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The evolutionary route of coal matrix during integrated cascade pyrolysis of a typical low-rank coal

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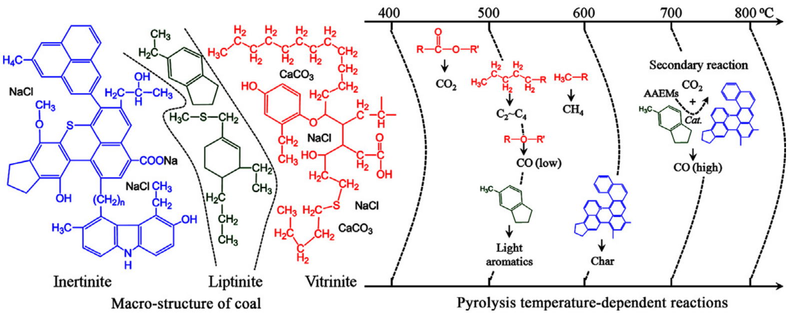
HIGHLIGHTS

- Mechanism on staged pyrolysis of inertinite-rich low-rank coal was proposed.
- Maceral-enriched coal fractions presented different activation energies.
- Secondary reactions could be catalyzed by AAEMs at high temperature.
- Reaction route and gaseous products in different pyrolysis stages were distinctive.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a typical inertinite- and AAEMs (alkali and alkaline earth metal species)-rich Chinese sub-bituminous coal was systematically investigated in terms of maceral component, mineral occurrence and molecular structure. Based on the experimental data, macromolecular-dependent evolutionary behavior during integrated cascade coal pyrolysis was unraveled, and further a mechanism on staged-pyrolysis was proposed. Compelling evidence shows that after heavy medium separation, the features of coal fractions with different densities were significantly varied in maceral compositions, AAEMs distributions and more importantly, in macromolecular structure. The various functional groups abundant in respective maceral-enriched (vitrinite, liptinite, and inertinite) coal fractions behaved distinctively during pyrolysis due to the different activation energies for the scission of these functional groups, thus resulting in temperature-dependent reactions. Specifically, at lower temperature (400–500 °C), carboxylic groups mainly inherent in vitrinite could be substantially decomposed into CO_2. Subsequently, at ca. 500 °C, aliphatic chains in vitrinite were cracked to C_2-C_4; while ether structures were broken and contributed to the generation of a small amount of CO. Meanwhile, the small aromatic molecules freely existed in liptinite could also be released in form of light aromatics. At higher temperature (ca. 700 °C), the volatiles including CO_2 would react with char and generate a larger proportion of CO; and particularly, this secondary reaction could be catalytically accelerated by AAEMs at higher temperature. Consequently, the pyrolysis route and gaseous products in different stages were varying in specific manner according to the reaction mechanism; and it was available to direct the production of methane-rich syngas, and provide a useful basis for optimization of cascade coal pyrolysis processes.

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1. Introduction

Since coal thermal processes, especially pyrolysis, is prevailingly associated with coal properties [1], many efforts have been paid in the last several decades to improve their conversion efficiencies. However, the fundamental mechanism on high-efficient coal conversion is still challenging in relevant energy industries. Therefore, it is particularly necessary to further clarify the correlation between coal features and specific conversion process.

Coal conversion heavily relies on coal reactivity, which is mainly affected by several factors, e.g., the thermochemical processing condition [2], coal rank as well as particle size [3]. Besides, AAEMs inherent in low-rank coal (e.g., lignite and sub-bituminous) could profoundly affect coal conversion [4–6]. And physically, coal is a heterogeneous organic-sedimentary rock comprised of macerals (i.e., liptinite, vitrinite, and inertinite), which are mutually combined with inherent minerals. Therefore, the occurrence and transformation behavior of AAEMs in respective maceral groups are supposed to be one of the key factors impacting coal reactivity; however, those features are rarely investigated in previous studies. On the other hand, the reactivity of coal principally depends on coal organic matrix, i.e., maceral groups; so the study on chemical structure of coal is expected to provide valuable insight into the thermal behavior of coal samples [7,8]. Consequently, various molecular representations for coal structure have been progressively proposed by employing advanced analytical technologies [9]; nevertheless, the true nature of the coal macrostructure is still elusive. Essentially, the critical challenges herein are the complex heterogeneity and non-repeatability of the macromolecular network [10]. However, the models associated with the structural characteristics of the maceral groups were claimed to be able to interpret the macrostructure more straightforwardly [11]. In fact, the maceral groups with different molecular structures had different activation energies, hence would certainly contribute to distinct reaction routes [12,13]. Though representations of vitrinite- [14], inertinite- [10], and liptinite-rich coal [15] had been referred, most models were based on Carboniferous vitrinite-rich coals due to its abundance and industrial importance [16], leading to their restricted applications in relevant industries [17]. Since much of the uncertainty in coal conversion mechanism is somewhat associated with the relatively scarce investigations on separated coal maceral components [18], therefore it is still necessary to clarify the features of individual maceral group during specific processes.

Recently, many attempts had been performed to enhance the quality and quantity of tar and/or gaseous products through controlling either the primary reactions or the secondary gas phase reactions by employing well-designed processes under immoderate conditions [2,3,19–21]. By coupling pyrolysis and gasification process in one fluidized bed reactor (FBPG) using pulverized coal particles to generate methane-rich syngas is one of the most efficient coal utilization technologies, as shown in Fig. 1. The pulverized coal particles are fed into the dilute zone at the bottom of the transport bed and contacts with high-temperature gas and char particles to perform rapid pyrolysis under oxygen-free atmosphere. The formed char after rapid pyrolysis would then pass through a two-stage cyclone to thoroughly separate the particles from the syngas. Large char particles from the first stage cyclone are circulated into the gasification zone for further gasification, while fine particle chars with low reactivity obtained from secondary stage cyclone are injected into the combustion zone to provide heat for gasification and fast pyrolysis. Such methods are practically effective. However, coal/char particles strongly varied depending on their maceral and mineral features; thus, the overlapped reactions in those integrated processes inevitably result in the ambiguity of the staged generation of various products [22]. The decoupling of the reactions, according to feedstock's properties, especially in consideration of molecular structure and mineral occurrence, might be beneficial to optimize the reaction conditions.

Accordingly, the main purpose of this work is to identify the essential changes in pyrolysis reactivity and products during the pyrolysis of a typical high-AAEMs and inertinite-rich Xinjiang coal. The evolution behavior of macrostructure for coal and maceral groups and their pyrolysis characteristics were studied using solid-state nuclear magnetic resonance (SSNMR) and thermogravimetric analyzer combined with a Fourier Transform Infrared Spectrometer (TG-FTIR) in real time, respectively. The relationship between structural features of the individual maceral group and activation energy was comprehensively elaborated, and the mechanism on staged pyrolysis of coal was further proposed. This study systematically clarifies the essential of reactivity, gaseous generation, and evolutionary route of coal matrix in bench-scale, and it is expected to provide useful information for simulation study or optimization of the operational condition for high-efficient coal conversion during pilot-plant cascade pyrolysis processes.

2. Experimental section

2.1. Sample preparation and characterization

A typical Chinese sub-bituminous coal from the Shaerhu, Zhundong coal field in Xinjiang province China was used in this study; and its proximate, ultimate and ash composition analyses are presented in Table 1. The chemical compositions of coal ashes prepared at 500 °C and 815 °C were analyzed using X-ray fluorescence (XRF, Thermo esca I ab 250Xi, American) in triplicate and showed good repeatability.

Prior to the floatation experiments, raw coal was ground and sieved to 40–75 μm [23]. Benzene, tetrachloroethane and tribromethane solvents were chosen to prepare the flotation heavy liquids for heavy medium separation. Flotation heavy liquids with densities ranging from D1: -1.3 g/cm^{-3} (C_6H_6 = 100 wt%), D2: 1.3–1.4 g/cm^3 (C_6H_6/CCl_4 = 40 wt%/60 wt%; C_6H_6/CCl_4 = 26 wt%/74 wt%), D3: 1.4–1.5 g/cm^3 (C_6H_6/CCl_4 = 26 wt%/74 wt%; C_6H_6/CCl_4 = 19 wt%/81 wt%), and D4: +1.5 g/cm^3 (CCl_4 = 100 wt%) were respectively tuned to separate coal into four different fractions. Approximate 1.0 kg raw coal samples were firstly poured into heavy liquid with density of D1, and then the mixture was subjected to a magnetic stirring of 500 rpm for 2 min, followed by the stratification and precipitating for 30 min to obtain the lighter flotation fraction. Sequentially, the sinking product was collected and further separated in the heavier liquids. Consequently, coal macerals were successfully enriched in different fractions according to the various densities. The residual organic heavy liquids remained within coal particles were completely removed in a vacuum drying oven at 60 °C for 24 h. Though, the solvents used in this process might affect the local crosslinking bond and thus break partial molecular structure of coal [24], such influence can be neglected because the flotation condition was very mild with low temperature (room temperature) and short time (32 min in total) [23].

The enriched coal maceral groups were identified by an automatic observation system combining a polarizing microscope according to the Chinese Standard (GB15588-2001) with each sample being scanned for 1000 points and repeated at least in triplicate. Those samples were quantitatively measured through visual counting and reported on mineral-matter-free (mmf) basis. The weight percentages of those coal fractions from the floatation experiment and their proximate and ultimate analyses are shown in Fig. 2 and Table 1, respectively. Clearly, fraction D3 with density of 1.4–1.5 g/cm^3 was dominated (77.84 wt%); whereas, fraction D1