In Situ Catalytic Pyrolysis of Low-Rank Coal for the Conversion of Heavy Oils into Light Oils

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Lighter tars are largely useful in chemical industries but their quantity is quite little. Catalytic cracking is applied to improve the yield of light tars during pyrolysis. Consequently, in situ upgrading technique through a MoS$_2$ catalyst has been explored in this research work. MoS$_2$ catalyst is useful for the conversion of high energy cost into low energy cost. The variations in coal pyrolysis tar without and with catalyst were determined. Meanwhile, the obtained tar was analyzed using simulated distillation gas chromatograph and Elemental Analyzer. Consequently, the catalyst reduced the pitch contents and increased the fraction of light tar from 50 to 60 wt.% in coal pyrolysis tar. MoS$_2$ catalyst increased the liquid yield from 18 to 33 (wt.%, db) and decreased gas yield from 27 to 12 (wt.%, db) compared to coal without catalyst. Moreover, it increased H content and hydrogen-to-carbon ratio by 7.9 and 3.3%, respectively, and reduced the contents of nitrogen, sulphur, and oxygen elements by 8.1%, 15.2%, and 23.9%, respectively, in their produced tars compared to coal without catalyst.

1. Introduction

Coal is heterogeneously complex structure having organic and inorganic macromolecules. Low-rank coals have great importance in utilization but have some problems due to low efficiency and higher CO$_2$ emissions compared to high-rank coals. These coals are difficult for storage and transportation and are not suitable for direct combustion [1–5]. The utilization of a low-grade coal could be achieved through pyrolysis which converts the coal volatiles into high valuable fuels and fine chemicals. A coal tar in bulk quantity is produced during pyrolysis, but it contains high range of heavy organic components having boiling point greater than 360°C called pitch. The high boiling point range organic components are not easy to be treated since they can easily precipitate in the pipelines with dusts, so they will create problems during operation of downstream equipment like engines and turbines and block the pipelines in the industry. High valuable tar can be achieved to crack high range organic heavy components into desired components having boiling point less than 360°C. However, the thermal cracking of tar generally occurs at high temperature through appropriate energy supply and reaction time which leads to decreasing the energy efficiency and tar yield. So, the catalytic coal pyrolysis is the most promising technique to upgrade the coal pyrolysis tar under moderate conditions and increase the energy efficiency of industrial equipment [6–21].

To improve the tar yield and fraction of light components in coal tar, catalytic coal pyrolysis experiments have been performed through mixing or without mixing of coal with catalysts in previous study [22–31]. Li et al. [25] were reported to improve aromatic components yield like BTExN on zeolite catalysts. Liu et al. [26] studied improving the yield of tar over Ni-MgO and obtained the higher tar yield, when the coal during pyrolysis was incorporated to CO$_2$ for reforming methane. Jin et al. [27] studied improving the tar yield on zeolite catalyst (Mo-HZSM-5) for integrating the aromatization of methane during coal pyrolysis and obtained yield of coal tar about 21.5% at the pyrolysis temperature of 700°C. Li et al. [28] investigated the long flame Huang Tu Miao
2. Experimental Portion

2.1. Synthesis of Raw Coal and Catalyst. Low-rank Shengli coal was grounded to the required size (20–40 mesh) for testing of experiments. Table 1 shows the results of raw Shengli coal. Raw coal was held for drying overnight at 120°C before each testing. A material MoS$_2$ (≥98%) as a catalyst supplied by Sinopharm Chemical Reagent Co., Ltd., was selected and amount of MoS$_2$ catalyst (2.5 g) was used in each experiment. The powder MoS$_2$ material was heated at 120°C and then calcined at 500°C within 4 h. It was pelletized with machine (769YB-24B) at 10 MPa pressure and then sieved to particle size of 20–40 meshes.

2.2. Testing Method. The testing section consisted of gas supply, a dual-stage fixed bed reactor, electric ring furnace, and tar and gas collection system as shown in Figure 1 as reported in our last research [33]. It was prepared through glass tube containing three parts including upper section, lower section, and a cover. The upper section containing a porous sintering quartz plate was used for the coal pyrolysis having 30 mm inner diameter and 200 mm length. The lower section was adopted for primary products during pyrolysis having 34 mm inner diameter and 550 mm length. Both parts were externally heated by an electric ring furnace. Two K-type thermocouples were kept inside the reactor for temperatures such as pyrolysis and cracking.

High purity N$_2$ carrier gas (Beiwen, Beijing, China, 99.99%) was controlled with a mass flow meter. It gave pyrolysis initial reaction in the dual-bed reactor. A 5 g coal was kept in the upper part of the pyrolysis and 2.5 g catalyst was kept in lower part of the catalytic upgrading of coal. The pyrolysis products from the upper section were transformed and go through the catalyst bed in lower part. Finally, obtained product was passed through condenser; it was cleaned with acetone thoroughly to get coal pyrolysis tar. Noncondensable pyrolysis gases were dewatered through calcium chloride block and received in gas bags. All pipelines were cleaned using acetone and then the liquid was obtained. The obtained liquid (acetone plus water) including tar was filtrated and the acetone was removed at 30°C in a rotary machine to get coal pyrolysis tar.

The experiments represented that reaction can finish within about 40 min during pyrolysis. The testing methods for coal with and without catalyst were as follows. A 5 g coal was pyrolyzed without catalyst in the upper part through electric furnace. It was performed for heating the coal through a temperature controller with 100°C per minute to 600°C temperature. Coal (5 g) was pyrolyzed and catalyst (2.5 g) was also put in lower part during upgrading of coal pyrolysis tar. Both parts were heated with a rate of 100°C per minute at 50 mL per min of gas flow from ambient to 600°C temperature. Both pyrolysis and cracking temperatures were kept within 30 min at 600°C. All performed tests were repeated three times and average was calculated as the final reading.

2.3. Coal Derived Products and Catalyst Analysis. Noncondensable and hydrocarbon gases were measured through a gas chromatograph as described in our last work [33]. The coal pyrolysis tar having aromatic and hydrocarbons was measured through analysis equipment as reported in our last study [33]. The boiling point range less than 360°C refers to the light tar and heavy tar having more than 360°C.

The catalyst characterization was analyzed through X-ray pattern machine and micropore analyzer as described in our last article [33]. The catalyst morphology was seen through scanning electron microscopy (SEM) with a JOEL machine (JSM-6700F) and transmission electron microscopy (TEM) was adopted to measure the catalyst with a JOEL (JEM-2000F).

### Table 1: Results of Shengli raw coal.

<table>
<thead>
<tr>
<th></th>
<th>Proximate (air-dried base, wt.%)</th>
<th>Ultimate (dry-free base, wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>M</strong></td>
<td><strong>A</strong></td>
<td><strong>Vol.Mat.</strong></td>
</tr>
<tr>
<td>15.0</td>
<td>4.2</td>
<td>32.04</td>
</tr>
</tbody>
</table>


In foregoing work, mechanical mixing and impregnation of MoS$_2$ catalyst with lignite coals were applied on the basis of research aims during catalytic hydropyrolysis [29, 30]. Thus, low-grade coal in this research's aim and MoS$_2$ catalyst were used separately in a dual-stage reactor having two sections through atmospheric pressure for the enhancement of coal pyrolysis tar. Moreover, the catalytic effect of MoS$_2$ on coal tar quality in terms of distilled temperature difference was investigated and also the behavior of catalytic upgrading in the conversion of heavy tar components was studied.
3. Results and Discussion

3.1. Temperature Influence on Coal without Catalyst. Coal having tar yield from 300 to 700°C is shown in Figure 2. It determined the suitable temperature that led to the maximum tar yield. More volatile matters were released at more than 600°C temperature and moved towards large cracking reactions to reduce coal tar yield during pyrolysis. Therefore, the temperature 600°C was selected. The product yields including gas, liquid, and char during coal pyrolysis without catalyst are depicted as in Figure 3. It can be stated that increase in gas yield occurred with the temperature from 300 to 700°C. The gas yield was increased which might be due to evolution of micro compounds due to the secondary tar reactions.
and large amount of volatiles was achieved at 600°C during pyrolysis. It was also observed that liquid yield increased from 300 to 400°C and then decreased. The reduction in liquid yield from 500 to 700°C indicates high reaction rates during decomposition. The expression of increase and reduction in liquid yield with temperature was reported in literature [34, 35]. The declining in char yield occurred from 300 to 500°C and then became stable above 500°C temperature. The stability of char yield above 500°C showed the complete burning of coal during pyrolysis. The temperature more than 600°C is attributed to the increment of gas yield and reduction in coal tar yield.

3.2. Catalyst’s Influence on Pyrolysis Product Yields. The catalyst having influence on yield of pyrolysis products during coal pyrolysis is described in Figure 4. It can be noted that the increment in liquid yield from 18 to 33 (wt.%, db) occurred due to catalytic effect during coal pyrolysis. The liquid yield increment might be due to high condensation reaction during catalytic coal pyrolysis, while gas yield decreased from 27 to 12 (wt.%, db) after catalysis and char yield (55 wt.%, db) remained constant before and after catalyst. These results showed that decrease in gas yield might be due to the catalytic effect on the released volatiles during coal pyrolysis. The liquid yield increment and gas yield reduction with the catalyst were studied in literature [31].

3.3. Gas Composition without and with Catalyst during Coal Pyrolysis. Pyrolysis gas components and hydrocarbon gases \((C_{m}H_{n})\) without and with catalyst are shown in Figure 5. It can be thought that gas components yield declined after catalyst. The pyrolysis of low-rank coal produces rich oxide of carbon due to large content of oxygen in raw material. The pyrolysis gases can provide energy requirement for plant during pyrolysis due to high content of carbon oxides [36]. The yields of gas components (\(H_2\), \(CH_4\), and \(CO\)) generated through the condensation reactions, whereas the yield of \(CO_2\) was produced due to the cracking of carboxyl group from coal during pyrolysis [37]. Thus, carbon oxide gases also decreased after catalysis. Therefore, the catalyst might be catalyzing the forward and reverse water gas reactions, which are attributed to declining gas yields.

3.4. Tar Characterization. Tar fraction as a function of simulated distillation temperature without and with catalyst is shown in Figure 6. It is noted that initial and final temperatures of tar decreased after catalysis which indicated that tar evaporated rapidly. These results showed that the amount of light weight tars was higher than that without catalyst. The composition of tar before and after catalyst during pyrolysis is shown in Figure 7. The light weight tars fraction increased after catalysis; meanwhile the variations
Table 2: Analysis of produced coal pyrolysis tars before and after reaction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O*</th>
<th>H/C (ratio of moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without</td>
<td>68.92</td>
<td>10.56</td>
<td>5.58</td>
<td>1.12</td>
<td>13.82</td>
<td>1.84</td>
</tr>
<tr>
<td>MoS₂</td>
<td>72.0</td>
<td>11.40</td>
<td>5.13</td>
<td>0.95</td>
<td>10.52</td>
<td>1.90</td>
</tr>
</tbody>
</table>

* By difference.

Figure 6: Tar fraction as a function of simulated distillation temperature without and with catalyst.

Figure 7: Tar composition of coal without and with catalyst.

Figure 8: Yields and fraction of coal pyrolysis tar without and with catalyst.

of wash and anthracene oils fractions were small. The pitch was also decreased after catalysis. For all compared data, the pyrolysis temperature in the upper layer was 600°C, the adopted catalyst was 50 wt.% of the pyrolyzed coal, and the cracking temperature was 600°C. Moreover, it is clear from Figures 5 and 6 that the catalyst had ability to produce more lightweight tars during pyrolysis.

The tar yield, light tar fraction, and yield are represented in Figure 8. In this case, the fraction of light tar is the sum of all oil components in Figure 7 except pitch. Moreover, it can be seen that the light tar fraction increased from 50 to 60 wt.% for the secondary upgrading over MoS₂ catalyst. The results showed that the secondary upgrading had greatly enhanced the overall tar quality, so that the downstream treatment could become more efficient and easier. In comparison to the coal pyrolysis without catalyst, the light tar yield with the catalyst increased significantly. It can be considered from light tar yield and fraction that MoS₂ catalyst might have the best upgrading effect. The elemental analysis data of tar before and after catalyst is shown in Table 2. The coal pyrolysis with catalyst increased hydrogen-to-carbon ratio and also reduced nitrogen, sulphur, and oxygen elements in coal pyrolysis tar. After the catalysis, tar yield is declined, while hydrogen and hydrogen-to-carbon ratio are increased as 7.9 and 3.3%, accordingly. Overall, MoS₂ catalyst was highly efficient in producing lighter coal pyrolysis tar fraction, upgrading the
coal tar products, and reducing the pitch contents in coal
pyrolysis tar.

3.5. Catalyst Characterization. The XRD pattern of MoS$_2$
catalyst is shown in Figure 9. A detailed view of diffraction
peaks of the catalyst showed the formation of single-phase
molybdenum sulfide (MoS$_2$) hexagonal structure as indicated
by the index at 14.4°, 32.7°, 39.6°, 44.3°, 49.8°, and 60.4°
corresponding to the (002), (100), (103), (104), (105), and
(112) crystal planes, respectively. The entire XRD diffraction
pattern was attributed to exhibit pure MoS$_2$ hexagonal form,
which had well adjustment to the values as shown (JCPDS
65-1951). XRD pattern represented no other peaks, exhibiting
pure form of MoS$_2$ material. The strong and clear diffraction
peaks showed that MoS$_2$ material is highly crystalline. The
highest intensity peak in the diffraction peaks shows high
crystal formation.

The porosity of fresh and spent catalysts was calculated
from nitrogen adsorption/desorption isotherms. The BET
surface areas of the fresh and spent catalysts are 3 and 5 m$^2$g$^{-1}$,
respectively, and there was no significant difference between
fresh and spent catalysts. The volume of pore in spent catalyst
increased from 0.015 to 0.025 cm$^3$/g, while pore diameter was
reduced from 23.65 to 16.66 nm. It is realized that BET surface
area and volume of pore increment might be attributed to the
breakdown of pore which was suffered from high volatiles
during pyrolysis and the cracking of coal pyrolysis tar.

The surface structure of fresh and spent catalysts with
high magnification is shown in Figures 10(a) and 10(b). From
Figures 10(a) and 10(b), it can be seen that both catalysts
were composed of MoS$_2$ platelets. Figure 10(a) shows MoS$_2$
crystals in the form of platelets. After the reaction, the
MoS$_2$ platelets formed a large lump which might be due
to high temperature and upgrading the coal pyrolysis tar
during pyrolysis. TEM diagrams of both catalysts (fresh and
spent) are shown in Figures 11(a) and 11(b), respectively. From
Figure 11(a), it is noted that the catalyst had nanoscale layer
on its structure. The nanoscale accumulated phenomenon
reduced the edge surface of the catalyst. It showed that sul-
phur atoms had strong molybdenum adsorption on the sur-
face of the edges, while molybdenum had strongly adsorbed
sulphur atoms. After the reaction, the edges on the surface of the catalyst reduced and changed into small nanolayers. The formation of small nanolayers after the reaction might be due to high temperature and decomposition of the coal pyrolysis tar during catalytic coal pyrolysis. Moreover, TEM showed highly crystalline material; its size was around 100 nm.

4. Conclusions

It was testified that MoS$_2$ catalyst was able to increase liquid product yield and produced the highest liquid yield. Moreover, it is found that the catalyst decreased the pitch in the tar and showed the increment in the lighter weight tars fraction. Therefore, the catalyst was also active for the increment in hydrogen-to-carbon ratio and reduction in nitrogen, sulphur, and oxygen elements in coal pyrolysis tar. The catalyst in this study was more effective to upgrade the coal pyrolysis tar to decompose the coal catalytically, although MoS$_2$ catalyst can promote the energy efficiency during the operation of industrial equipment.

Competing Interests

The authors declare that they have no competing interests.

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