

COAL STRUCTURE AND PROPERTIES

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Keywords: Coal structure, Characterization of coal, Coal properties, Solvent extraction, Structural parameters, Functional groups, Model structure, Macromolecular structure, Solvent swelling.

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Summary

Coals have many structural features such as aromaticity, various oxygen, nitrogen, and sulfur functional groups, covalent and noncovalent cross-links, physical associations, and several surface structural features that determine physical properties and reactivities. Many characterization techniques have been applied to coals, and new techniques such as solid state ^{13}C NMR are being refined. However, at present the structures of coal are not well understood and there are several vague parameters that make little physical and chemical sense.

In the past, the average structures of coals have been investigated and many average molecular models have been proposed. The concept of average structures is important for comparing many kinds of coals, but may not be completely accurate. Coal is composed of mixtures of thousands of constituents, and every structural factor in coal, such as the distribution of aromatic rings and molecular weights, is widely variable. Physical and chemical techniques may not be able to reveal precise detail on coal structure, but the knowledge accumulated will guide molecular simulation techniques that may provide significant insights into the structure-property relations of coals.

1. Introduction

Coals are complex heterogeneous solids that vary widely in their chemical and physical properties. Coal consists of organic and inorganic compounds. The organic portions of coal are composed of carbon, oxygen, hydrogen, nitrogen, and sulfur.

The carbon content is 65–95% and increases during coalification with a concomitant decrease in the percentages of oxygen and hydrogen, which typically range between 2–30% and 2–7%, respectively. Nitrogen and sulfur content is only 1–4%, and is independent of coal rank.

The widely used ASTM classification system defines lignite, sub-bituminous coal, high-, medium-, and low-volatile bituminous coals, and anthracite according to their heating value, percentages of volatile matter and fixed carbon content (Table 1.).

Van Krevelen introduced the use of H/C and O/C atomic ratios, generally called “Van Krevelen Diagrams,” as the main parameters for the study of coal (Figure 1.).

Class	Group	Abbreviation	Fixed carbon %, dmmf	Volatile matter %, dmmf	Calorific value Btu/lb, mmmf
Anthracite	metaanthracite	ma	98 -	- 2	
	anthracite	an	92 - 98	2 - 8	
	semi-anthracite	sa	86 - 92	8 - 14	
Bituminous	low volatile	lvb	78 - 86	14 - 22	
	medium volatile	mvb	69 - 78	22 - 31	
	high volatile A	hvAb	- 69	31 -	14000 -
	high volatile B	hvBb			13000 - 14000
	high volatile C	hvCb			11500 - 13000
Subbituminous	subbituminous A	subA			10500 - 11500
	subbituminous B	subB			9500 - 10500
	subbituminous C	subC			8300 - 9500
Lignite	lignite A	ligA			6300 - 8300
	lignite B	ligB			- 6300

Table 1 ASTM classification of coal by rank.

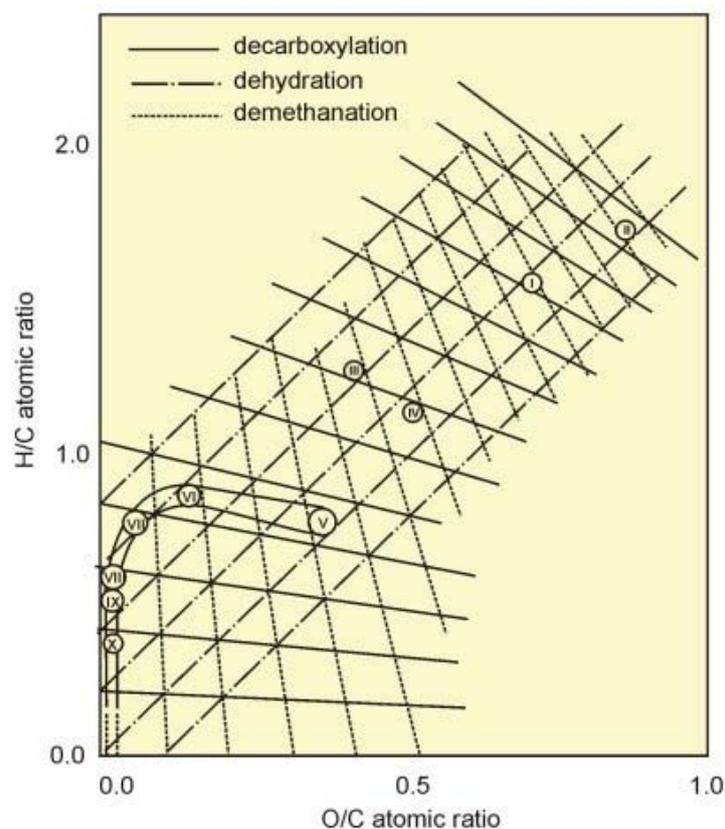


Figure 1. The H/C versus O/C diagram. I wood, II cellulose, III lignin, IV peat, V lignite, VI low-rank bituminous coal, VII medium rank bituminous coal, VIII high rank bituminous coal, IX semi-anthracite, X anthracite: Van Krevelen (1950)

Dehydration is the most common reaction in the conversion of wood, cellulose, lignin, and peat to lignite. In the conversion of lignite to bituminous coal, decarboxylation is the most important reaction, and demethanation reaction converts bituminous to anthracite coal. However, there are several unsolved questions concerning the coalification process; for instance, it is unclear whether all bituminous coals pass through the lignite stage.

Coal consists of thousands of organic compounds that are mainly hydroxyl- and alkyl-substituted aromatic and heteroaromatic rings that are connected by methylene and ether linkages. The size of aromatic rings and the types of functional groups vary widely even in a given coal. Many characterizations have been conducted in attempts to understand such a mixture or its separated constituents. Despite these attempts, only several vague factors that make little consistent physical and chemical sense have been elucidated. On the other hand, elemental analysis and infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy of raw coals and coal-derived materials such as solvent extracts and residues, suggest that the organic constituents have similar structures.

2. Characterization of Coal

2.1 Solvent Extraction

Solvent extraction is one of the most commonly-used techniques for the characterization of coal constituents. Its primary purpose is to isolate the soluble constituents that can be easily characterized with various modern techniques. Soxhlet extractions with pyridine, one of the best solvents for coal, produce extraction yields in the range of 2–40 wt% on a water- and mineral matter-free basis. The dependence of pyridine extraction yields on the carbon percentage of coals has a maximum of around 85–88 carbon %. Quinoline extraction at 300°C produces a yield of 50% for bituminous coals, although it is possible that weak covalent bonds in coals are broken at this temperature. Iino et al. have found that 1:1 (v/v) carbon disulfide / *N*-methyl-2-pyrrolidinone mixed solvent gives more than 50 wt% extraction yields for several bituminous coals at room temperature (Figure 2.). The maximum extraction yield for the mixed solvent also occurs around 85–88 carbon percentage.

Before characterization, coals are often depolymerized or solubilized by chemical reactions such as hydrogenation and alkylation. A mild depolymerization reaction has been carried out using phenol and acid as catalyst. *p*-Toluenesulphonic acid is an effective catalyst for the solubilization of coals in pyridine. A HF-BF₃-H₂ system effectively depolymerizes coals under mild condition; this treatment increases the extraction yield with pyridine and cyclohexane. Reductive and non-reductive alkylations have also been carried out. Coal is reduced by potassium in dry tetrahydrofuran for three hours at 60°C, alkylhalide is added, and, after hydrolysis, the alkylated coal is separated. Alkylation greatly increases the solubility of coals; for example, untreated Bruceton coal is 25% soluble and the alkylated product is 95% soluble in pyridine. In non-reductive alkylation reactions, coal is treated with NaNH₂ in liquid ammonia. An excess of the alkyl halide is added and the alkylated coal is separated. Oxidation is also one of the most effective methods to solubilize low-rank coals.

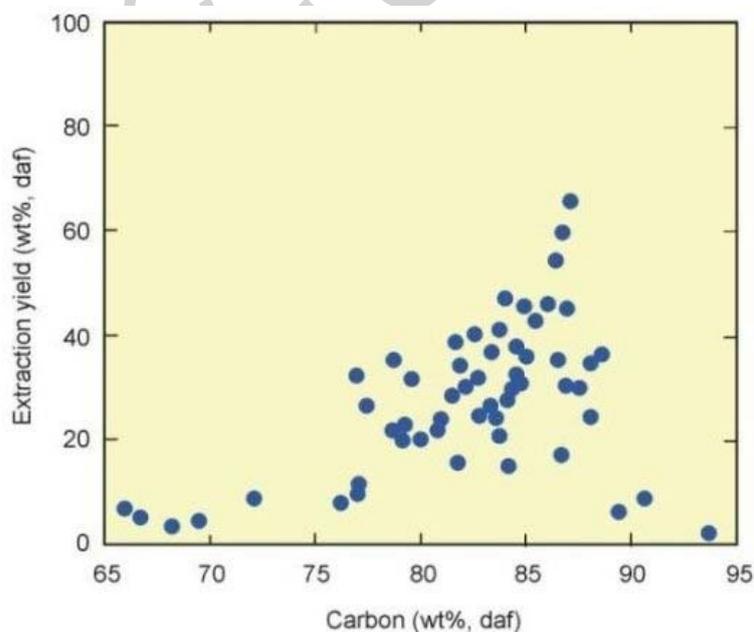


Figure 2. Plot of the extraction yield with the carbon disulfide / *N*-methyl-2-pyrrolidinone mixed solvent versus carbon % of coals. Iino M., Takanohashi T., Ohsuga H., and Toda K. (1988)

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Biographical Sketch

Toshimasa Takanohashi is a Research Scientist at the Energy Resources Department, National Institute for Resources and Environment, Tsukuba, Japan. His current research includes: modeling of molecular structure of coal and petroleum heavy oil; studies on the relationship between chemical structure-property for coal (or petroleum heavy oil) using computer simulation techniques; production of hyper-coal (non-ash coal) by dissolution of coals under mild condition; the mechanism of softening and fusibility of coals; and studies on coal–solvent interactions.