

## THERMAL DECOMPOSITION OF COAL

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**Keywords:** Coal, Thermal decomposition, Pyrolysis, Flash pyrolysis, Hydropyrolysis, Pyrolysis product, Pyrolysis technology, Gas, Tar, Char, Coke, Low-temperature pyrolysis, Weight loss, Thermal treatment, Homolysis, Devolatilization, Maceral, Atmosphere, Chemicals, Heating rate, Reaction, Coal rank, Temperature, Pressure, Hydrocarbonization, Hydrogenation, Laser, Microwave, Flash tube, Plasma, Electric arc, Shock tube, Electric current, Entraining gas, Hydrogen, Acetylene, Clean fuels, Mechanism, Aromatic, Hydrocarbon, Pyrolytic conditions.

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### Summary

When coal is heated progressively in an inert atmosphere, coal starts to decompose and evolves a mixture of hydrogen and/or oxygen-rich products, and aromatics units until coal comes to resemble a micro-crystalline graphitic solid at a high enough temperature. This process of thermal decomposition, on one hand, depends upon the nature and prior

history of the coal; on the other hand, is influenced by the particular conditions under which the process proceeds.

At a temperature above  $T_d$ , the complicated structure of coal is dissociated into aromatic ring units by rupture of bridge carbons. Meanwhile “free-radicals” are formed. Recombination of the smaller radicals results in the formation of small aliphatic gas molecules, and water and tar components of medium molecular weight. These volatile compounds diffuse from the interior of the coal/char particle into the bulk gas phase. Nevertheless, polynuclear aromatics of high molecular weight are easily trapped in the solid particle. Therefore, these compounds form the char fraction via condensation of the ring systems with the elimination of hydrogen. However, both the residual solid char and gaseous products from the primary decomposition will still proceed with a series of consecutive or parallel reactions, that is, secondary reactions. At high temperatures, carbon monoxide will be also produced from cracking of heterocyclic oxygen groups.

The amount of volatile products and their composition depends on coal type, coal size, and the conditions prevailing in the apparatus. Higher yield of tar and BTX is obtainable by using medium-rank bituminous heated at higher heating rate in the hydrogen-rich atmosphere. High yields of PCX and oxides are obtained from low-rank coal and/or in the hydrogen-poor atmosphere.

## 1. Introduction

The terms of thermal decomposition, pyrolysis, and carbonization are often interchangeable. However, the term pyrolysis is more usually applied to a process that involves extensive thermal decomposition of coal (with the ensuing production of a char or carbonized residue.) Pyrolysis is generally defined as the thermal decomposition of coal in the presence of air or other additives. Carbonization is more correctly used to describe the process for the production of char or coke when the coal is heated at temperatures in excess of about 773 K. The ancillary terms of devolatilization and destructive distillation are also used from time to time, but more correctly refer to the formation and removal of volatile products (gases and liquids), during the thermal decomposition process. Thermal decomposition of coal is important since it is the initial step in most coal conversion processes and is the step that depends mostly on the coal properties. Early research in the thermal decomposition of coal was concentrated on coal carbonization, for example, slow heating of dense coal samples, and conditions pertaining to coke making. By contrast, recent work has emphasized rapid heating of dilute coal samples, technically termed as “flash pyrolysis”. Behind this shift in emphasis there has been the desire to elucidate the role of pyrolysis in coal combustion and gasification, and hence the possibility of conversion of coal to liquid fuels or other desired chemicals.

Coal represents a substantial fraction of the estimated non-renewable fossil fuel resources of the world and may become an increasingly important source of hydrocarbon fuels and feedstock. Recognition of immediate and long-range potential of coal has resulted in substantial efforts toward the development of new or modified technologies in coal gasification, liquefaction, and direct combustion. Thermal decomposition of the coal occurs in all these approaches and in some case dominates the

process characteristics. Because of decreasing reserves of good coking coals, it is also the central issue in metallurgical coke production by adoption of coal blending technology. In liquefaction, pyrolysis controls the initial yield of soluble products, their molecular-weight distribution and the competitive yield of gas species. The same processes prevail in combustion and gasification in which the pyrolysis products are further reacted by ignition or gasification. Furthermore, the physical form and reactivity of the nonvolatile char are controlled by the pyrolysis reactions. Analysis of pyrolysis products can supply important clues for the structure of the parent coal in coal processing, especially since many structural units of coal are reserved in the heavy volatile products (tar).

Coals of potential commercial interest for conversion processes have typically the atomic hydrogen to carbon ratio of 0.6 to 1.0, which is substantially less than the value of liquid and gaseous fuels commonly used (see Table 1).

| Fuel Type                       | H/C, Atomic* | Fuel Type             | H/C, Atomic* |
|---------------------------------|--------------|-----------------------|--------------|
| Natural gas                     | 3.5-4.0      | No.6 fuel oil         | 1.3-1.6      |
| Water gas (H <sub>2</sub> , CO) | 2.0          | Lignite               | 0.8          |
| Air producer gas                | 1.2          | Bituminous            | 0.5-0.9      |
| Methanol                        | 4.0          | Anthracite            | 0.3          |
| Gasoline                        | 2.0-2.2      | High-temperature coke | 0.06         |

\* Mineral-matter-free C and total organic H (including H bound with O, S, and N).

Table 1. Hydrogen-to-Carbon Ratio of Selected Fossil and Process-Derived Fuels

Therefore, the primary requirement of most coal conversion schemes is either to increase the hydrogen content or to reject carbon, thereby upgrading the hydrocarbon fraction. This can be accomplished directly by coal pyrolysis, which yields a hydrogen-rich volatile fraction and carbon-rich solid residues (char and coke).

Coal undergoes a series of complex physical and chemical changes when it is heated. The nature of these changes, though primarily dependent on the type of coal, is greatly modified by the temperature, heating rate, soaking period, pressure, and gaseous environments. Reactor type, sample amount, particle size, and hydrodynamic conditions are other factors that also influence chemical and physical changes in coal pyrolysis.

This article examines fundamentals of coal pyrolysis, hydroxyrolysis, and low-temperature carbonization. It includes the following:

- Fundamentals of thermal decomposition of coal.
- Parameters affecting on thermal decomposition of coal.
- Processes of thermal decomposition.

## 2. Fundamentals of Thermal Decomposition of Coal

There arise physical and chemical changes when coal is heated to the temperature at which thermal decomposition occurs. However, some changes may be noted before the onset of what is often referred to as the “thermal decomposition proper,” and may manifest themselves as the formation of low molecular weight species. During the thermal decomposition of coal a substantial weight loss occurs because of the evolution of volatile matter. The amount and composition of volatile products depends on coal type, coal size, and the conditions prevailing in the apparatus. After the decomposition a series of consecutive and parallel reactions, which involve both the residual solid char and the gaseous products of the primary decomposition stage, take place.

### 2.1 The Patterns of Thermal Decomposition

Thermogravimetric measurements that follow the progress of decomposition by recording weight losses that accompany coal pyrolysis suggest that there is little change below a temperature  $T_d$ . The temperature  $T_d$  increases with coal rank from about 620K to 670K and that substantial breakdown of the coal substance occurs only beyond that temperature.  $T_d$  is therefore commonly identified as the decomposition temperature of coal. It is more appropriate to associate  $T_d$  with the onset of active thermal decomposition (which causes weight loss), and to view the overall decomposition process as composed of three successive stages, viz.

- (a) Limited thermal alteration of the original molecular structures (mostly by condensation reactions) at temperatures below  $T_d$ ;
- (b) Active decomposition at the temperature between  $T_d$  and about 820K, leading to generation and discharge of bulk of volatile matter, primary in the form of tars and light oils;
- (c) Secondary degasification, resulting in formation and evolution of a variety of hydrocarbon gases, elemental hydrogen and oxides of carbon over an extended temperature range beyond 820 K.

When coal is heated to temperatures below 473 K, water and adsorbed gas such as methane and carbon dioxide on the inner surface of the coal lump, will appear as products of the thermal treatment. On other hand, a lower rank coal such as lignite containing many carboxylic functional groups as part of the coal structure, will evolve carbon dioxide by thermal decarboxylation:  $Rh-COOH = R-H + CO_2$

Such changes are usually noted to occur at temperature just in excess of 373 K. More than 50 percent of the carboxylic functional groups can lose carbon dioxide over the temperature range from 373K to 473K.

As the temperature of the thermal treatment rises to the range of 473K to 643K, coal loses a variety of lower molecular weight organic species (especially aliphatic compounds). Some of the lower molecular aromatic species and sulfur compounds may also be obtained. At temperatures above 643K, methane, polynuclear aromatics, phenol, and nitrogen compounds are produced. With respect to the volatile matter produced by the thermal decomposition of coal, rapid thermal decomposition enables the yields of

the lower molecular weight hydrocarbons along with the char residue. For bituminous coals, the decomposition extent increases markedly above 673 K and reaches a maximum in the range 973K to 1173K.

### 2.1.1 Slow Heating Rate

The thermal decomposition of coal by slow heating rate is generally used to investigate carbonization of bituminous coal for coke making. It means that the thermal decomposition of coal under non-oxidizing conditions produces a residue (coke), which consists of carbon and mineral matter. During this process the coal passes through several stages. The heated coal is first cracked in a lateral chain of coal organic constituent, and becomes “plastic”, and softens. As the heating progresses the “plastic” mass may be the re-formation of the bonds or the formation of new bonds by solidification. This behavior, that is the “plastic” mass re-solidifies even before the onset of the coking reactions, allowing coals to be classified as caking or non-caking. The main characteristic in the process with slow heating rates is the secondary reactions that involve polymerization and /or thermal cracking of the heavier volatile products of coal pyrolysis.

### 2.1.2 Rapid Heating Rate

The thermal decomposition of coal by rapid heating rate has the potential of becoming one of the most effective ways to utilize hydrocarbons contained in coal. To achieve a rapidly pyrolytic coal rate, pulverized coal burners, fluidized beds, free-fall type reactors, entrained beds, and cyclone beds are often utilized. The weakly and middle strength bonds in the coal constituents crack to form a large number of gaseous and liquid products when coal is rapidly heated to the definite temperature (above 873 K.) The heavier volatile produces from decomposition are unlikely to undergo the secondary reactions. The gaseous and liquid yields by rapid heating are higher than that by slow heating.

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### Bibliography

Berkowitz N. (1985). *The Chemistry of Coal*. Amsterdam: 513 pp. Elsevier Science Publishers B.V. [This discusses the chemistry of coal pyrolysis.]

Gavalas G. R. (1982). *Coal Pyrolysis*, 168 pp. Amsterdam: Elsevier Scientific Publishing Company. [This expounds thermal reactions, experimental techniques and kinetics of coal pyrolysis.]

Guo Z. (1992). *Chemistry of Coal*, (Chinese). 149 pp. Beijing, China: Chemical Industry Press. [This reviews the chemistry of coal pyrolysis.]

Howard J. B. (1981). Fundamentals of coal pyrolysis and hydrolyrolysis. *Chemistry of Coal Utilization*, (Second Supplementary Volume, ed .Elliot, M. A. ), 2374 pp.. New York: John Wiley & Sons. [This reviews the fundaments and test results of coal pyrolysis and hydrolyrolysis.]

Liao H. (1998). Copyrolysis of coal with coke-oven gas. *Journal of Fuel Chemistry and Technology*, (Chinese) 26(2), 7–17. [This discusses the effects of different atmospheres on yields and composition of pyrolysis products.]

Speight J.P. (1994). *The Chemistry and Technology of Coal*, second edn. 642 pp. New York: Marcel Dekker, Inc. [This presents a comprehensive discussion on the thermal decomposition of coal.]

Tromp P .J. J. (1988). Slow and Rapid Pyrolysis of Coal. *New Trends in Coal Science*, (ed. Yurum Y.). 529 pp. Dordrecht, The Netherlands: Kluwer Academic Publishers. [This discusses mechanism and test results of coal pyrolysis.]

Wieckowski A.B. (1999). *Evolution of paramagnetic centers during thermal decomposition of coal and macerals*, Proceedings ICCS` 97 (ed. Ziegler A. et al.) pp657-660. Essen, Germany: DGMK. [This discusses variations of radicals in coal and maceral pyrolysis.]

### **Biographical Sketch**

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