COAL SCIENCE AND TECHNOLOGY 8

NATURAL GAS SUBSTITUTES FROM COAL AND OIL

SHAIK A. QADER

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PREFACE

Natural gas is the most versatile fossil fuel which provides about 20 percent of the energy consumed in the world. It is used for residential, commercial and industrial purposes. Because of local shortages and high demands in certain parts of the world, synthetic gases which are interchangeable with natural gas are produced from oil and coal. The technology to produce natural gas substitutes from light oils has been commercialized for quite some time in the United States, Japan and some European countries. Technologies for producing natural gas substitutes from coal are under development and at least one semicommercial plant is now in operation in the U.S.

The enormous world reserves of coal makes it the most potential source of synthetic natural gas and more coal based plants are likely to be built in different parts of the world in the future. Future increases in natural gas price and stabilization in oil price are likely to provide economic incentives for large scale production of natural gas substitutes from coal and oil, especially in those parts of the world where the demand of natural gas outpaces supplies and where there is an abundance of coal and availability of less expensive oil. No matter what happens in the future to commercial and industrial production of substitute natural gas, research and developmental activities will continue and there will always be a need for scientific and technological information on conversion of coal and oil to substitute gases. I hope that this book on "Natural Gas Substitutes from Coal and Oil" will provide useful state-of-the-art information.

This book is written with the objective of providing state-of-the-art knowledge on chemistry and technology of producing natural gas substitutes from coal and oil in a single volume. The text is designed to serve the needs of professionals in industry, research and engineering organizations and academic institutions. An attempt has been made to present the subject matter in a clear and comprehensive manner so that even the nontechnical reader will find it easy to understand. Equal emphasis is put on chemistry and technology of both coal and oil gasification. Commercial processes and evolutionary technologies having potential applications in the production of natural gas substitutes are described in this book. Processes designed for the production of low and intermediate heating value gases are not included.

The book is divided into eight chapters. Chapters 1 and 2 contain information on properties of coal and oil which are used as feedstocks in the production of natural gas substitutes. Chapter 3 contains the chemistry of coal gasification which includes chemical reactions, thermodynamics, kinetics and mechanisms. Chapter 4 contains catalysis of coal gasification and Chapter 5 contains information on coal gasification processes, both commercial and developmental. Chapter 6 contains chemistry of oil gasification and Chapter 7 contains information on oil gasification processes. Chapter 8 contains information on gas purification, shift conversion, methanation and interchangeability of synthetic gas with natural gas.

The book contains up-to-date information on important aspects of conversion of coal and oil to natural gas substitutes. Although the subject matter is covered in sufficient detail in this book, the coverage by no means is complete. I hope that the references provided at the end of each chapter will help readers in probing further wherever needed.

SHAIK A. QADER

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Chapter 1

PROPERTIES OF COAL

Coal is a heterogeneous material which is formed from vegetable matter by the action of heat and pressure. It is composed of organic and inorganic species in varying proportions. Coals of different type occur in nature with variations in physical and chemical characteristics. Coals behave differently under the action of heat and pressure, necessitating the use of different process conditions and equipment for conversion to fuel gases. An adequate knowledge of coal properties is therefore necessary to understand the conversion chemistry and select the right type of conversion process. This chapter provides a general understanding of the nature of different types of coal and a description of important properties which are relevant to gasification research and development work.

1.1 PETROGRAPHIC CONSTITUENTS

Coal is a carboniferous material formed from vegetable matter of plant debris due to the occurrence of biological and chemical changes. The conversion of plant debris follows a well-ordered and continuous change resulting in the formation of the series which can be represented as vegetable matter → peat → lignite → bituminous coal → anthracite. The process of transformation which converts vegetable matter to coal is known as Coalification. There is general agreement on the vegetable origin of coal but the manner in which coalification takes place is still controversial. During the conversion process, the plant debris sinks into earth and is subjected to the action of heat and pressure which promote coalification. Vegetable matter undergoes continuous change to varying degrees depending upon geological conditions. The process of coalification terminates itself at different stages which result in the formation of different coal types as end products.

All components of plant material contribute towards the formation of coal. Cellulose and lignin undergo degradative changes but waxes, resins, spore exines, bark and cuticles do not undergo any change. The organic matter of vegetable debris undergoes degradation by side chain cleavage, decarboxylation, demethylation, quinone formation, polymerization and condensation reactions. As a result of these reactions, carbonification takes place with elimination of hydrogen and heteroatoms and with formation of aromatic structures.

Coal is a heterogeneous material and contains organic and inorganic constituents in varying proportions. The heterogeneity of coal is caused due to variations in the nature of parent plant material and conditions of coalification. Inorganic sediments containing clay and sand infiltrate into the vegetable matter and get embedded in the coal structure during the process of coalification.

Coal occurs in seams ranging in thickness from a few inches to several hundred feet. Most U.S. coals of economic interest occur in seams of 14 inches to 20 feet thick with a few having thickness of 75 feet or more. Although the thickness is only a few inches or feet, coal seams extend over areas of hundreds of square miles horizontally. Each coal seam is built up of a number of pure coal laminations which are separated by rock bands of varying thickness. Within a seam, coal shows dull and bright banded structures with fossilized charcoal inclusions between the bands. The dull and bright parts are generally referred to as Dull and Bright coals respectively. Some coals are not made up of banded structures and they are generally referred to as Nonbanded coals. Cannel and Boghead coals are grouped as nonbanded coals and they occur only in a few parts of the world. They are richer in organic matter when compared to normal coals.

Coal is built up of macro- and micro-components known as Petrographic Constituents which are the physical building blocks of coal. The macro-constituents which are generally referred to as Rock and Litho types exist in coal as thin sections and bands visible to the un-aided eye. They are present in coal in different proportions with variations in appearance, composition and properties.

Two different designations are used in the classification of macro-constituents of bituminous coals. They are designated as Vitrain, Clarain, Durain and Fusain having significant differences in composition and properties (ref. 1, 2). Vitrain is bright black, brittle, translucent, amber red in color and is almost free from plant structures. Clarain is also bright black but is less bright than Vitrain. It has opaque bands which consist of fragmented plant remains. Durain is greyish black and opaque. It contains spore exines and woody fragments. Fusain is a soft black powdery material and shows the original cell structure of wood.

Table 1.1.1 contains some important properties of macro-constituents of a British coal. Vitrain, Clarain and Durain contain more volatiles and hydrogen while Fusain contains more carbon and ash. Tar and gas yields in low temperature carbonization (Gray-King Assay) vary in the order of Vitrain > Clarain > Durain > Fusain indicating that higher Vitrain content and lower Fusain content make coal more reactive.

In the United States, petrographic constituents are designated as Anthraxylon, Attritus and Fusain (ref. 3). Attritus is classified as Translucent Attritus and Opaque Attritus. Anthraxylon is derived from woody tissues and occurs in bands of several millimeters in thickness. Translucent Attritus contains resins, pollen, cuticles and algae whereas Opaque Attritus contains granular and amorphous opaque matter. Fusain has fibrous cellular structure.

Although macro-constituents of coal appear heterogeneous, microscopic examination indicates that they contain different types of micro-constituents which are homogeneous in appearance. The microscopic constituents are designated as Macerals which represent the organic constituents of coal. Macerals can be separated from coal in high purity to study physical and chemical properties. Coal is composed of three types of maceral groups which are designated by the International Nomenclature Committee as Exinite, Vitrinite and Inertinite. Each of these groups has subgroups of micro-constituents which are similar in composition and properties.

Table 1.1.2 contains classification, origin and properties of macerals commonly found in coals. The macerals are formed from different parts of the parent vegetable matter by different reactions which take place during coalification. They have different chemical and physical properties and thus are expected to be different in their technological behavior.

Table 1.1.3 contains typical properties of macerals separated from a South African coal. Analysis of these macerals shows that the carbon and oxygen content varies in the order of Exinite < Vitrinite < Inertinite. But the volatile matter and hydrogen content varies in the reverse order of Exinite > Vitrinite > Inertinite. Exinite is high in hydrogen and volatile matter contents and yields more tar on heating (Fischer Assay). Vitrinite contains relatively less hydrogen and volatile matter and yields less tar. Inertinite is the least reactive maceral and yields very little tar. In lower rank coals, the relative abundance of macerals results in significant variations in composition but they converge in composition in higher rank coals.

TABLE 1.1.1
Macro-constituents of a British coal (Source: Brame and King, ref. 2).

Analysis, % wt.	Vitrain	Clarain	Durain	Fusain
Moisture	1.7	1.4	1.2	0.9
Volatile Matter	34.6	37.6	32.2	19.1
Ash	0.6	3.5	4.6	9.6
Carbon	84.4	82.2	85.8	88.7
Hydrogen	5.4	5.7	5.3	4.0
Sulfur	1.0	2.3	0.9	1.0
Nitrogen	1.5	1.9	1.4	0.7
Oxygen (by difference)	7.7	7.9	6.6	5.6
HHV, Btu/lb (dry, ash-free)	14,790	14,790	15,100	14,840
Low Temperature Assay (Gray-King) Yields, % wt.				
Coke	69.0	71.5	76.2	-
Tar	16.2	14.5	11.2	-
Liquor	4.6	4.2	3.6	-
Gas (c.c.)	13,440	12,800	11,340	-