sample.

Another factor that must be taken into account in determining coal quality is the degree of coal oxidation. Oxidation may affect both the organic and inorganic components and may lead to deterioration of the coal properties. Another possible consequence of coal oxidation is the spontaneous combustion (Misra and Singh, 1994; Lyman and Volkmer, 2001; Beamish et al., 2001; Beamish, 2005). The propensity to oxidation is mainly determined by the rank of the coal in conjunction with the maceral and mineral (e.g., pyrite) content. Low-rank coals are particularly prone to spontaneous combustion. Other factors, such as the access of air to coal stockpiles, may need to be controlled in order to reduce the risk of spontaneous combustion. Petrographic examination may help to identify coals that have become oxidized.

1.7.2 Petrography

Coal petrography (a branch of coal petrology) specifically deals with the analysis of the maceral composition and rank of coal and therefore plays an essential role in predicting coal behavior and should be an essential part of any coal analysis and testing program (Esterle and Ferm, 1986; Unsworth et al., 1989; Esterle et al., 1994). The fundamentals of organic petrography, maceral nomenclature, classification of coal components, and analytical procedures, have been well established by the International Committee for Coal and Organic Petrology (ICCP, 1963, 1971a,b, 1975, 1993, 1998, 2001; Sýkorová et al., 2005).

Coal is a rock formed by geological processes and is composed of a number of distinct organic entities called macerals and lesser amounts of inorganic substances (mineral matter). The essence of the petrographic approach to the study of coal composition is the idea that coal is composed macerals, which each have a distinct set of physical and chemical properties that control the behavior of coal. The organic units, composing the coal mass (macerals), are the descriptive equivalent of the inorganic units composing rock masses (minerals) and to which pathologists are accustomed to giving distinctive names (Stopes, 1919, 1935).

One of the most important aspects of coal petrography is an understanding of the effects that the petrographic constituents have on the behavior of coal during processing, in particular the processing sequences that are designed to produce gaseous and liquid fuels. While some data are available, a considerable amount of investigative work still remains to be carried out.

In keeping with the theme of this present text, a brief discussion of the influence of the petrographic composition of coal in relation to the technological properties of coal is warranted, although more specific reference will, as the data allows, be made to the various processes throughout the text.

Petrographically and chemically, coal is a complex material and it is often convenient to describe coal in several ways. The most common way, of course, is in terms of the elemental (ultimate) composition (Chapter 6) where coal may actually be classified on the basis of the general formula: $C_nH_yN_xO_zS_z$ where n is the number of carbon atoms, y is the number of hydrogen atoms, x is the number of nitrogen atoms, y is the number of oxygen atoms, and z is the number of sulfur atoms. Indeed, one of the most important outcomes from the petrographic analysis of coal is the understanding of the effect that the petrographic composition has on the technological properties. In fact, the behavior of the petrographic constituents during coal utilization is now being documented with some regularity.

1.7.2.1 Lithotypes Coal lithotypes represent the macrostructure of coal and are, in fact, descriptive of the coal. A piece of coal will usually exhibit a definite banded appearance due to the accumulation of different types of plant debris during the formation of the organic sediment (Smith and Smoot, 1990; Muller et al., 1990). This may be due to not only the deposition of a variety of different organic compounds that are believed to be the precursors of coal (Chapter 1) but also the accumulation of different parts of the plant (as well as different plants, e.g., trees, ferns, mosses, etc.) during the formation of the sediment (Murchison, 1991; Puttmann et al., 1991; Speight, 2013a and references cited therein). Each compound type, tissue type, or plant type then progresses through the various maturation stages that eventually lead to coal.

1.7.2.2 Macerals The organic constituents in coal and non-coal organic-rich rocks are termed macerals (in the broader sense, and particularly for dispersed organic material, the term kerogen is also used). Macerals are the (optical) microscopically identifiable constituents in coal, somewhat analogous to minerals in an inorganic rock (Stopes, 1935). By convention, maceral names always have an *-inite* suffix. Thus, macerals are generally divided into the vitrinite (or *huminite* in lower rank coals), inertinite, and liptinite groups (Speight, 2013a and references cited therein).

Huminite/vitrinite macerals are derived from humic substances, the alteration products of lignin and cellulose. Huminite refers to macerals in lignite and subbituminous rank (see below) coals (Sýkorová et al., 2005), and vitrinite to maceral of bituminous and anthracitic ranks. The distinction with vitrinite is based on the division of the maceral group into three subgroups: (1) telovitrinite, (2) detrovitrinite, and (3) gelovitrinite, which are each further subdivided into two macerals. The dominant parameter for these newly ordered and in part newly defined subgroups is the degree of destruction (degradation), whereas the macerals can be further distinguished by their morphological characteristics and their degree of gelification (ICCP, 1998).

Inertinite macerals are, to a certain degree, derived from the same starting materials as the huminite/vitrinite macerals (ICCP, 2001). In contrast to the latter maceral group, the inertinites have been oxidized, with fire thought to be the primary cause of their formation. The macerals fusinite and semifusinite are the products of such oxidation and, in most coals, are the most abundant inertinite macerals. Secretinite

is a product of the oxidation of plant secretions. Macrinite is problematical, in part, because it has been confused with what is now recognized as secretinite. Multiple pathways have been proposed for macrinite (ICCP, 2001). Funginite, with a fungus origin, is grouped with inertinites derived from plant cells by ICCP (2001). Fungi, however, are not plants, but encompass two distinct eukaryote kingdoms, *Fungi* and *Protoctista*-kingdom slime molds. Micrinite is thought to have originated as a secondary maceral from the breakdown of hydrogen-rich liptinite.

The method of preparation of the samples for microscopic examination may vary according to the methods favored by a particular laboratory. However, there are standard methods described for the examination of coal samples by microscopic techniques. For example, a crushed coal sample will be formed into a briquette with a cold-setting epoxy resin. When the resin is set, the surface is ground using water-resistant, adhesive-backed silicon carbide papers of grit size numbers 240, 320, 400, and 600. Then, polishing is carried out using aluminum oxide powders of specified sizes followed by treatment with a nap-free cloth of cotton and silk and chemo-textile material backed with water-resistant adhesive. There are, of course, suggested sequences for this procedure to produce a surface suitable for microscopic examination.

1.7.3 Microlithotypes

Microlithotypes are the microscopic analogs of the coal lithotypes and, hence, represent a part of the fine microstructure of coal(s). The microlithotypes are, in fact, associations of coal macerals with the proviso that the “associations” should occur within an arbitrary minimum bandwidth ($50\ \mu$, $50 \times 10\text{ mm}$). The composition of the microlithotypes in coal(s) appears to be limited by the types of organic matter present in the original coal precursor.

In more general terms, the microlithotype vitrite is composed predominantly of vitrinite and is a common constituent of humic coals (Table 1.4), especially vitrains. On the other hand, clarite (which also contains exinite in addition to vitrinite) is more commonly found as thick bands in clarains but does not occur in many other coals; clarite may also contain inorganic impurities such as clay, pyrite, and carbonates. Fusite consists predominantly of inertinite and also contains impurities such as kaolin (as well as other clays), pyrite, and carbonate minerals. Durite is composed predominantly of exinite and inertinite and has actually been classified as existing in two forms: durite and durite I; the former (durite E) indicates that the durite is relatively rich in exinite whereas the latter (durite I) indicates the durite to be relatively rich in inertinite.

1.7.4 Inorganic Constituents

Inorganic elements can be included in coal as minerals or as elements incorporated in the organic structure (Chapter 4). The most common example of the latter is the incorporation of sulfur into macerals as organic sulfur. Minerals can be incorporated into the peat during deposition, result from epigenetic processes, or be the consequence

TABLE 1.4 United States Bureau of Mines System and International System of Coal Nomenclature

System	Coal Type	Characteristics
Bureau of Mines	Banded coal	Anthraxylon ^a present Opaque matter present
	Bright coal	<20% w/w opaque matter
	Semi-splint coal	20–30% w/w opaque
	Splint coal	>30% w/w opaque matter
	Non-banded coal	Anthraxylon absent
	Cannel coal	Spore debris present
	Boghead coal	Algal debris present
International System	Humic (banded)	Low hydrogen content
	Clarain	Striated, glossy
	Durain	Nonstriated
	Fusain	Charcoal-like
	Vitrain	Black, vitreous
	Sapropelic	High hydrogen content
	Cannel	Liptobiolithic (non-banded)
	Boghead	Liptobiolithic (non-banded)

^aThe glossy jet-black constituent of banded bituminous coal.

of metamorphic changes within the coal. Clay minerals, quartz, calcite, siderite, and pyrite/marcasite are the most common minerals in coals. All naturally occurring elements have been found in coal.

Coal petrography techniques, in addition to determining maceral/microlithotype composition, also includes microscopic measurements of certain parameters that are indicators of the degree of coalification (metamorphism) termed coal rank. The coal rank series, from the lowest to the highest degree of metamorphism, is as follows: lignite, subbituminous, high volatile bituminous, medium volatile bituminous, low volatile bituminous, semi-anthracite, anthracite, and meta-anthracite (Table 1.5).

1.7.5 Petrology, Petrography, and Behavior

Although *coal rank* plays an important role in defining coal use, *coal type* and *coal grade* are also extremely important consideration (Table 1.6). These parameters are the primary factors that influence a coal's specific physical and chemical properties and these properties in turn determine the overall quality of the coal and its suitability for specific purposes.

In general terms, the behavior of coal during combustion, carbonization, pyrolysis, gasification, and direct conversion to liquids depends on the type and amount of the macerals present (Fryer et al., 1975; Falcon, 1978; Stach et al., 1982; Bend et al., 1991; Derbyshire, 1991; Kalkreuth et al., 1991; Murchison, 1991; Sen, 1992; Speight, 2008; Suárez-Ruiz and Crelling, 2008; Gagarin, 2010). Indeed, it would be

TABLE 1.5 General Description of Different Ranks of Coal Including Peat for Comparison

Rank (Excluding Peat)	Properties
Peat	A mass of recently accumulated to partially carbonized plant debris that is not classed as coal; an organic sediment that has a carbon content <60% w/w on a dry ash-free basis.
Lignite	The lowest rank of coal (also called <i>brown coal</i>), which may contain recognizable plant structures; the heating value is <8300 Btu/lb on a mineral matter free basis and a carbon content from 60% to 70% w/w on a dry ash-free basis.
Sub Bituminous	Coal with a carbon content on the order of 71–77% w/w on a dry ash-free basis) and a heating value between 8300 and 13,000 Btu/lb on a mineral matter free basis; on the basis of heating value, this coal is subdivided into sub bituminous A, sub bituminous B, and sub bituminous C coals.
Bituminous	Coal with a carbon content on the order of 77% and 87% w/w on a dry ash-free basis and a heating value that is much higher than lignite or sub bituminous coal; on the basis of volatile matter production, bituminous coal is subdivided into low volatile bituminous coal, medium volatile bituminous coal, and high volatile bituminous coal; often referred to as <i>soft coal</i> (in relation to anthracite).
Anthracite	The highest rank of coal with a carbon content greater than 87% w/w on a dry ash-free basis and the highest heating value per pound on a mineral matter free basis; often subdivided into semi-anthracite, anthracite, and meta-anthracite on the basis of carbon content and <i>hard coal</i> (in relation to bituminous coal).

most surprising if this were not the case in view of the differences in ultimate composition alone of the various macerals (Table 1.7). Furthermore, it appears that no two coals (no matter how close their relationship in the various classification systems) have exactly the same petrographic composition and, consequently, the same reactive properties.

The basic chemical parameters of a coal are determined by proximate analysis (moisture, ash, volatile matter, and fixed carbon percentages) and ultimate analysis (carbon, hydrogen, nitrogen, sulfur, and oxygen contents). Other analyses that may be carried out include determining the forms of sulfur in the coal (pyritic, sulfate, and organic) and the carbon (or CO₂) content, which is derived from the carbonate fraction. Chlorine content (Spears, 2005), which is mainly associated with inorganic salts (relatively high proportions of chlorine may give rise to corrosion in coal utilization) and phosphorous content (an undesirable element in coals destined for use in the steel industry) may also be determined. The ash content of a coal may be analyzed to determine the presence of metal oxides (these influence coal and ash behavior during

TABLE 1.6 Differentiation of Coal Rank, Coal Type, and Coal Grade*Rank*

- Indicative of the degree of metamorphism (or coalification) to which the original mass of plant debris (peat) has been subjected during its burial history.
- Dependent on the maximum temperature to which the *proto-coal* has been exposed and the time it has been held at that temperature.
- Also reflects the depth of burial and the geothermal gradient prevailing at the time of coalification in the basin concerned.

Type

- Indicative of the nature of the plant debris (*proto-coal*) from which the coal was derived, including the mixture of plant components (wood, leaves, and algae) involved and the degree of degradation before burial.
- The individual plant components occurring in coal, and in some cases fragments or other materials derived from them, are referred to as *macerals*.
- The kind and distribution of the various macerals are the starting point for most coal petrology studies.

Grade

- Indicative of the extent to which the accumulation of plant debris has been kept free of contamination by inorganic material (mineral matter), before burial (i.e., during peat accumulation), after burial, and during coalification.
- A high-grade coal is coal, regardless of its rank or type, with a low overall content of mineral matter.

industrial usage) whereas the proportions of certain trace elements, some of which could be potentially hazardous to human health are worth evaluating.

The analytical procedures used to determine the petrographic, physical, and chemical properties and these tests are standardized in a number of international test methods (Peters et al., 1962; Karr, 1978a,b,c; Diessel, 1980; Stach et al., 1982; Ward, 1984; Diessel, 1992; Van Krevelen, 1993); Taylor et al., 1998; Thomas, 2002; Speight, 2008; Suárez-Ruiz and Crelling, 2008). The organic constituents of coal (liptinite, inertinite, and huminite/vitrinite) are, individually and in combination (microlithotypes), fundamental to many coal properties.

The inorganic constituents of coal are often expressed using simple parameters such as ash yield, mineral matter, and sulfur content. Knowledge of the inorganic constituents including trace elements in the coal may take on a more complex role if emissions of the so-called hazardous air pollutants (HAPs) are regulated. Hazardous air pollutants generally include antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), nickel (Ni), lead (Pb), selenium (Se), mercury (Hg), cobalt (Co), chromium (Cr), and manganese (Mn), with chlorine (Cl) and the radionuclides, thorium (Th) and uranium (U), also being included in some assessments.

TABLE 1.7 Analysis of Macerals

Property	Maceral		
	Exinite	Vitrinite	Fusinite
Carbon, % w/w	82.0 ± 1.0	82.5 ± 1.0	93.0 ± 1.0
Hydrogen, % w/w	8.5 ± 0.5	5.5 ± 0.2	2.85 ± 0.2
Nitrogen, % w/w	1.0 ± 0.5	1.6 ± 0.4	0.9 ± 0.1
Oxygen, % w/w	6.8 ± 0.5	9.5 ± 0.5	2.3 ± 0.2
Sulfur, % w/w	0.5 ± 0.1	0.5 ± 0.1	0.5 ± 0.1
Volatile matter, % w/w	45 ± 5.0	12 ± 2.0	5.0 ± 1.0

In summary, certain waxy and resinous macerals are reactive to coal conversion processes while other macerals, notably those of the inertinite group, are notoriously unreactive. Thus, as petrography facilitates the qualitative and quantitative identification of the constituents of coal, it will, no doubt, find increasing application as a method for predicting and elucidating the behavior of any coal to conversion processes designed for the production of synthetic gaseous and liquid fuels (ASTM D2793).

1.8 COAL AND COAL ANALYSIS

It has been (and often still is) presumed that coal formation invokes the concept of a *regular* progression from lignite (in a stepwise manner) to the higher-rank members of the coal series, ultimately leading to the anthracite coals. However, even using modern analytical techniques, it is difficult to assemble evidence in favor of only one or the other of these theories insofar as each theory has its own particular merits and, moreover, the chemical makeup of the starting material and end product (coal) is, at best, extremely speculative making the task that much more difficult. Indeed, there may be some merit in accepting both theories as part of the coal-forming process.

To confuse the issue of the analytical chemistry of coal even further, it has been suggested that there exists a somewhat lesser dependence of the molecular chemistry of coal on rank and the chemistry of coal is heavily influenced by its source as well as by the early formation history (Berkowitz, 1988). It is also possible that coals of similar rank may, therefore, be chemically much more diverse than is usually supposed, which may not be detectable by analytical test methods. Indeed, this concept is in agreement with similar conclusion about the formation of petroleum insofar as the chemical nature of the crude oil, with particular reference to the asphaltene constituents, is dependent not only upon the types of precursors but also on the relative mix of these precursors that formed the *protopetroleum* (Speight, 2014) as well as on regional variations in the maturation conditions due to variations resulting from climatic differences between various geological eras/periods (Bend, 1992; Speight, 2013a, 2014).

The concept of source material and formation history playing a larger role in the determination of coal chemistry and coal analysis is quite logical. In fact, the potential

(and the more likely reality) that there are localized variations in precursor-type, mix of the precursors, as well as variation in maturation conditions are given little consideration as part of the coal-forming processes. The age-old concept of *high heat and pressure*, which one assumes would be a chemical equalizer insofar as all chemical and physical reactions proceed toward a graphite-type material, are given much more credence, for whatever reasons. Perhaps it is also time to cease considering coal as a graphitic material and look to coal as a natural product that is subject to local and regional variations in maturation conditions rather than as a conglomeration of large polynuclear aromatic sheets. Indeed, the perception of the chemical and physical behavior of coal has, for many years, been *guided* by the results of a series of tests that, at best, give only gross properties and afford no information whatsoever (or at the most optimistic, very little information) about the nature of coal.

Finally, although all test methods can provide important information about the suitability of coal for a particular use, in addition to data from proximate analysis (Chapter 5) and from ultimate analysis (Chapter 6), other coal quality parameters that need to be taken into account (e.g., in coal combustion, coal carbonization, and coking processes) include information from the following tests (which are listed alphabetically rather than by preference:

- *Ash fusion temperature* (Chapter 5) indicates the behavior of the ash residues from the coal at high temperatures and is mainly related to the chemical composition of the ash and the nature of the coal's mineral matter; the data are used to indicate whether the ash will remain as a fine powder within the furnace system after the coal is burned or whether some of it might melt to form a slag on the heat exchange surfaces of the boiler.
- *Free-swelling index (FSI)* (Chapter 8) is a measure of the increase in volume of the coal when it is heated in the absence of air; this test is also used to characterize coals for combustion and the data are in part rank-dependent parameter as well as dependent on the maceral composition of the coal – the vitrinite maceral group is the main contributor to the swelling properties.
- *Gieseler plastometer* (Chapter 8) monitors how the coal behaves as the different macerals melt, devolatilize, and resolidify at different temperatures during the carbonization process; the data are particularly significant when different coals are blended for coke production to ensure compatibility of the different blend components – coal-blending strategies, for example, coke production are generally decided on the basis of a combination of rheological and petrographic parameters using individual coal samples and the data are used to select coals to make up a blend with specific coking properties.
- *Gray-King assays* (Chapter 8) determine the proportions of coke or char (carbonaceous solids), tar (organic liquids), liquor (ammonia-rich solutions), and gas produced when the coal is carbonized (heated in the absence of air); the data provide a basis for estimating the yields of coke and coke byproducts obtained from the coal in an industrial coke oven or oil-shale processing plant.
- *Hardgrove grindability index (HGI)* (Chapter 9) indicates the ease with which the coal can be ground to fine powder; the data are related to the maceral and

maceral group composition but is also dependent on rank and mineral content.

- *Heating value (calorific value)* (Chapter 8) indicates the amount of heat liberated per unit of mass of combusted coal; this is a rank-related parameter but is also dependent on the macerals in the coal and mineral composition.
- *Roga index* (Chapter 8) provides information on the caking properties of the coal; the index is derived from the strength or cohesion of the coke produced in the crucible, as evaluated by a subsequent tumbler test.

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