Study on the rheology of coal–oil slurries during heating at high pressure

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Abstract Using the self-developed viscosity measuring device, the viscosity variations of coal–oil slurries with temperature increasing during coal–oil co-processing were studied. The results show that the viscosity of coal–oil slurries prepared by different kinds of oil varies differently during heating. The viscosity of the coal–oil slurry prepared by the catalytic cracking slurry (FCC) generally decreases during heating. However, the viscosity of the coal–oil slurry prepared by the high-temperature coal tar (CT) will peak at 338 °C during heating. The differences in viscosity variations of coal–oil slurries are analyzed. In addition to the temperature, the properties of the solvents and coal are the main influencing factors. Because the used coal contains a large number of polar functional groups, the swelling behavior of the coal in polar solvent (CT) is stronger than that in non-polar solvent (FCC). The swelling effect of the coal can result in the appearance of the viscosity peak. Therefore, before 100 °C, the solvent molecules entering into the coal pores is the main influencing factor of coal–oil slurries viscosity variations. After 100 °C, the increasing of particle size of coal particles is the main influencing factor of coal–oil slurries viscosity variations.

Keywords Coal–oil slurry · Rheology · Swelling · High temperature and pressure

1 Introduction

In coal–oil co-processing, the temperature of coal–oil slurry after heating by the preheater is generally up to 380–400 °C. The coal will decompose and generate a large amount of free radicals during heating. The free radicals are very unstable. If there is sufficient active hydrogen, the free radicals can combine with the active hydrogen to generate small molecular substances. The small molecular substances can reduce the viscosity of coal–oil slurry. However, if the active hydrogen is insufficient, the free radicals themselves will aggregate to produce macromolecular substances. The macromolecular substances can increase the viscosity of coal–oil slurry. Generally, the viscosity of coal–oil slurry changes significantly during heating. Viscosity is an important parameter of the preheater design. Viscosity is also important to determine the flow status of slurry and to calculate pressure drop and heat transfer. Therefore, it is necessary to study the viscosity variations of coal–oil slurry during heating at high pressure. The study on the viscosity variations of coal–oil slurries is mainly in direct coal liquefaction (Okutani et al. 1984; Tsutsunmi and Yoshida 1986; Deng et al. 1987; Xiong et al. 2009). However, in coal–oil co-processing, the study on the viscosity variations of oil–coal–oil slurries is little (Xue et al. 2013; Gao et al. 2015). In this paper, the viscosity variations of coal–oil slurries during heating were studied by a self-developed viscosity measuring device, and the reasons for the changes of viscosity of coal–oil slurries were analyzed.
2 Experimental

A low rank bituminous coal from Xinjiang was used. Its properties are listed in Table 1. Two kinds of oil were used. One is high-temperature coal tar from Xinjiang, marked CT. The other is the catalytic cracking slurry from Shanghai Petrochemical Company, marked FCC. Their properties are listed in Table 2. Iron based catalyst was used. The addition amount of catalyst is 1% of the weight of coal and oil.

3 Measuring apparatus and method

3.1 Measuring apparatus

The self-developed viscosity measuring apparatus (Fig. 1) is mainly composed of a 0.5-liter autoclave, a stirring unit and a torque measuring unit. Autoclave can simulate the heating process of the co-processing, the stirring unit is to prevent the deposition of coal particles, and the torque measuring unit is to record the torque changes of the coal–oil slurry. Torque changes can reflect the viscosity variations of coal–oil slurry.

3.2 Power number method

For a stirring device, there is only one power curve. If the swirl phenomenon is not obvious, the relationship between Power number ($P_o$) and Reynolds number ($Re$) is as follows (Wu et al. 2007):

$$P_o = KR e^x$$

(1)

where, $K$ is the overall shape factor of the system geometry, $x$ is a parameter. According to the definition of Power number ($P_o$) and Reynolds number ($Re$), there are the following formulas:

$$P_o = \frac{N}{\rho n^2 D^5}$$

$$Re = \frac{D^2 n \rho}{\mu}$$

(2)

where, $N$ is the stirring power, $\rho$ is the density, $n$ is the rotating speed, $D$ is the diameter of impeller, $\mu$ is the viscosity, $M$ is the torque.

3.3 The relationship between viscosity and torque

23 kinds of Newtonian fluids with different viscosity were used to determine the relationship between viscosity and torque. The maximum viscosity of the Newtonian fluids is 1713.7 mPa s, and the minimum viscosity is 11.9 mPa s. The viscosity of the 23 kinds of Newtonian fluids was measured by capillary viscometers according to GB/T 265–1988. While the torques of the 23 kinds of Newtonian fluids were measured at 400 r/min using the self-developed measuring apparatus (Fig. 1). The viscosity-torque curves of the 23 kinds of Newtonian fluids are shown in Fig. 2. The viscosity-torque correlations are shown in Table 3.\n
If Eq. (2) is substituted into Eq. (1), it will get the following relationship:

$$\mu = a M^b$$

$$a = \left(\frac{2\pi}{\rho n^2 D^5 K}\right)^{\frac{1}{-x}} D^2 n \rho$$

(3)

$$b = -\frac{1}{x}$$

If the viscosity of substances is known, and the torque of substances is also measured, the values of $a$ and $b$ in Eq. (3) will be determined. Then for the unknown viscosity substance, if its torque is measured, its viscosity can be calculated by Eq. (3).

4 Results and discussion

4.1 Viscosity of coal–oil slurries

The viscosity of coal–oil slurries during heating was measured under the initial hydrogen pressure of 12.3 MPa. The results are shown in Fig. 3.

As the temperature increasing, the viscosity variations of coal–oil slurry prepared by CT can be divided into three stages. The first, when temperature is less than 100 °C, the
viscosity decreases rapidly with temperature increasing. The second, when temperature is between 100 and 320 °C, the viscosity is almost constant. The third, when temperature is more than 320 °C, the viscosity increases sharply, and reaches a maximum at 338 °C. The maximum at 338 °C is 3156.4 mPa s, then the viscosity decreases rapidly, and after 390 °C, the viscosity is less than 10 mPa s.

As the temperature increasing, the viscosity variations of coal–oil slurry prepared by FCC can be divided into two stages. The first, when temperature is less than 160 °C, the viscosity decreases rapidly with temperature increasing. The second, when temperature is more than 160 °C, the viscosity decreases slowly with temperature increasing.

From Fig. 3, it can be seen that the viscosity variations of coal–oil slurry prepared by FCC is different from that prepared by CT. When temperature is less than 100 °C, the viscosity of the two kinds of coal–oil slurries differ by more than 100 mPa s. When temperature is between 100 and 160 °C, the differences of the viscosity of coal–oil slurries are reduced to tens mPa s. The differences of viscosity of coal–oil slurries before 160 °C are caused by the properties of FCC and CT. The viscosity of FCC is larger than CT, so the viscosity of coal–oil slurry prepared by FCC is also larger than that prepared by CT. However, the effect of the property of oil on the viscosity variations decreases with temperature increasing. When temperature is between 160 and 240 °C, the viscosity of the coal–oil slurries is almost the same. This means the properties of FCC and CT have no effect on the viscosity variations of the coal–oil slurries. This finding is consistent with Wang’s findings (Wang et al. 2007). However, when temperature is more than 240 °C, the effect of the property of FCC and CT on the viscosity variations is also significantly different.

Table 2 The properties of CT and FCC

| Category | ρ(20 °C) (g/cm³) | η(60 °C) (mPa s) | Saturate (%) | Aromatic (%) | Resin (%) | Asphaltene (%) | TI (%) | H/C | f_a |
|----------|----------------|------------------|-------------|-------------|----------|----------------|-------|-----|-----|
| CT       | 1.1690         | 73               | 0.00        | 21.18       | 43.04    | 32.29          | 3.49  | 0.75| 0.90|
| FCC      | 1.1088         | 1212             | 9.54        | 68.46       | 19.54    | 2.37           | 0.09  | 0.96| 0.72|

Note TI is the Toluene insoluble. f_a is the aromatic carbon ratio, and was calculated on 1H-NMR spectra and elemental composition

Fig. 1 Viscosity measuring apparatus 1—torque meter; 2—electronic coupling meter; 3—outer magnetic jar; 4—thermocouple; 5—stirring impeller

Fig. 2 The viscosity-torque curve at 400 r/min
4.2 Analysis of viscosity-temperature curves

In order to analyze the causes of the viscosity variations, it is important to know when the coal–oil slurries begin to react. Figure 4 shows the pressure changes in autoclave with temperature increasing. When CT is used as the solvent, and temperature is less than 280 °C, the relationship between pressure and temperature is linear. That means coal–oil slurry has not yet react with hydrogen. When temperature is higher than 280 °C, the pressure rise slowly, and then begins to drop as temperature increasing. That means coal–oil slurry is carrying out hydrogenation reaction. When FCC is used as the solvent, the coal–oil slurry starts hydrogenation reaction at 300 °C.

### 4.2.1 Analysis of viscosity variations before hydrogenation reaction

It is found that the increase of viscosity of coal–oil slurry at low temperature is mainly caused by swelling (Okutani et al. 1980; Deng et al. 1989; Hao et al. 2008). According to the swelling mechanism of coal particles, the viscosity of the solvent itself and the volume fraction of coal particles are the main factors that effect on the viscosity of coal–oil slurry (Shi 2012). The viscosity variations of the solvents with temperature can be expressed by Aandrade equation (Poling 2006):

\[
\ln \mu_L = A + \frac{B}{T}
\]

where, \( A \) and \( B \) are constants related to solvent properties, \( \mu_L \) is the solvent viscosity, \( T \) is the absolute temperature.

The viscosity variations of coal–oil slurry can be expressed by Mooney formula (Mooney 1951):

\[
\mu_r = \frac{\mu_s}{\mu_L} = \exp \left( \frac{2.5\%_V}{1 - \%_V/\%_m} \right)
\]

where, \( \mu_r \) is the relative viscosity, \( \mu_s \) is the slurry viscosity, \( \mu_L \) is the solvent viscosity, \( \%_V \) is the volume fraction of solid particles, \( \%_m \) is the maximum volume fraction, 2.5 is the shape factor of spherical particles.

The Mooney formula can be changed into a logarithmic form, and combined with Aandrade equation, then a new formula will be got as follows:

\[
\ln \mu_s = \frac{2.5\%_V}{1 - \%_V/\%_m} + \left( A + \frac{B}{T} \right)
\]

According to formula (6), if the swelling effect is little with increasing temperature, the relationship between \( \ln \mu_s \) and \( \frac{1}{T} \) is close to linear. While if the swelling effect is strong, the relationship is nonlinear. The relationship between viscosity and temperature of two kinds of coal–oil slurries is analyzed. The results are shown in Table 4 and Fig. 5.

![Viscosity-temperature curves](image)

**Fig. 3** Viscosity-temperature curves

**Table 3** The viscosity-torque correlations at 400 r/min

| Re   | Equation                  | Correlation coefficient \((R^2)\) | Mean fit relative deviation (%) | Mean fit absolute deviation (mPa s) |
|------|---------------------------|-----------------------------------|---------------------------------|------------------------------------|
| ≤36  | \( \mu = 32222M - 300.63 \) | 0.9973                            | 1.31                            | 13.2                               |
| >36  | \( \mu = 2 \times 10^7 \times M^{0.8926} \) | 0.9990                            | 3.73                            | 7.0                                |

In order to find the reasons for the viscosity variations, the viscosity of coal–oil slurries at different temperatures and time are measured, and the particle size of coal particles at different temperatures are also measured. The results are shown in Figs. 6 and 7. When FCC is used as the solvent, the viscosity variations of coal–oil slurry is mainly affected by temperature from Fig. 5, but there is a
mutation at 100 °C. This is due to the reduction of lubricated solvent. Because the molecular structures of FCC and coal are different, the swelling of coal particles is not obvious. It can be seen from Fig. 7 that the particle size of coal particles at 100 °C does not become larger than original coal particles. When FCC is used as the solvent, the particle size of coal particles at 100 °C is even smaller than original coal particles in Fig. 7. The reason is that the coal particles at 100 °C is separated by Tetrahydrofuran (THF) from coal–oil slurry. The coal particles are partially dissolved by THF. That leads to the particle size become smaller (Zhang et al. 2004). When temperature is less than 100 °C, the movement of FCC solvent molecules is slow at low temperature. Therefore, the solvent molecules entering into the coal pores will need a long time. When temperature is at 70 °C, the swelling equilibrium time is 96 h in Fig. 6. However, when temperature is at 100 °C, the swelling equilibrium time is reduced to 0.5 h. The time from room temperature up to 100 °C is about 27 min, which is consistent with the swelling equilibrium time. Therefore, the FCC molecules entering into the coal pores leads to the appearance of mutation at 100 °C.

Because CT contains a small number of small molecules, the small molecules can quickly enter into the coal pores at low temperature. That results in the first change in the relationship between ln μs and 1/T at 60 °C. Then the macromolecules of CT gradually enter into the coal pores. That results in the second change at 100 °C. As temperature increasing, the solubility of CT to coal particles increases. The substances in the coal are constantly being dissolved, and the coal particles are expanding. It can be seen from Fig. 7 that the particle size of coal particles at 220 °C increases significantly. The substances are mainly composed of asphaltene and preasphaltene. They may play a role in viscosity increasing (Han et al. 2003).

4.2.2 Analysis of viscosity variations in hydrogenation reaction

When the coal samples begin pyrolysis reaction, the intermediate products such as asphaltene and preasphaltene are generated. They may affect the viscosity variations of coal–oil slurries (Tsutsumi and Yoshida 1986; Sawatzky et al. 1992). In order to know the effect of the intermediate products on the viscosity variations. The liquid–solid products of coal–oil slurries under different conditions are extracted by Hexane, Toluene and Tetrahydrofuran (THF) respectively. The Hexane soluble is defined as oil. The Hexane insoluble and Toluene soluble is defined as asphaltene (A). The Toluene insoluble and THF soluble is defined as preasphaltene (PA). The THF insoluble is composed of unconverted coal and catalyst, which is marked as THFI. The extraction results are shown in

| Solvent | t (°C) | Equation | Correlation coefficient (R²) | Note |
|---------|-------|----------|-----------------------------|------|
| CT      | 40–60 |ln μs = 7.9227 × 1000/T – 18.016 | 0.9950 | Linear |
|         | 60–100|ln μs = 4.5312 × 1000/T – 7.8134 | 0.9942 | Linear |
|         | 100–280| – | – | Nonlinear |
| FCC     | 70–100|ln μs = 5.223 × 1000/T – 8.4319 | 0.9987 | Linear |
|         | 100–300|ln μs = 2.3766 × 1000/T – 8.4319 | 0.9768 | Linear |
It can be seen that the yields of asphaltene and preasphaltene do not show a maximum at 338 °C.

When CT is used as the solvent, there is a viscosity peak in Fig. 3. If the asphaltene and preasphaltene play a role in viscosity increasing, the yields of asphaltene and preasphaltene will also appear the maximum at 338 °C (Yan et al. 2009; Xiao and Zhang 2010). However, there is no maximum between asphaltene and preasphaltene at 338 °C. It means that the asphaltene and preasphaltene do not play a key role in the viscosity changes.

The viscosity variations of coal–oil slurries may be caused by the properties of solvents and coal. Because the oxygen content of coal is up to 15.81%, the coal contains a large number of polar functional groups. The polar functional groups may form hydrogen bonds or other bonding forms in the coal molecules. When the functional groups encounter with polar solvent molecules, they may form more stable hydrogen bonds, so the interactions between coal molecules will be destroyed and result in a large swelling ratio of the coal. The oxygen content of CT is 1.86%, which is mainly in the form of phenolic hydroxyl groups, so CT is a polar solvent. When CT is used as the solvent, there may be a larger swelling ratio of the coal than that FCC used as the solvent. In order to confirm this inference, the particle size distribution of coal particles (THFI) at 320, 338, and 390 °C was analyzed respectively. The results are shown in Fig. 8. At the beginning, the particle size becomes larger than original coal particles with temperature increasing. When temperature is up to 338 °C, the particle size is the largest, and the particle size at 338 °C is much larger than original coal particles. This is due to the aggregation of coal particles into larger particles (Ren et al. 2011). As temperature continues to rise, the polar functional groups of the coal are removed, and the skeleton of the coal is destroyed, which result in a decrease in particle size and volume fraction of coal particles. The oxygen content of FCC is 0.22%, so it can be seen a nonpolar solvent. There are little interactions between nonpolar solvent and coal molecules, so the swelling ratio of the coal is smaller than CT as the solvent (Chang et al. 2005).

5 Conclusions

The viscosity variations of coal–oil slurries during heating at high pressure were studied by self-developed viscosity measuring device. It is found that the viscosity of coal–oil slurries varies differently with different solvents as temperature increasing. When FCC is used as the solvent, the viscosity of coal–oil slurry generally decreases with temperature increasing. However, when CT is used as the solvent, the viscosity of coal–oil slurry generally decreases with temperature increasing. However, when CT is used as the solvent, the viscosity of coal–oil slurry appears a viscosity peak at 338 °C. It is found that the properties of solvents and coal are the main influencing factors causing the viscosity changes of coal–oil slurries. Because the coal samples contained a large number of polar functional groups, the swelling ratio of coal in polar solvent (CT) was larger than in nonpolar solvent (FCC). The aggregation of coal particles result in the appearance of a viscosity peak. It is also found that when temperature is less than 100 °C, the viscosity variations of coal–oil slurry are caused by the solvent molecules entering into the coal pores. However, when temperature is more than 100 °C, the viscosity variations of coal–oil slurry are mainly caused by the increase of particle size of coal particles.

| Solvent | Temperature (°C) | Oil (%) | A (%) | PA (%) | THFI (%) |
|---------|------------------|---------|-------|--------|----------|
| CT      | 320              | 36.28   | 11.68 | 18.95  | 33.10    |
| CT      | 338              | 38.58   | 9.90  | 23.01  | 28.51    |
| CT      | 390              | 38.70   | 16.25 | 33.42  | 11.63    |
| FCC     | 450              | 65.02   | 1.57  | 28.37  | 5.03     |
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