Research article

Product distributions and characterizations for integrated mild-liquefaction and carbonization of low rank coals

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ABSTRACT

This paper proposed an integrated mild-liquefaction and carbonization technology for the efficient conversion of low rank coals. Simultaneously, preliminary investigations on the product distributions and characterizations of the proposed technology were made in simulated process conditions. In suitable mild-liquefaction conditions (390–450 °C, 8.4–11.6 MPa), the yields of liquid products and semi-cokes are up to 23.4–33.3% and 49.6–68.7%, respectively. The produced liquid products, which are predominantly abundant with paraffins (i.e., alkanes and alkanes), alkyl benzenes (i.e., benzene and its derivatives), and alkyl naphthalenes (i.e., naphthalene and its derivatives), are potentially utilized to produce liquid fuels by further refining. The produced semi-cokes are suitably utilized as high carbonaceous solid fuels. Also, some semi-cokes can be potentially utilized for the coking of blending coals. The adopted carbonization process in the proposed technology is convenient and efficient for the separation of liquid and solid mixtures from liquefaction. Summarily, the proposed technology is greatly potential for the conversion of low rank coals into liquid products and semi-cokes.

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1. Introduction

Low rank coals, such as lignite and subbituminous coal (probably including bituminous coal with relatively high volatiles), can be regarded as an abundant and inexpensive resource accounting for 50% of the coal deposits around the world [1,2]. Consequently, low rank coals will play a great role in the utilizations of energy and chemicals in this century [3]. Compared to high rank coals with more poly-aromatic structures, low rank coals with high volatiles, which are abundant in aliphatic C—O and C—C structures, present a higher reactivity for thermo-chemical conversions [4,5]. Therefore, more attention has been paid recently to develop a reasonable method for efficient utilization of low rank coals [6–8].

Direct coal liquefaction, industrialized in the western counties of the past century, is considered as an effective way to produce transportation fuels and chemicals. However, the severe conditions are required to perform a considerable productivity [9]. Besides, coal liquefaction residue as an inevitable by-product in direct coal liquefaction is generally used

for the hydrogen production by gasification to meet the hydrogen demand of other processes [10–13]. However, the coal liquefaction residue still contains 30–50% coal liquids, which are composed of oils and asphaltenes for further extraction or upgrading to obtain more value-added products [14–17]. Consequently, it is imperative to explore and develop a suitable technology for liquefaction of low rank coals.

In view of the characterizations of low rank coal, a novel technology for its conversion was proposed, patented and named as ECOC by our group [18]. Fig. 1 gives the schematic diagram of the proposed ECOC process. The proposed technology has several main characteristics as follows. The mild liquefaction conditions with relatively low temperatures (<430 °C) and pressures (<10 MPa) [19] as well as replaceable hydrogen-donated gases (such as syngas) [20–24] are adopted to alleviate the rigor conditions of whole technical process and lower the cost for preparing H₂. An artful coupling of carbonization and gas blowing is favorable for liquid/solid separation, which is one of the confronted problems in the typical direct coal liquefaction technology [25,26]. An elevation of the overall efficiency can be achieved, owing to the convenient, reasonable and efficient utilizations of various products from the proposed process. These include the direct utilization of semi-cokes as solid fuels [27–30] and raw materials of coking [31,32], the extraction of chemicals from asphaltenes [33–35], the refining of light fractions to produce gasoline and/or diesel [12,36], and the preparation of carbon materials using heavy fractions as raw materials, etc. [16,17].
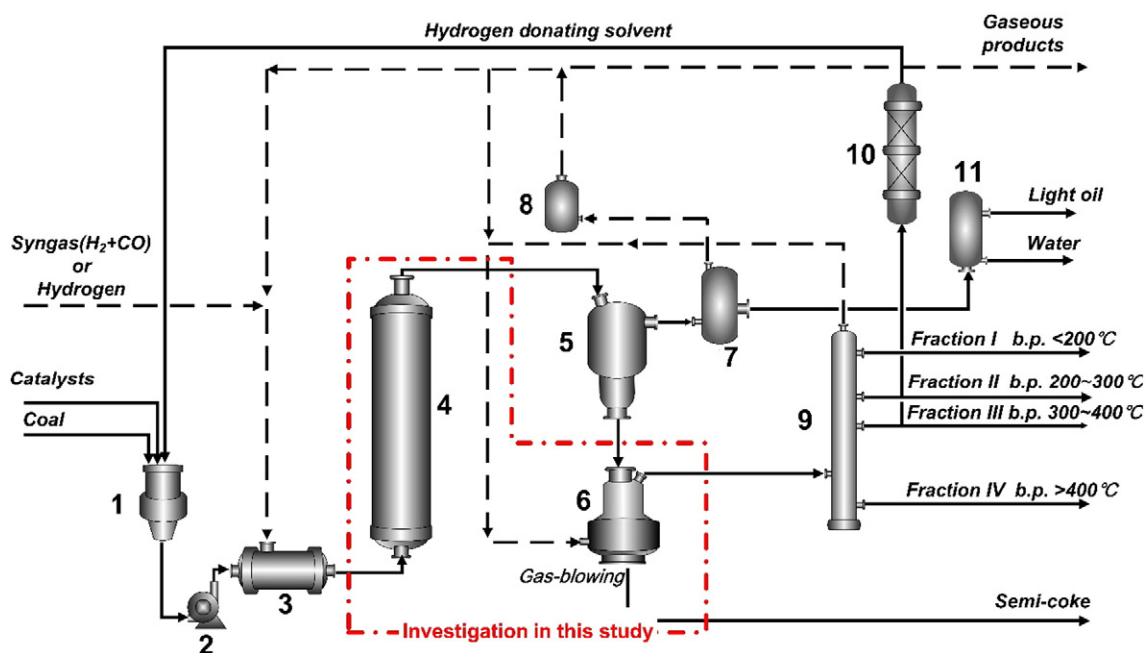
Fig. 1. Schematic processes of proposed ECOC technology. (1: slurry mixer; 2: coal slurry pump; 3: preheater; 4: liquefaction reactor; 5: flash tank; 6: carbonization reactor; 7: storage tank; 8: absorption tower; 9: fractionation tower; 10: hydrogenation reactor; 11: oil-water separator.)

In order to further promote the development of proposed technology, it is very imperative to understand its process and product characteristics. Thereby, this paper made a preliminary investigation on the distributions and characterizations of products from a simulated process, aiming at providing the basic data and references for the proposed technology.

2. Experimental

2.1. Materials

The used raw coal (Hongliulin coal), which is a bituminous coal, was provided by Shaanxi Coal and Chemical Industry Group Co., Ltd. The coal was ground to below 0.2 mm, subsequently dried under vacuum at 80 °C, and stored hermetically as experimental samples. The γ-FeOOH prepared according to literatures [37,38], was used as catalysts for liquefaction. The tetralin (THN) which was of chemical pure, was used as hydrogen-donating solvents for liquefaction. Other used solvents and reagents, including tetrahydrofuran (THF), toluene (TN), n-hexane (HEX), and sulphur, were commercially pure chemical compounds and used as received without further purification.

The proximate analysis of raw coal was made according to the National Standard of China (GB/T 212-2008), and its elemental compositions (C, H, S, and N) were determined using an elemental analyzer (Vario MICRO Cube, Elementar Trading Shanghai Co., Ltd.). Table 1

Table 1
Proximate and ultimate analyses of raw coal.

Proximate analysis (wt %)				Ultimate analysis (wt %)					H/C
M_{ad}	A_d	V_{daf}	FC_{daf}	C_{daf}	H_{daf}	N_{daf}	$S_d{}^a$	$O_{daf}{}^b$	
2.82	5.15	37.32	62.68	84.34	5.17	1.04	0.38	9.05	0.74

M: moisture; A: ash content; V: volatile matters; FC: fixed carbon; ad: air dry basis; d: dry basis; daf: dry and ash-free basis.
[a] Total S.
[b] By difference.

gives the proximate and ultimate analyses of raw coal. It is found that the raw coal has relatively high volatile content (37.32%) and relatively low ash content (5.90%). The thermogravimetric analysis of raw coal was carried out by a thermogravimetric analyzer (TG/DTG-DSC, SETARAM Inc., France) at a heating rate of 5 °C/min under a N_2 flow with 60 mL/min.

2.2. Integrated mild-liquefaction and carbonization experiments

As presented in Fig. 1, the proposed technology includes the two main processes of mild-liquefaction and carbonization. For this, each run for the integrated mild-liquefaction and carbonation (IMLC) was simulated as two separated experimental processes: the initial liquefaction of raw coals and the subsequent carbonization of liquid/solid mixtures from liquefaction. The liquefaction experiment was carried out in a 500 mL autoclave reactor [39], and the carbonization experiment was conducted by a self-built setup (Fig. 3), which was composed of carrier gas system, carbonization system and liquid phase recovery system. The schematic experimental procedures for each run are shown in Fig. 4.

In each run, the liquefaction reactor was charged with 30 g coal, 45 mL solvent, 300 mg catalyst, and 128 mg sulphur. Subsequently, the reactor was sealed and purged by H_2 for six times before being pressurized to the desired initial H_2 pressure of 4.0 MPa, and then was heated to the desired liquefaction temperature (390–450 °C). After the liquefaction process was maintained for 60 min, the reactor was quenched quickly by cooling water to 25 °C, and the gaseous products (LGs) were collected by an aluminum foil bag for composition analysis. The yield (Y_{LG}) of LGs was calculated according to Eqs. (1)–(2).

$$Y_{Gi} = (V_R/22.41) \times (P/0.101325) \times (273.15/298.15) \times (C_i \times M_i)/m_{daf} \qquad (1)$$

$$Y_{LG} = \sum Y_{Gi} \qquad (2)$$

where m_{daf} is the mass of coal on the dry and ash-free basis, Y_{Gi}, C_i and M_i are separately the yield, concentration, and molecular mass of i component in LGs (i = CO, CO_2, CH_4, and C_2–C_4) [40], V_R is the volume of gaseous phase in the liquefaction reactor, and P is the pressure of