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Study on the stability of hydro-liquefaction residue of Shenfu sub-bituminous coal

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HIGHLIGHTS

• DCLR and its components have different pyrolysis behaviors.
• THFI formed by the condensation of oxygen containing functional groups.
• THF soluble is more prone to form the THFI at lower temperature.

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ABSTRACT

The stability of direct coal liquefaction residue (DCLR) has significant effects on the DCL technology and the utilization of DCLR. In this paper, the pyrolysis behaviors of the DCLR from 6 t/d Shenhua BDU technology and its components including tetrahydrofuran soluble (THFS) and insoluble (THFI) were investigated by thermogravimetric analysis (TGA). Then, its thermal stability and THFS hydrogenation activity were studied by thermal treatment and hydrogenation treatment, respectively. Results show that DCLR and its components have different pyrolysis behaviors. Inorganic components existed in DCLR and THFI show a catalytic effect on the pyrolysis of organic matrix, but THFS inhibits the decomposition of carbonates in DCLR. The weight loss of THFI mainly results from the decomposition of carbonates and the dehydrogenation rather than the cracking of organic matrix. The thermal stability of DCLR mainly depends on the hydrogen donating ability and the solvency of solvent, and THFI formed in the thermal treatment mainly originates from the condensation between oxygen containing functional groups. The spent catalyst in DCLR can inhibit the condensation of THFS, which is more prone to form THFI at lower temperature.

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1. Introduction

DCL is a promising approach for producing clean liquid fuels and valuable chemicals from coal [1,2]. The only industrial DCL plant in the world since WWII had been built in China. At present, the efficient utilization of a large amount of DCLR is becoming a challenge for current DCL [3]. Generally, DCLR separated by vacuum distillation accounts for 20–30% of coal consumed [4]. It not only contains of THFI consisted of minerals, spent catalyst, semi-coke and unreacted coal, but also has a large amount of the heavy materials (THFS) as heavy oil, asphaltene (AS, n-hexane insoluble/toluene soluble) and preasphaltene (PA, toluene insoluble/THF soluble) [5–7]. Since these heavy materials, especially PA, are prone to aggregate and coke by retrograde reaction [8–10], DCLR is unstable at high temperature, for example in the processes of separation and vacuum distillation. So investigating DCLR stability is essential for the improvement of DCL technology and its efficient utilizations.

In the process of DCL, the benzene insolubles (similar to toluene insolubles) of coal liquid had deemed as precursor of carbon deposited on the catalyst [10,11]. Masuyama et al. [10] suggested that PA contained in the coal liquid bottoms is responsible for the deactivation of hydrogenation catalyst. Burke et al. [8] found that the principal retrograde reactant to form THFIs at SRC-I liquefaction conditions (450 °C, 10 MPa) is PA fraction, which was expected to significantly impede separator operation by forming anisotropic carbon. Tao and Brown [9] found that an improvement in solvency of solvent is only effective in decreasing the coking tendency of AS, and the hydrogen donor solvent is effective in reducing the coking
tendency of AS and PA. The donor hydrogen content of the solvent
is the important solvent property controlling coking severity in the
DCL process. In our previous works [12,13], some regressive trans-
formations of AS and PA to form coke were also observed in the
DCL process at high temperature. However, little formation has been
available for the thermal stability of DCLR to the best of our
knowledge, though it has significant effects on the process of
DCL, especially the separation of slurry product.

Recently, the researches on the utilization of DCLR mainly focus
on gasification [14–17], pyrolysis [18–20], hydro-liquefaction [21–
24] and preparation of advanced carbon materials [25–27]. Cui
et al. [14] found that DCLR has good reactivity of gasification
because of the catalysis of spent catalyst and enriched minerals.
Chu et al. [15] thought that the enriched mineral has catalysis on
the steam gasification of the DCLR char, but the spent catalyst
has no remarkably positive effect. Although the minerals, espe-
cially the alkaline earth metal minerals such as CaO, CaS and
CaCO3, can promote gasification of DCLR as catalyst [16,17], the
gasification of DCLR is unfavorable for the high valuable utilization
of heavy materials. In order to obtain more liquid fuels, the pyro-
lysis of DCLR has attracted much intention in China [7,18–20]. Li
et al. [18] found a synergetic effect between different fractions of
DCLR, which can inhibit the devolatilization of DCLR in the pyro-
lysis process. Xu et al. [7] investigated the pyrolysis of DCLR from
China Shenhua industrial coal liquefaction plant, suggesting that
the interaction among its fractions is unfavorable for the evolution
of volatile matter, and the inorganic compounds in DCLR have
catalysis on the DCLR pyrolysis. Due to hydrogen donor of DCLR,
it can improve the tar yield of the co-pyrolysis of DCLR and lignite,
but the minerals and the spent catalyst have no catalytic effect on
the co-pyrolysis [19]. As another important utilization approach,
the hydro-liquefaction of DCLR had also been studied [21–24]. Li
et al. [21] observed that there are some synergetic effects in the
hydro-treatment of DCLR as whole, and the PA as individual frac-
tion is the most active during the hydro-treatment. However, the
PA fraction is a main problem to yield non-soluble materials in the
hyrogenation of the heavy liquids of DCLR catalyzed by NiMo/Al2O3. [22]. Wang et al. [23] found that the catalytic hydrotreatment of
demineralized DCLR under microwave irradiation at relatively low
temperature can increase the solubility of DCLR in methanol and ethanol solvents, especially using Ni as cata-
lyst. In our previous work, it was found that SO42-/ZrO2 solid acid is in favor of the catalytic hydropyrolysis of PA, and inhibits the regressive reactions of PA [12]. Therefore, understanding stability of
DCLR, especially pyrolysis and hydrogenation activity, is very
important in its efficient utilization and the improvement of DCL
process.

In the present study, the pyrolyses of DCLR from 6 t/d Shenhua
BDU and its components were carried out by TGA to investigate the
effects of THFS and THFI components on the pyrolytic property of
DCLR. Then, the stabilities of DCLR at lower than the temperature
of DCL were investigated by thermal treatments of DCLR under dif-
f erent conditions and the hydrogenations treatments of THFS. The
influences of thermal treatment and hydrogenation conditions on
the thermal stability of DCLR were discussed.

2. Experimental section

2.1. Samples

DCLR comes from a 6 t/d Shenhua BDU. Its true density and
softening point are 1.59 g/cm3 and 148 °C, respectively. As a solid
block at room temperature, it is ground to sizes smaller than
0.5 mm before use. Since the DCLR contains very little of the n-
hexane soluble (ca. 6.5%), it was only separated into THFS and THFI
by tetrahydrofuran (THF) solvent extraction in this study. Ultimate
and proximate analyses of DCLR, THFS and THFI are listed in
Table 1.

2.2. Pyrolysis experiment

The pyrolysis behaviors of DCLR and its components, including
THFS and THFI, were investigated using a STA 449 F3 Jupiter ther-
mogravimetric apparatus. Firstly, approximately 10 mg of sample
was heated from room temperature to 900 °C at 10 °C/min under
100 ml/min N2 flow (99.999%). In order to obtain the semi-cokes
of pyrolysis at different temperatures, the sample of DCLR was
heated from room temperature to different setting temperatures
under above conditions, subsequently cooled to room temperature
under N2 flow. All obtained semi-coke samples were used to deter-
mine FTIR spectra and element compositions.

2.3. Thermal treatment experiment

Thermal treatment of DCLR was carried out in a 30 mL tubing
reactor shaken vertically. In a typical process, 2.0 g of DCLR and
4 mL solvent were charged into the reactor. The reactor was pres-
surized to 5.0 MPa with H2 or N2 after purged several times. Then it
was submerged into a salt bath and maintained at desired temper-
ature for 1 or 2 h. Finally, the reactor was quenched to ambient
temperature in a water bath. Toluene, tetralin, decalin and methyl
naphthalene (MN) are respectively used as thermal treatment sol-
vent. The treated product was filtrated and washed with THF sol-
vant. Then the filter residue was exhaustively extracted by THF
solvent in Soxhelt extractor. The extraction residue was dried
under vacuum at 80 °C for 24 h to obtain THFI. Finally, THF solvent
was evaporated from the mixed solution of filtrate and extraction
liquid to obtain THFS. THFI yield of thermal treatment sample
was calculated by the mass of THFI.

2.4. THFS hydrogenation experiment

The procedure of THFS hydrogenation was similar to that of
thermal treatment. In a typical process, 2.0 g of THFS and 4 mL tet-
ralin solvent were used. The initial pressure of H2 was set at
5.0 MPa, and the treatment time was 1 h. 0.1 g of catalyst was
added in the catalytic hydrogenation experiment. Since the separa-
tion temperature of liquefaction products in the commercial plant
is lower than the reaction temperature, the hydrogenation of THFS
was carried out at 200, 250 and 300 °C, respectively. Six home-
made Ni-base catalysts, including Ni/γ-Al2O3 (Cat-A), Ni–Cu/γ-
Al2O3 (Cat-B), Ni–Cu2P/γ-Al2O3 (Cat-C), Ni/OMMT (Organic Mont-
morillonite) (Cat-D), Ni–Cu/OMMT (Cat-E), Ni/MMT single crystal
(Cat-F), were used. The hydrogenised product was separated into
THFS and THFI by THF solvent extraction, and THFI yields were
calculated.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ultimate analysis (wt%)</th>
<th>Proximate analysis (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adaf</td>
<td>Madf</td>
</tr>
<tr>
<td>DCLR</td>
<td>20.6</td>
<td>0.4</td>
</tr>
<tr>
<td>THFS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>THFI</td>
<td>41.7</td>
<td></td>
</tr>
</tbody>
</table>

Dry and ash-free base; Madf: moisture (air dried base); Adaf: ash (dry base, i.e., moisture-free base); VMdaf: volatile matter (dry and ash-free base); Sdaf: total sulphur (dry base).

* By difference.
3. Results and discussion

3.1. Pyrolysis of DCLR and its components

Table 2 shows that DCLR consists of 50.5% THFS and 49.5% THFI. The ash content of latter is 41.7% as shown in Table 1. Based on the TGA results shown in Fig. 1a, the weight losses of DCLR, THFI and THFS at 900 °C are 27.7%, 19.3% and 42.3%, respectively. DCLR and THFI weight losses of the dry free-ash basis were further calculated as 34.9% and 33.1%, respectively. So the pyrolytic reactivity of THFS is obviously higher than those of the organic matrix in DCLR and THFI. Further, their derivative thermogravimetric (DTG) curves show that DCLR and THFS display a large DTG peak at 457 °C and 476 °C, respectively, but THFI shows only a weak peak at 458 °C. In general the DTG peak in the range of 400–500 °C is attributed to the pyrolysis of organic matrix to devolatilize [28]. It is speculated that the inorganic materials in DCLR and THFI, such as minerals and spent catalyst, can catalyze the pyrolysis of organic matrix. Meanwhile, other three well-defined DTG peaks at 208, 721 and 798 °C can be observed from the DTG curve of THFI, which can be ascribed to the dehydration of hydrogen bonded OH, the decomposition of carbonates and the dehydrogenation of organic matrix, respectively [28]. Except of the DTG peak at 457 °C, DCLR displays a weak DTG peak near to 763 °C, which should also be assigned to the decomposition of carbonates [29]. Owing to the inhibition of the coking of THFS on the decomposition of carbonates, the DTG peak temperature shifts from 721 °C (THFI) to 763 °C (DCLR). So the results of DTG analyses suggest that the inorganic components in DCLR and THFI can promote the pyrolysis of organic matrix, but the THFS in DCLR inhibits the decomposition of carbonates. In addition, the main weight loss of THFI occurred at above 680 °C should originate from the dehydrogenation and the decomposition of minerals such as carbonates, suggesting that most of carbonaceous components in THFI are very stable.

According to the method of Ref. [7], the fitting TG/DTG curves of DCLR were calculated from its composition and the DTA data of THFS and THFI to understand its pyrolysis behavior. Fig. 1b shows that the fitting DTG curve in the range of 300–570 °C is similar to that of THFS having a strong peak at 476 °C, but other part is similar to the one of THFI having two peaks at 721 °C and 800 °C. So the fitting DTG peak temperatures for the pyrolysis of organic matrix and the decomposition of carbonates are obviously different from the experimental values. Meanwhile, there is obvious difference between the fitting TG curve and the experimental TG curve. The fitting weight below 670 °C is slightly higher than the experimental result, but the fitting weight above 670 °C is obviously lower than the experimental value. So there should be interaction between the THFS component and the THFI component in the pyrolysis process of DCLR, which generally inhibits the evolution of volatile matter [7,19].

Further, a series of pyrolytic residues (semi-coke) at different temperatures were obtained from the TGA experiments of THFS and THFI, and their FTIR spectra and elemental compositions were determined respectively. Fig. 2 shows that there is no obvious difference between different THFS semi-coke except of a broadening aromatic ring vibration peak (near to 1600 cm⁻¹) with increasing temperature, which is caused by the condensation and the dehydrogenation. However, the pyrolysis temperature has significant effects on the semi-coke of THFI. A weak –SH peak (2510 cm⁻¹) and a strong CO$_3^-$ peak (1420 cm⁻¹) are observed only at no higher than 600 °C, suggesting that the carbonates and the C–SH begin to be decomposed at above 600 °C. Similarly, the THFI also shows a broadening aromatic ring peak. In addition, the peak of Si–O at 1038 cm⁻¹ becomes weak after 600 °C. So the minerals are responsible for the different pyrolysis behaviors between THFI and THFS.

Fig. 3 shows the element residual yields (R) of semi-coke formed at different temperatures, which were calculated by the following equation. $R (%) = Y \times W/Y_0 \times 100$, where $Y$ and $Y_0$ are the element contents in the sample and its semi-coke, and $W$ is the semi-coke yield. In the process of THFS pyrolysis the removal of carbon mainly occurs in the range of 300–500 °C, and the removal of hydrogen continuously happens after 300 °C, suggesting that the devolatilization of THFS is responsible for the removal of carbon and hydrogen at 300–500 °C, and the dehydrogenation above 500 °C mainly results from the condensation. In the pyrolysis process of THFI, the removal of carbon is very low, and mainly occurs in the range of 600–750 °C due to the decomposition of carbonates. The removal of hydrogen form THFI is very obvious after 300 °C, especially at above 750 °C. The H/C of THFI semi-coke sharply decreases at above 750 °C as a result. So the removal of hydrogen above 750 °C mainly results from the dehydrogenation, which is also responsible for the DTG peak at 798 °C. The above-mentioned results suggest that the weight loss of THFI results mainly from the decomposition of carbonates and the dehydrogenation rather than the cracking of organic matrix. In addition, the desulfurization of THFI is similar to the decarboxylation, and most of sulphur in the form of sulphur is remained in the coals, even at 900 °C.

3.2. Thermal stability of DCLR

In the present work, the variations of the THFI content of thermal treated DCLRs were determined under different conditions in order to investigate the influences of THFS pyrolysis on the thermal stability of DCLR. Fig. 4 displays that the thermal treatment solvent has significant effects on the THFI content in treated DCLR. In toluene solvent, the decreasing THFI content is seen only under $H_2$ for 1 h, and increasing treatment time and $N_2$ atmosphere increase the THFI content. On contrary, almost all of thermal treatments in tetralin solvent decrease the THFI content of treated DCLR. However, only some thermal treatments under $N_2$ atmosphere at higher temperature increase the THFI content when decalin and MN are used as solvent. It is concluded that tetralin as a hydrogen donor solvent can inhibit the formation of THFI, and promote the hydro-cracking of DCLR. Meanwhile, it may be due to high dissolving capacity that MN and decalin solvent also show varying inhibition on the formation of THFI at lower temperature [24]. In addition, MN shows a certain promotion on the hydro-cracking of DCLR under $H_2$ atmosphere due to its shutting hydrogen [30]. Therefore, the effect of solvent on the thermal stability of DCLR depends on its hydrogen donating ability and solvency.

Secondly, it can be found that the thermal treatment temperature has significant effects next to solvent on the stability of DCLR. The THFI content basically increases with increasing temperature. Thermal treatments at 380 °C almost decrease the THFI content except of those in toluene. The highest THFI content is obtained in the thermal treatment in MN solvent under $N_2$ at 430 °C for 2 h. It is in agreement with the afore-mentioned pyrolysis performances of DCLR and THFS which the condensation and the hydro-cracking of heavy products such as THFS should be responsible for the stability of DCLR. Increasing temperature is favorable for the condensation and the hydro-cracking, but the latter needs enough active hydrogen provided. Thirdly, the atmosphere and the treatment time have also obvious effects on the thermal stability of DCLR. In general the THFI

<table>
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<tr>
<th>Sample</th>
<th>THFI (%)</th>
<th>THFS (%)</th>
</tr>
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<tbody>
<tr>
<td>DCLR</td>
<td>49.5</td>
<td>50.5</td>
</tr>
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</table>
contents of DCLRs treated under H₂ are lower than those under N₂. Due to the presence of spent catalyst in DCLR, obvious hydrocracking can be observed in the thermal treatments under H₂ for 1 h regardless of the hydrogen donating ability of solvent. Increasing time is favorable for the formation of THFI under non-hydrogen donor conditions, but can decrease the THFI content under hydrogen donor conditions.

In order to investigate the formation of THFI, the THFIs obtained under different treatment conditions were characterized by TG/DTA and element analysis. The results of elemental analysis of THFI

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**Fig. 1.** TG/DTG curves: (a) DCLR, THFS and THFI, (b) experimental (Exp) and fitting (Fit) curves of DCLR.

**Fig. 2.** FTIR spectra of THFS and THFI semi-cokes obtained from their TGA at different temperatures.

**Fig. 3.** Element residual yields and H/C ratios of THFS and THFI semi-cokes obtained from their TGA at different temperatures.
in Fig. 5 display an obvious relativity between THFI content and O %daf, which the O %daf of THFI decreases linearly with the increase of THFI content. However, thermal treatment hardly influences the H/C of THFI. It was speculated that the THFI mainly results from the condensation between oxygen containing functional groups. Further, Fig. 6 displays that the TG/DTG curves of THFIs from thermal treated DCLR are very similar to those of original THFI shown in Fig. 1. Regardless of thermal treatment conditions, all THFIs show three DTG peaks without obvious pyrolysis of matrix near 480 °C, suggesting that THFI should be stable at thermal treatment temperature used.

3.3. Effects of hydrogenation on stability of THFS

Although THFS is soluble in THF solvent, Fig. 7 shows that there is about 13.7–15.8% THFI formed after non-catalytic hydrogenation treatment in THN solvent at 200–300 °C. So the thermal stability of THFS is very poor without hydrogenation catalyst. By comparison...
with the afore-mentioned thermal treatment of DCLR in THN solvent, it is found that the spent catalyst in DCLR can inhibit the condensation of THFS. Meanwhile, it may be the hydrogen donor of THN that the yield of THFI slightly decreases with the increase of temperature, suggesting that the THS is more prone to the formation of THFI at lower temperature. Further, the catalytic hydrogenation treatments of THFS by using a series of homemade catalysts at 250 °C show lower THFI yield than the non-catalytic hydrogenation treatment. The yields of THFI vary from catalyst to catalyst. Cat-A and Cat-F display better catalysis on the hydrogenation of THFS so that the formation of THFI is inhibited. Therefore, the highly active catalyst can improve the stability of THFS to depress the coking of DCLR in the process of DCL.

Further, the results of elemental analysis as shown in Fig. 8 disclose that there is an obvious relativity between the C/H and the yield of THFI formed in the THFS hydrogenation treatment except for that used Cat-D as catalyst, in which very little THFI (0.58% of yield) obtained should influence its element analysis result. The C/H of THFI formed increases with increasing THFI yield in the hydrogenation treatment of THFS. The non-catalytic hydrogenation shows the highest THFI yield, and its THFI also has the highest C/H. It is suggested that the catalytic hydrogenation treatment can not only suppress the condensation of THFS into THFI, but also reduce the C/H of THFI formed.

4. Conclusion

DCLR and its components show different pyrolysis behaviors. The pyrolytic reactivity of THFS is obviously higher than those of the organic matrix in DCLR and THFI. The inorganic components in DCLR and THFI show catalysis on the pyrolysis of organic matrix, but the THFS in DCLR inhibits the decomposition of carbonates. Most of carbonaceous components in THFI are very stable so that the weight loss of THFI mainly results from the decomposition of carbonates and the dehydrogenation rather than the cracking of organic matrix.

The hydrogen donating ability and the solvency of solvent have significant effects on the thermal stability of DCLR. Increasing temperature is favorable for the condensation and the hydro-cracking of DCLR, but the latter needs enough active hydrogen provided. In the process of thermal treatment, the THFI mainly formed by the condensation between oxygen containing functional groups. Further, the thermal stability of THFS is very poor without hydrogenation catalyst. The spent catalyst in DCLR can inhibit the condensation of THFS. The THFS is more prone to form the THFI at lower temperature, and the highly active catalyst can improve the stability of THFS to inhibit the formation of THFI.

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