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Physicochemical structure and gasification reactivity of co-pyrolysis char from two kinds of coal blended with lignocellulosic biomass: Effects of the carboxymethylcellulose sodium

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HIGHLIGHTS

- Influence of organic sodium on structure and reactivity of co-pyrolysis char were investigated.
- Carboxymethylcellulose sodium promoted the pore structure of bituminous and anthracite char.
- Surface fractal dimension indicated CMC promoted uniformity of the co-pyrolysis char.
- Deconvolution of Raman spectra revealed the microcrystalline structure of the co-pyrolysis char.
- Synergistic effect was observed during the gasification process of co-pyrolysis char.

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ABSTRACT

To investigate the influencing mechanism of alkalis on char structure evolution and gasification reactivity during co-pyrolysis of coal and lignocellulosic biomass, carboxymethylcellulose sodium (CMC) was selected as a typical organic sodium salt and introduced to the pyrolysis of bituminous coal (BC) and anthracite coal (AC) respectively. Physicochemical characteristics of the char samples were examined by N_2 adsorption/desorption measurement, scanning electron microscopy (SEM) and Raman spectra under different CMC mass ratio. Fractal theory and deconvolution method were applied to quantitatively analyze the surface morphology, pore property and microcrystalline structure of the char. Thermogravimetric analyzer and non-isothermal kinetics method were used to determine the gasification reactivity and kinetic parameters of the char. The results indicated that the addition of CMC promoted the development of pore structure from both BC and AC char samples. The fractal dimension can quantitatively describe the complexity and heterogeneity of pore structure and surface morphology of char sample. The fractal dimension obtained from SEM images of co-pyrolysis char was in range 1.41–1.68 and higher than that of the coal char, which meant CMC promoted the heterogeneity of co-pyrolysis char. 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, indicating that addition of CMC reduced the ordering of co-pyrolysis char structure. Synergistic effect was observed during the gasification process of co-pyrolysis char. The evolution of physicochemical structure and organic sodium lead to higher reactivity and lower activation energy during gasification of co-pyrolysis char than the raw coal char. This paper provides insight on the effects of organic sodium salt on products evolution during co-pyrolysis of coal and biomass.

1. Introduction

Coal remains as one of the primary source of energy worldwide, which provides 42% of global electricity although with the high emission of CO_2 and other pollutants [1,2]. Developing clean coal technology (CCT) and partially substituting coal with alternative energy are essential with the increasingly stringent environmental policies [3,4]. Lignocellulosic biomass, a renewable and CO_2 neutral energy, can be applied for mitigating greenhouse gas (GHG) emissions through thermochemical conversion [5]. However, due to the low energy density and seasonal material supply, large-scale

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Nomenclature

A	pre-exponential factor/s^{-1}
A_{All}	area of all the band from Raman spectrogram/–
A_D	area of the D band from Raman spectrogram/–
A_G	area of the G band from Raman spectrogram/–
C	constant/–
D	fractal dimension of pore structure/–
D_s	fractal dimension of the char sample from graph of scanning electron microscopy/–
E	activation energy/kJ mol^{-1}
$f(X_c)$	reaction model and $f(X_c) = (1 - X_c)$
I_D	height of the D band, and represents the large aromatic systems with no less than 6 rings/–
I_G	height of the G band, and represents small aromatic systems with less than 6 fused rings/–
M_c	mass ratio of the coal/%
M_b	mass ratio of the CMC/%
m_o	initial mass of char sample/mg
m_t	mass of the char at gasification time t/mg
m_a	mass of the ash in char/mg
N_r	measurement results from the determinate ruler/–
r	selected ruler during the calculation of D_s/–
P	equilibrium pressure of the gas/Pa
P_0	saturated vapor pressure of gas/Pa
$P(u)$	temperature integral
R	universal gas constant/J mol^{-1} K^{-1}
R_c	index of gasification reactivity/
R_{gmax}	maximum gasification rate/mg min^{-1}
R^2	correlation coefficients/–
t	time/s
T	temperature/°C K
T_{gin}	initial gasification temperature og the char sample/°C
T_{gmax}	temperature of maximum gasification rate/°C
V	adsorbing capacity of N_2 under P/P_0/ml g^{-1}
V_0	gas volume of the monolayer/ml g^{-1}
Xc	conversion of the char sample/%
$X_{c,calculate}$	calculated conversion of co-pyrolysis char/%
$X_{c,c}$	conversion of coal char under the same of the co-pyrolysis char/%
$X_{c,b}$	conversion of CMC under the same of the co-pyrolysis char/%
β	heating rate/°C min^{-1}
$\tau_{0.5}$	time when the conversion of char sample was 50%/min
u	E/RT

Abbreviations

AAEM	Alkali and alkaline-earth metal
AC	anthracite coal
ACCMC3-1	mixture of AC and CMC, and the mass ratio of CMC was 25%
ACCMC1-1	mixture of AC and CMC, and the mass ratio of CMC was 50%
ACCMC1-3	mixture of AC and CMC, and the mass ratio of CMC was 75%
BC	bituminous coal
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%
BET	Brunauer, Emmett and Teller
BJH	Barrett, Joyner and Halenda
CCT	clean coal technology
CE	cellulose
CMA	calcium magnesium acetate
CMC	carboxymethylcellulose sodium
EDS	energy dispersive spectrometry
IUPAC	International Union of Pure and Applied Chemistry
SEM	scanning electron microscopy
SM	Shenmu bituminous coal
SS	sewage sludge
TGA	thermogra vimetric analyzer
PAW	paulownia wood
PET	polyethylene terephthalate
PW	platanus wood
PZ	pingzhuang lignite
PVC	poly(vinyl chloride)

applications of biomass are limited. Co-thermochemical conversion of coal and biomass can provide a potential solution for the above problems, including co-combustion, co-gasification, co-pyrolysis and co-liquefaction [2–4,6,7]. During the co-thermochemical conversion processes, the gasification or combustion of co-pyrolysis char, a heterogeneous reaction, is usually the rate controlling step [7–10]. The heterogeneous reactions reactivity of co-pyrolysis char was significantly influenced by the physicochemical structure (specific surface area, pore structure, surface morphology, elementary compositions and microcrystalline structure., *etc.*) of the char. The adding of biomass could affect the physicochemical structure of co-pyrolysis char during the co-thermochemical process. Thus investigation of the structure evolution and reactivity are necessary for the process design and optimum.

Previous research mainly focuses on the influence of integral components in biomass on the physicochemical properties of co-pyrolysis char. Both Krerkkaiwan et al. [11] and Ellis et al. [12] found that the experimental values of the specific surface area and pore volume from co-pyrolysis char are higher than that of calculated values. While Yuan et al. [13] reported an opposite result about the specific surface area evolution of the co-pyrolysis char. Furthermore, the microcrystalline structure of co-pyrolysis char was also investigated with various conclusions [13–15]. Recently, Wu et al. [7,10] reported that the main organic components (cellulose, hemicellulose, and lignin) in the lignocellulosic biomass have different effects on the morphology and microstructure of the co-pyrolysis char. Various conclusions on the physicochemical structure evolution of co-pyrolysis may be partly attributed to the integrative action of the three main organic components. However, besides the organic components, inorganic matters in biomass, especially the alkali and alkaline earth metals (AAEM), also affect the co-pyrolysis process and the evolution of co-pyrolysis char structure [6,16,17].

Generally, there are mainly three forms of AAEM in biomass and coal, which are mineral matter (silicates), inorganic salts (NaCl, KCl) and salt of carboxylic acids (–COOM, and M is a kind of AAEM) [18–21]. Salts and carboxylates are the typical and abundant forms of AAEM in biomass. Influence of inorganic salts of AAEM on the product distribution and characteristics have been investigated [22,23]. Wang et al. [16] reported that hydrocarbon yields were reduced by the adding of inorganic AAEM salts, and the influence order was: $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$. However, little attention has been devoted to the effects of carboxylates AAEMs in the