Pyrolysis of coal hydroliquefaction residue in a dual loop reaction system

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Graphical Abstract

ARTICLE INFO

Keywords:
Coal hydroliquefaction residue
Pyrolysis
Fluidized bed
Caking

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
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 caloric 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 CHR itself by general method such as TGA and DTU-2B thermal balance. The thermal gravimetric analysis (TGA) was performed using a vario EL elemental analyzer. The ultimate analysis was made by a 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 (THFPS) were obtained.

The coking 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: 1.0–1.1) 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.

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 N2 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.
The superficial gas velocity in the upper zone of the fluidized bed is 1.5–3.7 times of the minimum fluidization velocity of bed material particles. When all the reactors reached to the desired temperatures, CHR (60–80 mesh) mixed with quartz sand of the same size in a mass blending ratio from 1:0 to 1:6 was fed into the pyrolyzer at a feeding rate of 50–100 g/h by the feeder. The cooling water of the feeder was controlled at about 100 g/h. During feeding, the water was vaporized and injected into the fluidized bed and finally recovered together with the pyrolysis water from CHR. The fine particles entrained in pyrogas from the pyrolyzer was captured in the filter. The pyrogas then passed through several ice water cooled condensers in series and finally through a THF absorption trap at −15 °C to capture the condensable components in it. The incondensable gas passed through a wet flow-meter to record the gas volume and then was sampled using gas sampling bag and analyzed by a gas chromatography GC-7900 equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The gas was sampled every 10 min and the final gas compositions excluding nitrogen are averaged values of at least three samplings in the steady operation stage. After experiment, the condensers were rinsed with THF. The substances scrubbed from the condensers were vacuum filtrated using a Buchner funnel. The weight gain of the filter paper is composed of THFIS of the condensates and the fine particles passed through the filter. The filter paper was then burned in the muffle furnace. The remaining mass after burning is defined as dust of the pyrolysis tar. It accounts approximately 0.1–0.3 percent of the tar. The recovered mixture of tar and water after filtration was extracted with dichloromethane (DCM) to get the tar. The obtained tar was weighted and stored for further extraction analysis using n-hexane and toluene solvent. The water from the pyrolysis of CHR could not be measured appropriately because it is about two orders of magnitude lower than that of the cooling water. The operation conditions are summarized in Table 1.

### Table 1: Operation conditions of the DLRS system

| Size (mm), weight of bed material and circulating rate in combustor-pyrolyzer loop (kg)/(kg/h) | 0.150–0.250/3.3/6 |
| Size (mm), weight of bed material and circulating rate in combustor-filter loop (kg)/(kg/h) | 0.425–0.850/5.0/6 |
| Feeding gas volume flow rate (m³/h) | 0.05 |
| U₀/Umf | 1.5–3.7 |
| Grading gas volume flow rate (m³/h) | 0.9–1.1 |
| Combustion rising air volume flow rate (m³/h) | 5–6 |
| Pyrolyzer temperature (°C) | 450–600 |
| Filter temperature (°C) | 500 |
| Combus temperature (°C) | 850 |
| Particle tank temperature (small and big) (°C) | 800 |

*U₀, Umf denote the superficial gas velocity and the minimum superficial velocity of bed materials based on upper zone diameter respectively.

### 2.3. Characterization of the tar

Solvent extraction of the tar was conducted the same way as that of CHR. The compositions of HS from the CHR and the tar were analyzed by GC/MS (Agilent 6890N gas chromatograph coupled with Agilent 5975 mass detector).

### 3. Results and discussion

#### 3.1. Basic properties of CHR

The basic properties of CHR are listed in Table 2. It is shown that CHR is carbon-rich and ash-rich with relatively low softening point. The tar yield obtained from the Fischer assay analysis is 11.0 wt%.

Fig. 3 shows the distribution of solvent extraction components of CHR. The HS which contains the lowest average molecular weight
molecules accounts for 10.5 wt% of CHR. The A and PA composed of highly aromatic mixtures account for 36.9 wt% and 8.7 wt%, respectively. In other words, the CHR contains more than 50 wt% of extractable components which is responsible for its relatively low softening point. The CHR was characterized to be a non-Newtonian pseudoplastic fluid at temperature 483—523 K [12,29,30].

Fig. 4 shows the TG and DTG analysis profiles of CHR under N2 atmosphere at the heating rate of 20 °C/min. At about 460 °C there is a devolatilization peak on the DTG profile. Two gentle wide shoulder peaks around 140 °C and 800 °C are attributed to the weight loss of water or light hydrocarbons and the decomposition of minerals, respectively.

Upon heating, CHR undergoes melting, boiling and expanding and finally forms a hard coke. To alleviate the caking property of CHR, it was mixed with quartz sand. The caking properties of the CHR-quartz sand mixture at varied blending ratio of CHR/quartz sand are shown in Fig. 5. With the increase of the quartz sand addition, the caking properties of the samples tend to be weaken.

3.2. Pyrolysis of CHR in DLRS

As discussed above, the caking property of CHR could be alleviated by blending it with quartz sand. So a blend of CHR and quartz sand was used as feedstock of the pyrolysis in DLRS. To optimize the blending ratio, tests with different blending ratio of CHR/quartz sand were conducted in DLRS. In the condition of no quartz sand blending, the experiments lasted less than 15 min (one cycle retention time of the fluidized bed materials) due to the defluidization and the blocking of the circulation pipe by the bulk cakes formed from CHR and the bed material quartz sand. When the quartz sand was blended with CHR at the blending ratio from 1:2 to 1:4, a more and more steady operation of pyrolysis could be achieved which indicates that the addition of quartz sand favored the dispersion of the CHR particles and prevented it from caking to unbreakable bulks. Due to intensive solids mixing and heat transfer in the fluidized bed pyrolyzer, rapid devolatilization of CHR particles would inhibit them to be agglomerated. In consideration that an even higher blending ratio like 1:6 or more will lower efficiency of the fluidized bed pyrolyzer, the CHR/quartz sand blending ratio of 1:4 was adopted to conduct the further pyrolysis experiments.

Fig. 6 shows the yield of pyrolysis products and the gas composition under different pyrolysis temperature, in which the char yield was calculated by difference. According to Fig. 6(a), the tar yield increases at the lower temperature and then keeps constant at about 20 wt% at the higher temperature. The tar yield is about two times of the Fischer Assay value and is higher than those from the fixed bed pyrolysis reported in the literature [16,17]. Under rapid heating condition by the circulated hot bed materials in the fluidized bed pyrolyzer, the devolatilization of CHR particles was enhanced and the secondary reactions of the volatiles were restrained which favored the tar yield in the pyrolysis of CHR. During the pyrolysis temperature range investigated, the gas yield shows no obvious changes and stabilizes at a low level of 3–4 wt%. It indicates that the increase of tar yield at the lower temperature might be contributed from the evaporation of those light components in CHR, i.e. HS, while the gas yielded mainly from the

| Property                      | Moisture | Ash    | Volatile | C    | H    | N    | S    | O    | Tar | Water | Char | Gas  |
|-------------------------------|----------|--------|----------|------|------|------|------|------|-----|-------|------|------|-----|
| Proximate analysis (wt%, ad)  | 0.18     | 14.76  | 35.11    | 90.25| 4.98 | 0.83 | 2.92 | 1.02 |     |       |      |      |
| Ultimate analysis (wt%, daf) |          |        |          |      |      |      |      |      |     |       |      |      |     |
| Fischer Assay analysis (wt%, d) |         |        |          |      |      |      |      |      |     |       |      |      |     |
| Softening point [17,28,29] (°C) |         |        |          |      |      |      |      |      |     |       |      |      |     |
|                               | 11.0     | 1.5    | 77.5     | 10.0 |      |      |      |      |     |       |      |      |     |
| By difference.                |          |        |          |      |      |      |      |      |     |       |      |      |     |

Fig. 3. The distribution of solvent extraction components of CHR.

Fig. 4. The TG and DTG profiles of CHR under N2 atmosphere (heating rate: 20 °C/min; flow rate: 100 ml/min).

Fig. 5. The caking properties of the CHR-quartz sand mixtures.

Fig. 6. The yield of pyrolysis products and the gas composition under different pyrolysis temperature.
polycondensation of those heavier components attributed to A and PA.

As depicted from Fig. 6(b), H$_2$ and CO$_2$ components are the main pyrolysis gases especially at lower pyrolysis temperature. With the increase of pyrolysis temperature, H$_2$ and CH$_4$ concentrations in product gas increase gradually while CO and CO$_2$ decrease. The evolution of H$_2$ is the result of polycondensation of the highly aromatic components of CHR, i.e. A and PA, as mentioned above, while that of CH$_4$ may come from the break of Ar-CH$_3$ or Ar-CH$_2$-Ar, and both would be enhanced at the higher temperature. The CO and CO$_2$ are mainly generated from the cleavage of the relatively weak C=O bond which is seen to release intensively at lower temperature.

3.3. Analysis of pyrolysis tar

Table 3 shows the Soxhlet extraction results of the pyrolysis tar. The tar is composed of mainly HS and A and a small amount of PA. The total of HS and A accounts for nearly 94 wt% of the tar obtained from the pyrolysis between 450 °C and 600 °C. When increasing the pyrolysis temperature, the HS content increases from about 50 wt% of the tar at 450 °C to 60 wt% at 600 °C while the PA keeps constant at around 5–6 wt%. Table 4 compares the Soxhlet extraction of the tar on the mass basis of CHR with that of CHR. It can be found that the HS yield of the tar is near that of CHR, while the A and PA yields are much lower. In association with the discussion above, it could be concluded that the major part of HS in the CHR was transferred into the tar. A large amount of A and PA in the CHR were transformed into THFIS as the results of polycondensation, which is in accordance with the high char yield as shown in Fig. 6. The polycondensation of PA might happen at the temperature as low as 450 °C. Higher temperature facilitates the transformation of A to HS because that the cracking of A was enhanced [31].

The GC/MS total ion chromatograms (TIC) of the HS extracted from CHR, 550 °C tar and 600 °C tar are shown in Fig. 7. They have similar compositions, indicating that there is no obvious change of the HS after the pyrolysis of CHR. Approximately 80–100 compounds (relative content higher than 0.5%) were detected. The four most prominent compounds are fluoranthene, 1-methylpyrene, methylchrysene and indeno(1,2,3-C,D)pyrene. Fig. 8 shows the results of classification of the composition of HS determined by GC/MS analysis. Aromatics are the main compositions in the HS of CHR and tar in which 3–6 rings polycyclic aromatic hydrocarbons (30–40%), substituted polycyclic aromatic hydrocarbons (20–30%) and partially hydrogenated polycyclic aromatic hydrocarbons (15–20%) were detected. Aliphatics account for about 10% of total in the form of long chain alkanes (from hexadecane to hexacosane were detected). In addition to some unknown compounds that cannot be ascribed through the mass spectrometry database, a very small amount of phenolic, ester and heterocyclic compounds were also detected.

4. Conclusion and perspective

Basic properties of CHR were investigated and the pyrolysis of CHR was conducted in DLRS under atmospheric pressure. The CHR is carbon-rich and ash-rich and has relatively low softening point and high caking property. The caking property of CHR could be alleviated by blending it with quartz sand. To obtain a steady pyrolysis of CHR in DLRS, the CHR mixed with quartz sand was rapidly injected into the fluidized bed pyrolyzer by a gas driven feeder. Under optimized blending ratio of CHR/quartz sand, i.e. 1:4, the caking of CHR to unbreakable bulks could be avoided. At the pyrolysis temperature from 500 °C to 550 °C, a tar yield of 20 wt% and a gas yield of 3–4 wt% were obtained. The tar was dust-free because that the dust entrained with the volatiles from the pyrolyzer was captured efficiently by the particulates filter. The Soxhlet extraction of the pyrolysis tar showed that the HS and A account for nearly 94 wt% of the tar. Almost all the HS and a

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**Table 3** The solvent extraction results of tar.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HS (wt%, on the mass basis of tar)</th>
<th>A (wt%, on the mass basis of tar)</th>
<th>PA (wt%, on the mass basis of tar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tar-450 °C</td>
<td>48.99</td>
<td>45.00</td>
<td>6.61</td>
</tr>
<tr>
<td>Tar-500 °C</td>
<td>55.24</td>
<td>38.08</td>
<td>6.68</td>
</tr>
<tr>
<td>Tar-550 °C</td>
<td>57.87</td>
<td>36.20</td>
<td>5.93</td>
</tr>
<tr>
<td>Tar-600 °C</td>
<td>64.68</td>
<td>29.13</td>
<td>6.19</td>
</tr>
</tbody>
</table>
small part of A and PA in the CHR were transferred into the tar during the pyrolysis. The GC/MS analyses of the HS extracted from CHR, 550 °C tar and 600 °C tar showed that they have the same four most prominent compounds, i.e. fluoranthene, 1-methylpyrene, methylchrysene and indeno(1,2,3-C,D)pyrene, and there was no obvious change of the HS after the pyrolysis of CHR.

For pyrolysis of CHR in DLRS, there are some key issues to be resolved in the technology development towards commercialization:

1) The contact mode between the feed and the bed materials not only determines the bogging tendency and operability, but also determines the conversion and product yields. The fact that CHR finally dries out and solidifies as pyrolysis progresses to completion is the key. Currently, continuous operation of DLRS has been enabled by blending the feed with excess quartz sand, resulting in the circulating ratio varying between 60 and 120. Usually, to supply the heat required for pyrolysis by hot solids, a circulating ratio of 15–20 should suffice for a temperature difference of 150 °C or larger.
between the combustor and pyrolyzer. Actually, excessively high circulating ratio is both unnecessary and unfavorable for large-scale industrial systems because of high energy consumption to drive the solids around the loop, plus materials erosion and particle attrition (fines) issues. An alternative solution to the caking and bogging problem of CHR is to pump and atomizing it at suitable temperature, possibly by mixing it with some oil or solvent. In this case, the rheological characteristics of CHR and design of atomizing nozzle should be major research topics.

2) In the present study, the pyrolyzer operates at a super fluidization velocity (SGV) about 1.5–3.7 \( \frac{\text{m}}{\text{s}} \), which is quite low compared to similar processes. The bed is more resistant to bagging as SGV increases, which suggests trade-offs between the SGV and operating temperature and sand/feed blending ratio. One can operate at slightly lower temperature (promising higher tar yield) with less quartz sand addition if the pyrolyzer runs at higher SGV. An additional benefit of higher SGV is that it enhances mass and heat transfer in the bed, which not only reduces the temperature gradient in the bed but also allows the fresh tar vapor to be stripped from the reacting particle surfaces as fast as possible, which in turn would encourage more tar vapor production due to improved vapor–liquid equilibrium conditions. Steam or nitrogen can be used as fluidizing/stripping agent. This is another point to consider for future technology development.

Acknowledgements

This work was supported by the Shanghai Research Institute of China Shenhua Coal to Liquid and Chemical Corporation Ltd. The reviewers’ valuable suggestions are highly appreciated.

References