Coliquefaction Reactivity of Biomass and Coal under Moderate Conditions. Part 2: Effect of Cornstalk Dosage on Viscosity of the Coliquefaction System

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Coliquefaction Reactivity of Biomass and Coal under Moderate Conditions. Part 2: Effect of Cornstalk Dosage on Viscosity of the Coliquefaction System

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ABSTRACT: The viscous characteristics of the liquefaction system play a crucial rule during liquefaction, and these characteristics of the coal−oil slurry (COS) have been studied. In this paper, the viscosity of the coal−biomass−oil slurry (CBOS) at three stages while not systematically studied by forerunners was investigated by the torque current in the autoclave during coliquefaction of coals and cornstalk. The results, therefore, show that, at the thermal calefaction stage, the torque current of the CBOS system, predicted with the exponential decay model, was larger than that of the COS. At the pyrogenation and hydrogenation stage, the torque current of COS varies slightly in the Shengli coal system compared to the Shendong coal system, which presents a maximum. At the cooling stage, the torque current of the COS system, increasing with the quantity of the CS, was greater than that of the CBOS system. The study, thus, in the thesis indicates three aspects for industrial practices as well as fundamental research: the pumpablility of feedstock in the calefaction stage, the anticarbonization in the pyrogenation and hydrogenation stage, and the kinetic foundation in coliquefaction.

1. INTRODUCTION

The rheological property, including the viscosity and fluidity, determining the pumpability of the coal−oil slurry (COS) or coal−solvent slurry, plays crucial rule during coal liquefaction (DCL) and has attracted more interests, especially in China, recently, with the increasing development of direct coal liquefaction as a result of the speedy exhaustion of petroleum and energy supply security. In our previous work, we studied the rheological characteristics of the Shengli COS[1−3] and Shenhua COS, and different factors in different situations, such as low temperature and atmosphere[4] and during heating at atmosphere,[5] and the effect of the particle size distribution of Shenhua coal,[6] solvents, and moisture[7] have been investigated systematically. These factors included solvent properties, granularity of coals, ratio of coal/solvent, temperature, solvent swell, and shear rate on the viscosity of COS prepared with coals and recycled oil or tetralin on the rheological property of the COS.

The coliquefaction of coal and agricultural waste, the abundant and predominant renewable solid combustibles that can be converted into liquid and gaseous fuels,[8] is becoming a focal issue of the energy study ascribed to the recent severe environmental regulations as well as exhausting oil supplying. However, up to the present, the rheological characteristic of the coal−biomass−oil mixture or coal−biomass−oil slurry (CBOS), which deserves to be seriously considered, has not been reported systematically, in detail, or comprehensively.

The aim of this work is to investigate the flow behavior of CBOS of Shengli coal (SLC), Shendong coal (SDC), and cornstalk (CS). The torque current, drawn by the stirrer motor at a constant stirring speed, corresponding to changes in the viscosity of the fluids in the vessel,[9] has been proven to be used to determine the tendency of viscosity of COS in accordance with that obtained by an appropriative viscometer at high temperature and pressure.[10] Consequently, the torque current was selected as the main parameter to investigate the viscosity of the coliquefaction system at three stages, including thermal elevation, pyrolysis−hydrogenation, and thermal degradation.

2. EXPERIMENTAL SECTION

2.1.1. Materials and Reagents. *Materials.* The coals used in this study were lignite (SLC) and bituminite (SDC). The coal samples were crushed and sieved to the 75−105 μm particle size range, dried in a vacuum oven at 105 °C for 24 h, and then stored in a desiccator saturated with nitrogen for latter use without any other further processing.

The CS, obtained locally from the Chang Ping District of Beijing, was crumbled and sifted to a particle size between 0.1 and 0.5 mm. Then, moisture was removed by drying the sample to a constant weight in a vacuum oven at 105 °C and stored in the same manner as the coal samples.

The proximate and ultimate analysis results of the materials above are listed in Tables 1 and 2, respectively.

2.1.2. Reagents. All reagents used in this work were of analytical quality/grade. Tetralin was used as a hydrogen donor solvent. The catalyst and its accelerator employed were Fe_3O_4 and sulfur, respectively. The reagents were products of Beijing F&F Chemical Industrial Company and used as received.

Table 1. Proximate Analysis of Coals and Biomass

	moisture$_{da}$ (%)	ash$_d$ (%)	volatile matter$_{daf}$ (%)	fixed carbon$_{daf}$ (%)
CS	6.85	4.71	45.73	26.71
SLC	19.89	14.51	46.88	53.12
SDC	6.64	4.13	35.49	64.51

Table 2. Ultimate Analysis of Coals and Biomass

	C$_{daf}$ (%)	H$_{daf}$ (%)	O$_{daf}$ (%)	N$_{daf}$ (%)	S$_{daf}$ (%)
CS	45.9	6.3	46.9	0.7	0.1
SLC	71.66	4.75	21.42	0.91	1.27
SDC	89.53	4.63	4.18	1.19	0.47

Hydrogen and nitrogen gases (99.999%) were supplied by Beijing Huayuan Gas Chemical Industry Co., Ltd.

2.2. Methods. Liquefaction runs were conducted in a 500 mL mechanically stirred and electrically heated stainless-steel reactor (Parr series 4575A HP/HT pressure reactor) equipped with a 4843 controller, manufactured by Parr Instrument Company, Moline, IL. After the coal, biomass, and tetralin (coal + biomass/solvent = 1:1.5) were charged and mixed in the inner cylindrical vessel of the reactor, the bomb was sealed, flushed with hydrogen, and then pressurized with 8 MPa of hydrogen at room temperature. Thus, the system was then heated to 668 K with agitation at a constant shearing rate of 400 rpm.

After 90 min of thermal retention at 668 K, the heat supply to the reactor was shut off. Then, the mixture was cooled until the desired temperature of less than 313 K was attained, and the final temperature and pressure were recorded.

In the course of the above-mentioned coliquefaction, the changes in the torque current was recorded every 5 min and treated mathematically to reveal the rheological nature of the CBOS. Therefore, the relationship between the torque current and temperature or reacting time at diverse stages of the coliquefaction was discussed.

3. RESULTS AND DISCUSSION

3.1. Rheological Property of the Coal–CS Slurry at the Thermal Elevating Stage. The composition of the coliquefaction system was kept unchanged at the thermal elevation stage below the pyrolyzing temperature of the feedstock. The viscous property, on the one hand, for one definite system is a function of the temperature, denoted as $\eta = F(T)$. On the other hand, for the different series, the viscosity is a function of the dosage of the biomass under the same conditions.

When CS was added to the direct liquefaction systems of SLC and SDC, the torque current of the systems was investigated at first stage, and the results were illustrated as Figures 1 and 2.

In Figures 1 and 2, the torque current of all systems decreased with the increase of the temperature of the system. Furthermore, when the CS was added to the liquefaction of ether the SLC or SDC system, the torque current of all coliquefaction systems was larger than that without CS to some extent and it increased with an increase of the CS quantity.

According to Peker et al.,[11] the systems were non-Newtonian flow, because all of the systems were solid–liquid suspensions. The rheological behavior of these systems was dependent upon the interactions between the solid components and the solvent, the strength of the attractive and repulsive forces, and the ratio of the time for reorientation of the components to their original configuration to the time scale of measurement.

With the increase of the dosage of CS, the absorbed dose of the solvent increased because of the lower metamorphosis of
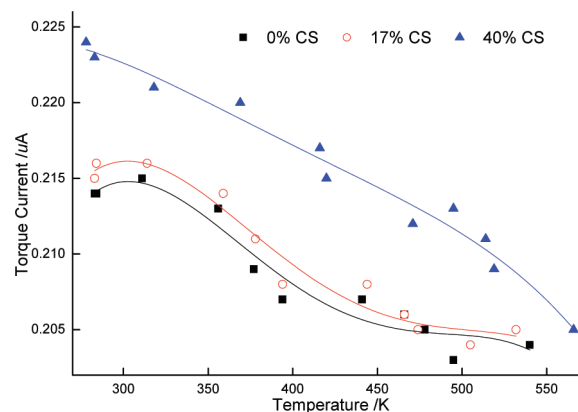

Figure 1. Torque current during thermal calefaction of coliquefaction of SLC and CS.
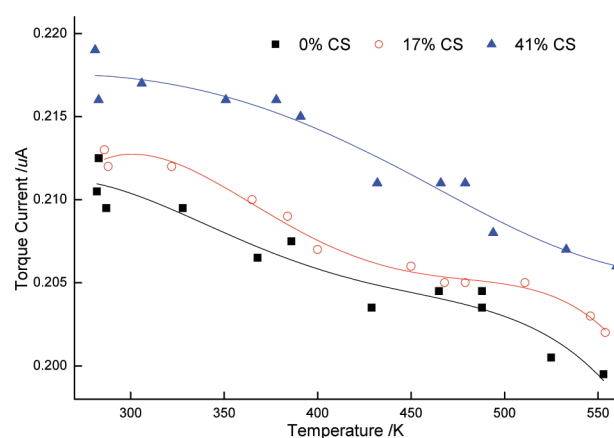

Figure 2. Torque current during thermal calefaction of coliquefaction of SDC and CS.

the CS. The swell of the CS resulted in the relative solid concentration increase and, finally, resulted in the increase of the torque current.

To canvass the influence of CS dosage on the torque current, a set of nonlinear models were established using the least-squares fitting method in accordance with Figures 1 and 2. The results were listed in Table 3.

From Table 3, all of the adjusted coefficients of determination, $\overline{R}^2$, which determined the quality of nonlinear

Table 3. Nonlinear Regressive Results of the Rheological Property of CBOS

| nonlinear model: $y = y_0 + A \exp(-x/t)$			
systems	y_0	A	t	adjusted R^2
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SLC + 0% CS	−170.39	170.62	3.59×10^6	0.88
SLC + 17% CS	0.18	0.06	602.15	0.90
SLC + 40% CS	−2279.75	2279.99	3.81×10^7	0.95
SDC + 0% CS	0.25	−0.03	−1159.77	0.91
SDC + 17% CS	0.17	0.05	880.04	0.96
SDC + 41% CS	0.23	$−3.7 \times 10^{-3}$	−318.82	0.93

regression in coliquefaction systems of coal and CS were larger than 0.87, indicating that the tendency of CBOS viscosity could be predicted with the nonlinear model according to the dosage of CS, approximately, at the thermal calefaction stage.

**3.2. Rheological Property of the Coliquefaction System at the Pyrogenation−Hydrogenation Stage.** The rheological property of the coliquefaction system at the pyrolyzing−hydrogenating stage was defined as the variation of viscosity of the CBOS with the reaction time and temperature from which the biomass started to pyrolyze and to which the biomass began to decrease. Throughout the reaction, biomass and coal did undergo pyrolysis and hydrogenation, converting into pre-asphaltene, asphaltene, and small molecules of oil, gases, and water, a different particle flow from the initial one. Accordingly, the models or regular pattern mentioned before did not match the depiction of the rheological characteristics at the pyrogenation and hydrogenation stage, which redounded the comprehension of the behavior and mechanism in the coliquefaction of coal and biomass.

In this section, the systems of coliquefaction of coal and biomass were heated to 668 K for 90 min, while the rheological property versus time was investigated at this stage.

The viscosity variation in the coliquefaction systems of CS and SLC or SDC on the liquefying reaction time was studied in detail. The results are shown as Figures 3 and 4, respectively.
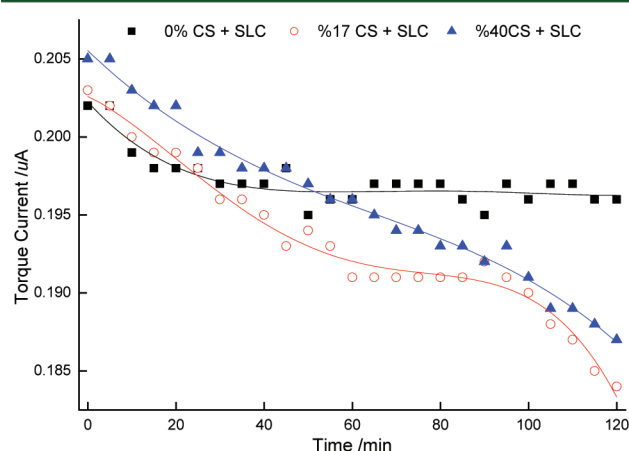
Figure 3. Torque current variation versus time during coliquefaction of SLC and CS.
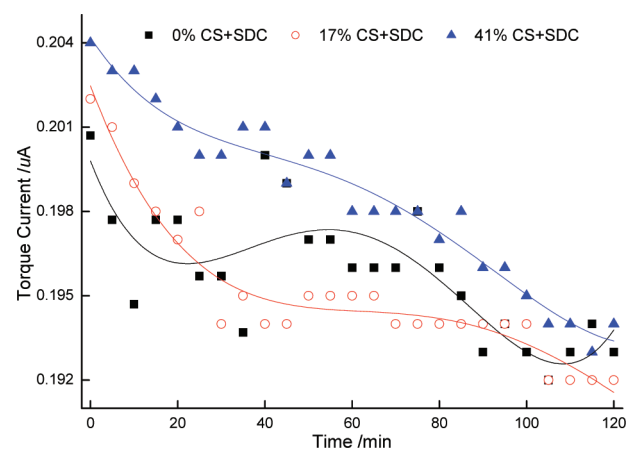
Figure 4. Torque current variation versus time during coliquefaction of SDC and CS.

Figures 3 and 4 illustrate that the torque current of the liquefaction systems decreased with the liquefying time of prolongation and the torque current of the coliquefaction systems of coal and CS decreased more markedly than that of the direct liquefaction system.

From Figure 3, it can be seen that the torque current of the direct liquefaction of SLC decreased rapidly at the thermal hoist before the temperature reached the designated reaction temperature. Then, the torque current of coliquefaction systems of SLC/CS kept decreasing with time, and this may be a result from the continuous conversion of the feedstock into small molecules.

In Figure 4, the torque current of the direct liquefaction system of the SDC decreased with time at first, then increased at the point of 20 min, and reached an extreme value at about 54 min, after which the torque current decreases with time. With the addition of CS to the direct liquefaction system, the torque current of the system kept decreasing with time, and this trended remarkably with the increase of the dosage of CS. In direct liquefaction, the coal particles swell and pyrolyze with the prolongation of the time and calefaction of the temperature. Especially, at the original reaction temperature, the coal pyrolyzed and converted into more viscous mediates, pre-asphaltene and asphaltene, rapidly, resulting in the increase of the torque current of the system. With the conversion of mediates into small molecules, the torque current of the system tends to decrease with time.

When CS was added to the direct liquefaction system, on the one hand, the particulate liquid was diluted by the small molecule product of pyrolysis of CS and, on the other hand, the pyrolysis of mediates, asphaltene and pre-asphaltene, derived from the coal was accelerated by the pyrolysis product of CS. Thus, both kinds of aforementioned effectiveness resulted in the continuing decrease of the torque current in the systems. Furthermore, both kinds of effectiveness were reinforced with increase of the dosage of CS.

3.3. Rheological Property of the Coliquefaction System at the Cooling Stage. After thermal retention time, the heater was turned off, the temperature of the liquefaction system began to decrease, and the system turned into the cooling stage. In this stage, the pyrogenation−hydrogenation stopped or finished approximately. Consequently, the rheological property of the liquefaction systems was regarded as the variation of the torque current of the CBOS with the temperature. The mixture in the system was considered as a very different flow from the initial paste or the reacting slurry. Therefore, it will be helpful to discuss the rheological characteristic of the system for selection of the separation method and the storage stability of the liquid product.
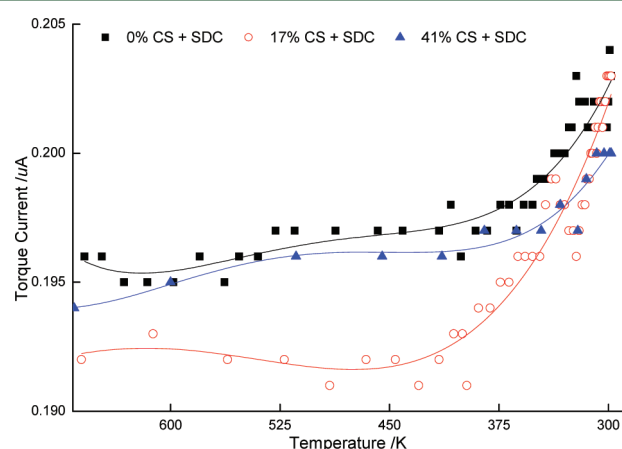
In the course of the cooling, the temperature decreased from 668 to 300 K, and the torque current of the systems was depictured in Figures 5 and 6.

In Figures 5 and 6, the torque current of the systems increased to some extent with the decrease of the temperature from 688 to 300 K. Furthermore, the torque current of the direct liquefaction system was greater than that of the coliquefaction systems of coal and CS for SLC and SDC, respectively. However, the torque current of the coliquefaction systems increased with the increase of the dosage of CS.

The dominant causality between the above-mentioned phenomena and the intrinsic factor was that the mediates of DCL systems, asphaltene and pre-asphaltene, may pyrolyze and
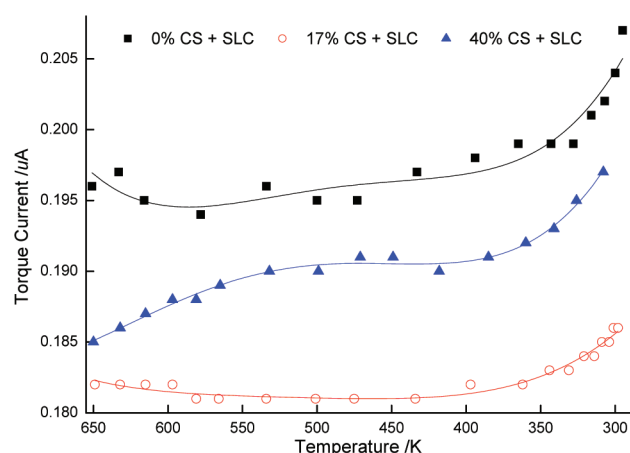
Figure 5. Torque current versus temperature of the coliquefied product of SLC and CS during the cooling phase.

Figure 6. Torque current versus temperature of the coliquefied product of SDC and CS during the cooling phase.

be hydrogenated tardily and incompletely, resulting in the flow product with a strong torque current with a decrease of the temperature. Therefore, in the coliquefaction systems, the diluent and promotive effectiveness of the liquid product derived from CS in the system and the conversion of mediates into the small molecular oil may bring on the decrease of the concentration and torque current of the system with a relative weak flow resistance compared to that of the DCL. However, with the increase of the dosage of CS and the content of polar compounds, such as the oxygen-contained component, an increase in the final liquefaction product strengthened the interaction of the molecules, finally resulting in the increase of the flow resistance of the mixture.

4. SUMMARIZATION AND CONCLUSION

In the course of coliquefaction of coal and CS, the feedstock undergoes pyrogenation and hydrogenation, converting into pre-asphaltene and asphaltene mediates and an oleic, gaseous, residual product, sequentially. Therefore, the system at the final stage is very diverse from the initial stage. As a result, the rheological property of the system cannot be described with a universal model. In this work, the viscosity of the coliquefaction system at three stages was investigated by employing the torque current as the predominant parameter, and some primary conclusions are as follows: (1) At the thermal calefaction stage,

the torque current of all systems decreases with the increase of the temperature. In comparison to the COS, the torque current of the CBOS system is greater and increases with the dosage of CS. The torque current of CBOS can be depictured with a nonlinear exponential decay model at this stage. (2) At the pyrogenation and hydrogenation stage, the torque current of all systems decreases with the increase of the thermal retention time. For the COS of the SLC system, the torque current varies slightly with the thermal retention time because of the weak reactivity of the mediates. The torque current of the COS of the SDC system possesses a maximum at this stage. For CBOS systems, the torque current decreases ascribed to the diluted and promotive effectiveness of the product derived from CS pyrolysis on the system and the mediates. (3) At the cooling stage, the torque current of the systems tends to increase with the decrease of the temperature. The torque current of the COS system is greater than that of the CBOS system, and the torque current of CBOS increases with the dosage of CS.

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Notes
The authors declare no competing financial interest.

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