



## Full Length Article

# Product distribution and interactive mechanism during co-pyrolysis of a subbituminous coal and its direct liquefaction residue



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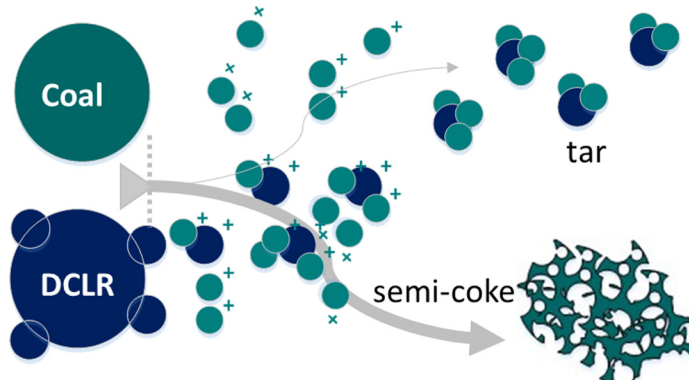
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## HIGHLIGHTS

- Experiments verify the interaction between coal and DCLR during co-pyrolysis.
- The interaction comes from the redistribution of free radicals between coal and DCLR during co-pyrolysis.
- More large free radicals from DCLR are stabilized by free radicals from coal in co-pyrolysis.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Compared with individual pyrolysis of Shendong coal or the direct coal liquefaction residue, co-pyrolysis has an improved tar yield. However, the synergistic mechanism in the integrated process is still controversial. In order to explore the interactive effect in co-pyrolysis of coal and the direct coal liquefaction residue, elemental analysis, gas chromatography, Fourier – transform infrared spectrometer, thermogravimetric simulation distillation, nuclear magnetic resonance and gas chromatograph – mass spectrometer were employed to analyze the structure and chemical composition of products (gas, semi-coke, and tar) obtained in co-pyrolysis at 600 °C. The results show that the actual product yields are different from the calculated values and elemental redistribution occurs in co-pyrolysis. Instruments characterization suggests an increased loss of aromatic hydrogen and carbon in co-pyrolysis, in comparison with individual pyrolysis. The increasing tar is mainly composed of heavy components with boiling points higher than 400 °C. Co-pyrolysis favors the minimization of the dealkylation of phenolic species. Furthermore, the synergistic mechanism analysis using two-stage reactor indicates that the increase in tar yield should be attributed to the change in the free radical reaction during the pyrolysis of Shendong coal and the direct coal liquefaction residue. In co-pyrolysis, more radicals generated from coal pyrolysis are used to stabilize the radicals generated from the pyrolysis of tetrahydrofuran soluble fraction of the direct coal liquefaction residue.

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## 1. Introduction

Coal is the dominant fossil energy in China, which provides a significant incentive for the development of competitive processes to convert this resource into a clean liquid fuel. Among the proven

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processes of producing liquid fuels from coal, direct coal liquefaction (DCL) must be considered seriously in any strategic plan for coal utilization [1]. The only commercial DCL plant after World War II was built by the Shenhua Group in Inner Mongolia, China. It was designed to produce liquid fuels, naphtha and liquefied petroleum gas (LPG) [2]. One of the challenges to further development of DCL is to find ways to add value to the direct coal liquefaction residue (DCLR), since this residue accounts for 30 wt.% of the feed and contains 30–50 wt.% coal liquids [1,3,4]. The conversion of this DCLR to lighter, high-value products is an important goal in helping to make this technology both commercially viable and environmentally acceptable [5]. Low-temperature pyrolysis could effectively recover heavy oil from DCLR, and derived DCLR semi-coke could be gasified to compensate hydrogen consumption during liquefaction [6]. However, the low thermal fluidity and high viscosity of DCLR during low-temperature pyrolysis is the main limitation detecting during amplification tests [7].

The co-pyrolysis of DCLR and low rank coal received considerable attention because it can inhibit lignite pulverization and increase granulation. The high sulfur content for all feeds are beneficial because acid gas removal costs can be limited by reducing the amount of gaseous sulfur in the system [8]. Besides the change in physical properties, there are also changes in chemical, such as the product distribution and composition. When a DCLR was impregnated into coals at 200–250 °C and pyrolyzed by using three types of reactors, negative synergism was found in the yield of hydrogen gas, hydrocarbon gases, and inorganic gases, indicating that the hydrogen transferred from DCLR to coal and that cross-linking reactions were suppressed [9]. From kinetic analysis, it was found that activation energies for the pyrolysis of coal liquefaction residues were lower than that for the mean values of coals [10]. Our previous study also inferred the existence of an interactive effect from the increase in tar yield in co-pyrolysis. This interactive effect is attributed to the hydrogenation of organic components (THFS) in the DCLR and the mass transfer process in pyrolysis [11].

DCLR is more hydrogen deficient than lignite comparing their H/C ratio, but there is less oxygen in DCLR than lignite. During pyrolysis, large amounts of hydrogen combine with oxygen to produce water, suggesting that in co-pyrolysis, DCLR may produce more hydrogen to promote radical stabilization. However, there are also other factors impacting the process of co-pyrolysis, which may produce adverse interactive effects. In Liu's research on co-pyrolysis at 900 °C, the difference between experimental yield and calculated yield ( $\Delta Y$ ) is variable at different DCLR/Coal ratios, but the experimental water, gas, and tar yields are all lower than their calculated values ( $\Delta Y \leq 0$ ). It is suggested that DCLR is not only a hydrogen donor, but also a hydrogen shuttle [12]. This result partly disagrees with our own results [11], in which  $\Delta Y$  of tar and water are both greater than zero. Further study is needed to fully understand the mechanism of co-pyrolysis. From the mechanism of pyrolysis, it is well recognized that the reactions occurring during coal pyrolysis can be categorized mainly into two general steps: thermal cleavage or rupture of covalent bonds to generate free radical fragments; and coupling or condensation of the free radical fragments to form stable products [13]. The difference in structure between coal and DCLR may lead to the difference in the cracking and condensation reactions involved in individual pyrolysis of coal and DCLR. For example, the coupling of the free radical fragments generated in pyrolysis is not simple because the probability of the free radical fragments finding each other varies with their size and the pyrolysis conditions [2,14–16]. DCLR is highly aromatic and resistant to thermal cracking. Hence, liquid recovery is effected by limited cracking and extensive vaporization of lighter oil and asphaltic fractions [17]. In contrast, due to the high concentration of thermally labile functional groups (such as

–OH, –COOH, and –OCH<sub>3</sub>) and the aliphatic side-chain in low rank coal, there are more smaller-molecular free radicals generated in coal pyrolysis than in DCLR pyrolysis. In co-pyrolysis, those free radicals which come from coal pyrolysis are more likely to stabilize the radical fragments and contribute to the reaction of asphaltene (A) and preasphaltene (PA) to oil, than the larger-molecular free radicals generated in DCLR pyrolysis.

There are still many uncertainties about the interactive effect in the co-pyrolysis of coal and DCLR. The purpose of this paper is to further investigate the interactive effect between the devolatilization of coal and DCLR. We adopted a two-stage reactor to explore the source of synergism. Investigations into the distribution of pyrolysis products and elements, and the physical and chemical characterization of tar and semi-coke were conducted to find the varieties of products being produced during individual pyrolysis or co-pyrolysis.

## 2. Experimental

### 2.1. Feedstock

Shandong long-flame coal (SD) and its direct coal liquefaction residue (DCLR) obtained from Shenhua Coal to Liquids plant were used as the feedstock in this study. The SD and DCLR were ground and sieved to 0.425–0.85 mm. Feeds were then dried at 110 °C for approximately 10 h and stored in a desiccator. SD, DCLR, or SD and DCLR mixture with 100/15 mass ratio were used as feedstock to feed into the reactor, respectively.

The proximate analysis, ultimate analysis of the SD and DCLR are presented in Table 1. It can be seen that the H/C molar ratio of SD is relatively high compared to DCLR, which suggests that SD act as a hydrogen donor in co-pyrolysis. This indicates that SD will be more hydrogen deficient than DCLR if a large amount of hydrogen is consumed by oxygen to produce water.

### 2.2. Experimental setup and procedure

One-stage pyrolysis with a fixed bed reactor was first performed to test the product distribution by pyrolyzing approximately 10 g feed of size 0.425–0.85 mm at 600 °C. According to our previous results, the highest tar yield in DCLR pyrolysis and SD pyrolysis was achieved at 550 °C and 600 °C. The mass transfer resistance was increased due to the stickiness of sample if DCLR addition was more than 20 wt.% coal in co-pyrolysis of DCLR and lignite [11]. We conduct the co-pyrolysis of DCLR and SD at 600 °C because the SD is the majority. In co-pyrolysis of different DCLR ratio at 600 °C, the difference of the experimental data and calculated values for tar yields ( $\Delta Y$ ) are 0.9% (SD + 10%DCLR), 1.9% (SD + 15%DCLR), 1.3% (SD + 20%DCLR). In the subsequent experiments, we conducted the co-pyrolysis at 600 °C and the addition of DCLR is 15 wt.% coal. As shown in Fig. S1, a special quartz reactor with a height to diameter ratio of 1:1 was designed to reduce the residence time of volatiles with an effort to minimize the occurrence of secondary pyrolytic reactions. The sample was loaded into the reactor, which was placed into a furnace preheated to a temperature for 30 min pyrolysis. Experiments were conducted using a nitrogen sweep gas with flow rate of 180 mL·min<sup>-1</sup> under atmospheric pressure. Gaseous and liquid products were rapidly removed from the reactor by the sweep gas during the pyrolysis. In co-pyrolysis, the mass ratio of DCLR to SD is 15:100 [11]. Each test was repeated three times to ensure the accuracy of data. A two-stage quartz reactor (Fig. S1) was employed to study the interactive mechanism in co-pyrolysis. In the two-stage reactor, the separate pyrolysis of SD and DCLR could occur in the upper layer (U) and lower layer (L), with the pyrolysis volatiles/radicals from

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