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Full Length Article

Pyrolysis of coal hydroliquefaction residue in a dual loop reaction system

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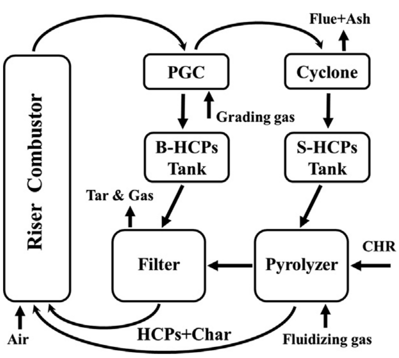
GRAPHICAL ABSTRACT



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ABSTRACT

To utilize the coal hydroliquefaction residue (CHR), a dual loop reaction system (DLRS) has been developed and upon which the pyrolysis of CHR was conducted under atmospheric pressure. The DLRS combines three reactors, i.e. a fluidized bed pyrolyzer, a radial-flow moving bed filter and a riser combustor followed by a particles grading cyclone. These three reactors form two parallel circulating loops, i.e. pyrolysis loop and filtration loop with small and big quartz sand particles as circulating bed materials, respectively. CHR mixed with quartz sand was injected into the fluidized bed pyrolyzer rapidly by a gas driven feeder, which makes it possible to dispose the CHR continuously. Under optimized blending ratio of CHR/quartz sand (1:4) and pyrolysis temperature from 500 °C to 550 °C, a dust-free pyrolysis tar with the yield of 20 wt% could be obtained, which was about two times of the Fischer Assay yield. The hexane soluble part (HS) and the hexane insoluble but toluene soluble part (asphaltene, A) account for nearly 94 wt% of the tar. Almost all the HS in the CHR was transferred into the tar during the pyrolysis.

1. Introduction

Coal-to-liquid technology has been attractive to many countries with local supply shortage of oil but abundant coal. With the rapidly growing demand for transportation fuels and the increasing concerns about energy security, China has made great effort on the development of coal hydroliquefaction. China Shenhua's Direct Coal Liquefaction Project is operating the largest demonstration plant of coal hydroliquefaction in the world [1,2]. The coal hydroliquefaction residue (CHR) as the main by-product discharged from the vacuum distillation unit of this plant accounts for 1/3 of coal feed. It contains high boiling point liquefied oils, asphaltenes, unreacted coal, mineral matter and liquefaction catalysts [3]. The oils and asphaltenes composed mainly of polycyclic aromatic hydrocarbons account for nearly half of the CHR, so

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both economic and environmental considerations will drive the recovery and utilization of CHR [4].

CHR could be used through combustion, gasification and pyrolysis and so on [5–15]. Though CHR is of high calorific value, it is not suitable to be burnt to generate heat and electricity due to its high sulfur content. The high content of the spent catalysts and the minerals-rich unreacted coal makes the CHR an unsatisfactory feedstock for gasification. Pyrolysis, instead, could pick up the high-value oils and asphaltenes and would be a favorite route for CHR conversion. Research on the pyrolysis of CHR focused on the basic pyrolysis characteristics of the CHR itself by general method such as TGA and fixed bed reactor [16]. The co-pyrolysis of CHR and lignite in a fixed bed reactor was made to improve the tar yield [17], but high blending ratio of CHR to lignite would hinder the release of volatiles. The co-pyrolysis of CHR and lignite in a rotary kiln was investigated to understand the inhibitory effect on lignite pulverization [18]. Due to low softening point and high caking property, CHR melted and captured the fine particles to reinforce the structure of particles during the co-pyrolysis process. However, bonding on the furnace wall cannot be avoided which may affect the normal operation of the reactor.

To pyrolyze CHR continuously, dual fluidized bed (DFB) might provide a favorable condition because the fluidization with the circulating bed materials would alleviate the caking of CHR. DFB has been applied in pyrolysis of variety of fuels [19–23] except for CHR. The feeding of CHR into DFB could be a key problem raised by its low softening point and high caking property. In addition, the fine particles derived from minerals-rich unreacted coal and spent catalysts entrained in pyrogas during pyrolysis would cause the additional operations of dust separation and purification of the pyrolysis product. For this issue, moving bed filtration could be one of the most promising technologies, which has been applied in some advanced coal conversion technologies [24–27].

In this study, a dual loop reaction system (DLRS) coupled with fluidized bed pyrolysis and moving bed filtration has been developed and successfully applied to the pyrolysis of CHR. By blending CHR with quartz sand before being fed into the pyrolyzer with a gas driven feeder, the phenomenon of caking to bulks could be alleviated, thus making it possible to operate the reaction system continuously and steadily. The effects of pyrolysis temperature and the blending ratio of CHR/quartz sand have been studied. Moreover, the pyrolysis tar of CHR has been analyzed.

2. Experimental section

2.1. The samples

The CHR used was provided by Shanghai Research Institute of China Shenhua Coal to Liquid and Chemical Corporation. The proximate analysis and Fischer Assay analysis of the sample were conducted according to Chinese standard GB/T 212-2008 and GB/T 480-2010, respectively. Ultimate analysis was made by a vario EL elemental analyzer. The thermal gravimetric analysis (TGA) was performed using a DTU-2B thermal balance.

The solvents extraction of CHR was carried out in a Soxhlet extractor by GB/T 30044-2013 standard, in which the hexane soluble part (defined as hexane soluble, HS), the hexane insoluble but toluene soluble part (asphaltene, A), the toluene insoluble but tetrahydrofuran (THF) soluble part (preasphaltene, PA) and the THF insoluble part (THFIS) were obtained.

The caking property of CHR was measured by the following method. The sample of CHR ground and sieved to 60–80 mesh, 0.5 g was mixed with quartz sand of the same particle size (CHR/quartz sand mass blending ratio: 1:0–1:10) in a crucible. The crucible with cap was then put in a muffle furnace at temperature of 900 °C ± 5 °C for 7 min to remove the volatile matter. After cooling down to room temperature, the residual char cake was dropped from a fixed height of 30 cm and the fragmentized sample was sieved using a 20-mesh sieve. The mass fraction of those particles larger than 850 μm (20 mesh) is a measure of the caking property of CHR.

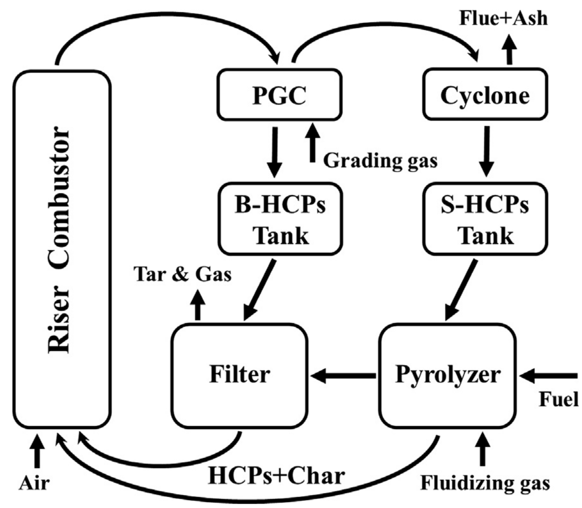

Fig. 1. Principle of the DLRS reaction system (B-HCPs: Big Heat Carrier Particles; S-HCPs: Small Heat Carrier Particles; PGC: Particles Grading Cyclone).

2.2. Apparatus and test procedure

The principle of DLRS is shown in Fig. 1. It is composed of three reactors, i.e. a fluidized bed pyrolyzer where pyrolysis of solid raw material takes place, a radial-flow moving particulate bed filter where fine particles in pyrogas from the pyrolyzer is filtered, and a riser combustor where the pyrolysis char is burned with air. These three reactors form two parallel loops, i.e. the combustor-pyrolyzer loop, where small quartz sands as heat carrier particles (S-HCPs) are circulating, and the combustor-filter loop, where big quartz sands as heat carrier and dust capturing particles (B-HCPs) are circulating. The two parallel loops are connected by the riser combustor followed by a particles grading cyclone (PGC). Through the PGC, the mixed sizes particles are segmented into two different size ranges using the grading gas. A scrubber unit after cyclone is set up to recover the entrained dust and the sulfur dioxide from the flue gas of char burning.

Fig. 2 presents the schematic diagram of the lab-scale experimental facility of DLRS. The pyrolyzer is a fluidized bed reactor which consists of a lower zone of 56 mm i.d. and 80 mm height and an upper zone of 98 mm i.d. and 190 mm height. The feeder of the pyrolyzer consists of a screw feeder combined with a gas driven feeder. The gas driven feeder is a concentric double layer tube with an inner tube of 4 mm i.d. and 5 mm o.d. and an outer tube of 8 mm i.d. and 10 mm o.d. The inner tube is for CHR feeding with N_2 as carrier gas. The annular space between the inner tube and the outer tube is filled with room-temperature deionized water as cooling agent to keep the CHR from softening during feeding. The moving particulate bed filter is a gas–solid radial cross flow moving bed reactor which has an annular bed of 28 mm i.d., 100 mm o.d. and 250 mm height. The riser combustor is a fast fluidized bed reactor of 20 mm i.d. and 2.6 m height. All the reactors are made of SUS 310S stainless steel and externally heated by electrical furnaces. The operating parameters including temperature, reactor pressure and differential pressure between reactors and gas flow rate were monitored in a smart touch monitor and recorded by a data acquisition computer.

For each experiment, about 3.3 kg fine particle quartz sand (0.15–0.25 mm) and 5.0 kg coarse particle quartz sand (0.43–0.85 mm) were added to DLRS. The bed material circulating rates of both loops were controlled at 6 kg/h. Nitrogen gas was preheated and fed into the bottom of pyrolyzer through the gas distributor as the fluidizing gas.