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LECTURE TEXT

Chemistry and geology of coal: nature, composition, coking, gasification, liquefaction, production of chemicals, formation, peatification, coalification, coal types, and ranks

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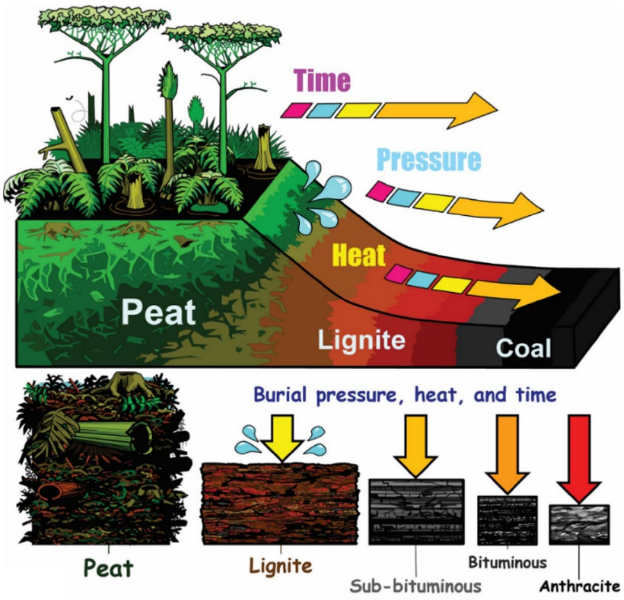
Abstract

As probably the most complex natural (geological) material, as well as a parent of the industrial revolution and the most important source of heat and electricity in the world, coal has attracted and continues to attract special attention of scientists and the entire world population. In this context, this lecture text is intended to provide both chemistry and geology students as well as teachers of courses on the chemistry and geology of coal with a solid background of the chemistry and geology of coal. Various aspects of coal chemistry are covered, including the nature of coal, its composition, coking, gasification, liquefaction and production of chemicals. Coal geology concerns major eras of coal formation as well as the processes of peatification, coalification and the chemical processes of coalification, coal types and their properties, coal lithotypes and coal ranks. Each of these topics is an important subject in its own, and this text is aimed to give only a brief overview of each, emphasising the relationship between the geology and chemistry of coal.

Graphical Abstract



Keywords Coal Chemistry · Geology · Formation · Peatification · Coalification Types · Composition · Liquefaction · Gasification · Coking · Chemical production

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Introduction

Depending on the language, historical period, geographical area, etc., there are various explanations related to the etymology of the modern word coal (in English). Thus, the word most often mentioned is *coal*, which originated from the Old English *col* and means charcoal, live coal, a piece of wood or other combustible substance. It is often related to Proto-Germanic *kula(n)*, Old Frisian *kole*, Middle Dutch *cole*, Dutch *kool*, Old High German *chol*, German *Kohle*, Old Norse *kol*, etc. [1].

To understand the differences in the composition, properties and uses of coal, it is first important to understand the nature of its origin. Coal is the result of an accumulation of organic and inorganic material and its follow-up transformation over geological times by the process of coalification into a fossil fuel with relatively high energy density [2, 3] (the coalificiation process is explained in detail further down). The energy density increases as coalification progresses, which explains the wide variation in coal quality that exists in the world today. To increase the energy density, the amount of inorganic material present must be reduced using various techniques. When using coal to generate electricity, the most common practice is to pulverise the coal before combustion. During combustion, the organic phases are consumed while the remaining inorganic components, such as minerals and trace elements, are converted into coal ash. The composition, properties and use of the residual ash depend on both the inorganic materials present in the fuel and the combustion conditions. Various clean coal technologies (CCTs) have been developed to reduce sulphur and nitrogen oxide emissions generated during coal combustion. Consequently, the composition and properties of the ash they produce are also quite different [2].

Coal is a combustible black or brownish-black sedimentary rock that contains a variable amount of carbon (usually more than 50 wt%) and variable amounts of other elements (mainly hydrogen, sulphur, oxygen and nitrogen) [4–6].

Unlike mineral rocks, which are composed of inorganic material, coal is formed over millions of years by the decay and transformation of plant material into peat (sole-like, partially decayed plant material that accumulates in wetlands), which is later converted into coal under the pressure and heat of deep burial [6–11].

Coal occurs in underground formations called "coal beds" that are about 30 m thick and 1500 km long. It is widespread on all continents (the largest reserves are in the USA, Russia, China, Australia and India) and occurs in the form of *peat, lignite, sub-bituminous coal, bituminous coal, anthracite, graphite, cannel coal and coking coal* [11–13]. Coal can also be classified based on its macroscopic appearance (commonly referred to as coal rock type, lithotype or kohlentype). Four main types are distinguished: *vitrain, clarain, durain and fusain* (which will be discussed later) [14–16].

Depending on the types of coal and their degree of purity, coal may produce upon burning different amounts of ash. Coal ash is the mineral substance that remains after the coal is burned. It contains very little organic matter. Chemical constituents of coal ash may include nitrogen and sulphur compounds, unburned carbon, heavy metals, radioactive elements and polycyclic aromatic hydrocarbons (PAHs). Depending on the location of coal mining, coal ash typically contains heavy metals such as As, Pb, Hg, Cd, Cr, Se as well as, Al, Sb, Ba, Be, B, Cl, Co, Mn, Mo, Ni, Tl, V and Zn, mostly in chemically bonded form. In general, coal ash consists of fly ash (the fines part of the ash carried by the flue gases) and bottom ash (non-combustible material). Among them, fly ash accounts for a major component (80% to 90%) of the total ash, and bottom ash accounts for between 10 and 20% [6, 17–20].

Coal, along with petroleum and natural gas, is the most abundant non-renewable fossil fuel resource currently in use worldwide and is expected to continue to be an important component of the world's energy resources (electricity) for the foreseeable future [21]. It can be considered the forefather of the industrial revolution and the principal source of heat and electricity in the world [22].

Nevertheless, in the recent decades and even in the present time, continuous efforts have been made to replace the use of coal with various alternative energy sources (solar, hydro, wind, nuclear) [23–25]. The use of coal as a fossil fuel resource and the damage caused by its use to the environment and human health will be discussed in the next issues of ChemTexts.

The studies in the field of coal geology and chemistry have been the subject of interest of many researchers, the results of which have been published in a plethora of scientific papers, monographs, books, educational texts, websites, etc. [7, 8, 13, 18, 21, 26–44].

In his modern and comprehensive book *Coal Geology*, Larry Thomas [41] mentions that no single model has been identified that can predict the occurrence, evolution and type of coal, even though the origin of coal has been studied for over a century. A variety of models attempt to identify the environment of deposition, but none can provide a satisfactory explanation for the cyclic nature of coal sequences, the lateral continuity of coal beds and the physical and chemical properties of coals. With the advent of sequence stratigraphy, however, the geological events leading to the different phases of deposition and erosion within the coal-bearing sequences has been recognised.

According to Peter Warwick [21], the various disciplines of coal geology aim to better understand the factors that influence the formation and distribution of coal beds, such as climate, eustacy, tectonics, diagenesis and thermal history. The study of coal geology helps scientists to understand the complex nature of the many different types of coal and how the various disciplines of coal geology can be used together to address the environmental problems associated with coal utilisation.

As expected, the texts in the above-mentioned monographs and books are quite extensive and comprehensive, being presented on hundreds of pages. On the other hand, in the abundance of scientific papers on coal (including coal chemistry and coal geology), the texts are of a very high scientific level and most refer to the specific topics of coal investigations, in which the obtained results are discussed in detail, but often not comprehensively. Therefore, we have prepared a manuscript on coal chemistry and coal geology in which various aspects of coal chemistry (nature of coal, its composition, coking, gasification, liquefaction and production of chemicals) and coal geology (various types of coal formation, peatification, coalification, chemical processes of coalification, coal types and their properties, coal lithotypes and coal rank) are presented together. To our knowledge, there is no manuscript of this type and content in the literature that presents all the mentioned aspects of coal chemistry and geology in a paper of about 20 pages. We hope that this type of text will be useful for chemistry and geology students as well as for teachers of courses on the chemistry and geology of coal.

Chemistry of coal

Composition

Chemical composition is the underlying criterion for the oldest coal-classification system, later improved in the systems that classified coals based on their hydrogen and carbon content [16]. However, because the relationships between chemistry and other coal properties are complex, these types of classifications are rarely used for practical purposes nowadays.

The physical and chemical properties of coal are determined using proximate, ultimate and calorific value analysis [5, 38].

The *proximate analysis* is used to determine moisture, volatile matter, fixed carbon and ash. The volatile matter does not exist by itself (with the exception of some adsorbed methane), but denotes the volatile compounds that are formed and expelled when the coal is heated. For economic reasons, it is important to know the moisture and ash content of coal as they do not contribute to the heating value of coal. The calorific value mainly comes from the volatile matter (excluding moisture) and the fixed carbon content.

The *ultimate analysis* is used to determine ash, carbon, hydrogen, nitrogen, oxygen, sulphur and moisture content of coal. Additionally, specific chemical analysis may be also employed to determine the presence of different forms of sulphur in coal (its minerals pyrite, marcasite, gypsum or organically bound sulphur) as well as the presence of trace elements (e.g. mercury and chlorine).

The calorific value of coal is determined by using the bomb calorimeter method.

It should be noted that the results of both proximate and ultimate analysis vary slightly depending on the country (locality) where the coal is excavated and the type of coal. For example, a typical bituminous coal may have an ultimate analysis on a dry, ash-free basis of 84.4% carbon, 5.4% hydrogen, 6.7% oxygen, 1.7% nitrogen and 1.8% sulphur (on a weight basis) [18]. In this context, the ash composition of a typical bituminous coal can vary (SiO_2: 20–40; Al_2O_3: 10–35; Fe_2O_3: 5–35; CaO: 1–20; MgO 0.3–4; TiO_2: 0.5–2.5; $Na_2O + K_2O$: 1–4; SO_3: 0.1–12, expressed as oxides, wt%) [18]. The average content of minor components of ash includes: Hg (0.1 ± 0.01 ppm) [45], As (1.4–71 ppm) [46] and Se (3 ppm) [47]. It should be noted that coal is probably the most complex natural (geological) material. Table 1 presents chemical composition (wt%) of one of the typical bituminous coals.

Figure 1 gives a structural model representation of the lignite coal ($C_{39}H_{35}O_{10}NS$), bituminous coal ($C_{18}H_{14}O$) and anthracite coal ($C_{45}H_{29}O_2NS$) [50–53].

Coking

Coking coal is an essential raw material for the production of iron and steel. Coke is a solid carbonaceous residue formed from coking coal (a low-ash, low-sulphur bituminous coal, also known as *metallurgical coal*), which is used in make steel and other iron products [54]. Coke is produced by burning coal at temperatures up to 1000 °C in the absence of

Table 1 Bituminous coal composition [48, 49]

Analysed parameter	As received (wt%)
Carbon	63.75
Hydrogen	4.50
Nitrogen	1.25
Sulphur	2.51
Chlorine	0.29
Ash	9.70
Moisture	11.12
Oxygen	6.88

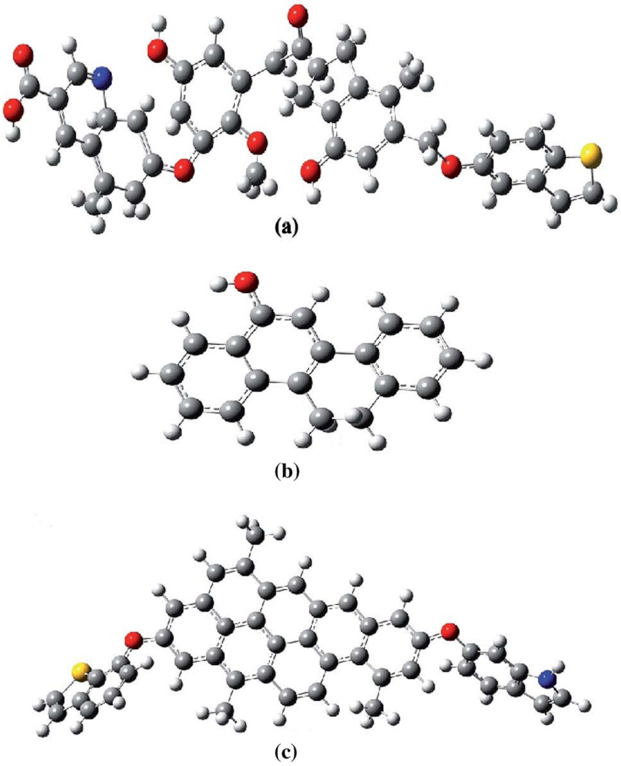

Fig. 1 Structural models of **a** lignite coal ($C_{39}H_{35}O_{10}NS$), **b** bituminous coal ($C_{18}H_{14}O$) and **c** anthracite coal ($C_{45}H_{29}O_2NS$) (yellow-sulphur, blue-nitrogen, grey-carbon, red-oxygen, white-hydrogen atoms respectively) (reproduced from Ref. [50] with permission from the Royal Society of Chemistry)

oxygen to remove the volatile hydrocarbons contained in the coal. The resulting coke is mechanically strong, porous and chemically reactive, all of which are critical properties for stable blast furnace operation. Coke making is extremely problematic from an environmental perspective, as many of the hydrocarbons expelled during the coking process are hazardous (the damage to the environment and human health caused by the use of coal will be discussed in a separate article in an upcoming issue of ChemTexts).

In addition, not all types of coal are suitable for the production of coke [55, 56].

Metallurgical coke is used as a fuel and as a reducing agent in the smelting of iron ore in a blast furnace. The addition of carbon as a heating material during the ongoing process of reducing iron ore (hematite, Fe_2O_3) to iron results in the formation and emission of carbon dioxide:

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$$

The impurities in the coal affect the quality of the coke produced. Such impurities are moisture, volatile matter, ash, sulphur, phosphorus and alkali content. Their levels should be kept as low as possible to avoid their migration into the metal [54]. Sulphur and ash are of particular importance because if their content increases, coke productivity in the blast furnace decreases. The ash content should be below 8% [55, 56].

The coke must be strong enough to withstand the weight of the overburden in the blast furnace, which is why coking coal is so important in conventional steelmaking. Coke from coal is grey, hard and porous and has a calorific value of 29.6 MJ/kg. Coal tar, ammonia, light oils and coal gas are byproducts of coke production.

The rank and chemistry of the coal have a strong effect on the textures of coke (coal types and coal rank are discussed later in the individual subchapters). The coking carbonisation characteristics of the individual constituents of in the coal determine the type of coke produced. For coking to occur, the coal must fall within a certain rank range. The coal must have a comparatively high content of vitrinite (a type of maceral) to form a hard metallurgical coke [55, 56].

Gasification

In coal gasification, coal reacts with oxygen, steam and carbon dioxide to form syngas containing hydrogen (H_2) and carbon monoxide (CO). Gasification is, in fact, a process of incomplete combustion. From a chemical and physical point of view, these two processes are quite similar, the main difference being the nature of the final products. The main difference is that gasification consumes heat evolved during combustion. In gasification, the sulphur from the coal is released as hydrogen sulphide rather than sulphur dioxide, and the nitrogen from the coal is mostly converted to ammonia rather than nitrogen oxides. These reduced forms of sulphur and nitrogen are easily isolated, captured and utilised. Therefore, gasification is a clean coal technology with a better environmental performance than coal combustion [37, 57].

Depending on the type of gasifier and the operating conditions, gasification can produce a fuel gas suitable for various applications (low heating value fuel gas, medium heating value fuel gas and high heating value gas).

Syngas can also be converted into transportation fuels such as gasoline and diesel through the Fischer-Tropsch process. Alternatively, syngas can be converted to methanol, which can be blended directly into fuel or converted to gasoline via the methanol to gasoline process [37].

In gasification, coal is mixed with oxygen and steam and simultaneously heated and pressurised. During the reaction, oxygen and water oxidise the coal to carbon monoxide (CO), also releasing hydrogen gas (H_2). The process was formerly used in underground coal mines, but was also used to produce town gas, which was piped to customers for lighting, heating and cooking.

$$3C \text{ (as coal)} + O_2 + H_2O \rightarrow H_2 + 3CO$$

When the refiner wants to produce gasoline, the syngas is routed into a Fischer-Tropsch reaction. This is called indirect coal liquefaction. However, if hydrogen is the desired end-product, the syngas is directed to the water gas shift reaction, which releases more hydrogen:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Liquefaction

Coal liquefaction is a process of converting coal into liquid fuels or petrochemicals. There are several processes to accomplish this task. The two most common are the *indirect route* and the *direct route* [58, 59].

The *indirect route* consists of two steps: In the first step, coal is gasified with steam and oxygen to produce a synthesis gas (syngas), which is then purified to remove dust, tar and acid gases. In the second step, the synthesis gas (syngas) goes through the Fischer-Tropsch process in the presence of catalysts, which converts the syngas into a range of hydrocarbon fuels such as gasoline, diesel and methanol [60].

Direct coal liquefaction involves contacting coal directly with a catalyst at elevated temperatures and pressures in the presence of a solvent with the addition of hydrogen (H_2) to produce a raw liquid product that is further refined into liquid fuels. It is referred to as direct liquefaction because the coal is converted to liquid without the prior formation of syngas (which in turn be converted to liquid products) [60].

Coal liquefaction emits more carbon dioxide than the production of liquid fuels from crude oil. Biomass blending and the use of carbon capture and storage (CCS) would emit slightly less than the oil process, but at a high cost [61].

Production of chemicals

The production of certain chemicals from coal dates back to its beginnings in the 1950s. Coal is used to produce a variety of chemical substances, chemical fertilisers as well as dyes, drugs, plastics, explosives, etc. The processes used to produce certain chemicals from coal are usually proprietary systems with specialised processing equipment. The main route for obtaining the above chemicals and fertilisers is coal gasification to produce syngas [62, 63]. Figure 2 shows a simplified purification scheme of cryogenic partial condensation of syngas (CO/H_2).

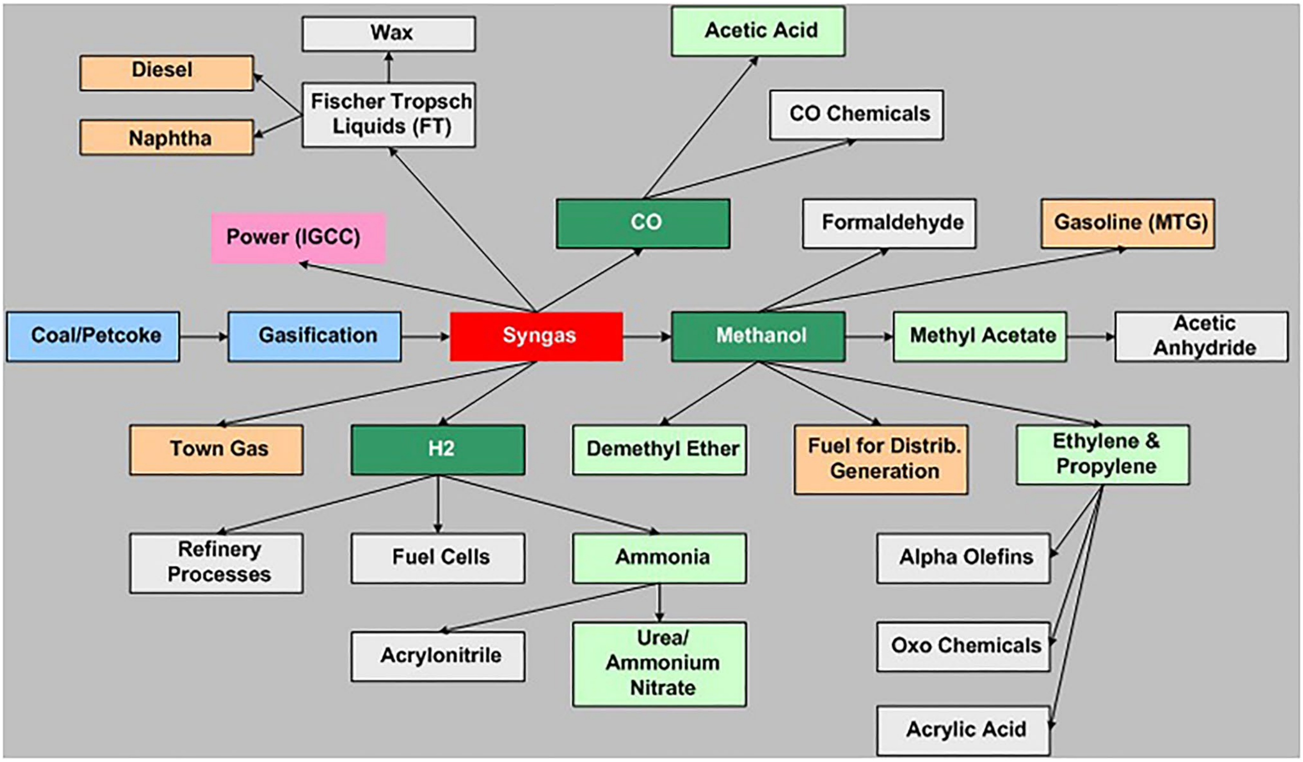

Fig. 2 Scheme of the production of chemicals from coal [63] (provided by the US Department of Energy's National Energy Technology Laboratory)

Chemicals produced directly from syngas include methanol, hydrogen and carbon monoxide (highlighted in dark green in Fig. 2). They are subsequently the chemical building blocks from which various chemical derivatives are manufactured, including olefins, acetic acid, formaldehyde, ammonia, urea and others. The versatility of syngas as a feedstock for primary chemicals and high-value downstream products provides the opportunity to use coal to produce a wide range of products. However, it should be mentioned that in the twenty-first century, the use of coal bed methane is becoming increasingly important [63].

In the following discussion, a very brief description of the valuable properties and processes of some important chemicals such as carbon monoxide, acetic acid, formaldehyde and olefins is given [62, 63].

Methanol

In recent years, there has been growing interest in the use of methanol as an alternative liquid fuel. Methanol is produced by conversion or derived from syngas, natural gas, coal, refinery off-gas or petroleum:

$$2H_2 + CO \rightarrow CH_3OH$$

Coal-derived methanol contains no sulphur or other impurities and could replace petroleum in transportation, provide a hydrogen source for fuel cells or be used as a peak fuel in combustion turbines.

In addition to using the methanol directly as a fuel, it can be converted into gasoline using a special catalyst. Methanol is also used in the process of production of dimethyl ether and also for gasoline according to the reaction [64]:

$$\text{Methanol} \rightarrow \text{dimethyl ether} \rightarrow \text{ethylene} \rightarrow \text{oligomerization} \rightarrow \text{gasoline}$$

Hydrogen

Various methods are used for the production of hydrogen. The most common among them is the so-called steam methane reforming. In this process, methane is converted into a mixture of hydrogen and carbon dioxide:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CH_4 + H_2O \rightarrow CO + 3H_2CO + H_2O \rightarrow CO_2 + H_2$$

The process of partial oxidation of hydrocarbons (coal, natural gas, heavy oils and solid biomass) is also used to produce hydrogen. Below is given an example reaction for this type of partial oxidation:

$$2C_8H_{18} + 2H_2O + 9O_2 \rightarrow 12CO + 4CO_2 + 20H_2$$

Syngas ($CO + H_2$) obtained from coal:

$$C\ (\text{as coal}) + H_2O \rightarrow CO + H_2$$

can be further converted to hydrogen:

$$CO + H_2O \rightarrow H_2 + CO_2$$

Ammonia

The fuel-bound nitrogen of coal is transformed during the pyrolysis of coal (gasification) to ammonia. Then, the residual gas containing ammonia is washed with a spray of sulphuric acid so that ammonium sulphate is formed.

In addition to using syngas as a feedstock for the production of a variety of organic and inorganic materials, it can also be used as a source of hydrogen (H2) for the synthesis of ammonia:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Carbon monoxide

Syntheses of certain chemicals require high purity carbon monoxide (CO) as a feedstock. This is obtained by separation from syngas, which can be accomplished by several commercial processes: cryogenic purification, pressure swing adsorption, membrane separation and salt solution absorption. Cryogenic purification is usually the preferred method unless the syngas feed contains large amounts of nitrogen (N_2), since the boiling points of CO and N_2 are close [$T_B(CO) - T_B(N_2) = -\ 4.3$ K)]. Under this situation, copper salt solution absorption can be used instead.

Acetic acid and derivatives

Acetic acid (CH_3COOH), an important industrial chemical, can be produced from coal-derived methanol indirectly through carbonylation of methanol over rhodium or iridium catalysts (with various iodide or other additives) according to the following reaction:

$$CH_3OH + CO \rightarrow CH_3COOH$$

The rhodium catalysed process is highly selective (> 98% acetic acid) and operates under mild reaction pressure (~3.45 Pa) in a liquid phase reactor. Acetic acid reacts with methanol to form methyl acetate (CH_3COOCH_3), which further reacts with CO to produce acetic anhydride, $(CH_3CO)_2O$.

Formaldehyde

Formaldehyde can be produced from coal indirectly through dehydrogenation and partial oxidation of methanol using a silver catalyst, based on the following reactions:

$$CH_3OH \rightarrow HCHO + H_2$$

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow HCHO + H_2O$$

Equilibrium conversion and potential side reactions are highly temperature dependent. The overall reaction temperature is controlled by the quantity of air (oxygen) used and the addition of inerts, such as water and/or nitrogen.

Olefins

Olefins, such as ethylene and propylene, can be produced from coal gasification indirectly by catalytic cracking of methanol (CH_3OH), commonly called the methanol-to-olefins (MTO) process. The final product from distillation separation typically consists of polymer grade ethylene and propylene, a methane-rich fuel gas, plus a small amount of ethane, propane, butane, pentane and higher molecular weight liquids.

Humic substances

Interest in soil humus has increased during the last years [103]. Humus is formed by the decomposition of plant and animal residues by microorganisms in soils, composts, peat bogs and water basins [65]. It is a complex material of brown- to dark-coloured substances. Humic substances consist of complex aromatic macromolecules with amino acids, peptides and amino sugars [66], while humic fertilisers are derived from brown coal [67]. Details of the procedures used to isolate humic acids from brown coal have been described by Hänninen et al. [68] and Demirbas [69].

Geology of coal

Formation

In general, most of the coal (and the other two fossil fuels, oil and natural gas) excavated today is thought to have originated from plants that grew in and adjacent to swamps in warm, moist regions hundreds of millions of years ago [7, 8, 16, 36, 70–72]. At various times in the geological past, material from these dense forest plants in low-lying wetlands (which remained wet most of the time) was converted to peat (soil-like, partially decayed plant material) by the activity of microorganisms. This organic plant material continued to accumulate and was later converted to coal. There are three main sources of evidence that coal was derived from plants. The first relates to lignite (the lowest coal rank), which often contains recognisable plant remains. The second evidence is sedimentary rock layers above, below and adjacent to coal seams that contain plant fossils (leaves and stems) in the form of imprints and charred films. The third piece of evidence is related to the fact that even high rank coal may contain plant precursor material.

Precambrian coal is thought to have originated from residues of algae [7]. An example is anthracite, the highest coal rank material from the *Proterozoic Eon* (2.5 billion to 541 million years ago) of *Precambrian time*, which has this origin. Fossil algae and fungi (any of about 144,000 known species of organisms from the fungal kingdom, which includes yeasts, rusts, smuts, mildews, moulds and mushrooms) have also been found in the siliceous rocks of the same age.

Otherwise, two major eras of coal formation in geology are registered [16, 73]. The older one includes the *Carboniferous Period* (358.9 million to 298.9 million years ago) and the *Permian Period* (from 298.9 million to 251.9 million years ago) of the *Paleozoic Era*. Much of the bituminous coal in Europe and eastern North America, for example, is of Carboniferous Period, while most of the coal in Siberia, eastern Asia and Australia is of *Permian Period*.

The younger era of coal formation began about 145 million years ago, during the *Cretaceous Period*, and peaked about 66 million to 2.6 million years ago, during the *Paleogene* and *Neogene periods* of the *Cenozoic Era*. Most of the coals formed during this later era are lignites and subbituminous (brown) coals, which are widely distributed in western North America (including Alaska), southern France and central Europe, Japan and Indonesia [16, 74] (see Fig. 3).

Although coal is known from most geological periods, about 90% of all coal beds were deposited in the *Carboniferous* and *Permian periods*, accounting for only about 2% of Earth's history [8].

In addition to favourable geographic conditions (temperature, sea level, river delta erosion, etc.), other factors (such as a high oxygen content > 30%, a high carbon dioxide content that promotes plant growth and the nature of the Carboniferous forests, which included lycophyte trees) contribute to the rapid deposition of coal through the formation of extensive coal beds [8].

Peatification

Peat is a soil-like, partially decayed plant material that accumulates in wetlands (distinct ecosystems that are inundated by water) and is the precursor material from

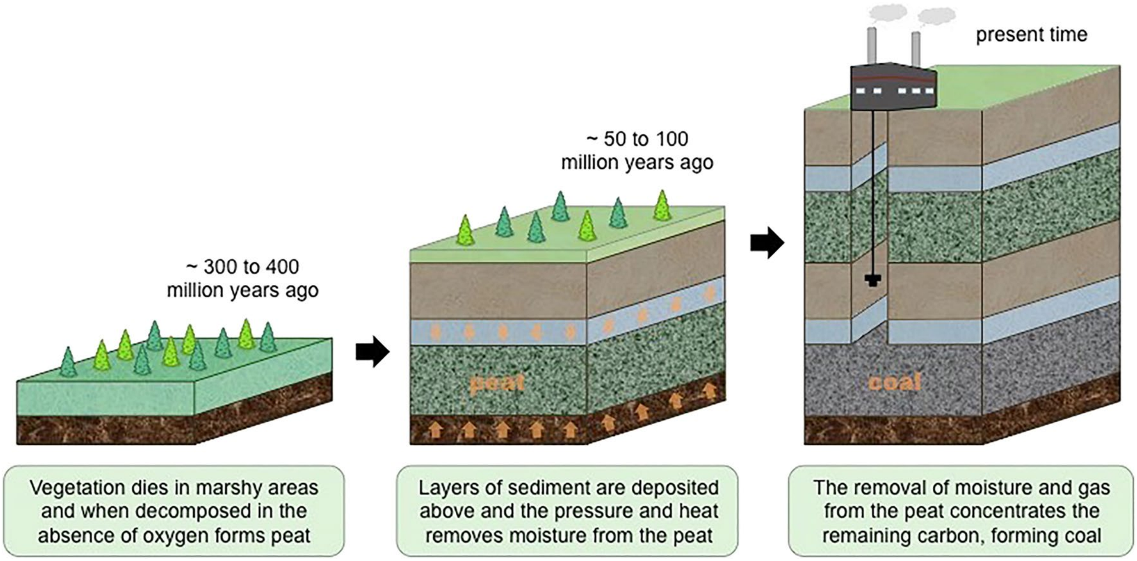

Fig. 3 Schematic presentation of coal formation through the hundred million years [75]. (Credit: B. Cornell, available at http://ib.bioninja.com.au)

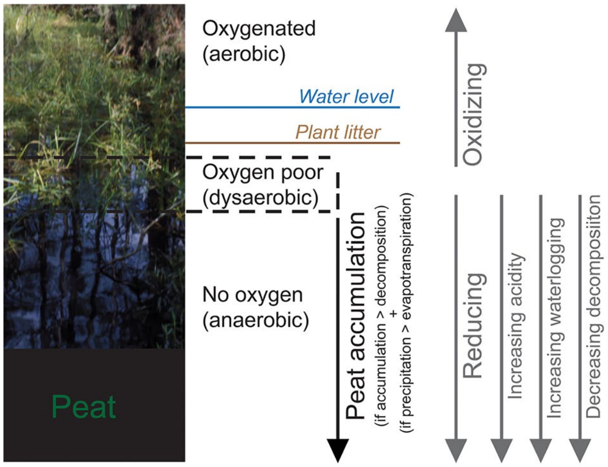

Fig. 4 Schematic presentation of peat formation process [6]. (Credit: Kentucky Geological Survey, University of Kentucky)

Fig. 5 Neat stacks of peat drying at the side of the area from which it was cut [80]. (Credit: Jonathan Wilkins, under https://creativecommons.org/licenses/by-nc/2.0/)

which coal is derived [6, 76]. Peat formation is controlled by at least three factors: (1) the evolutionary development of plant life; (*2*) the climatic conditions (warm enough to promote plant growth and moist enough to allow partial decomposition of plant material and preserve peat); (*3*) physical conditions of the area (its geographic location relative to the sea or other water bodies, subsidence or uplift rates, etc.) [16, 77, 78]. Warm humid climates are suitable for the production of bright coal, known as bituminous coal, which is characterised by its fine banding and high concentrations of nitrogen, sulphur and moisture. Cooler temperate climates, on the other hand, are favourable for the production of so-called detrital coal with relatively little bright coal.

The process of partial decomposition of plant material accumulated in wetlands is called *peatification* [6, 76, 77, 79] (see Fig. 4).

Figure 5 shows the peat cutting face and the cuttings obtained from the peat banks, which were formed during the process of coal formation at thick peat deposits developed at various conditions (explained below in the text) [80].

The area where the coal beds may have developed must have been elevated to allow plant growth to develop (areas near seacoasts or low-lying areas near streams remain moist enough for peat to form). The process of coal formation in thick peat deposits developed in places where the following conditions prevailed: slow, continuous subsidence; the presence of levees, beaches and bars that provided protection from frequent flooding; and a limited supply of incoming sediment that would have interrupted peat formation.

Microorganisms (bacteria) attack the plant material and convert it into peat. Very near the surface, where oxygen is still readily available (aerobic/oxidising conditions), decomposition of the plant material produces mainly gaseous and liquid products. As depth increases, conditions (increasingly anaerobic/reducing) become favourable for the development of moulds and peat. The process of peat formation (*biochemical coalification*) is most active in the upper few metres of a peat deposit. Fungi are not found below about 0.5 m, and most forms of microbial life are eliminated at depths below about 10 m. When either the rate of subsidence or the rate of influx of new sediment increases, the peat is buried and soon thereafter the coalification process (*geochemical coalification or physicochemical coalification*) begins. This cycle can repeat many times, which explains the numerous coal seams found in some sedimentary basins [16, 78, 81, 82].

Peat deposits vary and include former plant parts (roots, bark, spores, etc.) and decayed plant parts as well as other decay products, sediment and charcoal. A wide variety of organic and inorganic constituents in the resulting coals formed during the process of peatification are present, including various minerals derived from sediments carried by wind and water [6, 83, 84].

Coalification

The coalification process is characterised by chemical and physical changes in organic and inorganic compounds. It continues until the highest heating during the Earth's history [6, 78, 85, 86].

There are three important physical factors that can influence the coalification process: duration, increasing temperature and increasing pressure [29, 85, 87].

In general, the geological age of a coal was found to have no effect on rank, i.e. time was not considered to be an important factor influencing coal rang. However, modern research has shown that the length of time that the organic compounds and coal are exposed to elevated heating can also influence rank [88]. In addition, different rates of chemical and physical changes occur during coalification and organic maturation, which can be considered as time-influenced parameters [89].

The most widely accepted explanation is that coalification takes place in response to increasing temperature. In general, temperature increases with depth, averaging about 30 °C per kilometre. The temperature gradient ranges from < 10 °C per kilometre in regions undergoing very rapid subsidence to > 100 °C per kilometre in areas of igneous activity. Measurements of the thicknesses of the sedimentary cover and the corresponding coal ranks suggest that temperatures < 200 °C are sufficient to produce anthracite coal.

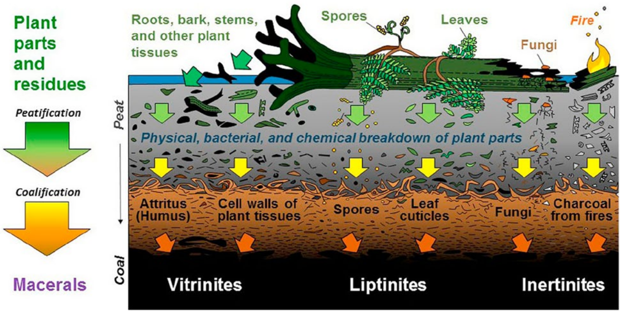

Fig. 6 An overview of the progression of plant and fungal tissues and burned material from peat [90] (under https://creativecommons.org/licenses/by-nc-nd/4.0/)

Increasing pressure due to depth of burial is not thought to cause coalification. In fact, increasing overburden pressure could have the opposite effect in retaining volatile compounds such as methane that must escape during coalification. The pressure may affect the porosity and moisture content of the coal [16, 29]. Figure 6 illustrates the coalification process (as the first step of coal formation), which is characterised by the physical, bacterial and chemical decomposition of plant parts (roots, bark, stems, leaves and other plant tissues) followed by the later process of formation of vitrinites (one of the main constituents of coal), liptinites (finely-ground remains in coal deposits) and inertinites (oxidised organic material). The formed coal beds contain organic components from plants and mineral components from various sources [90]. Vitrinites, liptinites and inertinates constitute the so-called macerals and can be identified by ore microscopy [91].

Chemical processes of coalification

Cellulose, hemicellulose and lignin are the main components of the woody tissue of plants. Peat consists largely of lignin, while the content of cellulose and hemicellulose ranges from 5 to 40% (in the text, the content is given in wt%). However, the presence of various other organic compounds, such as waxes and nitrogen- and sulphur-containing compounds, has also been noted [92]. Lignin contains ~ 54% carbon, 6% hydrogen and 30% oxygen, while cellulose contains ~ 44% carbon, 6% hydrogen and 49% oxygen. Bituminous coal has a composition of about 84.4% carbon, 5.4% hydrogen, 6.7% oxygen, 1.7% nitrogen and 1.8% sulphur, on a weight basis [18]. Clearly, during coalification, chemical processes remove most of the oxygen and much of the hydrogen, leaving carbon, which is why the process is called *carbonisation* [40].

The process of carbonisation consists of three sub-processes: dehydration, decarboxylation and demethanation.

In dehydration, water is removed from the maturing coal via the following reactions [30]:

$$2\,\mathrm{R{-}OH} \rightarrow \mathrm{R{-}O{-}R} + \mathrm{H_2O}$$

$$2\,\mathrm{R-CH_2-O-CH_2-R} \rightarrow \mathrm{R-CH=CH-R} + \mathrm{H_2O}$$

Decarboxylation removes carbon dioxide from the maturing coal, which occurs through a reaction [30]:

$$\mathrm{RCOOH} \rightarrow \mathrm{RH} + \mathrm{CO_2}$$

while demethanation proceeds through the next two reactions (R represents the remainder of a cellulose or lignin molecule to which the reacting groups are attached):

$$2\mathrm{R-CH_3} \rightarrow \mathrm{R-CH_2-R} + \mathrm{CH_4}$$

$$\mathrm{R-CH_2-CH_2-CH_2-R} \rightarrow \mathrm{R-CH=CH-R} + \mathrm{CH_4}$$

The processes of dehydration and decarboxylation take place at an early stage of coalification, while demethanation occurs much later, when the coal has already reached the bituminous rank [43].

During the process of carbonisation, aliphatic compounds (chain carbon compounds) are replaced by aromatic compounds (ring carbon compounds) and polyaromatic compounds (linked rings of carbon atoms) [93].

Coal types and their properties

Coal, as one of the three fossil fuels (along with oil and gas), generates ~ 40% of the world's electricity and about 25% of the world's primary energy). According to the World Coal Association, coal is the largest single source of electricity in the world and will still contribute 22% of electricity generation in 2040 [94]. The quality of coal is directly determined by its carbon content and the amount of thermal energy the coal can produce [95]. Higher-quality coal contains greater amounts of carbon and produces less smoke, burns longer and provides more energy than lower quality coal. Consequently, coal is generally classified into four main types or ranks (from highest to lowest): anthracite, bituminous, sub-bituminous and lignite [96].

Table 2 lists various types of coal, distinguished by their carbon content, moisture content, volatile content and heat content.

In the following fragment, an overview of the different grades of coal, ordered from the lowest to the highest quality, is given.

Peat is the first step in the formation of coal. It is a soft, crumbly, dark brown material formed over generations from dead and partially decaying organic matter. To be converted to coal, peat must be buried in sediment at a depth of 4–10 km [70]. Peat has the lowest carbon content (< 60%) and the lowest energy density (see Table 2 and Fig. 7 [97]).

Lignite or *brown coal* is the least valuable type of coal with a carbon content of 65% to 70% [96]. Compared to other types of coal, it contains the largest amount of compounds other than carbon, such as sulphur and mercury [98]. Lignite is the youngest fossil fuel, with an age of about 60 million years. It has a fairly low energy density of 18 MJ/kg (see Table 2). The higher moisture content and lower carbon content of lignite (Fig. 8, [99]) compared to other higher-grade coals (Table 2) results in lower carbon dioxide emissions compared to other coals.

Fig. 7 Lump of peat [97]

Table 2 Types of coal [96]

Coal	Dry, Carbon content (%)	Moisture content before drying (%)	Dry, volatile content (%)	Heat Content (MJ/kg)
Anthracite	86–92	7–10	3–14	32–33
Bituminous coal	76–86	8–18	14–46	23–33
Sub-bituminous coal	70–76	18–38	42–53	18–23
Lignite	65–70	35–55	53–63	17–18
Peat	< 60	75	63–69	15

Fig. 8 Lignite from Moab, Grand County, Utah, USA [99]

Fig. 9 Samples of sub-bituminous coal [101]

Sub-bituminous coal or *black lignite* is a greyish black to dark brown coal that ranges from hard to soft and is an intermediate stage between low quality lignite and higher-quality bituminous coal. The carbon content of sub-bituminous coal varies from 70 to 76% [71]. It belongs to the younger coals and is approximately 251 million years old. Therefore, the longer burial time compared to lignite increases its energy density, which ranges from 18 to 23 MJ/kg (Table 2). This type of coal is the most commonly used, with 30% of coal resources being sub-bituminous [100] (see Fig. 9, [101]).

Bituminous coal is the second highest quality of coal, with a carbon content of 76–86% [71]. It is the most abundant type and one of the longest buried fossil fuels with an age of about 300 million years. Therefore, its energy density is relatively high ranging from 23 to 33 MJ/kg (Table 2). The high carbon and low moisture content of this type of coal makes it ideal for the production of steel and cement as well as for power generation and coke production [73] (see Fig. 10, [102]).

Anthracite is a dark black form of coal with the highest quality. It is very hard, has a low moisture content and has a carbon content of almost 95% [71]. Anthracite is usually the oldest type of coal, having been formed from biomass buried 350 million years ago. With an energy density 33 MJ/

Fig. 10 Bituminous coal, Washington Township, Licking Co., Ohio, USA [102] (under https://creativecommons.org/licenses/by-sa/2.0/)

Fig. 11 Anthracite from Ibbenbüren, Germany [103] (under https://creativecommons.org/licenses/by-sa/3.0/)

Fig. 12 Coal burning image [104] (under https://creativecommons.org/publicdomain/zero/1.0/)

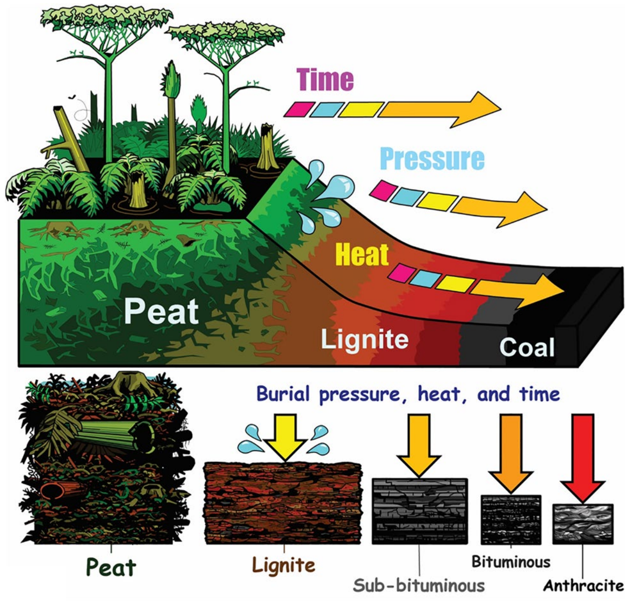

Fig. 13 Scheme of formation of different coal types [105]. (Credit: Stephen Greb, Kentucky Geological Survey, University of Kentucky)

Fig. 14 Sample of graphite [106] (under https://creativecommons.org/licenses/by-sa/3.0/deed.en)

kg [96], it has the highest calorific value of all coal types (see Fig. 11) [103].

This fuel is exceptional at heating up quickly and burns very hot [70]. As one of the cleanest coals, producing less smoke than other coals, anthracite is used for space heating. It burns longer than wood, which makes it attractive for use in home heating stoves [100] (see Fig. 12). The use of anthracite coal is necessary and useful especially in the current energy crisis in the world.

Schematic presentation of the process of formation of coal types is given in Fig. 13 [105].

Sometimes three other types of coal are mentioned in the literature: graphite, cannel coal and coking coal.

Graphite is difficult to ignite and is mostly used in pencils or as powder for lubrication, but not as fuel [26] (see Fig. 14, [106]).

Cannel coal (or candle coal) is a finely ground, high-rank coal with a considerable hydrogen content, consisting mainly of liptinite (finely ground remains in coal deposits) [14].

Coking coal (or metallurgical coal) is burnt at high temperatures to produce steel.

Otherwise, coal quality (coal rank) within a small area is defined by Hilt′s law, which is based on a geological observation that: the deeper the coal, the higher its rank (or grade). It should be noted that it applies when the thermal gradient is completely vertical, because regardless of depth, metamorphism can cause lateral changes in rank [107].

Coal types/lithotypes

"Coal type" is a specific geological classification based on the general appearance of the coal and refers to the rank of the coal (lignite, bituminous, etc.) or the grade of coal (low sulphur coal, steam coal, met-coal, etc.). However, most coals have internal layering, called banding. Coal types, and subsets of types, called *lithotypes*, are based on the presence or absence of banding and the brightness or opacity of each bands. Coal lithotypes are further subdivided into microscopic microlithotypes, which consist of different types of microscopic coal components, called macerals**.** Macerals are to coal what minerals are to rocks (building blocks) [14, 15, 108, 109]. From this perspective, there are two basic types

Table 3 Lithotypes and types of coal [6]

Coal type	Lithotype	Appearance
Humic (banded)	Vitrain	Bright, black, shiny and brittle bands, usually with cracks or fissures. Tends to break into small cubes
	Clarain	Semi-bright (between vitrain and clarain), black and finely interlayered bands (mm-scale) of vitrain, durain and sometimes fusian
	Durain	Dull, black to grey-black bands which have rough surface. Bands have less cracks (fissures) than vitrain. Tends to break into lumps
	Fusain	Black to grey bands with sily lustre (shine). Sometimes fibrous. Soft and friable, sometimes like charcoal
Sapropelic (non-banded)	Cannel	Black to dark grey, non-banded coal with dull to greasy lustre (shine). Often breaks with conchoidal (glass-like) fracture
	Boghead	Similar to cannel but brownish colour

of coal, and both can occur in a single coal seam: *humic* (banded) and *sapropelic* (non-banded) (see Table 3).

Coal rank

In general, the definition of coal rank is based on the recognisable changes in coal parameters during the stages of physical and chemical changes in the transformation of peat into coal (called coalification). Slightly different categories and parameters are used in different countries, but in general one proceeds in ascending order from lignite through sub-bituminous and bituminous coal to anthracite. The different ranks of coal cannot always be differentiated by appearance alone. Testing of various parameters is often required to distinguish the coal ranks (see Table 4) [31, 34, 35, 110, 111].

Conclusions

Coal is formed over millions of years during the decomposition of plant material into peat (sole-like, partially decayed plant material that accumulates in wetlands), which is later converted into coal under the pressure and heat of deep burial.

It is a combustible black or brownish-black sedimentary rock containing a variable amount of carbon (usually > 50 wt%) and variable amounts of other elements (mainly hydrogen, sulphur, oxygen and nitrogen).

Coal can probably be considered the most complex natural (geological) material and is also the origin of the industrial revolution and the most important source of heat and electricity in the world.

It occurs in underground formations called "coal beds" with a thickness of about 30 m and a length of about 1500 km, and it occurs in the form of peat, lignite, sub-bituminous coal, bituminous coal, anthracite, graphite, cannel coal and coking coal.

Coal can also be classified by its macroscopic appearance (commonly referred to as coal rock type, lithotype or kohlentype). Four main types are distingusihed: *vitrain, clarain, durain and fusain*.

The study of coal chemistry and geology makes it possible to understand the complexity of various types of coal both in terms of their composition and their nature, formation, types, rank, etc.

Next to petroleum and natural gas, coal is the most abundant non-renewable fossil fuel resource currently used in the world. It is expected to continue to be an important component of the world's energy resources (electricity) for the foreseeable future.

Nevertheless, continuous efforts have been made in the last decades and even in the present time to replace the use of coal with various alternative energy sources (solar, hydro, wind, nuclear).

Coal is used for the production of a wide range of chemical substances (e.g. methanol, hydrogen, carbon monoxide, acetic acid, formaldehyde, ammonia, urea, olefins and many others) as well as chemical fertilisers, dyes, drugs, plastics and explosives. The main way to obtain the above chemicals and fertilisers is coal gasification to produce syngas (containing hydrogen, H_2 and carbon monoxide, CO).

Table 4 US coal rank system showing the parameters used to define ranks [6]

	Low-rank coal					Medium-rank coal					High-rank coal			Method for determining rank (dmmf) (U.S. ASTM)
	Lignite		Sub-bituminous			Bituminous					Anthracitic			
Peet	B	A	C	B	A	high volatile C	high volatile B	high volatile A	medium volatile	low volatile	Semi-anthracite	Anthracite	Meta-anthracite	
5,000	6,300	8,300	9,500	10,500	11,500	13,000	14,000		*Less distinct for changing rank*					Caloric value (Btu/lb.)
			Less distinct for changing rank					31	22	14	8	2	~ 0	Volatile matter (%)
			Less distinct for changing rank					69	78	86	92	98	~ 100	Fixed Carbon (%)

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Data availability Authors can confirm that all relevant data are included in the article.

Declarations

Competing interests The authors declare no competing interests.

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