Full Length Article

Interactions during co-pyrolysis of direct coal liquefaction residue with lignite and the kinetic analysis

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ABSTRACT

Co-pyrolysis process of direct coal liquefaction residue (DCLR) with lignite was examined by thermogravimetric analyzer (TGA) and the kinetic characteristics were analyzed using Kissinger-Akahira-Sunose method. And different mass ratios of DCLR to lignite (10:0, 8:2, 6:4, 4:6, 2:8 and 0:10) were considered in this work. At the same time the influences of individual components in DCLR on co-pyrolysis process were investigated as well. Results showed that significant difference presented in experimental and calculated co-pyrolysis curves of DCLR with lignite. And such difference was related to pyrolysis temperature and mixed ratio of sample. The volatiles yield increased (experimental volatiles yield > calculated one) for the co-pyrolysis of DCLR with lignite at low temperatures (200–500 °C) while decreased at high temperatures (experimental volatiles yield < calculated one, 500–900 °C), and with the addition of DCLR, such increasement of volatile yield at low temperatures was weakened whereas the decrement at high temperatures was strengthened. The increase of volatiles of co-pyrolysis samples at low temperatures was ascribed to the heavy oils and asphaltenes in DCLR whereas all the individual fractions in DCLR could result in the decrease of volatile yield at high temperatures. And the activation energies of co-pyrolysis samples of lignite with DCLR decreased with the increase of DCLR dosage, which indicated that the co-pyrolysis reactivity of mixed samples increased gradually.

1. Introduction

Direct coal liquefaction technology is a promising approach for producing clean liquid fuels and valuable chemicals from coal. The only and commercial-scale direct coal liquefaction plant was built and put into production after World War II by Shenhua Group Corporation in Inner Mongolia, China. As the main by-product of liquefaction process, direct coal liquefaction residue (DCLR) accounts for 20–30 wt% of raw coal [1,2]. Rational utilization of DCLR is critical for improving the economic performance of direct liquefaction process. Generally, DCLR is separated by vacuum distillation [3,4]. It not only contains unreacted coal, minerals and residual catalysts, but also has considerable heavy components, including heavy oils, asphaltenes and preasphaltenes [4–7]. Currently, the research of DCLR utilization mainly concentrates on pyrolysis, gasification and hydro-liquefaction [4]. Among which pyrolysis is the initial step of these thermochemical processes which influences the subsequent reactions. In addition, pyrolysis can also recover heavy fractions from DCLR. Thus the researches on DCLR pyrolysis have caused extensive concern especially in China [6–8]. However, DCLR has strong cohesiveness and low soften point (< 180 °C),

and at the same time it will melt into liquid when heated [3,8]. This would lead to the difficulty in feeding system of pyrolysis process. In addition, the amount of DCLR is not enough for the operational capacity in terms of its individual pyrolysis. Thus coal blending technology are generally applied to DCLR pyrolysis process [7–9].

Low-rank coal, especially lignite, is one of the most common feedstocks to co-pyrolyzed with DCLR. Lignite has high moisture, high oxygen content, developed pore structure and low calorific value, which tends to spontaneously combust during transportation and storage [10,11]. Thus dewatering and upgrading of lignite have become the essential steps for its effective utilization [12]. Co-pyrolysis of lignite with DCLR is not only an attractive way to upgrade lignite in terms of enhancing heat value and stability, it can also decrease the cohesiveness of DCLR during pyrolysis process. Thus the co-pyrolysis characteristics of lignite with DCLR have been investigated by many researchers [7–9,13]. Several studies were conducted to analyze thermal behaviors and products distribution of co-pyrolysis of lignite with DCLR. And interactions were confirmed to exist in the co-pyrolysis process. Liu et al. [13] investigated the co-pyrolysis characteristics of Shenhua DCLR with its raw coal, and considered that the co-pyrolysis

Table 1
The basis properties of lignite and DCLR samples.

Sample	Proximate analysis (wt%)			Ultimate analysis (daf, wt%)				$S_{t,d}$	$Q_{gr,v,daf}$ (MJ/kg)
	A_d	V_{daf}	FC_{daf}	C	H	O*	N		
YNL	22.87	51.47	48.53	71.93	4.72	20.75	1.75	0.85	24.44
DCLR	14.95	43.53	56.47	89.84	5.20	1.66	0.97	2.33	37.46

d, dry basis; daf, dry and ash-free basis; S_t, total sulfur; *, by difference; $Q_{gr,v,daf}$, gross calorific value.

increased char yield while restrained the evolution of tar and gases. Similar results were observed by Xu et al. [9] in co-pyrolysis of Shenhua DCLR with lignite. However, Li et al. [7] found tar yield increased during co-pyrolysis of Shendong DCLR with Hulunbeier lignite, and they attributed the results to the hydrogen-donor effect of DCLR. It must be pointed out that the above-mentioned works were conducted in fixed-bed reactor and only a few temperature points were investigated. Compared with co-pyrolysis in fixed-bed reactor, thermogravimetric analysis (TGA) is a better option to understand the whole co-pyrolysis process [14–16]. Information about the pyrolysis characteristics and kinetic analysis can be obtained by TGA experiments. And these information are very important to understand the co-pyrolysis process, which can provide instructions for performance promotion and product yield control [17]. However, only a few researchers investigated the co-pyrolysis characteristics of coal with DCLR by TGA [9,13,18], and they did not reveal their interactions of both during co-pyrolysis. And at the same time the kinetic analysis is lacking in previous reports. In addition, DCLR can be separated into different components by extraction, including heavy oils (n-hexane soluble, HS), asphaltenes (n-hexane insoluble and toluene soluble, A), preasphaltenes (toluene insoluble and THF soluble, PA) and tetrahydrofuran insoluble fractions (THFIS) [5,6]. These individual components have significant influences on co-pyrolysis process. Previous literature considered that interactions presented in co-pyrolysis of HS, A, PA with lignite, whereas such interactions just were evaluated by final weight loss of samples [13]. The detailed effects of these individual components on co-pyrolysis process are ignored.

In this work, pyrolysis characteristics of lignite, DCLR and their mixed samples were examined, and influences of individual components in DCLR on co-pyrolysis process were discussed. The results are expected to well understand the presence and nature of interactions during co-pyrolysis of coal with DCLR.

2. Material and methods

2.1. Materials

Lignite from Yunnan province (YNL), in the south of China, was used in this study. DCLR was obtained from 6 t/d direct coal liquefaction pilot plant of Shenhua Group in Shanghai. Samples were ground to 100 mesh (< 154 μm) and then dried in a vacuum oven at 110 °C for 12 h to eliminate moisture. The basis properties of lignite and DCLR are listed in Table 1. And the chemical compositions of their ashes are shown in Table 2.

2.2. Characterization

Functional groups of samples were measured by a Fourier transform infrared spectrometer (VERTEX 70, Bruker, Germany). Samples were fully mixed with dried KBr powder at the mass fraction of 1:200. The spectra were recorded from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. Furthermore, to investigate the change of pore structure of samples during pyrolysis, char samples with different pyrolysis temperatures (200–900 °C) and DCLR fractions (0, 20, 40, 60, 80 and 100 wt%) were prepared. The procedure of char preparation and schematic flow diagram of experimental unit for pyrolysis can be seen in previous literature [8]. The pore structure properties of samples were estimated by a Micrometrics ASAP2020 adsorption apparatus (Micromeritics, United States of America) using N_2 and CO_2 as the probe gas. The adsorption of CO_2 was at 273 K whereas the adsorption of N_2 was at 77 K. The Brunauer Emmett Teller method was used to calculate the surface area of samples.

2.3. Co-pyrolysis

2.3.1. Co-pyrolysis of lignite with DCLR

The pyrolysis experiments were conducted using a thermogravimetric analyzer (TGA, Setsys Evolution, SETARAM, France) coupled with a mass spectrometer (MS, Omnistar, Switzerland) aiming at exploring the thermal degradation behavior of samples and release profile of gases. About 10 mg sample was used in each run to mitigate the influence of heat and mass transfer. First, sample was heated under 100 mL/min argon (99.95%) flow at heating rate of 10 °C/min from ambient temperature to 110 °C, and then held for 20 min at 110 °C to assure a complete removal of mositure. The pyrolysis experiments were performed from 110 °C to 900 °C at the heating rate of 10, 20 and 40 °C/min. In co-pyrolysis experiments, the mass fractions of 20, 40, 60 and 80% of DCLR were selected. To ensure fully blend of samples, mixed coal and DCLR were put into a mortar and ground for 15–20 min. And good repetition of experimental result indicates the uniformity of each sample.

2.3.2. Co-pyrolysis of lignite with individual components in DCLR

The co-pyrolysis characteristics of individual components (HS, A, PA and THFIS) with lignite were investigated. HS, A, PA and THFIS were separated from DCLR by Soxhlet extraction. The proportion of solid sample (g) and extractant (mL) in extraction is 1:50. DCLR was extracted for 72 h each solvents in a Soxhlet apparatus with n-hexane, toluene and tetrahydrofuran (THF) sequentially [5,6]. Finally the extracts were distilled in a rotary evaporator, then HS, A, PA and THFIS were obtained to use. To ensure the accuracy of experimental data, four parallel tests of extraction were conducted at the same time. Results showed that the extraction yield of each components in DCLR was quite close. The contents of HS, A, PA and THFIS in DCLR were 13.72 wt%, 28.60 wt%, 12.20 wt% and 45.48 wt% (the averages of four measurements). The mass fraction of co-pyrolysis of HS, A, PA and THFIS with lignite was 50%, and the mixed samples of which were defined as YNL-HS, YNL-A, YNL-PA and YNL-THFIS, respectively.

All the pyrolysis experiments were repeated to ensure accuracy and reliability of data. The relative error among the measurements of thermogravimetric curves was less than 0.26%.

Table 2
Ash composition (wt%) of YNL and DCLR.

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	TiO_2	K_2O	Na_2O	P_2O_5
YNL	46.01	21.54	7.57	10.71	2.05	5.94	1.51	2.20	0.30	0.26
DCLR	20.95	8.90	31.48	19.12	1.12	13.70	0.71	0.04	1.95	0.03