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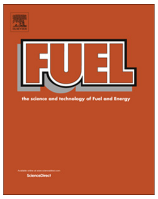

Review article

Mechanism of kerogen pyrolysis in terms of chemical structure transformation

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ABSTRACT

This article presents an overview on carbon chemical structure transformation to understand kerogen thermal decomposition based on the chemical structure of kerogen. Formation of kerogen is highlighted to distinguish the typical types of kerogen containing in oil shale and coal. The oil production potential for oil shale and coal is found to little correlate with their organic amounts but to depend on the quality or chemical structure of organic matters. Aliphatic and aromatic carbons in kerogen are correlative with the yield of oil and carbon residue from Fischer Assay retorting, respectively. The aliphatic carbon moieties largely produce oil and gas, while aromatic carbon portion is apt to be converted directly to carbon residue during kerogen pyrolysis process. On this basis, an updated lumped mechanism model is proposed for viewing kerogen pyrolysis and provides a basis for understanding the transformation of carbon chemical structures. Further quantization and analysis conclude that: 1) 10–20% aliphatic carbon leaves in carbon residue as methyl groups and methylene bridges attached to aromatic rings, 2) 45–80% aliphatic carbon is directly distilled into oil, and 3) 15–40% aliphatic carbon is aromatized into aromatic carbon. The aromatization degree of aliphatic carbon varies with secondary reactions and its intrinsic chemical structure (alkyl chains, naphthenic and hydroaromatic hydrocarbons). Thus, the article justifies that primary pyrolysis determines the potentially maximal oil yield according to original carbon chemical structure, while the subsequent secondary reactions should be selective and minimized to determine the final oil yield and quality.

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1. Introduction

The term "kerogen" covers a wide range of organic matters in solid fossil fuels typified by coal, oil shale or oil sand. These fuels can all be roughly described to have complex macro-molecular organic structures [1–3]. The structures are predominantly composed of carbon and have a significant proportion of hydrogen and small percentages of oxygen, nitrogen and sulfur [4]. The elemental composition makes kerogen as actually a storehouse of liquid fuels and chemicals. The problem is to find the key to this storehouse and to unlock it to utilize the elements as more valuable substances like oil, gas and coke, the fundamental feedstock supporting nowadays human life [5]. This kind of conversion and utilization of kerogen can usually be realized in three different ways: carbonization (pyrolysis or retorting) for oil and gas [6,7], gasification for combustible gas [8,9], and liquefaction for liquid fuel and chemicals [10]. The review concerns the first one.

A retort or pyrolyzer, in which the organic matters (kerogen) of oil shale and coal decomposes to produce oil (shale oil or tar), gas and char/coke, is the heart of the decomposition-based conversion process [11,12]. The performance of the reactor influences the viability of the process in many ways. Several literature studies have summarized the design considerations and performance characteristics for efficient pyrolysis reactors [13–16]. Surely, the selection and further design of a reactor are vital important to the success of an industrial process. In fact, the basis for reactor design and process optimization is to deeply understand the mechanism of kerogen pyrolysis under various processing conditions. The oil and gas generation potential from kerogen of solid fossil fuels is intrinsically dependent on chemical structures of kerogen [17–21]. Thus, increasing the knowledge of molecular and chemical structure transformations during kerogen decomposition becomes essential for controlling the yield and quality of coal and oil shale pyrolysis.

The mechanisms of kerogen pyrolysis have been extensively studied for more than half a century. In the late 1940s, Hubbard and Robinson [22] studied the conversion of kerogen and established a reaction mechanism shown as kerogen -->bitumen --> oil + gas + coke. In turn, several subsequent studies have reported similar mechanisms on basis of the thermal decomposition of organic matters (kerogen) in oil shale and coal [23–25], and a simple mechanistic picture of oil shale pyrolysis was derived from stoichiometric analysis [26]. Although considerable experimental refinements have been made, this model has remained as an empirical model of pyrolysis mechanism. In addition, some works reported the fate of aliphatic and aromatic carbon during pyrolysis [17–20] and the aliphatic-aromatic conversion mechanism of kerogen pyrolysis was proposed based on the component analysis of pyrolysis products [27–29]. Most recently, studies on pyrolysis mechanism were carried out using reactive molecular dynamics simulation method [30] or using model compounds for individual structural features in kerogen to clarify their pyrolysis characteristics at the atomic and molecular level [31]. Thus, there is a great need in pyrolysis mechanism models considering more fundamentals and applicable to different kerogens.

This review makes a special effort on scientific understanding pyrolysis mechanism in terms of chemical structure transformations occurring with kerogen pyrolysis. It will describe in detail the kerogen thermal decomposition and related chemical fundamentals for producing products through pyrolysis of coal and oil shale. The formation and classification of kerogen are addressed to distinguish the typical kerogen types of oil shale and coal. Also, it reports the chemical structure conversion of aliphatic and aromatic carbons, and reveals the correlations of oil yield and residual carbon with aliphatic and aromatic carbons in feedstock, respectively. Thus, an updated lumped mechanism model is proposed to offer a simple presentation for viewing kerogen thermal decomposition and subsequent secondary reactions in the process forming liquid and gas products. This review finally clarifies that the primary pyrolysis determines the potentially maximal oil yield according to original carbon chemical structure, while the subsequent secondary reactions have an essential effect on final oil yield and quality. This clear and deep understanding of kerogen pyrolysis mechanism is of great importance for pyrolysis process development and reactor design.

2. Formation and chemical structure of kerogen

2.1. Kerogen definition and classification

Kerogen refers to the naturally occurring solid organic matters presenting in oil shale, coal and other sedimentary rocks, and it is insoluble in common organic solvents and coexists with a fraction of bitumen [1–4]. Typical organic constituents of kerogen are algae and woody plant materials, which were converted into organic substance through conversion in millions of years under the action of pressure and heat from the Earth. Thus, kerogen indicates simply the carbonaceous organic matters existing in solid fossil fuels.

There are usually three types of kerogen [2–4,32,33]. The Type I is formed mainly from algal and amorphous constituents and it is rich in aliphatic chains by having low contents of aromatics and heteroatomic structures. For the Type-I kerogen its initial atomic H/C ratio is above 1.5 and O/C ratio is below 0.1. This type of kerogen has a good tendency to produce liquid hydrocarbons. The Type II consists of mixed terrestrial and marine source materials to have its atomic H/C ratio below 1.5 and O/C ratio above 0.1. The potential of oil generation for the type-II kerogen is generally lower than that for the Type I, but the Type-II kerogen has more aromatic and heteroatomic ketone and carboxylic acid groups. The Type III consists of woody terrestrial source material and is characteristic of coal and coaly shale. This kind of material has relatively low initial aromatic H/C ratio (<1.0) but high initial atomic O/C ratio (>0.2), leading to low oil-generation potential. In oil shale most organic matters belong to the Type-I kerogen, while in coal they are type III predominantly.

2.2. Oil generation potential of kerogen

Fig. 1 shows that the atomic H/C ratio of fossil fuels increases from anthracite to petroleum [34]. The origin of oil shale and petroleum is the similar organic materials, such as fat and protein of animals and plants. Thus, oil shale can also be considered as the precursor of petroleum [33,35]. The atomic H/C ratio between coal and oil shale reflects the difference between terrestrial and aquatic origins, essentially shown in their chemical structures. From the viewpoint of biochemistry, cell is the basic structure and function unit of organism consisting of cell membrane (mainly lignin, cellulose and hemicellulose) and cell inclusion (mainly fat, protein and carbohydrate) [4]. Lignin mainly includes aromatic structures to have low H/C ratios, while cellulose and hemicellulose are composed of five or six aliphatic rings to cause their relatively high H/C ratios [36,37]. The higher plants are rich in cell membrane (by weight), while the lower plants like algae have more cell inclusion. Thus, the lower plants have the higher H/C ratios than the higher plants do. It is the virgin materials forming kerogen that cause difference in organic properties among fossil fuels. For oil shale its virgin materials of kerogen are mainly lower plants very like phytoplankton (H/C≈1.87) that is rich in protein, fat and waxiness, complying with the high atomic H/C ratios and organic matters containing high aliphatic fractions in oil shale [3,36]. The other