

COAL TECHNOLOGY I

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Summary

Coal generally consists of organic and inorganic materials. The content of the organic portion is usually higher than 90%, and the inorganic portion mainly consists of mineral matters such as clay minerals (silicates). Generally, lignites have an aromatic ring structure of aromatic ring of 1–2 ring sizes and about one naphthenic ring with aliphatic chains and oxygen-containing functional groups such as hydroxyl and carboxyl groups. As coal-rank increases, i.e., coalification proceeds, both the number and size of aromatic rings increase, while oxygen-containing functional groups decreases. Bituminous coals with 85–87 carbon % have 3–4 aromatic ring size. Construction of an average structure model of coal is useful for the understanding of complex coal structure, reactivity, and reaction mechanism, and the development of new utilization processes, since coal does not have a simple and definite chemical structure. Solvent extractions of coal usually give low extraction yields. Recently, a mixed solvent including CS₂ was found to give more than 50 wt% of extraction yields for several bituminous coals at room temperature, resulting in the proposal of new non-covalently connected network models.

Pore structure, i.e., pore volume, surface area, and pore size distribution has a great influence on coal mining, preparation, and utilization. Surface areas of various coals measured from nitrogen adsorption at -196°C are usually in the range of $1\sim 50\text{ m}^2/\text{g-coal}$, and those from carbon dioxide adsorption at 25°C are $100\sim 300\text{ m}^2/\text{g-coal}$. Generally, coal is abundant with micro- and submicropores, compared to meso- and macropores. Various mechanical, thermal, and electrical properties, such as compressive strength, hardness, and grindability, calorific value, heat capacity, electrical conductivity, are measured.

Coal preparation is to effect the reduction in coal size and its adjustment to a size proper for transportation, handling, and utilization, as well as cleaning (beneficiation) to remove extraneous mineral matters, and drying to remove water. Coal transportation is carried out by rail-road, barge, ships, conveyor, and slurry pipe line.

Current annual world coal production is very large, i.e., about 5000 million tons of coal is used every year. “Clean coal technologies” are new coal utilization technologies, which are environmentally clean, highly efficient, and economically acceptable. Coals are largely used for the generation of electricity in power plants and of heat in industrial and residential boilers. Coal emits SO_x (mainly SO_2), NO_x , particulates, and solid wastes, when coal is burned. In addition to such pollutants, the combustion of fossil fuels evolves a great amount of carbon dioxide, which may be responsible for global warming through its greenhouse effect. Current emission standards for SO_2 , NO_x , and particulates vary from country to country, and there are also different standards for new or “in operation” plants. These standards will become more stringent year upon year.

Environmental problems arising from coal mining, cleaning, and transportation are air pollution from coal dust, water contamination, solids waste, and land disruption. Coal dust produces not only serious human health and environmental hazards, but also the danger of explosion. Dust collections are usually carried out by dry methods such as cyclones and fabric filters, and wet scrubber. Adding water to coal is effective to reduce dust emission.

The greatest environmental concern in coal utilization is air pollution by SO_x and NO_x emission from coal combustion. Air pollution and resulting acid rain by SO_x and NO_x emissions are responsible for the disruption of forest and human and animal life. SO_2 abatement and control are being effected by the desulfurization of raw coals, and the removal of SO_2 during and after combustion. Physical cleaning of raw coals can remove inorganic sulfur, but not organic sulfur. The removal of SO_2 from flue gas, i.e., flue gas desulfurization, is the most widely-used technology for controlling emissions. When coal is burnt, NO_x (mainly NO_2 and NO) and N_2O are emitted. Denitrogenation of raw coal by physical cleaning is not effective because most nitrogens in coal are bound in aromatic rings as pyridine and pyrrole rings. Currently, many new technologies controlling NO_x emission during combustion (primary measures), such as burner optimization and air staging, are being successfully developed. NO_x removal technologies from flue gas are also being developed. Removal of hazardous trace elements such as As, Cd, Hg, and Pb gives great environmental concern, because some of these are considered to be carcinogenic and/or toxic to human beings. On the other hand, coal combustion produces a very large amount of ash, which is discharged from

the bottom of the combustion furnace or is loaded in flue gas as fly ash. These ashes contain some hazardous components such as toxic trace elements.

The greenhouse gases produced by coal combustion are CO₂ and N₂O, in which CO₂ is emitted in a much larger amount and considered to have a more serious greenhouse effect than N₂O. Various measures are being considered for CO₂ concentration increase, including the recovery of CO₂ from flue gases. Of these, new technologies to increase the efficiency for the conversion of coal to electricity or heat by a few percent are surely promising and realistic measures against CO₂ concentration increase.

1. Introduction

Coal has a wide range of chemical compositions and properties, and ASTM classification defines anthracite, low, medium, and high-volatile bituminous coal, subbituminous coal, and lignite, according to their heating value, and the content of volatile matter and fixed carbon. The carbon percentage of coal, expressed as dry and mineral matter free basis (dmmf), is in the range of about 65–95% and increases with coal rank, i.e., from lignite to anthracite, with the accompanying decrease of oxygen and hydrogen percentage.

Coal also generally includes up to 20% minerals that can be largely removed by acid washing. The chemical structure of the organic portion of coal is considered to be that aromatic and heteroaromatic (sulfur and nitrogen) rings with hydroxyl and alkyl groups are connected through methylene and ether, and naphthene rings. But detailed chemical and network structures are still not well understood, though this knowledge seems important for the development of new environmentally-friendly coal utilization technologies. Current progress on coal structure research will be described below in detail.

In the 1990s, primary energy supply by the fossil fuels of petroleum, coal, and natural gas reached about 90% of the whole primary energy produced in the world, of which coal comprised about 25%. Current annual world coal production (therefore, consumption) is about 5000 million tons of coal used every year. Coal obtained by surface and underground mining is changed in size for transportation, handling, and utilization, and cleaning (beneficiation) to remove extraneous mineral matters, and drying to remove water.

Coal transportation is generally carried out by railroad, barge, or other water transport, and conveyor to coal utilization places such as coal-fire stations. Coal emits SO_x (mainly SO₂), NO_x, particulates, and solid wastes, when coal is burned at power plants. In addition to such pollutants, the combustion of fossil fuels evolves a great amount of carbon dioxide which may be responsible to global warming by its green house effect. Development of new coal utilization technologies which are environmentally clean, highly efficient, and economically acceptable are highly desirable.

The current situation of coal preparation, transportation, and utilization technologies, and their impacts on the environment and environmental measures will be described below.

2. Coal Structure and Properties

2.1 Physical Structure

Coal is a porous material. The most important physical structure for coal mining, preparation, and utilization is porosity, i.e. the pore structure of coal. The porosity of coal has a great influence on coal mining, in which coal bed methane is found in coal pore, and its diffusion is controlled by pore structure.

Coal preparation by the removal of mineral matters from coal often uses the difference in the densities of the coal and mineral matters, which are highly dependent on its porosity. In coal gasification and liquefaction, reacting gases or liquids diffuse into the pores of coal to react with the coal, and so the reaction rates are greatly influenced by coal porosity.

The IUPAC classification of pores of different sizes is; macropore: > 50 nm in diameter, mesopore: 2~50 nm diameter, micropore: 0.8~2 nm in diameter, submicropore: <0.8 nm in diameter. Until this classification was introduced in 1972, pores with < 20_ were classified as micropores. For the characterization of coal porosity pore volume, surface area and pore size distribution are estimated. Pore volume can be estimated from the difference between the densities measured by using helium, which is supposed to be capable of penetrating into the whole pore, and mercury, which does not penetrate at all at low pressures, as displacement fluids.

Surface area and pore size distribution can be determined from physical absorption of gases, and nitrogen and carbon dioxide are often used. However, this method has following several problems which affect its reliability: (1) the ambiguity of the cross-sectional area of an absorbed molecule which is needed to calculate the surface area; (2) the possibility of volume filling of a gas, instead of layer filling; and (3) the possibility of coal swelling (change of pore structure) by a gas diffusion into the bulk of the coal. Small-angle X-ray scattering and nuclear magnetic resonance spectroscopy (NMR) are also used for the estimation of coal porosity.

Pore volumes estimated from the difference of the density using helium and mercury were reported to be in the range of 0.033 to 0.232 cm³/g-coal for 12 American coals with a wide range of coal rank. Generally, anthracite (high coal rank) and lignite (low coal rank) have smaller pore volume than middle rank bituminous coals. Surface areas of various coals measured from nitrogen adsorption at -196°C are usually in the range of 1-50 m²/g-coal, and those from carbon dioxide adsorption at 25°C are 100-300 m²/g-coal.

The reasons for this large discrepancy are considered as being: (a) pore deformation and shrinkage at the measurement temperature (-196°C) using nitrogen, and (b) the very slow rate of adsorption of nitrogen at -196°C. So, the surface area from carbon dioxide seems reliable. There are also many problems for accurate pore size distribution. But it may be sure that, generally, coal has more micro- and submicropores, compared to meso- and macropores. The shape of coal pores is not clarified at present, though this is an important area of enquiry for the better understanding of coal.

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Biographical Sketch

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