
Experimental Study of Supercritical Ethanol Deoxygenation of Shengli Lignite

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To cite this article:

Zhou Jianming, Hu Xiuxiu, Wang Yiwei, Rao Tianxi, Xu Deping. Experimental Study of Supercritical Ethanol Deoxygenation of Shengli Lignite. *American Journal of Chemical Engineering*. Vol. 6, No. 6, 2018, pp. 121-125. doi: 10.11648/j.ajche.20180606.11

Received: October 24, 2018; **Accepted:** November 20, 2018; **Published:** December 24, 2018

Abstract: In this study, supercritical ethanol process is employed to remove the oxygen-containing functional groups in lignite and the effects of temperature, residence time and ethanol/coal mass ratio on the deoxygenation were systematically investigated. Specifically, the solid and liquid products after supercritical ethanol deoxygenation were characterized by FT-IR and GC/MS. Considering the deoxygenation rate (61.40%) and solid yield (89.62%), the optimal deoxygenation was achieved at 270°C with the residence time of 90 mins and alcohol/coal mass ratio of 5:1. In the liquid products generated at 220°C, the content of aromatic compounds was about 80% while the content of phenols and ester compounds was less than 5%. However, for the liquid products obtained at 270°C, the content of aromatic compounds was decreased by 31.69 % while the volume fraction of O-containing compounds was increased by 2.81 % and the content of phenols and ester compounds was increased to about 35%. During supercritical ethanol process, ether oxygen bonds were cracked. For the O-containing species in the products, phenol and its derivatives were the main components in solid products and esters (mostly ethyl esters) in liquid products.

Keywords: Lignite, Supercritical Ethanol, Deoxygenation Rate, Solid Product Yield, Phenols, Esters

1. Introduction

Lignite reserve is about 130 billion tons in China, which approximately accounts for 13% of total national coal reserve. However, the annual production of high-rank coal is gradually reduced, so the efficient utilization of lignite is becoming increasingly important. Low calorific value and spontaneous combustion of lignite are the main reasons for limiting lignite application. During lignite liquefaction, abundant oxygen could react with hydrogen to generate water, which increases hydrogen consumption and negatively affects economic effectiveness, restricting its utilization [1-5]. Therefore, developing an appropriate process for deoxidization of lignite is the key to elevate its value. Supercritical fluid (SCF) is the fluid with higher temperature and pressure above the critical point and it has dual properties of gas and liquid, such as high solubility/diffusivity and low viscosity. The density of supercritical fluid is close to that of liquid [6], but hundreds of times higher than that of gas. Close to the critical point, slight changes in pressure or temperature could lead to significant variation in fluid density, making it an ideal

solution for dissolving organic matter [7]. These unique properties of supercritical fluid enable it to enter into lignite macromolecule, resulting in higher solubility for small molecules in lignite. Haiyan Luan [8] and other researchers used supercritical methanol treatment to remove oxygenates from Xilinhaote lignite. Specifically, the coal powder was immersed in methanol for 8 h with the solid/liquid ratio of 5:1 using 1% NaOH solid as catalyst. Then the coal sample was treated at 330°C and 8.2 MPa for 60 min where the disintegration rate of 32.94% was reached. Qian Zhang [9] employed high-temperature and high-pressure equipment to treat Xilinhaote lignite with supercritical methanol at 300°C and ~8.5 MPa and concluded that the carboxyl and phenolic hydroxyl groups in the coal are almost completely removed.

In this study, the supercritical ethanol process was used to treat the Shengli lignite. The effects of temperature, residence time and alcohol/coal mass ratio on the removal of oxygen-containing functional groups in Shengli lignite were studied. And additionally, the solid and liquid products were characterized by FT-IR and GC/MS. Meantime, the chemical reactions, functional groups and the distribution of oxygenates in the liquid products were discussed.

2. Experimental Condition

2.1. Raw Coal Properties

The experimental samples (Shengli lignite) were obtained from Xilinhaote, Inner Mongolia. According to GB 475-2008 "Artificial Adoption of Commercial Coal Samples",

Table 1. Proximate and ultimate analysis of lignite sample.

| proximate analysis (Wt%) | | | ultimate analysis(Wt%) | | | | |
|--------------------------|----------------|------------------|------------------------|----------------------|----------------------|----------------------|----------------------|
| M _{ad} | A _d | V _{daf} | w(C _{daf}) | w(H _{daf}) | w(N _{daf}) | w(S _{daf}) | w(O _{daf}) |
| 16.57 | 16.60 | 50.14 | 70.83 | 5.36 | 1.37 | 0.86 | 21.58 |

2.2. Experimental Method

During supercritical alcoholysis, the ethanol and coal sample are mixed according to a certain mass ratio and placed into a high-pressure reaction kettle(Model 4570 High Pressure Reactor from Parr USA), which is then closed and sealed. N₂ is used to purge the air out of the kettle at first, followed by increasing the pressure to 275.8kPa. Subsequently, the cooling water is switched on, heating to the desired temperature at a rate of 5°C /min. After retaining at the constant temperature for a desired residence time, the autoclave was naturally cooled to room temperature in the air. the solid-liquid mixture in the reaction kettle was filtered by vacuum filter. the filtrate was concentrated by evaporation in a rotary evaporator and the liquid product was collected and stored. The solid products was washed in triplicate with chloroform and ethanol, and dried in vacuum oven at 50°C for 12h and before being stored in a brown sample vial under low-temperature for further analysis.

The single factor experiment method was used to study the effect of different conditions on the lignite deoxidization rate. As shown below, the solid yield Y was defined as the mass ratio between solid products generated during supercritical ethanol deoxidization and raw lignite subjected to this deoxidization. While deoxidation rate R, which is used to measure the deoxidation effect of the supercritical ethanol deoxygenation process, is defined as the ratio between total oxygen mass reduction during the deoxygenation process and the total oxygen mass in raw coal.

$$Y = M_1/M_2 \quad (1)$$

$$R = (M_1 w_1(O_{daf}) - M_2 w_2(O_{daf})) / M_1 w_1(O_{daf}) \quad (2)$$

Where M₁ and M₂, are the mass of solid products and raw lignite after and before supercritical ethanol treatment respectively in a dry and ash free basis; w₁(O_{daf}) and w₂(O_{daf}) represent the total oxygen mass content in solid products and raw lignite.

FT-IR (GX II Fourier Infrared Spectrometer from Nicolet, USA) was used to analyze the solid and liquid products before and after alcoholysis. The composition of oxygenated organic compounds in liquid products was studied by GC /MS (PerkinElmer Instruments (Shanghai) Co., Ltd.).

Shengli lignite was crushed, ground and sieved into particles sizes less than 150 μm (80% of which is less than 74 μm). The prepared coal samples were dried in a vacuum oven at 50°C for 12 h and then stored in a dryer at low temperature and lightless environment prior to use. The properties of raw coal are shown in Table 1.

3. Experimental Result

3.1. Effect of Temperature on Deoxidation

The effect of temperature on deoxidation was investigated at 220, 250, 270 and 300°C while the initial pressure (0.1 MPa), residence time(60 min) and alcohol/coal mass ratio (5:1) were kept constant. It should be noted that the critical temperature and pressure of ethanol are 243.1°C and 6.38 MPa, respectively. When the temperature rises above 250°C, the pressure in the kettle is higher than this critical pressure, indicating that the ethanol reaches its supercritical state. The oxygen contents in solid products, the solid yields and the deoxidation rate after lignite supercritical ethanol under different temperatures are shown in Table 2.

Table 2. The effect of temperature on lignite deoxidation supercritical ethanol.

| Temperature/°C | W1(O _{daf})/% | Y/% | R/% |
|----------------|-------------------------|-------|-------|
| 220 | 13.53 | 99.44 | 37.64 |
| 250 | 10.04 | 97.15 | 54.81 |
| 270 | 10.12 | 91.35 | 57.16 |
| 300 | 10.60 | 66.58 | 67.28 |

Table 2 shows that ethanol is under subcritical state at about 220°C with a solid yield of 99.44%. However, due to the alcoholysis, most of the small molecules in the coal are separated from the macromolecules and dissolved in ethanol, so the oxygen content in the solid product is significantly reduced from 21.58% to 13.53%. When the reaction temperature reached 250°C under ethanol supercritical conditions, the solid yield was decreased to 97.15% with an increased weight loss, which could be attributed to the changes in fluid properties and the enhancement in the permeability of ethanol. Under this condition hydrogen bonds between ethanol molecules were substantially reduced while the role of coal molecules was promoted, enhancing the dissolution of some larger molecules into ethanol. However a slight decrease (3.49%) of total oxygen content was observed. When the temperature is further increased from 250°C to 300°C, the solid phase yield decreased to 66.58%, indicating that the volatile matter in coal begins to precipitate. Specifically, the side chain of the lignite molecular was thermally fractured while the small molecule gas and liquid generated from the heterocyclic ring were diffused from the coal surface into the solution, resulting in a decrease in the

mass of the solid products and an increase in the total oxygen content of the solid products. With the progress of the reaction, the adsorbed water, CO₂ and CH₄ in the coal are desorbed, and a small amount of side chain is cracked to form gaseous products. Overall, more volatiles are released and higher deoxidization rate is achieved under higher temperature. However the changes in total oxygen content in solid products turn to be insignificant when the temperature is higher than 250°C.

The increase in temperature contributes to the breakage of covalent bonds in the macromolecular structure of lignite, and also accelerates the thermal decomposition. However, too high temperature for supercritical ethanol deoxidation might, to a large extent, damage coal structure. Considering the deoxidation rate and solid phase yield, the optimum temperature for lignite supercritical ethanol is 270°C.

3.2. Effect of Residence Time on Deoxidation

In this section, 270°C was selected as the reaction temperature and the effect of different residence times (30, 60, 90, 120 mins) on deoxidation was investigated while the other experimental conditions remained the same as that of Section 2.1. The oxygen contents in solid products, the solid yields and the deoxidation rate after supercritical ethanol deoxidation with different residence times are shown in Table 3.

Table 3. The effect of residence time on lignite deoxidation supercritical ethanol.

| Residence time/min | w(O _{daf})/% | Y/% | R/% |
|--------------------|------------------------|-------|-------|
| 30 | 11.47 | 96.44 | 48.76 |
| 60 | 10.12 | 91.35 | 57.16 |
| 90 | 9.29 | 89.62 | 61.40 |
| 120 | 9.25 | 88.92 | 61.90 |

Clearly, longer residence time resulted in lower total oxygen content in solid products and higher deoxidation rate. However, after the residence time exceeds 90 min, the deoxidation rate has little change. As the reactions proceed, the relatively weaker bonds in the macromolecular structure of lignite would break first, generating products with smaller molecular weight. As the residence time increases, the energy of the whole system gradually increases, which causes the breakage of stronger bonds in the lignite macromolecules. Meanwhile, some organic species with larger molecular weight are also decomposed by supercritical alcohol, and some oxygen-containing functional groups are either dissolved into the supercritical solution or released into gas phase; therefore, the total oxygen content in solid products gradually decreases with the extension of the residence time. However, when the residence time is further increased, the alcoholysis and the polycondensation of the coal might simultaneously occur in the system due to the insufficient supply in active hydrogen radicals by supercritical ethanol in the system. When the condensation reaction is dominant in the reaction system, the extended residence time has little effect on the supercritical ethanol deoxidation rate of lignite. Summarily, of the best residence time within the investigated range in this study is 90 min.

3.3. Influence of Alcohol/Coal Mass Ratio on Deoxidation

In the supercritical alcoholysis reaction, ethanol acts as both a reactant and a solvent in the reaction system. During the experiment, the pressure in the autoclave is controlled according to the amount of ethanol added, and the pressure is a critical factor governing the alcoholysis efficiency. Therefore, the mass ratio of alcohol /coal might exert effect on the deoxidation rate of supercritical ethanol. Under the reaction temperature of 270°C with a residence time of 60 min, four mass ratios of alcohol/coal are examined, namely, 3:1, 5:1, 8:1, 10:1, as shown in Table 4.

Table 4. The effect of mass ratio of alcohol coal on the lignite deoxidation supercritical ethanol.

| mass ratio of alcohol to coal | w(O _{daf})/% | Y/% | R/% |
|-------------------------------|------------------------|-------|-------|
| 3:1 | 10.76 | 94.10 | 53.08 |
| 5:1 | 10.12 | 91.35 | 57.16 |
| 8:1 | 16.03 | 89.24 | 33.72 |
| 10:1 | 6.40 | 87.95 | 33.19 |

As shown in Table 4, when the mass ratio of alcohol /coal is increased from 3:1 to 5:1, the deoxidation rate has little change. This might indicate that there is an up-limit level of alcoholysis reaction with increasing addition of ethanol. Therefore, when the mass ratio of ethanol /coal reaches a certain value, the total oxygen contents in solid products are barely changed. Interestingly, when the mass ratio of alcohol /coal is increased to 8:1, the total oxygen content in solid products increases sharply while deoxidation rate decreases. Kunchana et al [10] found that the critical temperature of alcohol and oil mixtures gradually decreases with increasing the alcohol /oil mass ratio while the critical pressure for the system gradually increases. The increase fraction of ethanol has increased the supercritical pressure of the mixture, which converts the system to be subcritical state and thus weakening the solubility of ethanol. The macromolecular component of lignite tends to occur polycondensation reactions, resulting in the decrease in deoxidation rate. On the other hand, the increase in the ethanol fraction also increases the total oxygen content in the system, which might enhance the potential oxidation of coal structure and accordingly reduce the deoxidation rate. Overall, 5:1 should be the optimum mass ratio of alcohol / coal in this study.

Based on the discussion above, the optimum experimental conditions for the supercritical ethanol deoxidation of Shengli lignite would be at 270°C for 90 min with a mass ratio of the ethanol/coal of 5:1, where the deoxidation rate of 61.40 % could be achieved.

4. FT - IR and GC/MS Analysis

4.1. FT-IR Analysis

The solid products (deoxygenated coal) obtained under the aforementioned optimal process conditions and the original coal as well as the liquid phase products were subjected to FT-IR analysis, and the results are shown in Figure 1.

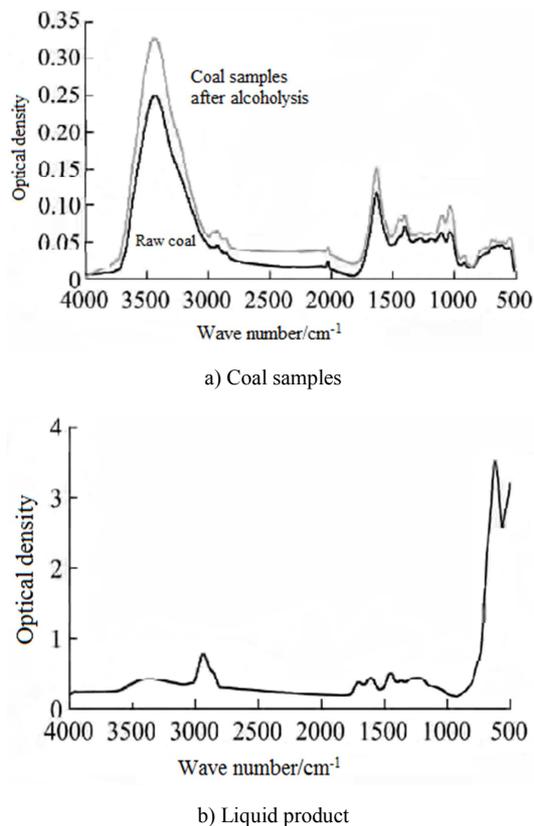


Figure 1. FT-IR analysis of coal and liquid products before and after supercritical alcoholysis.

As shown in Figure 1 the absorption peak at 1300 ~ 1200

Table 5. GC-MS analysis of liquid products from lignite supercritical alcoholysis.

| liquid product | compound volume fraction /% | | | | |
|----------------|-----------------------------|--------|------------------|----------|-------------|
| | phenols | esters | other oxygenated | aromatic | hetero atom |
| A | 0.43 | 4.29 | 11.29 | 79.76 | 4.57 |
| B | 15.04 | 20.23 | 14.10 | 48.07 | 2.51 |

About 80% of the liquid products A are aromatic compounds at 220°C while the volume fraction of phenols and ester oxygenates is less than 5%, and other oxygen-containing compounds are 11.29%. Comparatively, the volume fraction of aromatic compounds in the liquid phase yield at 270°C decreased by 31.69% while the volume fraction of oxygenated compounds increased by 2.81%, and the oxygen content of phenols and esters increased to about 35%. More than 50 organic compounds were detected in the liquid product B at 270°C, including 12 phenolic compounds, 5 esters, 9 alcohols, 3 carboxylic acids, 3 ethers, 2 ketones, 1 aldehyde, 12 kinds of aromatic hydrocarbons and a small amount of hetero atoms-containing compounds. The volume fraction of phenols (mainly phenol and its derivatives) and esters (Mainly ethyl ester) was 15.04% and 20.23%, respectively. These phenolic compounds might derive from the breakage of ether bonds. At 220°C, ethanol is in a subcritical state, where the reaction between ethanol molecules and the oxygen-containing bridge in coal is insignificant. When the ethanol reaches the supercritical state, the ether bonds in the lignite are cracked and promoting the

cm⁻¹ representing the ether oxygen bond in solid products is weaker than that of the original coal, indicating that the ether oxygen bond has been decomposed during alcoholysis process. The vibration peaks of many substituted aromatic hydrocarbons in the range of 900~700 cm⁻¹ become higher, suggesting that the aromatic alkyl side chain of lignite increased after the alcoholysis process due to the dehumidification of the humic acid in lignite during alcoholysis heating process to remove CO₂, and hydrogen radicals are added to the remaining carbon [11-13].

For the analysis of liquid products in Figure 1b, there are apparent absorption peaks at 600~3100 cm⁻¹, which is the -OH stretching vibration peak, indicating the presence of phenol or alcohol. Besides, there is the absorption peak of ethoxy at 1300~1000 cm⁻¹, and the peak at 1700 cm⁻¹ for a dialing C=O bond is also observed [14]. Therefore, the presence of the absorption peaks for hydroxyl, carbonyl and other bonds in the liquid product suggests that during supercritical alcoholysis of Shengli lignite, the coal sample undergoes the decarboxylation reaction and the breakage of the ether bond.

4.2. GC-MS Analysis of Liquid Products

The liquid phase product A obtained at temperature 220°C for 60 min with 5:1 of alcohol /coal mass ratio and liquid product B obtained under the optimum process conditions were all analyzed by GC/MS. The results are shown in Table 5.

formation of phenolic compounds [15]. The results of GC-MS analysis showed that the content of phenolic compounds in liquid B was higher than that of other oxygenates, in consistence with the mechanism on the ether bond cleavage presumed by Wang Yugao [16]. That is, the methylene carbon atom connecting the lignite macromolecule and the oxygen atom is attacked by the nucleophilic oxygen atom of the ethanol, causing the ether oxygen bridge bond on the aliphatic ether side to be broken, thereby generating phenol.

5. Conclusion

(1) With the increase of temperature and the extension of residence time, the supercritical deoxidation rate of lignite increased gradually, but the excessively high temperature could reduce the solid yield. The excessive residence time had no significant effect on the deoxidation rate. The changes in ethanol fraction varies the critical pressure of the mixture, altering the supercritical deoxidation effect on lignite. Optimum experimental conditions for supercritical ethanol

deoxidation of Shengli lignite is 270°C for 90 min with the alcohol/ coal mass ratio of 5:1, where 61.40% of deoxidation rate could be achieved.

(2) FT-IR results showed that during the alcoholysis process, the decarboxylation reaction and the breakage of ether bond might take place. GC-MS results showed that the volume fraction of phenolic and ester oxygenates in the liquid phase increased from less than 5% at 220°C to about 35% at 270°C. The results imply that during supercritical alcoholysis of lignite, the cleavage of ether and oxygen bridge occurs due to the reactions between ethanol and coal molecules, and also the decarboxylation reaction takes place in coal molecules. The liquid product contains a significant amount of phenols and esters.

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