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Thermochemical behavior and char morphology analysis of blended bituminous coal and lignocellulosic biomass model compound co-pyrolysis: Effects of cellulose and carboxymethylcellulose sodium

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HIGHLIGHTS

- Co-pyrolysis characteristic of lignocellulosic biomass major components and bituminous coal was evaluated.
- CE and CMC showed opposite synergistic effects on the char yields during co-pyrolysis.
- Kinetic parameter was calculated by iso-conversional approach (Flynn–Wall–Ozawa).
- Surface morphology of co-pyrolysis char were analyzed based on fractal theory.

ARTICLE INFO

ABSTRACT

Lignocellulosic biomass–coal co-pyrolysis is a promising approach for greenhouse gas reduction. The thermochemical behaviors and product distributions must be understood to optimize the process. This paper examines the effects of lignocellulosic biomass model components (cellulose and carboxymethyl-cellulose sodium) on the thermal behavior of bituminous coal (BC) using a non-isothermal thermogravi-metric analysis. The co-pyrolysis char surface morphology was evaluated using scanning electron microscopy technology (SEM) and a fractal dimension analysis. A positive char yield synergistic effect was observed between BC and CE. CMC exhibited a negative synergistic effect on BC pyrolysis, with char yields being higher than predicted. The additions of CE and CMC decreased the average activation energy of the co-pyrolysis process. A fractal analysis of SEM images provided quantitative information pertaining to the effects of CE and CMC on the co-pyrolysis char surface morphology. The BCCE (BC and CE mixtures) co-pyrolysis char fractal dimensions were less than those of BC and CE chars, indicating that the addition of CE promoted the uniformity degree of the co-pyrolysis char. The BCCMC (BC and CMCE mixtures) co-pyrolysis char fractal dimensions displayed the opposite trend.

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1. Introduction

As the largest coal producer and importer in the world, China faces energy-savings and emission reduction issues related to coal utilization [1,2]. Thus, efficient clean coal conversion technologies and clean alternative energies must be developed. Coal gasification is a key clean coal conversion technology, but the process is limited by its carbon capture capabilities. Lignocellulosic biomass, a net-carbon alternative energy, can be used for a wide range of applications [3,4]. However, large-scale commercial biomass gasification applications are limited by a seasonal material supply and secondary pollution from tar [5]. The co-gasification of coal blends with lignocellulosic biomass can serve as a fossil fuel substitute and solve the large-scale biomass seasonal supply problem [6–8]. Co-pyrolysis is the initial step of most co-thermochemical processes, but the process significantly influences the ensuing reactions [4,9,10]. In addition, co-pyrolysis is one of the most promising co-thermochemical technologies and can potentially be applied for energy utilization [11–13]. Therefore, the thermal behaviors and production evolutions that occur during the co-pyrolysis of lignocellulosic biomass–coal blends must be investigated.

Several studies have analyzed the thermal behaviors and product distributions of the co-pyrolysis process to explore the existence of synergistic effects. Some researchers reported the

Nomenclature

A	pre-exponential factor (s^{-1})
D_i	devolatilization index (mg min^{-1} °C^{-3})
D_s	fractal dimension of the char sample (–)
E	activation energy (kJ mol^{-1})
$G(\alpha)$	integration function of the reaction model (–)
m_0	initial mass of sample (mg)
m_t	instantaneous mass of sample (mg)
m_∞	final mass of sample (mg)
N_r	measurement results from the determinate ruler (–)
r	selected ruler during the calculation of D_s (–)
R	universal gas constant (J mol^{-1} K^{-1})
R_d	decomposition rate (mg min^{-1})
R_1	decomposition rate of the first DTG peak (mg min^{-1})
R_2	decomposition rate of the second DTG peak (mg min^{-1})
R_{max}	maximum decomposition rate (mg min^{-1})
R^2	correlation coefficients (–)
RMS	root mean square (–)
t	time (s)
T	temperature (°C K)
T_{in}	initial devolatilization temperature (°C)
T_1	temperature of the first DTG peak (°C)
T_2	temperatures of the second DTG peak (°C)
T_{max}	temperature of maximum decomposition rate (°C)
T_α	temperature of under conversion ratio of α (°C)
$\Delta T_{1/2}$	temperature interval when R_d/R_{max} = 1/2 (°C)
$W_{Experimental}$	experimental mass loss value (–)
$W_{Calculated}$	calculated mass loss value (–)

W_M	mass losses of CE/CMC (–)
W_B	mass losses of BC (–)
ΔW	relative mass loss difference (–)
X_M	mixing ratio of CE/CMC in the mixture (%)
X_B	mixing ratio of BC in the mixture (%)
α	conversion ratio of the raw sample (–)
β	heating rate (°C min^{-1})

Abbreviations

AAEM	alkali and alkaline-earth metal
BC	bituminous coal
CE	cellulose
CMC	carboxymethylcellulose sodium
BCCMC3-1	mixture of BC and CMC, and the mass ratio of CMC was 25%
BCCMC1-1	mixture of BC and CMC, and the mass ratio of CMC was 50%
BCCMC1-3	mixture of BC and CMC, and the mass ratio of CMC was 75%
BCCE3-1	mixture of BC and CE, and the mass ratio of CE was 25%
BCCE1-1	mixture of BC and CE, and the mass ratio of CE was 50%
BCCE1-3	mixture of BC and CE, and the mass ratio of CE was 75%
DTG	derivative thermogravimetric
TGA	thermogravimetric analyzer
FWO	Flynn–Wall–Ozawa
SEM	scanning electron microscopy

absence of synergy effects during co-pyrolysis, indicating that the products exhibited a linear additive relationship [6–8]. Other researchers suggested that volatile products cannot be linearly predicted based on the individual fuels used during the co-pyrolysis of biomass–coal blends [5,14–16]. The existence of synergy effects may depend on the experimental conditions (pressure, temperature, contact intensity and heating rate), experimental device types and samples types [11,17]. Various lignocellulosic biomass synergy mechanisms have been proposed, which mainly focus on the hydrogen transfer and catalytic effects from the alkali and alkaline earth metals (AAEM) [18–21]. However, specific mechanisms, including the hydrogen donor source and catalytic AAEM role, have not been clarified. Lignocellulosic biomass is mainly composed of cellulose (CE), hemicellulose and lignin. Cellulose possesses a higher H/C ratio than hemicellulose and lignin. Thus, cellulose–coal pyrolysis can be used to investigate the thermal behaviors and interactions between biomass and coal from a hydrogen transfer perspective. Furthermore, the existing AAEMs in biomass can be divided into organic and inorganic forms. Carboxymethylcellulose sodium (CMC) is a type of organic sodium salt, where the hydroxyl groups of cellulose are partly replaced by –COONa. Thus, CMC can be used investigate the effects of sodium on the co-pyrolysis process and distinguish the synergistic effect between the hydrogen transfer process and catalytic effects.

In addition, the co-pyrolysis product characteristics, particularly the co-pyrolysis char characteristics, significantly impact the co-gasification process. Co-pyrolysis char conversion is a rate-determining step during the co-gasification process. Co-pyrolysis char characteristics, particularly the surface morphology evolution, must be considered when designing and optimizing co-gasification equipment. The surface morphology affects the co-pyrolysis char reactivity, which is the controlling step during the co-thermal conversion of the coal and biomass [22]. Scanning electron microscopy (SEM) has been widely applied to qualitatively describe the surface

morphologies of char samples [23–25]. However, quantitative studies of the effect of biomass on co-pyrolysis char surface morphology are uncommon. This knowledge can be gained via a fractal analysis of the SEM image [26]. The fractal surface morphology characterization method is not dependent on the structural parameters, such as the surface roughness and degree of stereoscopic development. Therefore, the surface morphology can be quantitatively described by the fractal dimension D_s [26,27].

The goal of this study is to evaluate the thermal behaviors and char morphologies of bituminous coal and lignocellulosic biomass model compounds due to co-pyrolysis. Pyrolytic characteristics were explored via a thermogravimetric method, while kinetic parameters were calculated using the Flynn–Wall–Ozawa (FWO) method. The effects of cellulose and organic sodium salt on the surface morphology of co-pyrolysis char were quantified using fractal theory. This study helps to characterize the synergistic effect mechanisms that occurred during the co-pyrolysis of coal and lignocellulosic biomass.

2. Materials and methods

2.1. Materials

Cellulose (CE) and carboxymethylcellulose sodium (CMC) were purchased from Sigma–Aldrich Co., Ltd. CE and CMC were separately screened and particles smaller than 74 µm were collected. Fig. 1 illustrates the chemical structure of cellulose and sodium carboxyl methyl cellulose (CMC). The bituminous coal (BC) used in this study was from Shaanxi, northwest China. The coal was ground to a particle size smaller than 74 µm and mixed with CE or CMC. The BC and CE composition data are shown in Table 1. The BC and CMC mixtures were named BCCMC3-1, BCCMC1-1 and BCCMC1-3, with CMC mass ratios of 25%, 50% and 75%,