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Catalytic effects of the typical alkali metal on gaseous products distribution and char structure during co-pyrolysis of low rank coal and lignocellulosic biomass

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Abstract

In order to investigate the influencing mechanism of alkalis on gaseous products distribution and char structure during co-pyrolysis of low rank coal and lignocellulosic biomass, carboxymethylcellulose sodium (CMC) was selected as the typical organic sodium salt. Gaseous products distribution was explored in a drop tube furnace from 800 – 1000 °C under various CMC mass ratio, surface morphology of co-pyrolysis char was examined via scanning electron microscopy technology and fractal dimension analysis, and microcrystalline structure was evaluated using Raman spectra and peak deconvolution. The results indicated that the addition of CMC promoted the yields of H_2 and CO, and the yield of CO_2 was improved due to the content of carboxylate radical in CMC. Quantitative information on co-pyrolysis char surface morphology was obtained from fractal analysis on the SEM images. The fractal dimension of co-pyrolysis char was in range 1.61 to 1.78 and higher than that of coal char, which meant the uniformity of the co-pyrolysis char was promoted by CMC. Peak fitting analysis on the Raman spectra illustrated that the value of A_D/A_{All} and A_D/A_G increased with the mass ratio of CMC, indicated that CMC improved the ordering of char structure. This paper provides an insight on the effects of organic sodium salt on products evolution during co-pyrolysis of coal and biomass.

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Keywords: co-pyrolysis; low rank coal; lignocellulosic biomass; gaseous products; char structure.

1. Introduction

As a promising co-thermochemical conversation technology, co-pyrolysis of coal and lignocellulosic biomass has attracted much attention[1]. The co-pyrolysis process can provide various fuels and chemical

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products, including char, tar and gas. The upgrading of the gaseous product is very essential due to the wide application in industries. Previous research mainly focuses on the products distribution during pyrolysis of different ranks of coals blended with kinds of lignocellulosic biomass, also including the main constituent of the lignocellulosic biomass (cellulose, hemicellulose and lignin)[2, 3]. Several researchers reported synergistic effects on the yields of products, such as the gas and tar of mixtures can not be linearly predicted by the performance of individual coal and biomass [4-7]. And various synergy mechanism about lignocellulosic biomass were presented, which was mainly explained by catalytic effects from the alkali and alkaline earth metals (AAEM) and transformation of hydrogen from biomass. However, little attention has been devoted to the effects of alkali and alkaline earth metals (AAEM) in the lignocellulosic biomass, specific mechanisms on catalytic AAEM role have not been clarified [8, 9]. The AAEM mainly exists as organic and inorganic forms in biomass. And carboxymethylcellulose sodium (CMC) is a typical organic sodium salt, which can be chose to investigate the catalytic effects of alkali metal on the products distribution during the decomposition of coal.

Furthermore, the structure has a significant influence on the gasification or combustion performance of co-pyrolysis char, which is also the rate-determining step of co-thermochemical conversion. Thus the influence of CMC on the structure evolution can provide basic information about association between reactivity and structure characteristics. Usually, crystallite structure and surface morphology evolutions were investigated, and qualitative description on char surface can be obtained. However, for further understanding of microstructures of char sample, quantitative analysis on the influence of CMC on char surface morphology is necessary. Although the surface of char sample is irregular and complex, it also statistically self-similar, which meant that fractal theory can be used to describe the surface morphology[10]. The aim of this paper is to obtain the catalytic effects on gaseous products distribution and char structure evolution during co-pyrolysis process and provide possible reaction path for optimizing the co-pyrolysis conversion.

2. Experimental

2.1. Materials

The bituminous coal (BC) was collected from Shaanxi province, northwest China. And the proximate analysis results of the air-dried BC were as follows: moisture 4.18%, volatile 30.56%, fixed carbon 49.88% and ash 15.38%. The ultimate analysis results based on dry ash-free based were as follows: C 79.31%, H 4.72%, N 1.03%, O 13.38% and S 1.3%. The carboxymethylcellulose sodium (CMC) was bought from Sigma–Aldrich Co., Ltd. Both the samples were grinded into less than 74 μm then mixed well. The mass ratios of the CMC in the mixtures were 0.10, 0.30 and 0.50 respectively.

2.2. Methods

The pyrolysis of BC, CMC and their mixtures were carried out in a drop tube furnace (internal diameter 35 mm, length 800 mm) and the description of the DTF and the experimental procedure were described in previous research.[11] The pyrolysis temperature was from heated from 800-1000 ºC. For each trial, it was repeated three times to make sure the accuracy of the results. The gaseous products (CO, CO_2, CH_4, C_2H_4 and C_2H_6) distribution was quantitatively detected by BeiFen3420A gas chromatography. The Carboxen 1000 packed column with dimensions (60/80 mesh, 15 ft×1/8 in O.D.) and thermal conductivity detectors were used. The distribution of gas products was evaluated by molar yield.