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Co-pyrolysis of lignocellulosic biomass with low-quality coal: Optimal design and synergistic effect from gaseous products distribution

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ABSTRACT

Co-pyrolysis of lignocellulosic biomass and low-quality coal can alternate fossil fuel partially and utilize biomass on a commercial scale. Gaseous products from co-pyrolysis process can be widely applied in industries due to the advantage in transportation and compression. Thus, investigation of synergistic effect and optimal design about gas products is essential for efficiently and comprehensively design of the process. In this research, three model compounds of lignocellulosic biomass (cellulose, hemicellulose, lignin) and wheat straw were co-pyrolyzed with a kind of low-quality coal via a drop tube furnace. Based on the component insight of biomass and response surface methodology, synergetic effects from gas distribution were investigated. The influence of reaction condition (biomass ratio and pyrolysis temperature) on the yield and high heat value (HHV) of gaseous products were explored. Optimal result for the objective of the highest effective gas yield during co-pyrolysis were obtained. Results revealed that both positive and negative synergic effects on yields and composition of pyrolysis gas were presented. When pyrolysis temperature was 600 °C, both wheat straw and three model compounds promoted the formation of H_2 and CO. Negative effects on CO_2 were observed when co-pyrolysis of cellulose/wheat straw with coal at the temperature of 600 °C to 800 °C. Whether positive or negative synergy existed depended on the mixing ratio, temperature and combined action of lignin, hemicellulose, and cellulose. For coal and hemicellulose mixtures, the mixing ratio of 0.03 and temperature of 936 °C can get the highest yield of H_2 (20.56 mmol/g). Moreover, the maximum yield of CO and CO_2 was obtained at cellulose mixing ratio of 0.99 and 0.98 at 787 °C and 626 °C, respectively. Based on the view of biomass composition, the results can be used to optimize the gaseous products distribution during co-pyrolysis of coal and biomass.

1. Introduction

According to the coal information from International Energy Agency (IEA), coal still play an essential role in the energy supply and power generation. About 63.5% of the coal was used for power and heat supply, accompanied with environmental constraints [1]. Base on the formation age of the coal, it can be divided to four kinds from the younger one to older one, including lignite, sub-bituminous, bituminous and anthracite. For the lignite and sub-bituminous coal, they can also be called as low-rank coal or low-quality coal (LC). Especially in China, about 60% of the coal storage is LC [2]. How to use LC in an efficient and environmentally friendly way is very important for economic development. Moreover, the clean coal technology and alternative energy can be selected as the solutions for clean using of LC. Biomass has been considering as one of the most significant renewable energy resources [3]. Co-thermochemical conversion of coal and biomass can partially substitute the consumption of fossil fuel and promote the commercial scale application of biomass [2,4]. Co-pyrolysis is the initial procedure of the co-thermochemical process. Thus, investigation on the distribution and characteristics of products from co-pyrolysis is beneficial for the reactor design and optimization [5].

Previous investigations on co-pyrolysis have been performed on the influence of biomass on the thermal behavior and products distribution [6–12]. However due to the variety of biomass, different conclusions on the pyrolytic characteristics, kinetic analysis, quantity and quality of the products were obtained [13–15]. Above conclusion can be divided to two effects, the additive effect and synergistic effect, which corresponding with linear and non-liner relationship between biomass ratio and parameters. For additive effect, it could be used to predict the yield. For synergistic effect, researchers can select proper mass ratio and

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Nomenclature

A	mixing ratio of major biomass component or wheat straw/-
B	temperature of pyrolysis/°C
HHV	higher heating value of gaseous products/$\mathrm{MJ\cdot Nm^{-3}}$
H_i	higher heating value of the effective gas/$\mathrm{MJ\cdot Nm^{-3}}$
M_0	mass of coal or biomass sample/g
t	time for gas collected/min, which was 10 min in this paper
V_{ni}^{0}	flow rate of N_2/$\mathrm{ml\cdot min^{-1}}$, in this research it was 100 $\mathrm{ml\cdot min^{-1}}$
V_{ni}	volume content of N_2 in gas products/vol%
X_C	mass ratio of LC in the mixing sample
X_L	mass ratio of the three major model compounds (CE, HCE, and LIG) and WS
Y_C	gas yield from model compounds and WS at the same condition of the mixing sample
Y_L	gas yield from LC at the same condition of the mixing sample
Y_{Gi}	yield of gaseous product/$\mathrm{mmol\cdot g^{-1}}$
$Y_{Experiment}$	experimental value of gas yield from the mixture/$\mathrm{mmol\cdot g^{-1}}$
$Y_{Prediction}$	predicted value based on the mass of gas yield from the individual sample/$\mathrm{mmol\cdot g^{-1}}$
ΔY	synergistic value of the gas yield/$\mathrm{mmol\cdot g^{-1}}$
+	positive synergistic effect
–	negative synergistic effect

Abbreviations

AAEMs	alkali and alkaline earth metallic species
CE	cellulose
DTF	drop tube furnace
HCE	hemicellulose
LC	low-quality coal
LIG	lignin
WS	wheat straw
LCCE3-1	mixture of LC and CE, and the mass ratio of CE was 25%
LCCE1-1	mixture of LC and CE, and the mass ratio of CE was 50%
LCCE1-3	mixture of LC and CE, and the mass ratio of CE was 75%
LCHCE3-1	mixture of LC and HCE, and the mass ratio of HCE was 25%
LCHCE1-1	mixture of LC and HCE, and the mass ratio of HCE was 50%
LCHCE1-3	mixture of LC and HCE, and the mass ratio of HCE was 75%
LCLIG3-1	mixture of LC and LIG, and the mass ratio of LIG was 25%
LCLIG1-1	mixture of LC and LIG, and the mass ratio of LIG was 50%
LCLIG1-3	mixture of LC and LIG, and the mass ratio of LIG was 75%
LCWS3-1	mixture of LC and WS, and the mass ratio of WS was 25%
LCWS1-1	mixture of LC and WS, and the mass ratio of WS was 50%
LCWS1-3	mixture of LC and WS, and the mass ratio of WS was 75%

reaction condition to get the highest yield of target products. Haykiri-Acma *et al.* [6,16], Ulloa *et al.*[17], Krerkkaiwan, S., *et al.* [18]and Aboyade *et al.* [8] reported that the char yields from co-pyrolysis of lignite and biomass were smaller than the values obtained from individual fuels. A similar result was also reported in the apparent activation energy [7–8]. However, non-existence of synergies during co-pyrolysis was reported by some researchers [5,19–23]. Collot *et al.* [24], Meesri and Moghtaderi [22,25], Weiland *et al.* [21] observed no synergistic effect from char yield during the co-pyrolysis process, and the products distribution had a linear relation with biomass mixing ratio. An absence of synergistic effect on the apparent activation energy was reported by other researchers [5] Furthermore, whether there exist synergistic effects from the yield of pyrolysis products or not remains inconclusive [26].

Due to the various kinds of biomass, the major contents, including organic and inorganic components, are different [27]. Thus, the variation of the primary organic component (cellulose, hemicellulose, and lignin) and alkali and alkaline earth metallic species (AAEMs, mineral matter, inorganic salts and salt of carboxylic acids) would relate with the different conclusion on production from co-pyrolysis [27–29]. Wu *et al.* reported that both positive and negative synergetic effects were observed during co-pyrolysis of coal with cellulose, hemicellulose, lignin and carboxymethylcellulose sodium [27,30]. However, few attentions have been paid to the optimal design based on the synergistic effect during co-pyrolysis of organic compounds in biomass and LC.

This paper aims to investigate the optimal design of gaseous products from lignocellulosic biomass model compounds and typical biomass with LC during the co-pyrolysis process. Three main organic components of biomass, including cellulose, hemicellulose and lignin, wheat straw were introduced in the pyrolysis of LC. The individual materials and mixtures were pyrolyzed via a drop tube furnace, and gas chromatography was used to detect the gaseous products. The effects of components types, temperature and mixing ratio of the gaseous products distribution and optimal design on the effective gas yield was investigated.

2. Experimental

2.1. Materials

Cellulose (CE, CAS No: 9004–34-6), hemicellulose (HCE, CAS No: 9014–63-5) and lignin (LIG, CAS No: 8068–05-1) were bought from Sigma–Aldrich Co., Ltd, and detailed information can be found in previous research [30]. Wheat straw (WS) and low-quality coal (LC) were collected from north of Shaanxi, China. The procedure for preparing the individual sample and mixture were described in previous research [30]. The mixtures of LC and WS were named as "LCWS3-1", "LCWS1-1" and "LCWS1-3", indicating that the mass ratio of WS was 25%, 50%, and 75%, respectively. The mixtures of LC and CE, LC and HCE, LC and LIG were named in the same way. Analyses of the samples are shown in Table 1.

Table 1
Analyses of the raw samples.

	LC	CE	HC	LG	WS
Proximate analysis (wt%, ad)					
Moisture, M	4.18	3.67	5.76	3.38	6.82
Ash, A	15.38	0.07	3.61	3.62	10.52
Volatile, V	30.56	94.37	77.71	60.35	66.21
Fixed carbon, FC	49.88	1.89	12.92	32.65	16.05
Ultimate analysis (wt%, daf)					
Carbon, C	79.31	44.3	40.18	61.35	47.58
Hydrogen, H	4.72	6.17	5.53	5.05	5.79
Nitrogen, N	1.03	–	2.71	1.13	0.85
Sulfur, S^t	1.30	0.03	–	0.69	0.33
Oxygen, O^c	13.38	49.5	51.58	31.78	45.4
High-heating value ($\mathrm{MJ\cdot kg^{-1}}$, ad)	25.44	16.71	15.21	17.98	17.45

ad: Air-dried; daf: Dry ash-free; t: Total content; c: Calculated by difference.