Catalytic Liquefaction of Lignite by Supercritical Ethanol

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Abstract: Catalytic hydrogenation liquefaction by supercritical ethanol is an effective method for the efficient utilization of lignite. The liquefaction efficiencies of lignite 1(L1) and lignite 2(L2), which were collected from Zhaotong, Yunnan, were compared. It was found that the liquefaction efficiency of L1 was better than L2 but the gas yield of L2 was higher than L1 under the same reaction conditions, indicating that both of them could be effectively converted. The yields of lipids and phenols in the components of liquefaction products were significantly different, and the liquefaction of L2 could achieve the desired conversion effect by changing the reaction conditions. Increasing the amount of ethanol could promote liquefaction efficiency, however, when the ratio of ethanol to coal(E/C) were 20 and 30, the growth rate of the yield of liquefied oil was quite lower than the previous stages. This phenomenon indicated that with the decrease of lignite concentration, the mass transfer effect of ethanol as a solvent in the reaction was getting better and better, and the liquefaction rate increased rapidly. But the higher system pressure was not conducive to liquefaction in high temperature conditions. In addition, the esterification reaction between ethanol and the intermediates of hydrocracking reaction could facilitate liquefaction reaction.

1 Introduction

Supercritical fluid(SCF), with special physical and chemical properties, make supercritical technology become a widely used promising technology. The special properties of supercritical fluid are favorable for reactions [1]: the small diffusion coefficient allows the reactants to be sufficiently contacted, increases the reaction rate and easily controls the solubility and concentration of the reactants via the pressure. In the SCF system, the solubility of products varies markedly with the change of molecular weight, temperature and pressure, so the reaction products can be removed from the reaction system in time to obtain a higher conversion rate. The increase of pressure can increase the reaction rates constant and have different effect on different reaction rates, so the selectivity of the reaction can be changed by this property of SCF. Supercritical fluids are superior to the traditional reaction system, which can not be substituted in terms of reaction selectivity, reaction rate, chemical equilibrium and catalyst life.

The reserve of lignite in the world is very rich, but mainly lignite is low-quality. So it is an important way to ease the energy crisis by rational and efficient use of lignite. High water content, high volatility and low calorific value are the main characteristics of lignite, especially water content is greater than 40% and calorific value is less than 2000kcal/kg. But the price is only 1/4-1/2 of the other coals, and the development and utilization of lignite is very difficult. At present, lignite is mainly used for direct combustion power generation, gasification, pyrolysis and the preparation of montan wax and humic acid, etc, but the use of lignite is with low efficiency and serious pollution. Therefore, it is necessary to develop new direct liquefaction technology for the efficient conversion and use of Yunnan lignite.
Supercritical water has been used for liquefying lignite by many researchers without drying the lignite, but it still requires higher temperature and pressure and the oil and water of later stage should be separated which will increase cost. Some organic solvents instead of water are also used, like toluene, methanol and acetone. Among these supercritical organic solvents, supercritical ethanol has excellent liquefaction properties, such as lower temperature and pressure than water and hydrogen-rich environment producing by steam reforming reaction[5]. Moreover, the alcoholysis effect of ethanol can generate esterification reaction.

Previous studies have reported the upgrading of biomass, the liquefaction of biomass-coal and crude bio- oils in supercritical ethanol. The materials in these studies include lignocellulose[3], lignin[4], cellulose[3, 5], impurity sludge[6] and microalgae[7, 8]. However, most of the raw materials are required for dry pretreatment[9]. It is found that ethanol/water solvent mixed system has a synergistic effect, but the aqueous phase should be separated at the later stage [10-13], and the separation of water-soluble products was costly. Therefore, it is important to seek for more effective liquefaction method in water/ethanol systems to avoid water-soluble products and oil-water separation reactions to reduce operating costs and capital costs.

The development of efficient catalysts is the key to the development of coal liquefaction processes and applied to all of coal liquefaction processes. Although some liquefaction are claimed to run with no catalysts, most of coal itself contain large amounts of minerals such as pyrite and iron oxide that can act as catalysts in the liquefaction process[14]. Studies have shown that some metals are efficient for catalyzing deoxidation hydrogenation, such as Ru, Pt, Pd [15, 16], which are the key to liquefied petroleum refining. Therefore, the Ru/C catalyst was chosen to catalyze the liquefaction of lignite. On the basis of this, the catalytic liquefaction and quality improvement of lignite in supercritical ethanol system was studied. The reaction temperature was 400 ℃ and the reaction time was 60 min. By studying the impact of the ratio of E/C, a longer residence time of 120 min was chosen. The product distribution was analyzed by GC-MS to detect oil quality.

2 Experiments and Methods

2.1 Reagents
The lignite used in the study was collected from Zhaotong, Yunnan. In the laboratory, the coal is crushed and sieved to 80 mesh coal powder and stored in a brown vial keeping in a low temperature and away from light. Dry is not required. Table 1 is the industrial analysis and elemental analysis of L1, Table 2 is the industrial analysis of L2. The Ru/C catalyst, anhydrous ethanol and dichloromethane were purchased from Sigma-Addirich. The metal loading of Ru/C was 5%, anhydrous ethanol and dichloromethane are chromatograph pure.

| M  | A  | V  | FC | C  | H   | N | S  | O   |
|----|----|----|----|----|-----|---|----|-----|
| 29.19 | 7.14 | 36.09 | 27.58 | 45.43 | 4.31 | 1.49 | 1.25 | 29.99 |

| M  | A  | V  | FC |
|----|----|----|----|
| 23.9 | 23.44 | 45.02 | 7.65 |

1 Percent of weight; 2 By difference.

Ad—air dry basis; daf—dry ash free basis; M—content of moisture; A—content of ash; V—content of volatiles; FC—content of fixed carbon

2.2 Experimental apparatus and procedure
The reactor consists of four parts: the top of the Hip part valve, the middle slender buffer tube, the main reaction tube and card sets in the study of lignite supercritical ethanol liquefaction[17]. The volume of
reactor was 10 ml. The reactor needs to be assembled and tested for air tightness prior to the experiment. After adding the appropriate amount of pulverized coal, ethanol and catalyst into the reactor, it is necessary to press the helium several times to drain the air, and then pour 0.2 MPa of helium into the reactor as the reference gas. After sealing, the reactor is placed vertically in a sand bath (model SBL-2) to start the reaction. The temperature of the sand bath is controlled at ± 2 °C and the inside temperature of the reactor reaches the set temperature for only 2 min. After the reaction finished, the reactor was allowed to cool rapidly to room temperature by fan. The heating and cooling time of the device is relatively shorter.

2.3 Analysis
After cooling and stabilizing for 4 hours, the reactor was connected to a GC gas sampling valve for gas analysis. When the analysis progress completed, the residual gas in the reactor is completely discharged. The liquid fraction was collected with methylene chloride and the solid residue was separated. The liquid fraction is a mixture of ethanol, methylene chloride and liquefied petroleum oil. The mixture was placed in a rotary evaporator (water bath temperature 35°C, rotational speed 1.5-2 rad/s, and vacuum degree 0.072 MPa) to remove methylene chloride and ethanol for oil product. When the quality of the evaporation bottle remained unchanged and then cooled and wiped the water outside the evaporation bottle, the quality of the processed evaporation bottle minus the quality of the empty bottle is the quality of the oil. The liquefied oil was dissolved in 5 ml of dichloromethane and placed in a vial and then subjected to GC-MS analysis. GC-TCD for gas detection and GC-MS for liquid analysis have reported in our previous literatures[18, 19]. The syringe used for filtration (the syringe port was connected to an organic filter vacuum filter of 0.45 μ) was dried in a dry oven for 24 hours. After cooling and weighing, the resulting mass minus the mass of the original syringe and the catalyst is the mass of the residue.

3 Results and discussion
3.1 Liquefaction of different coal
Although the water content of L2 is relatively lower than L1, it still meets the characteristics of lignite high water content. In general, moisture is an unfounded inorganic substance in coal, which will increases the difficulty of lignite to transport, handle, store, process and coke. But it can convert the moisture in the lignite to be useful in the supercritical system. It is found that the conversion activity of L2 is higher than L1. Figure 1 shows three-phase product yield of two different coal. It can be seen from the figure 1 that the liquefied oil yield of L1 is 64.76%, which is twice as high as that of L2 (32.23%), but its gasification rate is only 35.15%, which is half of L2 (68.28%), indicating that L1 is more conducive to liquefaction and L2 gasification effect is good under the same reaction conditions.

![Figure 1 Three-phase yield of different coal under the condition of 400 °C, 60 min of the reaction residence time, 50% of the catalyst, and 9 of the ratio of E/C](attachment:image.png)
The product distribution of L1 and L2 is shown in Figure 2, where the components of the liquefied oil are divided into four main components: alkanes, lipids, phenols and others. It can be seen from the figure 2 that the yields of alkanes and others in L1 and L2 are similar, which is 47.17%, 50.54%, 13.09% and 15.46%, respectively. But the yields of lipid and phenolic are different, which is 24.082% and 3.129%, 11.248% and 23.243%, respectively. The difference in functional groups of lignite macromolecules is one of the possible causes of this phenomenon. In addition, the structure of lignite is very complex, and the corresponding liquefaction reaction process is also very complex, which may cause differences in the products. In short, although there are some differences among the gasification rate, residue rate and product distribution of L1 and L2 after liquefaction, they also have high conversion activity. The conversion effects of L1 and L2 is unlike, but the purpose of the use of L1 and L2 is same. In addition, we can change the reaction conditions of L2 to achieve the goal of the conversion activity.

![Figure 2 Products distribution of different coal](image)

3.2 Effect of the ratio of E/C on liquefaction

Ethanol as a hydrogen donor can enhance oil quality by hydrogenation, and react with water to remove water by steam reforming reaction. By changing the amount of ethanol, we want to investigate the effects of the ratio of alcohol to coal of 5, 9, 15, 20 and 30 on liquefaction in Fig 3. With the increase of the amount of ethanol and the decrease of the lignite concentration, the oil yield showed a trend of increasing gradually, indicating that the effect of ethanol was markedly under the condition of high temperature and long reaction time. Duan[20] et al pointed out that the H2 consumption in the system is related to the catalytic hydrogenation time, and the amount of hydrogen capture increases with the increase of time in the experiments of bio-crude oil catalytic hydrogenation of algae, which makes the oil quality rise. It is worth noting that the rate of liquefied oil growth in the ratio of alcohol to coal of 20 and 30 is significantly lower than that of the previous stages. It may be due to lignite concentration decreased with the increase of the ratio of E/C, , and the mass transfer effect of ethanol as a solvent in the reaction is getting better and better, which leads to liquefaction rate increase rapidly. But the system pressure will increase large in high temperature conditions, which may affect the liquefaction effect of lignite. Duan et al found that C2 and C3 decreased with the increase of hydrogen pressure in the pyridine catalytic hydrogenation denitrification study, indicating that hydrogen pressure could inhibit the formation of C2 and C3 in cracking reactions[21]. In addition, ethanol can react with the intermediates of hydrocracking reaction intermediates to generate alcoholysis reaction, which will promote the liquefaction progress.
Figure 3 Effect of ethanol addition on liquefaction at 400 °C, 60 min of the reaction residence time, 50% of the catalyst.

Figure 4 (a) Effect of the ratio of alcohol to coal on the three-phase product with alcohol density of 0.043 g/ml; (b) effect of ratio of alcohol to coal on the three-phase product with alcohol density of 0.086 g/ml; (c) effect of ratio of alcohol to coal on the three-phase product with alcohol density of 0.13 g/ml.

Figure 4 (a), (b) and (c) show the three-phase product changes with the ratio of alcohol to coal under the temperature of 380 °C, 45 min of the reaction residence time, 25% of the catalyst added, and the alcohol density are 0.043 g/ml, 0.086 g/ml and 0.13 g/ml respectively. It can be seen from Fig. 4 (a) that the liquefaction rate is rising, and the slight decrease when the ratio of E/C is 9, that is, when the coal slurry concentration is 10%, may be due to the better mass transfer effect, which leads to the liquefied short chain compound further gasify. Gas products are mainly CH4, CO, CO2 and a small amount of H2, C2H4 and C2H6, resulting in the reduction of liquefied products, and then the coal slurry concentration decreases. In the process of hydrocracking, lignite and ethanol generate esterification reaction to promote liquefaction and make the liquefaction rate increase, resulting in the yield of gas increase first and then decrease. In Fig. 4 (b), a similar reaction mechanism occurs when the ratio of alcohol to coal is 19, that is, when the coal slurry concentration is 5%.

It can be seen from Figure 4 (c) that the liquefaction rate is increasing, indicating that the conditions of alcohol density (0.13 g/ml), temperature, pressure and others promote liquefaction. But the pressure (nearly 30MP) is too large, which will increase the experimental loss. In short, to achieve higher liquefaction efficiency, it is necessary to avoid the induction conditions that easily facilitate gasification. And appropriate increase in reaction temperature and alcohol density can also obtain higher yield of liquefaction products.
4 Conclusion
The liquefaction of L₁ and L₂, which were collected from Zhaotong, Yunnan, was compared. It was found that the liquefaction efficiency of L₁ was better than L₂ but the gas yield of L₂ was higher than L₁ under the same reaction conditions, indicating that both of them could be effectively converted. The yields of lipids and phenols in the components of liquefaction products were significantly different, and the liquefaction of L₂ could achieve the desired conversion effect by changing the reaction conditions. Increasing the amount of ethanol can promote liquefaction in the supercritical reaction system. Gas products are mainly CH₄, CO, CO₂ and a small amount of H₂, C₂H₄, C₂H₆. We should pay attention to avoid the induction conditions of gasification, because the high yield of gas is not conducive to liquefaction. The growth rate of liquefied oil at the stage of the ratio of alcohol to coal of 20 and 30 is obviously lower than that of the previous stage, indicating that the high temperature and high pressure are not conducive to liquefaction. In addition, the esterification reaction between ethanol and the intermediates of hydrocracking reaction facilitates liquefaction.

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