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Pyrolysis behavior and kinetics of the trapped small molecular phase in a lignite

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ABSTRACT

Trapped small molecular phase is an important part in coal and strongly affects reactivity and volatile release during pyrolysis. In this work, it was separated by normal heptane leaching of extracts from thorough extraction of a lignite and was further fractionated into four sub-fractions by column chromatography. Chemical properties of each sub-fraction were evaluated first and then pyrolysis behavior, gaseous product evolution and kinetics of the raw coal and its four sub-fractions were systematically investigated using a thermogravimetric analyzer coupled with on-line Fourier Transform Infrared spectrometer. Determination results corresponding to the total yield and chemical properties of the sub-fractions proved the effectiveness of the separation procedure. Normal heptane eluate presented one mass loss stage and decomposition of aliphatic moieties in it mainly contributed to formation of methane, ethylene, and other high carbon number aliphatics. Toluene eluate exhibited one broad mass loss stage and produced largest quantities of light arenes and ether bond containing species, while two apparent mass losses occurred in pyrolysis profile of ethyl acetate eluate, during which ketonic bond containing species generated at the first pyrolysis stage. The formation of coke during pyrolysis was mainly caused by the presence of methanol eluate. Kinetic results revealed that distributed activation energy model was suitable for describing the pyrolysis process of raw coal and its four sub-fractions. Trapped small molecular phase could be easily pyrolyzed and the average bond energy of the components was in the order of raw coal $\gg$ ethyl acetate eluate > normal heptane eluate > toluene eluate > methanol eluate. In addition, the kinetic compensation effects were observed for almost the whole pyrolysis processes of both the raw coal and the four eluates.

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1. Introduction

Pyrolysis occupies an exceptional position in the field of efficient utilization of coals because it is the basic process for obtaining valuable feedstocks and also serves as the initial and accompanying reactions during thermal conversion processes [1]. Pyrolysis is also a useful tool to correlate coal structure with reactivity under the accurately controlled conditions [2]. Additionally, maturation process of coal organic matter could be altered at high temperatures in a short period of time, so that artificial pyrolysis was often employed to simulate natural coalification process [3]. Coupling pyrolysis and gasification in the fluidized bed reactor for methane-rich syngas production is also germane to coal pyrolysis because the methane is mainly generated from pyrolysis reaction zone rather than the gasification zone [4]. Therefore, coal pyrolysis has received much attention and great achievements have been made on some aspects [5].

It is commonly recognized that coal pyrolysis is a temperature-dependent process [6]. Desorption of water and gases takes place at about 120 °C when coal is heated from room temperature. Vaporization of the mobile phase begins near 250 °C and aliphatic species release. Emerging of aromatic tar and the organic gases induced by bond cleavage occurs above 400 °C and condensation of aromatic structures to char becomes dominated after 600 °C. Formation of CH_4 during pyrolysis of superfine pulverized coal can be divided into five constituents of reactions and the main precursors of CH_4 are alkyl side chains on the aromatic clusters [7]. The progress of analytical tools makes attempt for investigating the coal pyrolysis in the perspective of bond cracking possible. In-situ FTIR technique was adopted to investigate pyrolysis charac-

Nomenclature

A	pre-exponential factor	FTIR	Fourier Transform Infrared
CC	column chromatography	FWO	Flynn-Wall-Ozawa
DAEM	distributed activation energy model	NL	Neimeng lignite
D_i	devolatilization index	NMP	N-methyl-2-pyrrolidone
DTG	derivative thermogravimetric	R_{max}	maximum decomposition rate
E_a	activation energy	T_f	terminal devolatilization temperature
F_1	fraction eluted by normal heptane	TG	thermogravimetric
F_2	fraction eluted by toluene	T_{in}	initial devolatilization temperature
F_3	fraction eluted by ethyl acetate	T_{max}	temperature of maximum decomposition rate
F_4	fraction eluted by methanol	TSMP	trapped small molecular phase

teristics of a perhydrous bituminous coal based on the direct loss of functional groups and thus the kinetic method corresponding to the changes of functional groups could be established [8]. Pyrolysis of lignite could be interpreted with six kinds of functional groups and the reaction process of each functional group showed different mechanisms and kinetic characteristics [9]. It was found that coal pyrolysis in thermogravimetric analyzer (TGA) presented only the information of bond scission for the mass loss and therefore derivative TG curves of coals could be resolved by six sub-curves and each one represented cleavage of a specific series of covalent bonds with the same bond energy [10]. Furthermore, sulfur atoms are thought to enhance the reaction kinetics during coal pyrolysis due to weaker bond energies of aryl and alkyl C—S compared with that of C—C [11]. Although researchers contributed significantly to advancement in pyrolysis of coal in various aspects, most of the experiments were directly performed on raw coals while the trapped small molecular phase (TSMP) in coal was not generally recognized which acts key role on volatile production and reaction behavior during coal pyrolysis [12]. It is widely accepted that chemical structures of coal are a network of fused aromatic and hydroaromatic ring clusters that are cross-linked by aliphatic, ether, and heteroatoms bridges [13]. Mobile phase is in the holes or cages of three-dimensional networks which is governed by the secondary forces such as, hydrogen bonds, π–π interaction, electrostatic interaction, and Van der Waals' force [14]. The network is seen as immobile and trapped or embedded small molecules refer to those compounds in the mobile phase [15]. Extracts from mild extraction are regarded as the important part of TSMP in coal [16]. This approach for obtaining TSMP from coals, however, is not easy to be performed because in one respect, the yields of extract are closely related to the types of solvent and extraction methods, which will affect TSMP release [17]. Furthermore, some effective solvents, such as N-methyl-2-pyrrolidone (NMP)/CS$_2$ mixed solvent and pyridine, can give a maximum extract yield up to 50% for some selected coals. However, the soluble portions with these solvents were proven to be as complex as the raw coal and showed similar aromaticity, molecular weight distribution, and reactivity with the raw coal, which in fact did not represent the intrinsic TSMP in coal [18].

Therefore, thorough extraction through applying effective solvent and extraction method followed by leaching of the extract with proper extractant should be a useful strategy for capturing of the intrinsic TSMP in coal. The previous work proved that multistep extraction coupling heat reflux extraction with cyclohexanone and ultrasonic-assisted extraction with NMP/CS$_2$ mixed solvent in series could achieve higher extraction ability than the single step extraction to different rank coals. The improved extraction ability for coals was attributed to reasonable combination of extraction methods and solvents [19].

Understanding the pyrolysis kinetics is critical in the development of technologies to utilize coals in the most efficient manner and can help researchers improve the designs of reactors for engineering applications [20]. There are considerable methods that can be applied to calculate kinetic parameters due to the diverse integral formulas. The models used to obtain the kinetic parameters of pyrolysis are classified into two categories. One is model-free methods such as Friedman method, and Flynne-Walle-Ozawa (FWO) method. According to Friedman's kinetic model, conversion function $f(\alpha)$ is assumed to be constant while FWO integral method assumes the change in the apparent activation energy constant during the thermal process. These methods overcome the requirement of determining the $f(\alpha)$, in order to calculate the activation energy, E_a. This is realized by simultaneously analyzing decomposition curves generated under different heating rates to extract the apparent kinetics data, i.e., E_a and $\ln A$, corresponding to each degree of conversion (α). Model-free methods are popular in pyrolysis studies for coal and its derivatives due to the fact that they can get more reliable activation energy. The distributed activation energy model (DAEM) is another popularly used method to investigate kinetic characteristics of coal pyrolysis due to its capacity to describe the whole process of complicated pyrolysis of coal [21]. DAEM assumes that a series of irreversible first-order mutually independent reactions occur simultaneously and the activation energies of these reactions are described as a Gaussian distribution [22]. This assumption is appropriate because coal is a mixture of many components that decompose independently from each other. Even the same chemical species may have a different reactivity if its pyrolysis is influenced by other species in its vicinity and thus decomposition reactions have a wide range of activation energies [23]. To compare the reliability of the models, the combination of the model-free and DAEM methods is a reasonable way to evaluate the pyrolysis kinetics of coals and its derivatives.

In this work, multistep extraction coupling heat reflux extraction with cyclohexanone followed by ultrasonic-assisted extraction with NMP/CS$_2$ mixed solvent was employed to thoroughly dissolve the mobile phase from a lignite considering its huge reserve and unique structural features compared with higher rank coals. The total solvent soluble fraction was leached by normal heptane to obtain the intrinsic TSMP in coal and it was further fractionated into four sub-fractions in column chromatography using four different polar eluents. Pyrolysis behavior, gaseous product evolution, and kinetics of raw coal and its TSMP derived sub-fractions were systematically investigated by TG-FTIR after evaluating their chemical properties. The aim of this work is to clarify the pyrolysis behavior and the kinetics of TSMP, which is an important component in coal but not usually perceived. The determination of reliable data regarding to mass loss profiles, gaseous product species and evolution trend, and kinetics from TSMP