

Chapter 2

Physical Characteristics of Coal

Abstract To understand the behavior of coal, characterizing and understanding its physical properties is of paramount importance. The bulk properties of coal, and in particular the mechanical and thermal properties, have a significant impact on the various processes that are discussed in later chapters. In addition, the microstructure and porosity of coal are intimately involved in the complex heterogeneous reactivity of coal. In this chapter, the physical structures and properties of various coal types are described in terms of the most commonly used physical characterization techniques, including X-ray diffraction, X-ray scattering, surface area, and porosity measurement techniques. Other physical properties of coal such as optical, electrical and magnetic properties can also offer insight into the chemical structure and composition of coal. The physical properties of coal, including the mechanical, electromagnetic, and optical properties, are related to structural models of coal. The bulk thermodynamic properties of coal combustion are also introduced. Finally, the use of computational methods to determine the physical properties of coal is discussed.

2.1 Physical Properties of Coal

2.1.1 *Mechanical Properties of Coal*

The bulk mechanical properties of coal have major implications for designing coal-based processes. The mechanical properties of coal are related to coal type.

2.1.1.1 Mechanical Strength

The mechanical strength of coal refers to its capacity to resist external forces and is related to physical properties of coal such as shatter indices and grind ability index.

Table 2.1 Grading standards for mechanical strength of coal

Grade	Mechanical strength of coal	Proportion of particles >25 mm (%)
Grade I	High-strength coal	>65
Grade II	Medium-strength coal	50–65
Grade III	Low-strength coal	30–50
Grade IV	Ultralow-strength coal	≤30

The shatter indices of coal can be determined using the drop method. The method is to let coal lumps of size 60–100 mm fall freely from a point 2 m above a steel plate, sieve them with a sieve of 25 mm, and repeat the process for coal samples of size greater than 25 mm. After repeating the process three times, the mass of coal samples larger than 25 mm is determined, and the percentage with respect to the mass of the original coal samples is taken as the shatter indices of the coal. The grading standards for determining the mechanical strength of coal using the drop test are shown in Table 2.1.

The grind ability index of coal is determined using the Hardgrave method. The method is to break 1 kg of coal samples of size 6 mm in a Hardgrave grind ability analyzer, grade by grade, until all of them pass through a 1.25 mm screen, weigh the coal samples of size 0.63–1.25 mm, calculate the percentage of their mass to the total mass of the coal samples, and determine the corresponding grind ability index from a standard curve.

The mechanical strength of coal is related to factors such as the degree of coalification, lithotype, mineral content, and weathering. The mechanical strengths of high-rank and low-rank coals are greater than those of medium-rank fat coals and coking coal. In terms of the macroscopic lithotype of coal, the mechanical strength of fusain is lowest, followed by vitrain, and that of durain is the highest. The mechanical strengths of coals with high mineral contents are high, and are reduced by weathering.

2.1.1.2 Density

Density is an important parameter, and it reflects the nature and structure of a material. The density depends on the closeness of the molecular structure and the molecular arrangement and there is also a relationship between density and degree of coalification. The density can also be used for structural analysis of coal, using statistical methods. The coal density is the coal mass per unit volume. Coal volume has different meanings in different situations, because of the inhomogeneity of coal, so coal density has various definitions.

The true relative density (TRD) of coal refers to the coal mass per unit volume, excluding the pores in the coal. It is an important indicator for calculating the average mass of a coal seam and in coal quality research. The TRD can be determined in aqueous media using a pycnometer. When different substances (for example, helium,

methanol, water, *n*-hexane, and benzene) are used as the replacement substances for determining coal density, the values obtained vary. Usually, the result obtained using helium as the replacement substance is taken as the TRD (also known as the helium density). The diameters of the smallest pores in coal are about 0.5–1 nm, whereas the diameter of the helium molecule is 0.178 nm; therefore helium can completely penetrate the porous structure of coal. The general ranges of the TRDs of various types of peat, lignite, bituminous coal, and anthracite are about 0.72, 0.8–1.35, 1.25–1.50, and 1.36–1.80 g cm⁻³, respectively.

The apparent relative density (ARD) of coal is the coal mass per unit volume, including the pores in the coal. This parameter is necessary for calculating coal reserves and in the transportation, crushing, and combustion of coal. The ARD can be determined using the wax-coating method. The coal porosity can be calculated using the TRD and ARD of the coal:

$$\text{Porosity} = \frac{\text{True relative density} - \text{Apparent relative density}}{\text{True relative density}} \times 100\%.$$

The bulk density (BD) of coal is the ratio of the total mass of coal grains filling a container using the free-stacking method to the vessel volume. The BD is used when estimating the mass of a coal pile or calculating the coal capacity of a coke oven.

For the same coal sample, the value of the TRD of the coal is highest, followed by that of the ARD, and the value of BD is lowest. The densities of minerals are significantly higher than that of organic matter, so the content and composition of the minerals in coal has a significant influence on the coal density. In the study of coal structure, it is usually necessary to eliminate the impact of minerals. The density must be corrected roughly as follows: for every 1 % increase in coal ash, the coal density will increase by 0.01 %.

The general relationship between the density and the degree of coalification for various macerals is as follow [1]: the TRD of inertinite is the highest, followed by those of vitrinite and exinite; when the carbon content on a dry ash-free basis (C_{daf}) is greater than 90 %, the three become similar and increase sharply, indicating that their structures have undergone profound changes.

The general relationship between vitrinite density and the degree of coalification is as follows [2]: the vitrinite density begins to decrease slowly with increasing coalification, mainly because the reduction in the oxygen content is greater than the increase in the carbon content, and the atomic weight of oxygen is greater than that of carbon. The density of coal containing 85–87 % carbon is at least 1.3 g cm⁻³. For coal with a carbon content greater than 90 %, the density increases sharply with increasing coalification, mainly because of the increasing amount of more compact aromatic structures.

2.1.1.3 Hardness

Coal hardness reflects the coal's ability to withstand external mechanical actions. The representation and determination of coal hardness differ depending on the applied mechanical force.

The scratch hardness (Mohs hardness) is the relative hardness determined by scratching the coal surface with 10 types of standard mineral. The scratch hardness of coal is usually between 1 and 4. Coal hardness is related to coalification. Lignite, which has a low coalification degree, and coking coal, with medium coalification, have the lowest scratch hardnesses of 2–2.5, whereas anthracite has the highest scratch hardness that is close to 4.

The micro Vickers hardness is referred to as the microhardness (symbol MH or Hm). It is determined by pressing a diamond indenter with a static load into the maceral under a microscope. The greater the indentation is, the lower the microhardness of the coal. The value of the microhardness is expressed by the load capacity per contact area between the indenter and the coal (in kilograms per square millimeter). The microhardness determined by the indentation method is widely used in the study of coal chemistry.

2.1.1.4 Elasticity

Coal elasticity is the deformation produced under an external force, and the degree of recovery after removal of the external force. The elasticity of a material is related to its structure; in particular, there is a close relationship with the binding force between constituent molecules. The determination of coal elasticity is very important in the study of coal structure, e.g., the elastic modulus of coal is an indication of the characteristics of the chemical bonds between the units of coal structure.

The methods for determining material elasticity are divided into static and dynamic methods. The static method determines the relationship between stress and strain; for example, it can determine the bending degrees of coal briquettes produced under different loads. The dynamic method is based on determining the transmission speed of sound in the coal. The coal elastic modulus can be calculated as

$$v = k\sqrt{\frac{E}{\rho}},$$

where

v is the transmission speed of sound in the coal (m s^{-1});

k is a constant;

E is the coal elastic modulus ($10^{-5} \text{ N cm}^{-2}$);

ρ is the coal density (g cm^{-3}).

Fine cracks or other factors can lower the static elastic modulus, therefore the dynamic elastic modulus is considered to be more reliable. The elastic moduli of low-coalification and bituminous coals are generally isotropic, whereas that of high-coalification coal is anisotropic. Different macerals have different elasticity values. The values increase in the order liptinite, vitrinite, and inertinite. However, with increasing coalification degree, the differences gradually become smaller. In addition, the coal elasticity increases with increasing mineral and moisture content, because minerals have high densities.

2.1.2 Thermal Properties of Coal

2.1.2.1 Thermal Conductivity

The thermal conductivity of coal includes two basic constants: the thermal conductivity coefficient λ ($\text{kJ m}^{-1} \text{h}^{-1} \text{K}^{-1}$) and the thermal diffusivity coefficient α ($\text{m}^2 \text{h}^{-1}$). The thermal conductivity coefficient λ is the transmission rate for a temperature difference of 1 K over a unit distance when heat is transferred from a high-temperature area to a low-temperature area; it is the direct conduction speed of heat in an object, representing the heat-sinking capability of the object; $c\rho$ represents the heat-storage capacity of the object. The thermal diffusivity coefficient α is the ratio of the heat-sinking capability to the heat-storage capacity of the material and it represents the temperature-changing (heating or cooling) capability of an object; λ and α are related as follows:

$$\alpha = \frac{\lambda}{c\rho},$$

where c is the mass heat capacity of the coal ($\text{kJ kg}^{-1} \text{K}^{-1}$) and ρ is the coal density (kg m^{-3}).

The λ and α values of medium-coalification bituminous coal can be calculated using the empirical equation

$$\lambda = 0.0003 + \frac{at}{1000} + \frac{bt^2}{1000^2},$$

where a and b are specific constants; the values of a and b for caking coal are equivalent, i.e., 0.0016, and for weakly caking coal, the values of a and b are 0.0013 and 0.0010, respectively; t is the temperature ($^{\circ}\text{C}$).

The thermal diffusivity coefficient α of medium-coalification bituminous coal is given by the empirical equations

$$\alpha = 4.4 \times 10^{-4} [1 + 0.0003(t - 20)] \quad \text{when } t = 20-400^\circ\text{C},$$

$$\alpha = 5.0 \times 10^{-4} [1 + 0.0033(t - 400)] \quad \text{when } t = 400-1000^\circ\text{C}.$$

The thermal conductivity coefficient of coal is related to its moisture and ash contents, temperature, and type. The thermal conductivity coefficient of water is approximately 25 times that of air. The thermal conductivity coefficient of coal therefore increases with increasing moisture content. The thermal conductivities of minerals are much higher than those of organic materials; therefore if the amount of coal ash increases, the thermal conductivity coefficient increases. There is a positive relationship between the thermal conductivity coefficient and temperature of the coal, i.e., the thermal conductivity coefficient increases with increasing temperature. The thermal diffusivity coefficients of various coals have roughly similar variation rules. These variation rules reflect the characteristics of the internal structure of the coal. In the metamorphic process, the structure of the organic matter in coal gradually becomes more compact and regular; therefore the thermal conductivity gradually increases, approaching that of graphite.

2.1.2.2 Specific Heat

The quantity of heat needed to raise the temperature of a unit mass of coal by 1 K is referred to as the specific heat of the coal. The specific heat of coal at room temperature ranges from 1.00 to 1.266 kJ kg⁻¹ K⁻¹. The specific heat of coal changes with changes in coalification, moisture, ash, and temperature. The specific heat of coal at room temperature decreases with increasing coalification (expressed by the carbon content) [3]. The specific heat of coal increases approximately linearly with increasing moisture content, because the specific heat of water is high. The mass heat capacity decreases with increasing coal ash content, because the mass heat capacity of minerals is generally from 0.70 to 0.84 kJ kg⁻¹ K⁻¹ at room temperature.

The specific heat of coal varies with temperature. In the temperature range 0–350 °C, the mass heat capacity increases and reaches a maximum at about 350 °C. From 350 to 1000 °C, the specific heat decreases. Thermal decomposition of coal occurs above 350 °C, and it finally reaches the specific heat of graphite, 0.71 kJ kg⁻¹ K⁻¹ [3].

2.1.3 Optical Properties of Coal

The optical properties of coal provide important information on coal structure, such as coalification, anisotropy, sizes and arrangement of aromatic layers. They can also reflect the shape, orientation, and agglomeration of the internal particles of the coal.

This section focuses on the reflectivity and refractive index of coal. Spectroscopic properties such as infrared (IR) properties will be discussed elsewhere.

2.1.3.1 Coal Reflectivity

The capacity of a polished coal surface to reflect vertically incident light is referred to as the reflective capacity of the coal. The visual performance under a microscope is the brightness of the polished surface. The reflective capacities of different coal types are different. The reflectivity, R , of coal is defined as:

$$R = \frac{I_r}{I_i} \times 100 \%,$$

where I_r is intensity of the reflected light and I_i is the intensity of the incident light.

Reflectivity is an important property of opaque minerals, and is also an important indicator of the coalification degree. The reflectivity is usually determined using a relative method: the reflected light intensity of a standard sheet with a known reflectivity is measured under a certain intensity of incident light (typically monochromatic polarized light) and compared with the intensity of reflected light of the material under investigation. Materials such as optical glasses, quartz, and diamond are commonly used as standards. The equation for calculating the reflectivity is

$$R = \frac{I}{I_0} R_0 \times 100 \%,$$

where I is the intensity of the reflected light from the material being examined, I_0 is the intensity of reflected light of the standard material, and R_0 is the reflectivity of the standard material.

As the resolution of coal in an oil medium is far better than that in air, the reflectivity is generally measured under an oil-immersion objective (R^o). At least 20 points for each optical coal sample are used to measure the maximum reflectivity. Usually, the average value, $\bar{R}_{\max}^o$, of the maximum reflectivity measured under an oil-immersion objective is used as the analytical indicator. The range of reflectivities of different Chinese coal types is shown in Table 2.2.

The reflectivity of vitrinite in bituminous coal is related to other commonly used coal classification indicators such as volatile matter content determined on an ash-free basis (V_{daf}), C_{daf} , and calorific value. The general relationships between the maximum average reflectivity of vitrinite of Chinese coal under an oil-immersion microscope correlates well with the coalification, which is a good indicator of coal rank [4].

Table 2.2 Reflectivities (%) of different types of Chinese coal

Coal type	Metamorphic stage	Reflectivity	Coal type	Metamorphic stage	Reflectivity
Lignite	0	0.40–0.50	Lean coking coal	VI	1.50–1.69
Long-flame coal	I	0.50–0.65	Lean coal	VII	1.69–1.90
Gas coal	II	0.65–0.80	Meager coal	VIII	1.90–2.50
Gas-fat coal	III	0.80–0.90	Anthracitic	IX	2.50–4.00
Fat coal	IV	0.90–1.20	Anthracitic	X	4.00–6.00
Coking coal	V	1.20–1.50	Anthracitic	XI	>6.00

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2.1.3.2 Refractive Index of Coal

The definition of the refractive index is the ratio of the sine of the incident angle to that of the refraction angle when light passes through a material interface, is refracted at the interface, and enters the interior of the substance. The molecular refraction can be obtained from the additive refractive index, an important property in analytical studies of coal structure. The refractive index of coal cannot be directly measured, but the reflectivity and the refractive index of vertical incident light are related as follows:

$$R = \frac{(n - n_0)^2 + n^2 K^2}{(n + n_0)^2 + n^2 K^2},$$

where

R is the coal reflectivity (%);

n_0 is the standard medium refractive index, $n_0 = 1.514$ for cedar oil;

n is the refractive index of the coal;

K is the light absorption rate of the coal (%).

Based on the reflectivities of incident light measured in air and cedar oil, two equations can be obtained using the above equation. Simultaneously solving the equations gives n and K .

The refractive index increases with increasing coalification. When the carbon content is higher than 85 %, the increase is large [5].

Generally, lignite is optically isotropic. Coal is transformed from bituminous coal to anthracitic coal with increasing coalification. The layered structure of the aromatic nuclei in the molecular structure improves, and the arrangement becomes regular. Anisotropy of the optical properties parallel or perpendicular to the aromatic layers gradually becomes apparent. The reflectivity and refractive index can both reflect such changes, which are determined by the internal structure of the coal.

2.1.4 Electrical and Magnetic Properties of Coal

The electrical properties of coal include the conductivity and dielectric constant. The study of the electrical properties of coal can theoretically provide information such as the semiconducting nature of the coal, the size of aromatic structures in the coal, and the anisotropy. The main magnetic properties of coal are diamagnetism and paramagnetism.

2.1.4.1 Coal Conductivity

The conductivity of coal is the degree of difficulty of passing a current through the coal. The conductivity of a substance is commonly expressed in terms of the electrical resistivity ρ (Ω cm) or electrical conductivity κ (Ω^{-1} cm $^{-1}$). The reciprocal of the electrical resistivity is the electrical conductivity, i.e.,

$$\kappa = \frac{1}{\rho},$$

In terms of electrical conductivity, coal is generally considered to be close to a semiconductor. The κ value of young lignite is approximately $1 \times 10^{-14} \Omega^{-1} \text{ cm}^{-1}$.

2.1.4.2 Dielectric Constant of Coal

The ratio of the charging capacity of a substance between two parallel plate electrodes to the charging capacity when there is a vacuum is between the parallel plate electrodes is referred to as the dielectric constant, ε , of the substance. The relationship between ε and the refractive index, n , of a non-polar insulator is

$$\varepsilon = n^2.$$

2.1.4.3 Magnetic Properties of Coal

The internal magnetic field intensity, B , of a material placed in a magnetic field of intensity H is referred to as the magnetic induction intensity:

$$B = H + H' = H + 4\pi d\chi H,$$

where H' is the additional magnetic field intensity induced by magnetization of the magnetic medium. When $H' > 0$, a magnetic medium with a magnetic field H with the same direction as that of H' is referred to as a paramagnetic substance; when

$H' < 0$, a magnetic medium with a field H with the opposite direction to that of H' is referred to as a diamagnetic substance.

In chemistry, the specific magnetic susceptibility χ ($\text{cm}^3 \text{g}^{-1}$) and molar magnetic susceptibility χ_m ($\text{cm}^3 \text{mol}^{-1}$) are generally used to indicate the magnetic properties of a substance. The relationship between the specific magnetic susceptibility and the molar magnetic susceptibility is

$$\chi_m = \chi \cdot M,$$

where M is the molar mass of the substance (g mol^{-1}).

2.1.5 Surface Properties of Coal

During the process of coal change, chemical reactions occur on the reactant surfaces and coal solid surfaces. Most of the surfaces are related to the pore structure, i.e., the diffusion of products and penetration of reaction media are related to the coal pore structure in most cases. The porosity also affects the physical and chemical properties of coal. The surface and body of coal are full of holes composed of organic matter and minerals, and coal is a porous solid substance with different pore size distributions; micropores are the main type of pore. The correlation between coal porosity and coal rank is of great practical significance. This section describes the pore structures in coal.

2.1.5.1 Classification and Forms of Pores in Coal

There is no single standard for classifying the pores in coal. Dubinin suggests the following classification, which is widely used in the study of coal chemistry, to distinguish different-sized pores of a porous adsorbent: large pores, of diameter >20.0 nm; transitional pores, of diameter 2.0 – 20.0 nm; and micropores, of diameter <2.0 nm. Some researchers divide pores into macropores and micropores, and the dividing point is an effective pore radius of 10.0 nm.

The International Union of Pure and Applied Chemistry (IUPAC) proposed the following new standard aperture classification in 1978.

Micropores (<2 nm). The micropore size and pore diameter range can be measured and calculated using small-angle X-ray scattering (SAXS), CO_2 adsorption, or the pure helium adsorption.

Mesopores (2 – 50 nm). These can be observed using scanning electron microscopy (SEM), measured using transmission electron microscopy (TEM), and quantified using N_2 adsorption, small-angle neutron scattering (SANS), or SAXS.

Macropores (>50 nm). Pores larger than 1000 nm can be observed with an optical microscope, and smaller pores can be studied using SEM. The diameters of

larger pores can be quantified using image analysis technology or measured using the mercury intrusion method.

Physical properties of micropores. Micropores are almost the same size as the adsorbed molecules. The volume of a micropore is about $0.2\text{--}0.6\text{ cm}^3\text{ g}^{-1}$, the pore quantity is 10^{20} , and the total surface area of micropores in coal-based activated carbon is about $500\text{--}1000\text{ m}^2\text{ g}^{-1}$.

Physical properties of mesopores. A meniscus can be formed in the pore. A decrease in the vapor pressure causes capillary condensation, and liquefies the adsorbates. The pore volume is small, about $0.015\text{--}0.15\text{ cm}^3\text{ g}^{-1}$; the surface area is also small.

Physical properties of macropores. No obvious meniscus can be formed in the pores; no capillary condensation occurs. The causes of these pores have the following categories: holes and fissures. The hole types are air, residual plant material, corrosion, mold, intercrystal, interbioblast, and condensation water loss. Fissures are endophytic and tectonic.

Pores in coal have different forms: some pores form passages, some are blind holes, some are closed holes, and some are open holes. These hole structures can be observed using an electron or optical microscope.

2.1.5.2 Pore Size and Distribution in Coal

Surface area is one of the most important factors determining coal surface properties and micropore structure. The overall porosity can be calculated from the difference between the densities measured using helium and mercury:

$$V_t = \frac{1}{\rho_{\text{Hg}}} - \frac{1}{\rho_{\text{He}}},$$

where V_t is the total pore volume ($\text{cm}^3\text{ g}^{-1}$), ρ_{He} is the true density (measured using mercury, $\text{cm}^3\text{ g}^{-1}$), and ρ_{He} is the apparent density (measured using helium, $\text{cm}^3\text{ g}^{-1}$).

The pore size distribution of coal also depends on the coalification. Lignite pores are relatively uniform, long flame coal has micropores and few macropores and mesopores, bituminous coal has a large number of micropores, and anthracite is usually dominated by micropores, with only about 10 % of the pore volume contributed by macropores and mesopores.

2.1.5.3 Coal Surface Area

The surface area of coal consists of internal and external surface areas. However, the external surface area accounts for a very small proportion, and the internal surface area is the major component. Very fine capillaries and pores are formed within coal during coal generation. There are large amounts of such capillaries and

pores, and they are deeply and widely distributed; they have complex and well-developed internal structures. The coal internal surface area is the entire surface area of the internal pore structure, and is generally expressed by the specific surface area ($\text{m}^2 \text{g}^{-1}$). It is closely related to the microscopic structure and chemical reactivity of coal, and is one of the important physical indicators for coal.

There are many methods for determining the coal specific surface area, such as the wetting heat, Brunauer–Emmett–Teller (BET), gas chromatography, and micropore volume methods. The BET method is the classical method. As the coalification changes, the coal internal surface area increases significantly in both the early and late stages (lignite and anthracite), but decreases in the middle stages (medium-coalification coal); this reflects changes in the spatial arrangement of molecules during coalification. The results obtained using different gases and temperatures vary, and can be unreliable.

2.1.5.4 Distribution of Porosity and Pore Size in Coal

Coal contains many pores. The percentage of the total volume of these pores compared with the entire coal volume is referred to as the coal porosity; this can also be expressed as the void volume ($\text{cm}^3 \text{g}^{-1}$) in a unit mass of coal. The porosity can be calculated using the substitution method, TRD, or ARD. The principle of the substitution method is as follows: helium can fill all the coal pores, but mercury cannot enter the pores at all, so densities are obtained using helium and mercury as substitutes. The coal porosity is obtained as

$$\text{Porosity} = \frac{d_{\text{He}} - d_{\text{Hg}}}{d_{\text{He}}} \times 100 \%,$$

where d_{He} and d_{Hg} are the coal densities (g cm^{-3}) obtained using helium and mercury, respectively.

There is a minimum near $C_{\text{daf}} = 90 \%$, where the porosity is lowest, less than 3 %. Generally, the porosity of young bituminous coal is greater than 10 %. The amount of pores decreases with increasing coalification, because the coal structure becomes more compact under metamorphism. As coalification increases further, the porosity tends to increase, because of the increase in coal fractures with increasing coalification [6].

The pore diameters in coal are non-uniform in size, and can be roughly divided into three categories: micropores, transitional pores, and macropores. The pore diameter distribution can be determined using the mercury intrusion method or the liquid N_2 isothermal adsorption method. The mercury intrusion method is used to determine the distribution of pores of diameter 10–1000 nm. The liquid N_2 isothermal adsorption method can only be used to measure the volumes of transitional pores, and then translate them into pore diameters. Micropore diameters cannot be directly measured, but can be obtained indirectly by subtraction.

The pore diameter distributions of coals vary with different coalification degrees [7]: when the C_{daf} content is less than 75 %, macropores are predominant in lignite, with hardly any transitional pores; for coals with C_{daf} contents in the range 75–82 %, transitional pores are well developed, and the main contributors to the total pore volume are transitional pores and micropores; for coals with C_{daf} contents in the range 88–91 %, micropores remain predominant, and their volume accounts for more than 70 % of the total volume, with few transitional pores. With increasing coalification, the coal pore diameter decreases, the micropore proportion increases, and the physical structure of the coal gradually becomes more compact.

2.1.5.5 Coal Wettability

When coal is in contact with a liquid, the wetting of the coal differs depending on the properties of the liquid and the coal surface, and the liquid–solid surface properties. At the intersection of a gas, liquid, and solid, the included angle between the liquid surface and the solid–liquid interface is called the contact angle, θ . It is determined from the relative values of the interfacial tensions at the coal, liquid, and solid–liquid interfaces.

$$\cos \theta = \frac{\gamma_{\text{coal}} - \gamma_{\text{s-l}}}{\gamma_{\text{l}}},$$

where

γ_{coal} is the surface tension of the coal (N m^{-1});

γ_{l} is the surface tension of the liquid (N m^{-1});

$\gamma_{\text{s-l}}$ is the interfacial tension of the coal and the liquid (N m^{-1}).

2.1.5.6 Heat of Coal Wetting

The heat released when coal is wetted is referred to as the heat of coal wetting. The heat of coal wetting is the heat released when 1 g of coal is wetted; the unit is joules per gram. The heat of coal wetting is usually directly determined using a calorimeter. The heat of coal wetting is the result of interactions between the liquid and the coal surface, mainly van der Waals forces. The value of the heat of wetting is related to the liquid type and the specific surface area of the coal. The measured value of the heat of wetting can therefore be used to determine the total surface area of the pores in the coal. The coal surface areas obtained using the heat of wetting and BET methods show that 0.39–0.42 J is approximately equivalent to 1 m^2 , and the inner surface area of the coal is calculated to be approximately $10\text{--}200 \text{ m}^2 \text{ g}^{-1}$.

2.1.6 Coal Models

Among the models describing the physical structure of coal, the Hirsch model and the two-phase model are the most typical.

2.1.6.1 Hirsch Model

Hirsch [8] classified coal with different degrees of coalification into three physical structures, based on the physical model obtained using X-ray diffraction (XRD).

Open structure. This is observed for bituminous coal with a low degree of coalification, and features small aromatic lamellae and a large proportion of irregular amorphous structures. The aromatic lamellae are bound by cross bonds and more or less arbitrarily oriented in all directions, forming a porous three-dimensional (3D) structure.

Liquid structure. This is observed for bituminous coal with an intermediate degree of coalification, and is characterized by the orientation of some aromatic layer and formation of microcrystals comprising two or more lamellae. There are few cross bonds among the lamellae, resulting in high mobility. This type of coal has low porosity, low mechanical strength, and tends to be plastic during pyrolysis.

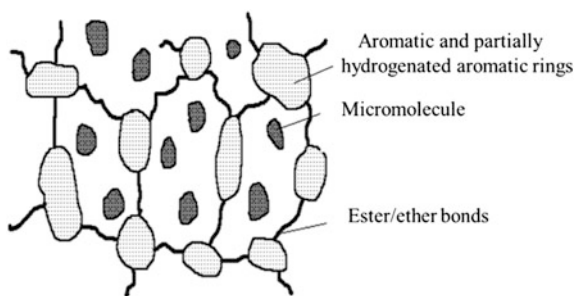
Anthracite structure. This is observed for anthracitic coal and is characterized by an increased number of aromatic lamellae and increased orientation. Condensation reactions result in a large number of micropores, so the porosity is higher than those of the former two structures.

The Hirsch model visually reflects the physical structural features of coal and explains many phenomena. However, the term “aromatic lamella” is not defined precisely, and the model fails to show the heterogeneity of the molecular constitution of coal.

2.1.6.2 Two-Phase Model

From the chemical point of view, coal has a 3D mesh structure composed of celluloses, lignins, lipids, proteins, tannins, and resins. In terms of the two components: one is a 3D carbon structure that consists of polycyclic aromatic hydrocarbons and hydrogenated aromatic hydrocarbons connected by aliphatic and ether chains; the other component is low-molecular-weight compounds in the network voids. Based on this idea, Haenel [9] found that ^1H nuclear magnetic resonance (NMR) spectroscopy shows that there are two coal proton relaxation times, one fast and one slow, and suggested a two-phase model, which is also known as the host–guest or macromolecular–molecular model, as shown in Fig. 2.1. In the figure, the macromolecular network is the stationary phase, and the micromolecular network is the mobile phase. This model suggests that the coal structure is an immobile, three-dimensionally crosslinked macromolecular phase, with embedded small

Fig. 2.1 Two-phase model.
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mobile-phase molecules of various structures. The polyaromatic ring is the host in the coal, and is the same for similar coal types. However, the mobile-phase small molecules, which act as guests, vary depending on the coal type. The host and guest can be separated by extraction with different solvents. This model shows that crosslinking of the molecules in coal is essential for covalent bonds and that physical associations are essential for intermolecular forces, and explains the bonding properties of coal during solvent expansion processes. However, the idea of a mobile phase consisting of small molecules with low molecular weights is still controversial.

2.2 Physical Methods for Coal Structure Characterization

Physical research methods can directly provide molecular structural information on coal and are usually used in combination with other research methods. Recently, progress in coal structural studies has mostly been achieved using physical methods, as a result of significant progress in instrumental and analytical techniques.

2.2.1 Infrared Spectroscopy

IR absorption occurs when the energy ($h\nu$) of IR light is absorbed by molecules. The energy of IR light is not high enough to cause an electronic transition, but matches the energy level required to induce bond vibrations. The sample is irradiated with IR light with continuous frequencies, and characteristic absorptions are observed at specific frequencies. Infrared absorption follows the Beer law.

The absorption frequency and intensity in an IR spectrum depend on the types of bond vibration and the adjacent substituents. Knowledge of the characteristic absorptions of various functional groups and the peak displacement patterns provides a basic understanding of molecular structure, and, in some circumstance, enable quantitative analysis of the compound or specific functional groups.

The IR absorption frequencies of various common functional groups are in the range $4000\text{--}400\text{ cm}^{-1}$; for convenience, this range is usually divided into four sections, as shown in Table 2.3.

The absorption peak at 3450 cm^{-1} is assigned to hydroxyl groups. The hydroxyl groups in coal are usually cross-linked via hydrogen bonds. IR spectroscopy has been widely used in the analysis of coals and coal derivatives, and the absorption peak shifts in the range 3300 cm^{-1} (--OH groups) to 3450 cm^{-1} can offer useful information about the functional groups present. The absorption intensity weakens with increasing coalification, which indicates that the number of hydroxyl groups decreases.

The absorption peak at 3030 cm^{-1} is attributed to C--H bonds in aromatic rings. The peaks at 870 , 820 , and 750 cm^{-1} are also associated with aromatic C--H vibrations. For coal samples with a low degree of coalification, the absorption

Table 2.3 Assignment of infrared absorption peaks of coal

Wavenumber (cm^{-1})	Wavelength (μm)	Peak assignment
>5000	<2.0	Multiple frequency absorptions and weak main frequencies
3300	3.0	--OH (or --NH) bonded, phenols
3030	3.30	Aromatic CH
2950 (shoulder)	3.38	--CH_3
2920	3.42	Naphthene or alkane --CH_3
2860	3.50	
2780–2350	3.6–4.25	Carboxylic groups
1900	5.25	Aromatics, 1,2- and 1,2,4-substituted Carboxylic group $>\text{C=O}$
1780	5.6	
1700	5.9	
610	6.2	$>\text{C=O}$, HO-- in carboxylic acid (bonded), --O- substituted aromatic C=C
1590–1470	6.3–6.8	Aromatics
1460	6.58	--CH_2 and --CH_3 , or inorganic carboxylate
1375	7.72	--CH_3
1330–1110	7.5–9.0	C--O in phenols, alcohols, ethers, and esters, ash
1040– 910 860 833 (weak) 815 750 700 (weak)	9.6– 11.0 11.6 12.6 12.3 13.3 14 0.3	CH in substituted aromatics, ash

intensity at 3030 cm^{-1} is weak, but increases significantly with increasing coalification.

The absorption peaks at 2925 , 1450 , and 1380 cm^{-1} are contributed by C–H bonds in alkanes and naphthene. The intensities of all these peaks initially increase with coalification but then decrease significantly as the degree of coalification approaches 81.5 %. The absorption ratio A_{3030}/A_{2925} is consistent with the H_a/H_{al} ratio, and reflects the degree of coalification [10]. The peak at 1380 cm^{-1} is the characteristic IR absorption of methyl groups, and can be used for quantitative calculation of the methyl group content.

The strong absorption at 1600 cm^{-1} is still not definitively assigned. The absorption gradually weakens with increasing degree of coalification.

The absorptions between 1000 and 1300 cm^{-1} are attributed to ether bonds.

The absorption between 900 and 650 cm^{-1} , normally consists of three wide absorption peaks, are attributed to aromatic rings.

IR spectroscopy also confirms that aliphatic C=C and C≡C bonds are not present in coal molecules; the amounts of carboxylic acid and methoxy groups in bitumite (C > 80 %) are low; there is a significant amount of carboxylic acid groups in lignite, but these groups are not detected in coal above bitumite.

IR spectroscopy is sometimes used for quantitative analysis. The absorptions at 1380 and $900\text{--}650\text{ cm}^{-1}$ are usually used for calculating the content of hydrogen in methyl groups and aromatic rings. The hydrogen in hydroxyl groups is measured by chemical titration, and the numbers of hydrogen atoms in methylene and methenyl groups are calculated using the equation:

$$H_{\text{CH}_2, \text{CH}} = H_{\text{total}} - (H_{\text{CH}_3} + H_{\text{OH}} + H_{\text{ar}}).$$

2.2.1.1 Infrared Spectroscopic Studies of Functional Groups in Coal

Eight coal samples with various coalification degrees, ranging from peat to anthracite, were studied using Fourier-transform (FT) IR spectroscopy (Bio-Rad FTS165). The proximate and ultimate analyses of the samples are shown in Table 2.4. The amount of sample to be used in the analysis was determined using a series of pilot IR experiments. The amount of sample was considered to be suitable when a linear correlation between the absorption intensity and sample amount at 3450 cm^{-1} was achieved. The results show that for coal samples in the range $0.8\text{--}1.5\text{ mg cm}^{-2}$, the IR absorption follows the Beer law. The coal test samples were prepared by mixing KBr (1:180) and pressing. The coal samples and KBr were dried in a vacuum oven at $110\text{ }^\circ\text{C}$ overnight before use.

The standard curves obtained are used for quantitative analysis of functional groups.

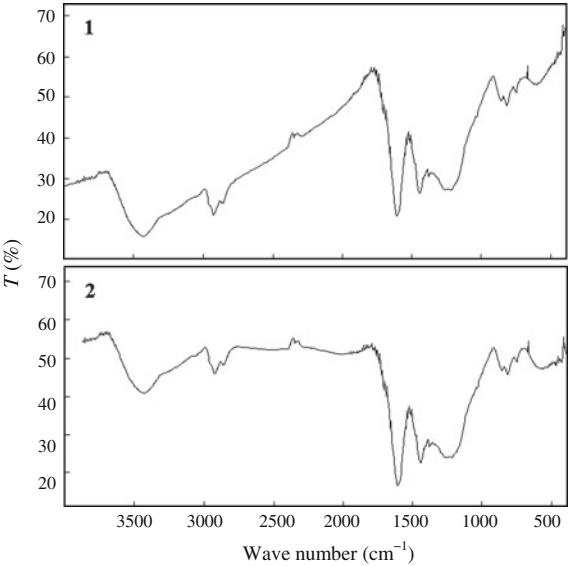
The raw IR spectrum is processed further to remove distortions. Spectrum 1 in Fig. 2.2 is the original spectrum; the baseline is clearly tilted. After calibration using the standard normal variate and Savitsky–Golay methods (spectrum 2), the baseline

Table 2.4 Coal proximate and ultimate analyses (%)

Coal sample	Proximate analysis			Ultimate analysis				
	M_{ad}	A_d	V_d	C_d	H_d	O_d	N_d	S_{td}
Huachuan peat	8.02	49.38	40.11	26.40	2.97	19.15	1.86	0.24
Pinzhuang lignite	13.49	5.72	43.68	66.44	4.57	21.90	1.08	0.29
Fuxin long flame coal	2.36	14.24	32.27	68.08	4.27	11.61	0.91	0.89
Xingzhi fat coal	0.81	14.52	29.52	70.69	4.45	7.33	1.13	1.88
Zaozhuang coking coal	1.25	7.96	33.60	76.25	4.67	9.55	1.05	0.52
French lean coal	0.79	6.82	11.05	75.85	4.85	7.56	1.45	1.01
Fengfeng meager coal	0.87	17.54	12.22	72.72	3.36	5.04	1.05	0.29
Jincheng anthracite	0.72	14.52	7.93	77.95	2.93	0.57	0.94	0.36

ad air dried basis; *d* dry basis; *td* total dry basis

Fig. 2.2 IR spectra of coal samples: 1 without calibration; 2 calibrated



is smoother and most of the distortion is removed. The IR spectroscopic information for the top seven coal samples are shown in Table 2.5 (except Jincheng anthracitic).

There is a broad and strong absorption at 3410 cm^{-1} in most of the coal spectra, which is assigned to hydrogen-bonded hydroxyl group vibrations. In the spectrum of peat coal, a strong absorption at 3285 cm^{-1} , assigned to the wagging vibrations of hydroxyl groups, is also present. This suggests that there are large numbers of condensed hydroxyl groups in peat coal, forming a coal-OH-OH-coal internal network structure. No absorption above 3600 cm^{-1} was observed in the peat coal spectrum, suggesting that free hydroxyl groups have been totally removed. With increasing coal rank from lignite to jet coal, the hydroxyl group absorption

Table 2.5 Relationship between coal type and the wave number and content of OH group

Coal	Free OH group (cm ⁻¹)	Content	Hydrogen bond (cm ⁻¹)	Content	Poly OH1 (cm ⁻¹)	Content	Poly OH2 (cm ⁻¹)	Content
Peat	3634	3.17	3518	3.23	3409	12.90	3292	7.20
Lignite	3622	2.35	3540	5.19	3425	14.81	3228	21.34
Long flame coal	3622	0.80	3524	9.75	3421	16.89	3230	5.28
Fat coal	3620	1.02	3544	0.84	3446	10.22	3244	5.68
Coking coal	3524	0.33	3412	5.87	3301	0.39	3213	1.73
Meager coal	3585	0.00	3544	0.27	3438	13.34	3227	1.73
Lean coal	3590	1.83	3443	33.28	3352	0.16	3247	4.43
Anthracite ^a	—	—	—	—	—	—	—	—

^aBelow detection limit

gradually splits into two absorption bands, at 3408 and 3221 cm⁻¹, and then gradually weakens and disappears completely in anthracite.

Hydrogen bonds are common linkages in coal structures, and play an important role in stabilizing and deconstructing the coal molecular network. As seen from Table 2.5, the amounts of intermolecular hydrogen bonds are highest in meager coal and lowest in Lean coal. The total content of polymerized hydroxyl groups (poly OH1 and poly OH2), which form the coal–OH–OH–coal internal network structure, decreases with increasing coal rank.

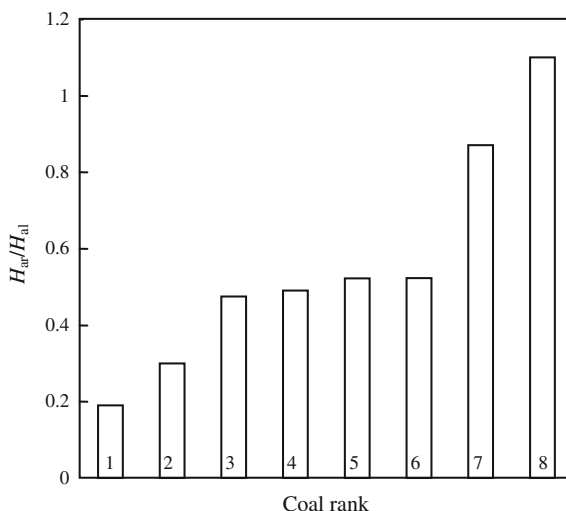
Ratio of Aromatic to Aliphatic Hydrogens

The ratio of H_{ar} to H_{al} , where H_{ar} refers to hydrogen atoms attached to aromatic backbones, and H_{al} refers to hydrogen atoms in alkane chains, is a key parameter in the coal average molecular structure. The ratio usually changes with increasing coal rank. The contents of H_{ar} and H_{al} reflect the coal activity during pyrolysis and the molecular-weight distribution of the pyrolysis products.

The absorption at 3065 cm⁻¹ is assigned to aromatic C–H stretching vibrations and indicates the content of condensed aromatic structures. A strong absorption at 3065 cm⁻¹ usually indicates low pyrolysis activity of the coal. In this section, the absorption intensities between 3030 and 3060 cm⁻¹ are used to calculate the H_{ar} content.

The sharp absorptions at 2920 and 2850 are attributed to alkane-chain C–H symmetric stretching and asymmetric stretching vibrations. In this section, the intensity of the peak at 2920 cm⁻¹ is used to calculate the H_{al} content and the absorption at 2850 cm⁻¹ is used for CH₂ and CH. The correlation between H_{ar}/H_{al} and coal rank is illustrated in Fig. 2.3.

Fig. 2.3 Correlation between H_{ar}/H_{al} and coal rank: 1 peat; 2 lignite; 3 long flame coal; 4 fat coal; 5 coking coal; 6 meager coal; 7 lean coal; and 8 anthracite



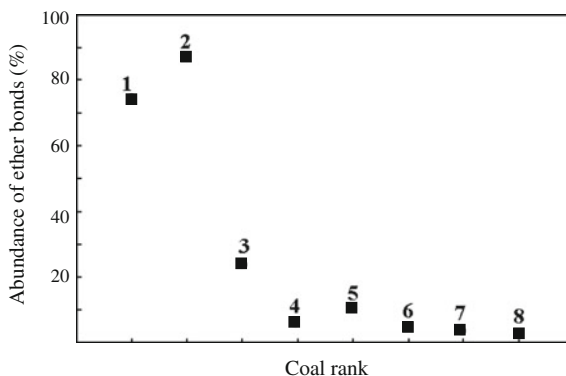
Assignment of the absorption at 1618 cm^{-1} remains controversial. Brown [11] and Solomon [12] believed that the 1618 cm^{-1} absorption arose from the rocking vibrations of hydroxyl-substituted aromatic backbones. However, Friedel [13] proposed it was more reasonable to assign the absorption to conjugated carbonyl groups. This author agrees with Brown and Solomon's conclusion, because a typical absorption at 1580 cm^{-1} , an important indicator of conjugated C=C structures, was not observed in the coal IR spectra. Eolfson [14] thought that an increase in the number of aromatic ring substituents weakened the intensities of absorption bands. The strong absorption band at 1450 cm^{-1} shifts to lower frequency and gradually disappears with increasing ring condensation degree.

The oxygen-containing functional groups in coal include carboxyl, carbonyl, hydroxyl, and ether groups. The ether group absorption is normally at 1225 cm^{-1} , caused by an asymmetric stretching vibration. The C=O absorption in peat is at 1716 cm^{-1} , assigned to C=O in aliphatic chains, which confirms that peat coal is of low coal rank, without condensed aromatic structures. Siskin et al. [15] confirmed that the rupture of ether bonds usually occurred on bonds linked to a single benzene ring. Figure 2.4 shows the relationship between the number of ether bonds and the coal rank. Figure 2.4 shows that the ether bond abundance is very low in all coals except peat and lignite. The low abundance of ether bonds does not indicate low pyrolysis reactivity.

Length of CH_2 Chain

The bimodal absorption at 725 cm^{-1} is usually assigned to CH_2 rocking vibrations, and its intensity is proportional to the amount of consecutive CH_2 groups. The CH_2 absorption shifts from 725 to 750 cm^{-1} , indicating increasing polarity of the coal

Fig. 2.4 Relationship between number of ether bonds and coal rank: 1 peat; 2 lignite; 3 long-flame coal; 4 fat coal; 5 coking coal; 6 lean coal; 7 meager coal; and 8 anthracite

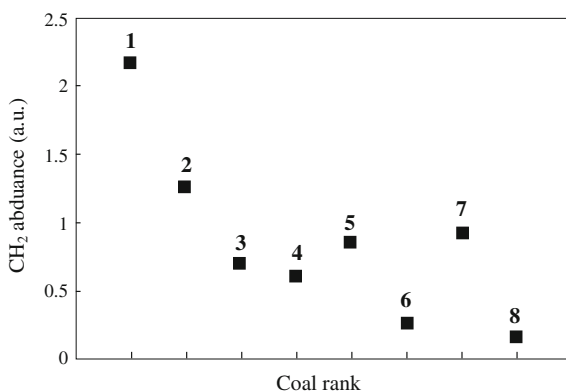


structure. In high-rank coal, the CH_2 absorption peak is sharp, the coal structure is unitary and $\text{CH}_2\text{--CH}_2$ bond cleavage depends on the bond energy rather than on the effects of adjacent functional groups. As Fig. 2.5 shows, the number of CH_2 groups decreases with increasing coal rank. The CH_2 absorption wavenumber increases as the coal rank increases, and reaches 779 cm^{-1} in lignite. In the lignite structure, large amounts of unsaturated electron-donating groups surround CH_2 groups, and these electron-donating groups significantly affect the cleavage of $\text{CH}_2\text{--CH}_2$ bonds. Heredy and Neuworth [16] showed that CH_2 attached to a single benzene ring was least active, CH_2 linked to a phenanthrene ring was moderately active, and a single CH_2 was more active than consecutive CH_2 groups in an aliphatic chain.

2.2.2 Nuclear Magnetic Resonance Spectroscopy

Since its invention in 1946, NMR has become a powerful tool for the determination of organic structures. The NMR spectrum provides a great deal of information about the structure of a compound, and some structural information can only be

Fig. 2.5 Correlation between abundance of CH_2 and coal rank: 1 peat; 2 lignite; 3 long flame coal; 4 fat coal; 5 coking coal; 6 lean coal; 7 meager coal; and 8 anthracite



obtained using NMR spectroscopy. NMR spectroscopy is widely used in research on coal structure.

NMR spectra provide information on chemical shifts, peak areas, and coupling and/or splitting. Peak coupling and splitting provide detailed information on the fine chemical structure. When NMR is used in the analysis of coal samples, it is usually a challenge to analyze the fine chemical structure, because the absorption signals overlap. In this section, therefore, only a brief introduction to chemical shifts and peak areas is given.

In NMR spectroscopy, nuclei in the same chemical environment generate only one absorption signal, and nuclei located in different chemical environments absorb magnetic waves at various frequencies, because of the magnetic shielding effects of adjacent atoms. A typical ^1H NMR spectrum is shown in Fig. 2.6.

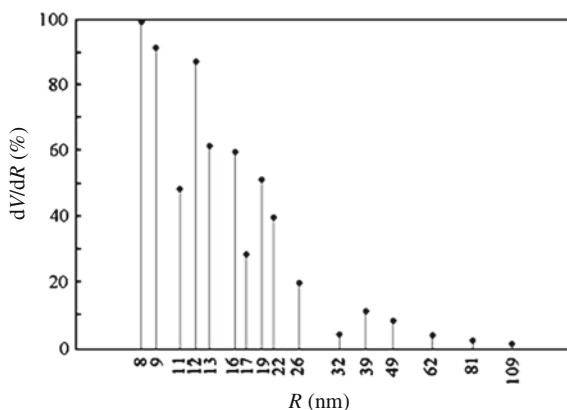
Many factors, including the adjacent functional groups, conjugated bonds, and hydrogen bonding, change the nuclear chemical shift, as a result of changes in the chemical environment surrounding the target nucleus.

The area under a peak is represented by the integration curve and proportional to the number of hydrogens contributing to that peak. This provides useful information for assigning the absorption peaks and classifying the environment of the nucleus.

The major elements (C and H) in coal samples have nuclei that are active in NMR spectroscopy, with significant differences among the signal intensities. The ^1H nucleus has a spin quantum number of $1/2$, and a natural abundance of 99.985 %. It is therefore easy to measure the ^1H NMR signal. The ^{12}C nucleus is not active in NMR and does not generate absorption signals, because its nucleus spin quantum number is 0. The ^{13}C nucleus has a spin quantum number of $1/2$, and a natural abundance of 1.107 %, making it more difficult to measure ^{13}C NMR signals.

^1H NMR was first used in coal structural analysis by Newman [17] in 1955, and has been widely used since then. ^1H NMR provides detailed information on the types and distribution of hydrogen atoms in coal and coal derivatives; for example, the chemical shifts of aromatic hydrogen atoms are 6–10 ppm; the chemical shifts

Fig. 2.6 Pore size distribution of Jincheng anthracite



of hydrogen atoms at the α positions of alkyl-group side-chains bonded to aromatic carbons are 2–4 ppm, and those of hydrogen atoms in alkyl groups attached at the β or further positions to aromatic carbons are around 0.2–2 ppm. Brown et al. [18] calculated three structural parameters using the following equations:

$$f_a = \frac{\frac{C}{H} - \frac{H_\alpha^*}{X} - \frac{H_0^*}{Y}}{\frac{C}{H}},$$

$$\sigma = \frac{\frac{H_\alpha^*}{X} + \frac{O}{H}}{\frac{H_\alpha^*}{X} + \frac{O}{H} + H_{ar}^*},$$

$$\frac{H_{aru}}{C_{ar}} = \frac{\frac{H_\alpha^*}{X} + H_{ar}^* + \frac{O}{H}}{\frac{C}{H} - \frac{H_\alpha^*}{X} - \frac{H_0^*}{Y}},$$

where

- f_a is the percentage of aromatic carbons, i.e., the ratio of aromatic carbons to total carbons;
- σ is the percentage of substituted aromatic carbons, i.e., the ratio of substituted aromatic carbons to total substitutable aromatic carbons;
- H_{aru}/C_{ar} is the condensation degree of aromatics, i.e., the hydrogen/carbon ratio in unsubstituted aromatics;
- H_{ar}^* is defined as H_{ar}/H , i.e., the ratio of aromatic hydrogens to total hydrogens;
- H_α^* is defined as H_α/H , i.e., the ratio of H_α (hydrogen atoms at the α positions in alkyl side chains bonded to aromatic carbons) to total hydrogen atoms;
- H_0^* is defined as H_0/H , i.e., the ratio of H_0 (hydrogen atoms at the β or further positions in alkyl side chains bonded to aromatic carbons) to total hydrogen atoms;
- X, Y are the ratios of hydrogen/carbon at the α or β positions of alkyl side chains bonded to aromatic carbons, usually assumed to be 2.

In Table 2.6 [19], the calculated key structural parameters of pyridine extracts from various coals are listed. With increasing coalification, H_{ar} and H_α gradually increase, and H_0 gradually decreases. This suggests that the extent of the aromatic structure increases and the alkyl side chains become shorter as the degree of coalification increases.

Coal extract samples were used in the ^1H NMR test, because dissolved samples are typically required. The chemical shifts of highly active hydrogen atoms, usually attached to the carbons in ether and ester groups and involved in crosslinking, are listed in Table 2.7.

^{13}C NMR spectroscopy provides direct information about the carbon backbone. Both liquid and solid samples can be used in ^{13}C NMR spectroscopy, so interference originating from the solvent extraction process can be eliminated. The chemical shift of ^{13}C may reach 200 ppm, which is a much broader range than that

Table 2.6 Hydrogen distribution and structural parameters of pyridine extracts

C_{daf} (%)	Extraction yield (%)	H distribution			Structural parameters		
		H_{ar}^*	H_{α}^*	H_0^*	f_a	σ	H_{ar}/C_{ar}
61.5	13.8	0.07	0.12	0.75	0.41	0.74	0.93
70.3	16.6	0.18	0.20	0.56	0.61	0.55	0.69
75.5	15.8	0.21	0.20	0.53	0.62	0.52	0.72
76.3	6.7	0.20	0.30	0.44	0.64	0.59	0.76
76.7	16.7	0.10	0.21	0.64	0.53	0.67	0.60
80.7	12.8	0.27	0.22	0.45	0.70	0.45	0.65
82.6	21.4	0.35	0.26	0.36	0.73	0.37	0.68
84.0	18.5	0.30	0.25	0.43	0.69	0.41	0.67
85.1	20.9	0.27	0.29	0.39	0.72	0.47	0.59
86.1	19.3	0.32	0.28	0.37	0.73	0.37	0.57
90.0	2.8	0.55	0.31	0.13	0.85	0.27	0.63
90.4	2.5	0.50	0.30	0.19	0.83	0.26	0.57

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Table 2.7 Chemical shifts for typical active protons (ppm)

Compound	δ	Compound	δ
ROH	0.5–5.5	Ar–SH	3.0–4.0
ArOH	10.5–16	RSO ₃ H	11.0–12.0
Ar–OH	4–8	RNH ₂ , R ₂ NH	0.4–3.5
C=C–OH (bonded)	15–19	ArNH ₂ , Ar ₂ NH, ArNHR	2.9–4.8
RCOOH	10–13	CONH ₂ , ArCONH ₂ , R	5.0–6.5
=N–OH	7.4–10.2	RCONHR, ArCONHR	6.0–8.2
R–SH	0.9–2.5	RCONHAr, ArCONHAr	7.8–9.4

of the ^1H nucleus. Overlap of absorption peaks is rarely observed in ^{13}C NMR spectra, which is helpful in analyzing individual carbons. However, ^{13}C NMR suffers from a low signal-to-noise ratio and low sensitivity (only 1/5800 that of ^1H NMR), but this can be greatly improved using Fourier-transform technology.

2.2.3 X-ray Diffraction

In a crystal structure, atoms are arranged in a periodic repeated pattern. The crystal lattice spacing is of the same order of magnitude (around 10 nm), so diffraction occurs when X-rays pass through the crystal. The diffraction pattern is recorded photographically for analysis of the crystal structural parameters. The fundamental theory of XRD is expressed by Bragg's law:

$$2d \sin \theta = n\lambda,$$

where

d is the spacing between layers of atoms (nm);

θ is the angle between the incident rays and the crystal surface;

n is an integer (1, 2, 3, and so on), because the reflected waves from different layers are perfectly in phase with each other;

λ is the X-ray wavelength (nm).

Graphite has a clear crystal structure and exhibits nine XRD peaks which are related to different crystal facets. Although coal is not crystalline, it still has diffraction peaks, which show the arrangement of the carbon atoms. Lignite and bituminous coal only have two diffraction peaks, and anthracite has four peaks.

Macerals from the same coal sample have significantly different molecular structures. This difference is observed in the XRD patterns. The inertinite group shows four diffraction peaks, which are similar to those from anthracite. Vitrinite only shows three diffraction peaks, and the peaks from exinite are indistinct.

As the degree of coalification increases, diffraction patterns become increasingly distinctive and similar to that of graphite, and the aromatic structure of the coal becomes more microcrystalline. The aromatic microcrystalline structure is composed of various layers of polyaromatic rings, and is described by three key parameters, L_a , L_c , and d , where L_a is the horizontal dimension of the aromatic microcrystal, L_c is the vertical dimension, and d is the average distance between the polyaromatic layers. The parameters L_a , L_c , and d can be calculated from the XRD pattern. With increasing degree of coalification, L_a and L_c increase, and d gradually decreases. The distance between polyaromatic layers increases with increasing coalification [20]; The parameters for the aromatic microcrystals of various coal macerals also differ significantly. Table 2.8 [21] lists the L_a , L_c , and d values for the macerals from Yanzhou coal (the maceral density gradually increases from group E to I₂).

Table 2.8 Percentages of aromatic carbon and microcrystal parameters for Yanzhou macerals

Maceral	f_a^a	d (nm)	L_c (nm)	L_a (nm)
E	0.56	0.492	0.638	1.824
V ₁	0.65	0.372	0.658	1.768
V ₂	0.69	0.360	0.790	1.490
V ₃	0.70	0.360	0.802	1.976
I ₁	0.73	0.357	0.946	1.868
I ₂	0.77	0.355	1.298	1.998

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^aCalculated from ¹³C NMR spectra

2.2.4 *Small-Angle X-ray Scattering*

SAXS is a scattering technique based on the deflection of collimated X-ray radiation from the straight trajectory after it interacts with structures that are much larger than the X-ray wavelength. Reich et al. [22] was the first to use SAXS in the study of coal structures. SAXS gives information about the sizes, shapes, and orientations of structures in a sample.

SAXS has significant advantages in porosity studies. No sample pretreatment is required and closed pores are measurable using SAXS. SAXS can be used under various conditions, with no pressure and temperature restrictions. It is applicable to solution and in situ reaction systems. In SANS, another small-angle scattering technique, neutrons are used instead of X-rays. SANS is very similar to SAXS in many respects and provides reliable porosity data. The limitation of small-angle scattering techniques is that they cannot be used to analyze the ultramicropore structures in coal. Bale et al. [23] first used SAXS techniques for fractal analysis. Johnston et al. [24] used SAXS to study drying and thermal processes of Victoria lignite. In the drying process, the volume fractal dimension and the area fractal dimension are significant before and after dehydration.

2.2.5 *Electron Microscopy*

Electron microscopy is used to investigate the micro-structures of a wide range of solid surfaces. The pore structures or spatial structures of large molecules in coal samples have also been extensively studied using electron microscopy. In work performed at Tokyo University, Japan three organic maceral groups from Pingshuo gas coal were investigated by high resolution transmission microscopy and was confirmed to be an effective method for studying coal internal structures and coalification processes. Other researchers have performed fractal analysis of coking coal using electron microscopy [25]. The 3D profiles of solid surfaces can be observed using the secondary electron imaging technology in scanning electron microscopy (SEM). If the incident intensity of the electron is I_p , the intensity of the secondary electron, I_s , is calculated using the following equation:

$$I_s = C \frac{I_p}{\cos \theta},$$

where θ is the angle between the electron beam and the solid surface, and C is a constant. When the electron beam is scanning through a concave-convex surface, θ is changing, so the amount of secondary electrons at each imaging point changes.

When a surface with fractal features is analyzed using electron microscopy, the SEM images reveal gray levels and gradients. The use of graphics-processing

software and computational tools enables the fractal dimension to be estimated using the discrete fractal Brownian increment random field mathematical model.

2.2.6 Surface Methods

2.2.6.1 Gas Adsorption

Gas adsorption is a classic method for investigating surface structures. Normally, low-temperature (77 K) N₂ adsorption or room-temperature (298 K) CO₂ adsorption is used, with the BET adsorption model:

$$\frac{X}{V(1-X)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} X,$$

where

X is the relative pressure, i.e., the ratio of the equilibrium and the saturation pressures of the adsorbates at the adsorption temperature, P/P_s ;

V is the adsorbed gas quantity at a relative pressure (m^3);

V_m is the saturated monolayer adsorbed gas quantity (m^3);

C is the BET constant related to adsorption heat.

The BET equation can be plotted as a straight line with $X/V(1-X)$ on the y -axis and X on the x -axis. The value of the slope, a , and the y -intercept, b , of the line are used to calculate the monolayer adsorbed gas quantity V_m :

$$V_m = \frac{1}{a+b},$$

If the adsorbed gas is N₂, which has a molecular cross-sectional area of $1.62 \times 10^{-19} \text{ m}^2$, the surface area in the BET model, S_{BET} , can be calculated using the equation:

$$S_{\text{BET}} = 4.353 \times \frac{V_m}{m},$$

where m is the mass of the sample (g). Anderson [26] used an empirical constant, K , in the classic BET equation for coal sample analysis to improve the accuracy (K is usually 0.8 for coal analysis):

$$\frac{X}{V(1-KX)} = \frac{1}{V_m CK} + \frac{(C-1)}{V_m C} X,$$

N₂ adsorption requires a relatively long equilibrium period and is inappropriate for micropore analysis. CO₂ adsorption at room temperature is also widely used in coal surface analysis. Gan et al. [7] studied coal surfaces using N₂ and CO₂ adsorption methods, and found that the surface areas obtained with N₂ were 1–88.4 m² g⁻¹, which were notably lower than those of 96–426 m² g⁻¹ obtained using CO₂ adsorption. These results suggest that only the macropores and mesopores in coal adsorbed N₂ molecules.

The D–P equation is also commonly used to calculate surface areas:

$$\ln V = \ln V_0 - \left(\frac{BT^2}{\beta^2} \right) \ln^2 \left(\frac{P_s}{P} \right),$$

where

V is the adsorbed gas volume (m³) under pressure P ;

V_0 is the volume of micropores (m³);

T is the adsorption temperature (K);

P_s is the saturation pressure (Pa) of adsorbates at the adsorption temperature;

B is a constant related to the average micropore size;

β is a coefficient.

Walker et al. [27] used CO₂ adsorption at 298 K to study several coals and calculated the surface areas using both the BET and D–P equations. Surface area tests with 28 types of Chinese coal showed an empirical relationship between the results obtained using the BET and D–P equations [28]:

$$S_{D-P} = -14.06 + 2.11S_{BET},$$

Although CO₂ adsorption is widely used in coal surface area analysis, it has been shown to be inconsistent in various independent studies. Dietz et al. [29] and Ghetti et al. [30] suggested that the surface hydroxyl groups and ash content of coal affected the CO₂ adsorption. However, Chinese researchers repeated the CO₂ adsorption tests with Chinese coal samples and found no significant variations in the results, confirming the feasibility of using CO₂ adsorption for coal surface area analysis. Gas adsorption was the first method used for surface fractal analysis.

Normally, N₂ and CO₂ are used as the adsorbed gas in fractal dimension analysis. Unlike the case of surface area analysis, discussed previously, Fairbridge et al. [31] found that using different adsorbed gases did not affect the results of the fractal dimension analysis. In a study of 28 types of Chinese coal, fractal dimension analysis was performed based on the data collected for surface area analysis, using mathematic tools, and the results agree with the fundamental theory of coal structure [32].

2.2.6.2 Mercury Porosimetry

Macropores cannot be analyzed using gas adsorption methods. Mercury porosimetry was developed for the study of macropores, based on the external pressure needed to force the liquid into a pore against the opposing force of the liquid's surface tension. The force balance equation is

$$p_{\text{Hg}} = \frac{-2\gamma \cos \theta}{r},$$

where

p_{Hg} is the forcing pressure (N m^{-2});

γ is the surface tension of the liquid (0.486 N m^{-1} is usually used);

θ is the contact angle of mercury (140° is usually used);

r is the pore radius (m).

The pressure required to intrude mercury into the coal pores is inversely proportional to the pore size.

Mercury porosimetry analysis is simple and quick, but it cannot be used for micropore analysis. So, to obtain the overall distribution of all the pores, a combination of gas adsorption and mercury porosimetry is required.

Mercury porosimetry is also commonly used for surface fractal analysis. Friesen et al. [33] showed that the volume of mercury intruded into the pores is related to the fractal dimension.

2.2.6.3 Case Study of Coal Surface Characterization

An investigation of five coals of various coalification degrees is presented: Fuxin long flame coal, Pingshuo gas coal, Xinzhi fat coal, Fengfeng meager coal, and Jincheng anthracitic coal. The proximate and ultimate analyses of the selected coal samples are displayed in Table 2.4. The five coal samples were ground and sieved; particles of diameter around $100 \mu\text{m}$ were chosen for gas adsorption tests.

Surface analysis was conducted using an automatic adsorption apparatus on 1 g samples in an adsorption tube cooled with liquid N_2 . The instrumental physical constant was determined before the analysis. The sample underwent degasing pretreatment under vacuum ($<6.7 \text{ Pa}$) at $100\text{--}300^\circ\text{C}$. The pressure of the high-purity N_2 gas for the adsorption tests was adjusted to $0.2\text{--}0.3 \text{ MPa}$.

The key surface structural parameters for five coals are displayed in Table 2.10. Figures 2.6, 2.7, 2.8, 2.9 and 2.10 show the pore diameter distributions of the five coals. Figure 2.11 shows the changes in the raw coal surface area with degree of coalification.

As can be seen from Table 2.9, micropores are the predominant pore type. For all five coals, the most probable diameters are lower than 1 nm and the mean pore diameters are below 3 nm . The coal surface areas are large, but the pore volumes

Fig. 2.10 Pore size distribution of Fuxin long flame coal

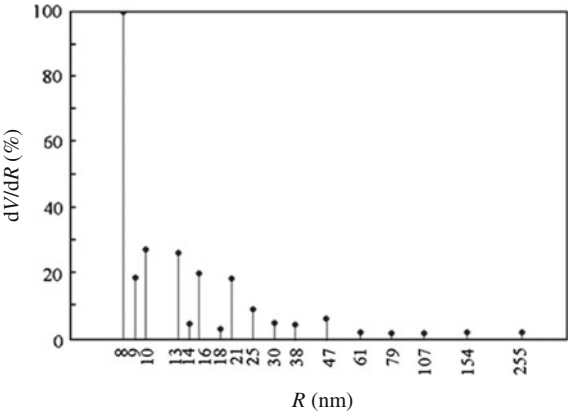


Fig. 2.11 Relationship between surface area and degree of coalification

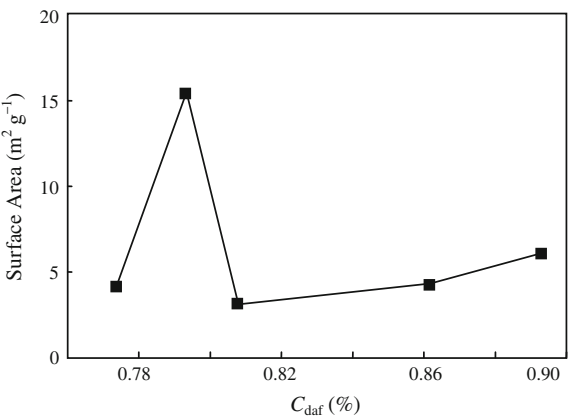


Table 2.9 Key surface structural parameters of five raw coals

Coal sample	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Most probable diameter (nm)	Mean pore diameter (nm)
Fuxin long flame coal	4.23	0.01	0.83	2.57
Xinzhi fat coal	3.12	0.01	0.87	2.73
Pingshuo gas coal	15.5	0.04	0.93	1.32
Fengfeng meager coal	4.30	0.01	0.94	2.76
Jincheng anthracite	6.03	0.01	0.84	2.19

are small, confirming that micropores are the main contributors to the surface area. The data also show that the order of the maceral surface areas is inertinite > exinite > vitrinite. The surface area of exinite is almost three times than those of exinite and vitrinite. Pingshuo gas coal has an inertinite content as high as 25 %, which explains why the surface area and pore volume of Pingshuo gas coal are around four times those of the other four coals. In the other four coals, the changes in surface area are related to the degree of coalification: with increasing degree of coalification, the coal surface area initially decreases and then gradually increases [34]. The surface area is minimum at a carbon content of 85 %.

Xinzhi fat coal, with a carbon content of 83 %, has the lowest surface area ($3.122 \text{ m}^2 \text{ g}^{-1}$), because it has the largest pore volume and most probable pore diameter. Fuxin long flame coal has a large surface area, in line with its low most probable pore diameter. Jinchen anthracite coal has the highest degree of coalification and an even pore size distribution of below 2.5 nm, which suggests that the coal has a high aromatic content with a regular arrangement of large molecules.

2.3 Statistical Constitution Analysis

Natural products can be classified into three categories: micromolecules with uniform molecular structures; large molecules with uniform molecular structures; and mixtures of micromolecules and polymers with various molecular structures. Coal belongs to the last category and contains large molecules with various molecular structures. Waterman [35] first suggested that the characteristics of a material can be described by certain critical structural parameters, which can be obtained using statistical methods. This method was introduced for structural studies of coal by van Krevelen et al. [36], who developed the statistical constitution analysis method, which is one of most powerful methods in coal studies.

2.3.1 Coal Structural Parameters

The complexity of coal structures makes determining the exact molecular structure challenging. Currently, structural parameters that describe an averaged coal structural unit are typically applied. In the following sections, the definitions and formulas for calculating the structural parameters are briefly introduced.

For saturated aliphatic alkane groups:

$$H = 2C + 2,$$

where, H and C represent the number of H and C atoms, respectively.

For the alkanes without conjugated double bonds and acetylene linkage (carbon triple bonds) in the molecules:

$$H = 2C + 2 - 2R - C_a,$$

$$2\left(\frac{R-1}{C}\right) = 2 - f_a - \frac{H}{C},$$

where, R is the number of rings in the structural unit. C_a and C are the number of aromatic and total carbon atoms in the structural unit, respectively. f_a is the aromaticity, defined as C_a/C .

In the above formula, $2(R-1)/C$ is defined as the ring condensation index. If heteroatoms are included in the molecules, the above formula is still applicable after adjustment of the value of H/C .

For coal or other polymeric compounds composed of a variety of structural units, an averaged structural unit is adopted. By considering the bridge bonds among structural units together with the additional rings within these linkages, the structural parameters of the average structural unit are calculated as:

$$H_u = 2C_u + 2 - 2R_u - C_{au} - 2b_u,$$

$$H_u = \frac{p-1}{p} + r_u,$$

$$2\left(\frac{R_u + r_u - \frac{1}{p}}{C_u}\right) = 2 - f_{au} - \frac{H_u}{C_u},$$

where: H_u , C_u are the number of hydrogen and carbon atoms in the average structural unit, respectively. R_u is the number of ring in the average structural unit; C_{au} is the number of aromatic carbon atoms in the average structural unit; f_{au} is the aromaticity of the average structural unit, defined as C_{au}/C_u ; b_u is the number of bridge bonds in an average structural unit, known as polymerisation intensity; r_u is the average number of additional rings that arise from bridging bonds among structural units; p is the number of the structural units included in a polymeric molecule, known as degree of polymerisation.

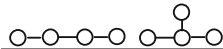
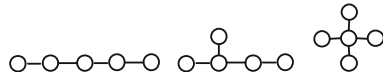
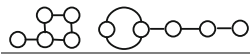
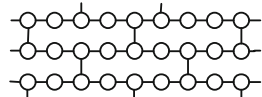
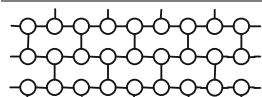
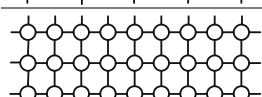
In coal, the parameter $f_{au} = C_{au}/C_u$ is similar to $f_a = C_a/C$, and H_u/C_u is similar to H/C . For the following calculations in this chapter only f_a and H/C are used. Thus the new parameters b_u , r_u and p are determined for the average structural unit. To further illustrate this relationship, examples with average structural units and associated structural parameters (b_u , r_u and p) are listed in Table 2.10.

The total number of rings in an average structural unit are the sum of rings in individual units and those additional rings from bridging bonds.

$$R'_u = R_u + r_u.$$

For a coal structural unit, $1/p$ is negligibly small so that the formula may be further simplified as:

Table 2.10 Examples of b_u , r_u and p in various polymeric structures

Polymeric structural models	p	r_u	b_u
	2	0	0.5
	4	0	0.75
	5	0	0.8
	5	1/5	1
	5	2/5	1.2
	5	4/5	1.6
20 structural units arranged in a linear or branching structure	20	0	0.95
An infinite number of structure units, arranged in a linear or branching structure	∞	0	1
A structure containing a large number of structure units with a ring in the molecule	p	$1/p$	1
	∞	0.25	1.25
	∞	0.5	1.5
	∞	1	2

$$2\left(\frac{R}{C}\right)_u = 2\left(\frac{R'_u}{C_u}\right) = 2 - f_a - \frac{H}{C}.$$

In the above equation, $2(R/C)_u$ is defined as the ring index of the average structural unit and $(R/C)_u$ means the average ring number for each carbon atom. In Table 2.11, the key structural parameters and their internal relations in the coal matrix are described.

2.3.2 Principle of Statistical Constitution Analysis

Statistical constitution analysis of coal is based on the additive molar function developed by van Krevelen [37]:

Table 2.11 Key structural parameters and their internal relations in coal matrix

Category	Structure parameters	Symbol and definition	Extremum	Note
Aromaticity	Fraction of aromatic carbons	$f_a = \frac{C_a}{C}$	0-non aromatic hydrocarbons 1-aromatics	The ratio of aromatic carbon, and hydrogen, and rings to the overall respective values in the structure unit
	Fraction of aromatic hydrogens	$f_{Ha} = \frac{H_a}{H}$		
	Fraction of aromatic rings	$f_{Ra} = \frac{R_a}{R}$		
Degree of ring condensation	Degree of ring condensation	$2\left(\frac{R-1}{C}\right)$	0-Benzene 1-Graphite	Reflects the degree of ring condensation
	Ring index for structural unit	$2\left(\frac{R}{C}\right)_u$	0-Aliphatic alkane 1-Graphite	The average ring number of each carbon atom in a structure unit
	Aromatic ring compactness	$4\left(\frac{R_a + \frac{1}{2}}{C}\right) - 1$	0-cata type condensed aromatics 1-peri type condensed aromatics	Reflects of how many aromatic rings are formed for a certain number of aromatic carbons
Molecular level	Size of aromatic unit	C_{au}	–	Aromatic carbons in structure unit
	Intensity of polymerization	b	0-monomer ≤1-liner polymer >1-cross-linked polymer	The number of bridge bonds in the average structure unit across the coal matrix
	Degree of polymerization	p	–	The number of structural units in the coal matrix

$$MF = C\varphi_C + HC\varphi_H + O\varphi_O + \cdots + \sum X_i\varphi_{X_i},$$

where

MF is the additive molar function;
 C , H , and O are the numbers of C, H, O atoms;
 X_i is the contribution factor i in an average structural unit;
 φ_C , φ_H , and φ_O are the contributions from C, H, and O atoms to the additive molar function;
 φ_{X_i} is the contributions from contribution factor i .

The structural parameters of an average structural unit can be developed using the MF function, even without a coal molecular weight. For example, coal true

density, d , is used as the additive molar function to calculate the ring number (R) and fraction of aromatic carbons (f_a). van Krevelen obtained the following equations, with the adoption of some reasonable assumptions:

$$\frac{M_C}{d} = 9.9 + 3.1 \frac{H}{C} + 3.75 \frac{O}{C} - \left(9.1 - 3.65 \frac{H}{C} \right) \cdot \frac{R}{C},$$

$$M_C = \frac{M}{C} = \frac{1200}{C_{daf}},$$

where M_C is the single-carbon molecular-weight, describing the molecular weight reflected by every single carbon atom; d is the true density (g cm^{-3}). van Krevelen et al. [38] verified the reliability of the above equations using 18 polymers with known structural parameters. The calculated densities were very close to their actual densities. In practical applications, the atom ratio, carbon content, and true density are determined by laboratory tests.

The correlations between f_a and the degree of coalification obtained using four methods are summarized. The results from statistical constitution analysis are slightly higher than those from other methods, but follow the same trend. The f_a increases with increasing degree of coalification. When the carbon content is higher than 95 %, f_a is almost equal to 1, which suggests that only anthracite is highly aromatized [39].

Different macerals of the same coal have different structural parameters. The fractions of aromatic carbons and the ring condensation index increase with increasing degree of coalification for almost all macerals. Exinite has a much lower aromaticity than vitrinite, and its fraction of aromatic carbon changes significantly in response to changes in the coalification degree. Fusinite is close to the highest stage of coalification [40]. Coal with a high degree of reduction usually has a high content of hydrogen atoms, making the H/C ratio an important indicator of the degree of reduction in this type of coal.

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