Research on Improving Low Rank Coal Caking Ability by Moderate Hydrogenation

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Abstract: The hydrogenation test of low metamorphic coal was carried out by using a continuous hydrogen reactor at the temperature of 350 ~ 400°C and the initial hydrogen pressure of 3 ~ 6Mpa. The purpose of the experiment was to increase the caking property, and the heating time was controlled from 30 to 50min. The test results show that the mild hydrogenation test, no adhesion of low metamorphic coal can be transformed into a product having adhesion, oxygen elements in coal have good removal, the calorific value of the product has been improved significantly and coal particles during pyrolysis, swelling, catalyst, hydrogenation, structural changes and the combined effects of particles a new component formed between financial and is a major cause of coal caking enhancement and lithofacies change, coal blending test showed that the product can be used effectively in the coking industry.

1. Introduction
China had the most coke production in the world in 2016, about 450 million Tons coke were generated. Coking process under the current conditions, which required coking coal with good adhesion. Moderate metamorphic bituminous coal is a conventional coking coal, but in the various types of coal in China, moderate metamorphic bituminous coal reserves are low, and conventional coking coal reserves account for only 26% of the national coal reserves, of which more than 50% are distributed in Shanxi Province, the geographical distribution is extremely uneven. Compared with the low rank coal, the coking coash and sulfur is relatively higher, and has a poor washability. Due to the influence of resource conditions, coking technology development and coke demand, the shortage of high quality coking coal will exist for a long time. [1,2]

Low rank coal is abundant in China, accounting for more than half of the total reserves. At the same time, characteristic of most low metamorphic bituminous coal with low ash, low sulfur, low phosphorus, but because there is no bond or bond is very weak, the current can not be used as the conventional coking coal use, even in the presence of strong caking coal, under the coke condition, the blending ratio is generally not more than 5%. [3] In the early study, some foreign experts have increased the coking characteristics of coal by thermal hydrogenation,, this study was conducted by using 4 kinds of thermal hydrogenation without nonagglomerating coal, including lignite, sub bituminous and sub bituminous coal and oxidized bituminous coal, the results show that the product of plasticity, free expansion coefficient has been compared to the raw coal some improvement, but still do not have adhesion. [4,5] therefore, the main goal of this paper is to increase the caking property of non caking coal by moderate solvent hydrogenation.
2. Experimental

2.1. Material and Equipment

|          | Ad  | Vad | Vadf | FCd | Qgr.d/ MJ/kg | Cdaf | Hdaf | Odaf | Ndaf | Sdaf |
|----------|-----|-----|------|-----|--------------|------|------|------|------|------|
| YulinCoal| 4.1 | 44.16 | 44.16 | 51.86 | 30.79 | 80.67 | 5.36 | 12.54 | 1.01 | 0.4  |

Table 1. Analysis of Yulin coal

Raw coal was selected which was long flame coal from Yulin mining area. The element analysis and industrial analysis of raw coal show table 1 (G was bituminous coal caking index). Table 1 shows that Yulin coal belongs to low metamorphic bituminous coal with high oxygen content and volatile content, and has no caking property. Broken about grinding to 0.16–0.18mm dry spare, hydrogenation solvent was anthracene oil. Hydrogenation experiments were carried out in continuous hydrogen type autoclave, autoclave by mechanical stirring, the stirring paddle makes the gas phase and liquid phase reactant mixing, stirring speed is 200r/min, using oil bath heating, the operating pressure is 0 ~ 35MPa, the operating temperature is 0 to 480°C, according to the temperature in the reactor, and regulation the control of oil bath, to achieve the purpose of indirect control of reaction temperature. The flow chart of the experimental device is shown in figure 1.

![Figure 1. Schematic diagram of the experimental apparatus.](image)

2.2. Procedures

The extraction flow chart is shown in figure 2. When the reaction temperature and pressure reached the set conditions, keep a certain amount of time, open the tank cover, get the products out, calculate reaction kettle liquid and solid volume, solid product into the vacuum oven; a part of the product was fractional extracted after drying; the reaction products all transferred to the quantitative filter tube, extracted by Soxhelt continuous extraction unit, followed by n-hexane, toluene and tetrahydrofuran, reflux extraction time for each solvent 48h, until the filtrate is clear.
Figure 2. The products extraction

2.3. Material Balance Calculation

Gas Yield

\[ \eta_g = \frac{m_g}{m_{C_{daf}}} \times 100\% \]  \hspace{1cm} (1)

- \( m_g \): weight of the gas products
- \( m_{C_{daf}} \): weight of the dry air free based coal.

\( \text{H}_2\text{O} \) yield

\[ \eta_{H_2O} = \frac{m_{O\text{coal}} - m_{Og}}{m_{C_{daf}}} \times \frac{18}{16} \times 100\% \]  \hspace{1cm} (2)

- \( m_{O\text{coal}} \): weight of oxygen element in the coal
- \( m_{Og} \): weight of oxygen element in the gas

Coal conversion rate

\[ \sigma = \left(1 - \frac{m_{THFI}}{m_{C_{daf}}} \right) \times 100\% \]  \hspace{1cm} (3)

- \( m_{THFI} \): weight of residue can’t dissolve in tetrahydrofuran
- \( m_\Lambda \): the weight of ash

asphaltene yield
\[ \eta_a = \frac{m_a}{m_{\text{daf}}} \times 100\% \]  \hspace{1cm} (4) \\

\[ \eta_{pa} = \frac{m_{pa}}{m_{\text{daf}}} \times 100\% \]  \hspace{1cm} (5) \\

\[ \eta_{pa} : \text{weight of asphaltene (dissolve in toluene, can’t dissolve in n-hexane)} \]

**preasphaltene yield**

\[ \epsilon_H = \frac{m_{H0} - m_{Ht}}{m_{\text{daf}}} \times 100\% \]  \hspace{1cm} (6) \\

\[ m_{H0} \text{ and } m_{Ht} : \text{weight of H}_2 \text{ in the autoclave (before and after reaction).} \]

**H}_2 \text{ consumption**}

\[ \eta_{oil} = \sigma + \epsilon_H - \eta_e - \eta_{H20} - \eta_a - \eta_{pa} \]  \hspace{1cm} (7) \\

In this experiment, 3 conditions were selected before optimization, 350°C was the initial reaction point; 380°C was the maximum temperature point of Yulin coal loss rate. 400°C, 6MPa was the best reaction condition. The reaction products were analyzed, the reaction conditions and the conversion rate under this condition were shown in table 2:

| Samples | Temperature/°C | Pressure/MPa | time/ min | σ/ % |
|---------|----------------|--------------|-----------|------|
| 1       | 350            | 4            | 30        | 35.47|
| 2       | 380            | 4            | 50        | 37.16|
| 3       | 400            | 6            | 50        | 54.14|

3. Results and Discussion

3.1. Products Properties

The properties of Yulin coal after moderate hydrogenation modification are listed in Table 3 (vacuum drying at 110°C for 2 hours).

| wt%, % | A_d  | Vdaf | Vdaf | Qgr.d/MJ/kg | C_daf | H_daf | N_daf | S_daf | O_daf | R_max |
|--------|------|------|------|-------------|-------|-------|-------|-------|-------|-------|
| 1      | 7.39 | 45.35| 45.35| 35.36       | 82.65 | 4.99  | 2.55  | 0.93  | 1.49  | 0.96  |
| 2      | 6.61 | 44.31| 44.31| 36.66       | 86.15 | 4.63  | 1.42  | 0.87  | 1.32  | 0.98  |
| 3      | 3.77 | 41   | 41   | 36.74       | 90.93 | 5.13  | 1.79  | 0.98  | 1.17  | 0.98  |

After the reaction, the properties of the product were analyzed. The results showed that the modified product had adhesive property. The caking index (G) can reach about 70 at 350°C, and the caking index (G) can reach more than 90 at 400°C.

From the analysis of the properties of hydrogenation products in Table 4, it can be seen that the
content of carbon in mild hydrogenation products is higher than that of raw coal, and the structure of the product is more compact than that of the raw coal. From the angle of coal hydrocracking, during the reaction, the bridging reaction of oxygen bridge and side chain of low rank coal macromolecular structure was formed, and other forms such as H₂O, COₓ, and H₂S were produced. On the other hand, the content of N in the mild hydrogenation product is much higher than that of the raw coal, which indicates that the N element in coal is difficult to be removed under the condition of hydro upgrading. From the structural analysis, the N element mainly exists in the aromatic structure.

From the results of industrial analysis in Table 3, it can be seen that the ash content has increased in comparison with the industrial analysis, which is due to the escape of some volatile components, and the heat value of the mild hydrogenation product is significantly higher than that of the raw coal. The reason is that in the process of mild hydrogenation, due to the fracture of the macromolecular side chain, the oxygen-containing functional groups and the intrinsic water in the low rank coal are removed, and the latent heat of vaporization of the water molecules during combustion is eliminated, and the calorific value is increased. [6-8]

The analysis of hydrogenation pyrolysis process, a large molecular fracture generated asphaltene, with activity of preasphaltene and other active components, with the increase of temperature and pressure, asphaltene substances increased, increasing coal pyrolysis, bond strong structural fracture and continue to generate free when the base fragments, these fragments are hydrogen stable liquid and gas production to small molecules, on the other hand, when the hydrogen pressure is conducive to inhibit the reaction process of the dehydrogenation, thus improving the yield of oil and gas, the higher the initial hydrogen pressure would be beneficial to solvent on molecular hydrogen solubility, increase the concentration of active hydrogen the solvent, solvent to dissolve hydrogen fast transfer to free radical fragments. The analysis of the composition of the products under different conditions is shown in figure 3.

From Figure 3 (condition 1, 2, 3 respectively in the picture: 1, 2, 3) can be seen, generation of oils and gas molecules products increase, reaction to obtain solid product having adhesion for the purpose of increasing the conversion rate will bring a solid product yield loss.

![Figure 3. Hydrogenation products composition](image-url)
3.2. Maceral Specification

![Microphotographs](image)

(a) 623K. Coal particle diameter increased, microlithotype of the modified coal change from monocomponent to vitrinitic.
(b) 653K. Microlithotype of the modified coal formed by vitrinite mainly.
(c) 673K. Microlithotype of the modified coal formed by vitrinite mainly, the particle of the Fe-catalyst and the particle of the inertinite spread in vitrinite base.
(d) Raw coal maceral specification

**Figure 4. Plasticized Coals Microphotograph (350°C ~400°C)**

The change of petrographic characteristics during the modification of low metamorphic bituminous coal was studied by polarizing microscope, and the main factors affecting the caking property of modified coal were analyzed. The petrographic characteristics of the modified products at temperatures from 350 to 400°C are shown in figure 4.

From Figure 4 (a) can be seen before in the reaction temperature reaches 350 °C, coal bond hasn't changed basically, vitrinite reflectance increased slightly with the rise of temperature, coal particle size increases, microlithotype by single component type into a micro mirror by inert coal; Figure 4 (b) can be seen, when the temperature reached 380°C, microlithotype in micro mirror inert coal; It can be seen from Figure 4 (c) that when the reaction temperature is 400°C, the micro coal type is dominated by micro mirror inert coal, and the catalyst particles and the inert group particles are dispersed in the vitrinite matrix. Figure 4 (d) is a micrograph of raw coal.

When the reaction temperature is higher than 380°C, the caking property of coal was obviously enhanced, and the characteristics of modified coal and coal rock changed significantly. The micro inert component is the main micro coal type in the mild hydrogenation product (microlithotype containing vitrinite and inertinite and exinite less than 95%, less than 5%). The structural changes and inter particle melting of coal particles under the combined action of pyrolysis, swelling, catalyst, hydrogenation and formation of new components are the main reasons leading to the increase of coal caking property and the change of petrographic characteristics. The caking property of modified coal mainly comes from the new soluble component at 350°C, and the increase of caking property caused by the change of coal structure needs higher reaction temperature.

3.3. Coal Blending of Yulin Coal

Choose the best modified products and coking performance of Shanxi 1/3 coking coal comparison, the use of these two samples and non caking coal blending. [9-12] At different ratios, the bond index between mild hydrogenation products and Shanxi coking coal and non caking coal is compared. The main coal quality characteristics of 1/3 Shanxi coking coal are shown in table 5.

| Table 5 Characteristics of Puxian coal |
|--------------------------------------|
| wt/% | A<sub>d</sub> | V<sub>daf</sub> | C<sub>daf</sub> | H<sub>daf</sub> | N<sub>daf</sub> | S<sub>daf</sub> | O<sub>daf</sub> | G | R<sub>max</sub> |
|------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---|------------|
| Puxian coal | 31.24 | 6.91 | 87.83 | 5.68 | 1.11 | 0.40 | 5.39 | 85 | 0.99 |

* R<sub>max</sub>: mean max reflectance of the coal
Overall, the modified product properties was between gas fat coal and coking coal. The modified products and 1/3 coking coal were mixed according to the amount of 0%, 20%, 40%, 50%, 60%, 70%, 80%, 90% and 100%, respectively, and non caking coal (the percentage of total mixed coal). The caking index(G) of modified products was determined by GB/T5477 method, then draw the corresponding curve, coal blending curve as shown in figure 5.

![Blending Curve of Coal](image)

**Figure 5.** Blending Curve of Coal

We can see from Figure 5, the mixing quantity is between 66%~81%, change coal caking index curve and hydrogen production after coal blending coking coal faster; in the mixing quantity of 74% previous bond index of hydrogenation products than blending coking coal blending high coal blending effect is good; and after 74%, and hydrogen bond index products with the high coal blending coking coal.

4. Conclusion
(1) The cohesiveness of mild hydrogenation products has been obviously improved, and the expected purpose has been achieved. The deoxidation effect is obvious, and the calorific value has been improved obviously.
(2) During the mild hydrogenation process, the coal particles experienced pyrolysis, swelling, hydrogenation and inter particle melting, leading to the micro coal type of the modified coal mainly with micro mirror inert coal, and the inert group was often dispersed in the vitrinite matrix in fine particles.
(3) From the coal blending results, between mild hydrogenation product properties between gas fat coal and 1/3 coking coal.

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6. References
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