

# Research on Supercritical Methanol Treatment of Lignite

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## ABSTRACT

China has rich lignite reserves which are the proper resources to be liquefied. As its low coalification degree, much hydrogen is wasted. Solvent extraction can save hydrogen and improve its liquefaction performance. The paper studies supercritical methanol treatment of lignite with a device at high temperature and pressure. Experiments mainly focus on the effects of temperature, pressure, catalysts and pretreatment ways on the extraction rate. Results indicate that the extraction rate increases with raising of temperature and pressure below 330°C, 10 MPa. When temperature exceeds 330°C, extraction rate decreases slightly. After swelling pretreatment in methanol for 8 h, the lignite is treated for 60 min at 330°C, 8.2 MPa with NaOH as catalyst(1% wt). The weight ratio of methanol/Xilinhaote lignite is 5/1. Under these conditions, the extraction rate can reach 22.88%.

**Keywords:** Lignite; Supercritical Methanol Treatment; Extraction Rate

## 1. Introduction

Lignite reserves cover 13% of all the coal reserves in China. As its rich reserves and fine liquefaction behavior, lignite becomes high-quality resource to be liquefied. But expensive hydrogen is wasted because water is formed during liquefaction process[1,2]. To treat lignite before liquefaction can help save hydrogen, improve the reactivity of lignite and increase oil yield during liquefaction[3]. Therefore, the pretreatment is of an important significance for its comprehensive utilization.

Solvent extraction of coal is a hot topic because it can study coal structure and get small molecule compounds. Li et al[4] did researches on the relationship of the extraction rate of ash-free coal and extraction temperature in NMP. Hu et al[5] extracted coal with water under its supercritical and subcritical state. They found that temperature and pressure were important factors which influence the extraction results. High temperature and pressure improve solvent diffusion speed and dissolving power as well exacerbate the resolvability of lignite. Yunus et al[6] studied the extraction performance of about 20 kinds of solvents with Soxhlet extraction. The extraction rate has a close relation with solvent polarity. It shows a higher extraction rate in polar solvents than in nonpolar solvents.

Coal structure and operation conditions are the key to extraction results. Coal is made up of condensation aromatic rings as basic framework and side chains. Basic units are connected with ether bonds and methylene bonds. Side chains include alkyls and other functional groups. There is strong acting force between coal molecules such as interionic force, hydrogen bonds and Van der Waals force[7]. Pretreatment should weaken the acting force between coal molecules and dissolve the extracts[8]. Besides coal structure and solvent properties, factors

which influence the speed during mass transfer process include permeation and diffusion [9]. Treatment include two parts. Solvent molecules permeate into coal micro pore structure and then soluble substance spreads outside.

Fluids under supercritical conditions are easier to enter coal molecules and can solve soluble substance better. So the paper adopts supercritical methanol to pretreat lignite. Carbon emission reduces because less CO and CO<sub>2</sub> is produced. Experiments aim at the extraction rate and study the effects of temperature, pressure, catalyst and pretreatment ways on the extraction rate. Optimized technologies lay the foundation for coal liquefaction.

## 2. Experiments

### 2.1. Instruments and Reagents

**Main instruments:** Sartorius BS2109 electronic scale; RE2000E Rotary Evaporator; FYXD2-20/400 autoclave ( $T_{\max}=450$ ,  $P_{\max}=20$ MPa,  $V=2$ L); ZDXS3-5-1200 muffle.

**Reagents:** methanol, tetrahydrofuran, NaOH, H<sub>2</sub>SO<sub>4</sub>. All the reagents are analytically pure.

### 2.2. Lignite Sample

The coal sample is Xilinhaote lignite from Inner Mongolia. The sample has been grinded and sifted(200 mesh). Proximate and ultimate analysis of the sample is shown in **Table 1**.

**Table 1.** Proximate and ultimate analysis of Xilinhaote lignite sample(wt,%).

Proximate analysis			Ultimate analysis, daf				
$M_{ad}$	$A_{ad}$	$V_{daf}$	$C$	$H$	$O^*$	$N$	$S$
9.95	10.21	47.49	65.87	5.13	27.37	1.07	0.56

\*by difference.

<sup>†</sup>High-tech Zones Development Guidance Special of Guangdong Province- Key Problems Tackling and Industrialization Type g(2010A011300038).

### 2.3. Experiment Methods

Mix 200 g coal sample, certain methanol and 2 g catalyst into slurry. After swelling for 8 hours, put it into the autoclave. Heat the mixture at rate of 5 °C/min and stir it at rate of 200 r/min. Pressure is controlled by the intrans volume of methanol. Treat at a constant temperature for a certain time. Turn on the tap to cold down the system. When the temperature is below 70 °C, take out all the material in the autoclave. Separate the solid and liquid after treatment using vacuum suction filtration. Filter residue is washed three times by methanol and tetrahydrofuran. When it is dried, test its ash content and calculate the extraction rate.

### 2.4. Analysis Methods

Define the mass of dry solid before and after treatment as  $M_1$ ,  $M_2$ , ash content as  $A_1, A_2$ , extraction rate as  $E$ . Suppose the weight of ash will not change during the treatment process, so:

$$M_1 \cdot A_1 = M_2 \cdot A_2 \quad (1)$$

$$E = \frac{M_1(1-A_1) - M_2(1-A_2)}{M_1(1-A_1)} \quad (2)$$

According to (1)(2):

$$E = \frac{A_2 - A_1}{A_2(1-A_1)} \times 100\% \quad (3)$$

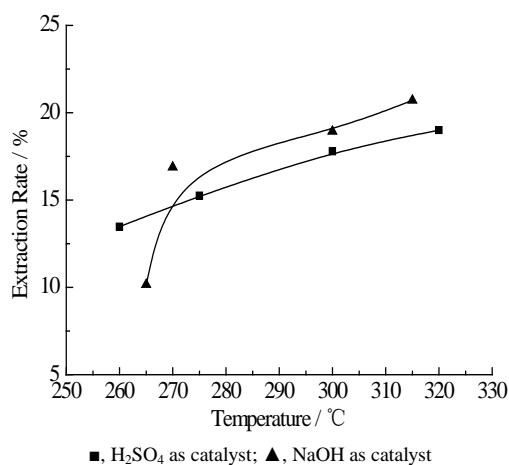
The ash content of the extracts is below 0.1% by the test. That is all the ash is still in the solid. It is feasible to calculate the extraction rate using the above ash balance method.

## 3. Results and Analysis

### 3.1. Effects of Different Treatment Conditions on Extraction Performance

#### 1) Effect of temperature on extraction performance

Take  $H_2SO_4$  and NaOH as catalyst separately. Treat the lignite for 60 min at  $9.0 \pm 0.5$  MPa. The weight ratio of methanol: Xilinhaote lignite is 5:1. Research the effect of temperature on extraction performance ( $T=260-320$  °C). The variation of  $E$  with  $T$  is shown in **Figure 1**.



**Figure 1. The effect of temperature on E.**

As is shown in fig1, with the increase of temperature (260-320 °C) at certain pressure,  $E$  increases obviously no matter the catalyst is sour or basic. At lower temperature, that is near or above the critical temperature of methanol,  $H_2SO_4$  is better than NaOH. When temperature surpasses 270 °C, NaOH is better than  $H_2SO_4$ .

With the rise of temperature, solvent viscosity decreases. Solvent molecules are easier to enter macro molecule structure, leading dissociation of ether bonds. The dissociation speed increase with the increasing temperature. Alcohols provide active hydrogen, therefore free radicals and micro molecules can be stable [13,14]. The solubility of compounds in methanol increases. Hence the extraction rate increases with temperature.

#### 2) Effect of pressure on extraction performance

Take  $H_2SO_4$  and NaOH as catalyst separately. Treat the lignite for 60 min at 260 °C. The weight ratio of methanol/Xilinhaote lignite is 5/1. Research the effect of pressure on extraction performance ( $T=260-320$  °C). The variation of  $E$  with  $T$  is shown in **Figure 2**.

As is shown in **Figure 2**, with the increase of pressure at certain temperature,  $E$  increases obviously no matter the catalyst is sour or basic. When the pressure surpasses 8.1 MPa, NaOH is better than  $H_2SO_4$ .

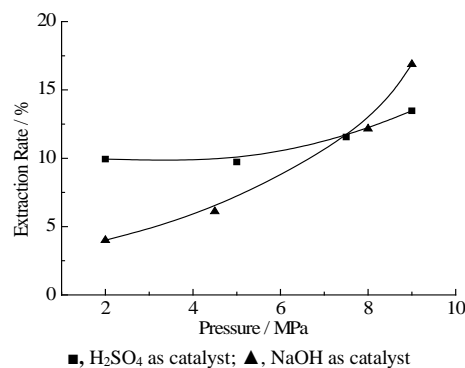
For supercritical fluids, the increase of pressure means increase of solubility. During supercritical treatment, fluids of high solubility makes free radicals move away from coal subjects. Secondary reactions are avoided. At the same time, high pressure can make fresh solvent permeate into coal molecules. The mass transfer speed is raised because of higher turbulivity. Hence the extraction rate increases with pressure.

#### 3) Effect of catalysts on extraction performance

Acid and base can help damage some strong chemical bonds. Through 2.1.1 and 2.1.2, we can make the conclusion that NaOH is better than  $H_2SO_4$  when pressure surpasses methanol critical pressure and temperature above 270 °C. Oxygen exists in coal in the form of carboxyl, hydroxyl and other functional groups. Carboxyl and hydroxyl are acid groups [16-18]. Base can also enforce hydrolyzation of oxygen bonds and increase the content of hydroxyl [19]. Hence to choose base as catalyst is better for raising extraction rate.

#### 4) Effect of pretreatment ways on extraction performance

All the experiment samples above have been swelled in methanol for 8 h. Pretreatment will influence coal molecule structure. The table below shows the effect of different pretreatment ways on the extraction rate at similar temperature and pressure.



**Figure 2. The effect of pressure on E.**

#### 5) Swelling

Compared 1<sup>#</sup> and 3<sup>#</sup> in **Table 2**, after swelling, the extraction rate increases 4.60% at similar treatment conditions. It is proper to make the conclusion that swelling can help increase the extraction rate.

Swelling can weaken the association between coal macro molecules[20]. New structure makes it easier for solvent molecules to touch coal. What's more, micro molecules enter supercritical fluids. Secondary reactions and reverse reactions can be avoided[21].

#### 6) Effect of moisture in coal

Compared 1<sup>#</sup> and 2<sup>#</sup> in **Table 2**, the extraction rate of 1<sup>#</sup> is 1.66% higher than 2<sup>#</sup>, in which the lignite sample is dried. Treatment temperature and catalyst are the same, but treatment pressure of the former is 1MPa higher than the latter. According to the analysis about the effect of pressure on the extraction rate, suppose treatment pressure was the same extraction rate should be similar to each other. It is difficult for H<sub>2</sub>O as an inorganic solvent to solve long-chain compounds, benzene rings and condensed rings in coal. The supercritical condition of H<sub>2</sub>O is  $T_r = 374.3^\circ\text{C}$ ,  $P_r = 22.12\text{MPa}$ . Under the conditions in this paper, H<sub>2</sub>O cannot damage the coal molecules. Compared with large scale of methanol solvent, the effect of moisture in coal can be ignored.

Through the analysis about effects of different experiment conditions on the extraction rate, some conclusions can be draw. To get high extraction rate, we should swell the coal sample, use base as catalyst and make the temperature and pressure above methanol critical point.

### 3.2. Further Discussion on Treatment Temperature

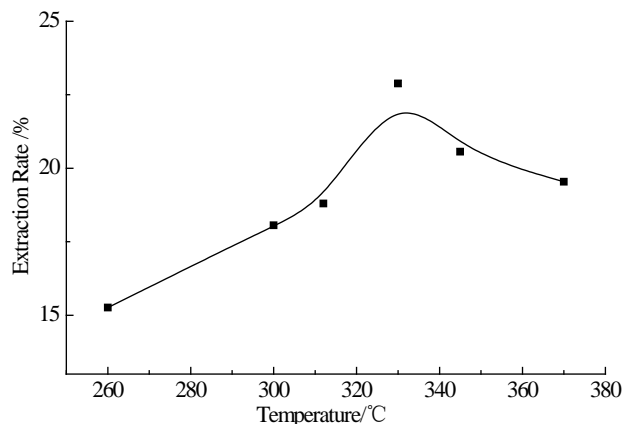
Effects of temperature and pressure on the extraction rate are preliminary investigated through above extraction experiments under different conditions. In fact, pressure of the autoclave is controlled by adjusting the volume of material. Considering that the increase of pressure will bring higher requirement of the equipments and subsequent liquefaction technologies, further studies focus on the extraction rate at higher temperature and pressure of 8.2 MPa. If temperature continues to increase, the weight ratio of solvent/coal will reduce on the basis of the 6:1. Treatment cost can be lower.

The experiment scheme is determined after comprehensive analysis above. Firstly, swell the sample in methanol. With NaOH as catalyst and pressure controlled at 8.2 MPa, increase the temperature gradually from 240°C, which is methanol critical temperature. When the temperature reaches the test temperature, stabilize for 60 min.

The result can be seen in **Figure 3**. During the procedure of temperature varies from 260°C to 320°C, the extraction rate increases obviously, which is consistent with the results of the

**Table 2. The effect of different pretreatment ways on the extraction rate.**

Pretreatment ways	T/°C	P/MPa	Catalyst	E/%
Original sample(1 <sup>#</sup> )	310	10.5	1%NaOH	17.87
Only drying(2 <sup>#</sup> )	310	9.5	1%NaOH	16.21
Swelling (3 <sup>#</sup> )	310	9.5	1%NaOH	22.47



**Figure 3. Variation of E with T.**

foregoing. When the temperature rises to 330°C, the extraction rate reaches the maximum. Continuing to rise the temperature to 370°C, the extraction rate decrease slightly.

The rise of temperature makes the coal pyrolysis accelerating and free radicals generate in a very short period. H-donor ability of methanol is limited and free radicals cannot be stable right away. As a part of free radicals poly-condense together, the extraction rate is decreased[13,14]. Therefore, to obtain a higher extraction rate, the reaction temperature should be maintained at about 330°C.

### 4. Conclusions and Prospect

The extraction rate increases with the raising of temperature and pressure below 330°C, 10 MPa regardless of NaOH or H<sub>2</sub>SO<sub>4</sub> as catalyst and reaches its maximum at 330°C. However, there is a downward trend when continuing to raise temperature. Experiment results show that taking NaOH as catalyst is more conducive to improve the extraction rate than H<sub>2</sub>SO<sub>4</sub>.

After swelling pretreatment in methanol for 8 h, the lignite is treated for 60 min at 330°C, 8.2 MPa with NaOH as catalyst(1% wt). The weight ratio of methanol/Xilinhaote lignite is 5/1. Under these conditions, the extraction rate can reach 22.88%.

In this paper, the influence factors such as temperature, pressure, catalyst and pretreatment on supercritical methanol processing lignite have been studied. But the analysis and separation for the extracts need further exploration.

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