



Physicochemical evolution during rice straw and coal co-pyrolysis and its effect on co-gasification reactivity



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HIGHLIGHTS

- Physicochemical evolution in coal-biomass co-pyrolysis was quantitatively measured.
- Order degree of co-pyrolyzed chars was distinctly promoted at high coal proportion.
- Co-pyrolysis obviously enhanced active K transformation at high coal proportion.
- Co-pyrolysis impact on co-gasification was related with physicochemical evolution.

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ABSTRACT

Physicochemical evolution (i.e. pore structure variation, carbon structure change and active AAEM transformation) during rice straw (RS) and Shenfu bituminous coal (SF) co-pyrolysis was quantitatively determined in this work. Moreover, the corresponding char gasification was conducted using a thermogravimetric analyzer (TGA) and relative reactivity was proposed to quantify the co-pyrolysis impact on co-gasification reactivity. The results showed that the development of pore structure in co-pyrolyzed chars was first inhibited and then enhanced with the decrease of SF proportion. The promotion effect of co-pyrolysis on order degree of co-pyrolyzed chars gradually weakened with increasing RS proportion. Co-pyrolysis mainly enhanced active K transformation in co-pyrolyzed chars and the promotion effect was alleviated with increasing RS proportion. The inhibition effect of co-pyrolysis on co-gasification reactivity weakened with increasing RS proportion and gasification temperature, which was mainly attributed to the combination of carbon structure evolution and active AAEM transformation in co-pyrolysis.

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1. Introduction

Gasification is the core technology for efficiently and cleanly utilizing carbonaceous materials. Biomass is an important renewable energy and shows great superiority in near-zero carbon emission, great available reserves and high reaction activity, whereas biomass gasification is seriously hindered owing to the low energy density, low calorific value, high tar yield and unstable supply (Fermoso et al., 2010; Rizkiana et al., 2014). Compared with biomass, advanced coal gasification has achieved widespread industrialization and exhibits high complementarity with biomass (Masnadi et al., 2015). Coal is favorable for effectively improving the deficiencies of biomass and promoting the industrialization of biomass gasification. On the other hand, biomass is conducive to remedy the limitation of coal in resource reserves, pollution emission, product distribution and reactivity. Moreover the ample alkali/alkali earth metal minerals (AAEM) in biomass could be served as natural catalyst and reduce the catalyst cost in coal gasification process (Jeong et al., 2014; Zhang et al., 2016; Ding et al., 2014). Consequently, it is very worthy to conduct studies on biomass and coal co-gasification.

Pyrolysis is the basic step of gasification reaction, and directly affects the product distribution, char structure evolution, internal mineral transformation and subsequent gasification reactivity (Ding et al., 2015). Recently, much attention has been focused on exploring co-pyrolysis characteristic of biomass and coal and its

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impact on co-gasification reactivity. Meesri and Moghtaderi (2002) pointed out that chemical interaction hardly existed during ligno-cellulosic biomass and coal co-pyrolysis at the temperature range of 200–1400 °C in a fixed bed reactor. Li et al. (2014) and Yuan et al. (2012) reported that biomass and coal co-pyrolysis at high temperature exhibited significant synergy in tar yield decrease and gas yield increase, whereas barely affected char yield. Ellis et al. (2015) found that the correlation between co-gasification reactivity of wood and coal and pore structure variation during co-pyrolysis in a fixed bed reactor was weak, but Kreckkaiwan et al. (2013) stated that the development of pore structure in co-pyrolysis of straw/wood and sub-bituminous coal advanced co-gasification reactivity. Zhu et al. (2008) conducted biomass and coal co-pyrolysis at 650–850 °C in a spout-entrained reactor and the results indicated that co-pyrolyzed char at 750 °C contained the greatest potassium content and showed highest gasification reactivity. Additionally, it was also demonstrated that the crystal structure was formed in co-pyrolysis process because of the reaction between inert mineral (i.e. SiO₂, Al₂O₃, etc) and AAEM, which had an inhibition effect on co-gasification reactivity (Ellis et al., 2015; Masnadi et al., 2014).

According to previous studies, the influence of co-pyrolysis on subsequent co-gasification reactivity was mainly attributed to the AAEM transformation and pore structure evolution in co-pyrolysis. However, the methods (X-ray diffraction (XRD), scanning electron microscopy coupled with energy disperse spectroscopy (SEM-EDS), etc) adopted to analyze the AAEM transformation in co-pyrolysis were short of quantification. Furthermore, the special researches on active AAEM transformation in co-pyrolysis and its effect on co-gasification reactivity were rarely reported. On the other hand, literatures about the correlation between carbon structure changes in co-pyrolysis and co-gasification reactivity were still few although some studies have been carried out to investigate the variations of char carbon structure during co-pyrolysis process (Wang et al., 2015; Lahijani et al., 2013; Meng et al., 2015).

The main purpose of this work was to study the physicochemical evolution during co-pyrolysis of rice straw (RS) and Shenfu bituminous coal (SF) and its effect on subsequent co-gasification reactivity characteristics. The evolution of pore structure, carbon structure and active AAEM content in co-pyrolysis was quantitatively determined by physisorption analyzer, Raman spectrum and flame atomic absorption spectrum, respectively, moreover char gasification reactivities were evaluated using thermogravimetric analyzer. It was not only beneficial to deeply understand the influence of co-pyrolysis on co-gasification, but also favorable for the further mechanism investigation on synergy behaviours during co-pyrolysis/co-gasification.

2. Materials and methods

2.1. Tested samples

Rice straw (RS, a typical biomass in China) and Shenfu bituminous coal (SF, a typical gasification coal utilized in China) were selected as raw materials in this work. SF and RS dried for 12 h were respectively smashed by coal pulverizer and cutting machine, and then respectively sieved to particle size range of 80–120 μm and 190–250 μm. Properties of SF and RS were listed in Tables 1 and 2.

High-frequency furnace reactor was adopted to pyrolyze raw materials and acquire char samples, and the schematic diagram of HFFR was given in Fig. 1. The pyrolysis atmosphere, pyrolysis temperature and dwell time were chosen as nitrogen (100 mL/min),

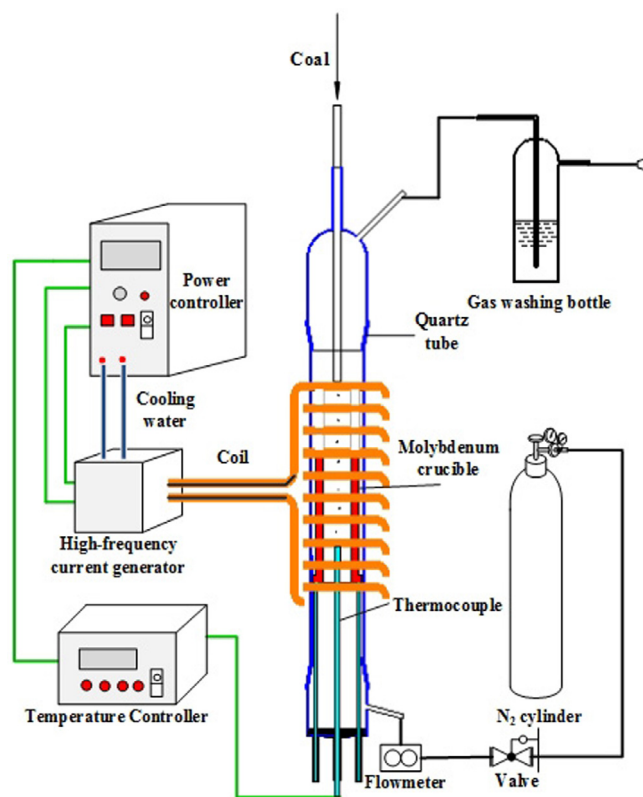


Fig. 1. The schematic diagram of high-frequency furnace reactor.

Table 1

The proximate analysis, ultimate analysis and ash fusion temperature of tested samples.

Samples	Proximate analysis/d, %			Ultimate analysis/d, %					Ash fusion temperature/°C			
	VM	FC	Ash	C	H	N	O	S	DT	ST	HT	FT
SF	35.42	58.29	6.29	79.14	2.32	1.12	10.36	0.77	1152	1167	1175	1179
RS	75.05	15.35	9.60	44.08	6.24	1.13	38.57	0.38	1198	1257	1290	1380

Table 2

The ash composition of tested samples.

Samples	Ash composition/%						
	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	CaO	Fe ₂ O ₃	MgO
SF	33.36	12.44	0.67	1.73	27.78	9.11	1.34
RS	58.88	0.18	21.97	1.13	4.20	0.26	2.73

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