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# Characterization of the liquid intermediates from gasification of lignite in supercritical water: Insights into the gasification process for hydrogen production

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## ABSTRACT

The liquid intermediates formed during supercritical water gasification of lignite have a significant influence on the process. To deeply understand the process, the effects of various process parameters on the components and their distribution in liquid intermediates were examined by GC–MS and FT–IR. GC–MS analysis indicated that the liquid intermediates can be principally grouped as alkenes, alkanes, aromatic hydrocarbons, phenols and oxygen containing compounds. Without adding Ru catalyst, the relative area % of aromatic hydrocarbons, phenols and oxygen containing compounds showed little changes, while that of alkanes increased and alkenes decreased with increasing time and temperature. In contrast, all the percentage area of intermediates, except aromatic hydrocarbons, decreased sharply with Ru catalyst. The unconverted aromatic hydrocarbons mainly consist of p-xylene (15.28%), o-xylene (12.87%), mesitylene (5.99%), naphthalene (8.96%), methylnaphthalene (3.88%), indicating these aromatic hydrocarbons can be regarded as the ‘last hurdle’ to get over for complete gasification of lignite in SCW. FT–IR experimental results correlated well with that obtained by GC–MS. According to the obtained results and previous studies, a simplified schematic diagram illustrating the possible reaction pathways for gasification of lignite in SCW with Ru catalyst was proposed to further understand the SCWG of lignite.

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## Introduction

Lignite have a relatively low heating value because of high moisture (containing 10–40%) and chemically bonded oxygen functionalities [1–3]. Among many approaches, gasification is

an efficient way to utilize the low-grade coal by converting it into gaseous fuel, especially gasification of lignite in supercritical water (SCW,  $P_c > 22.1$  MPa,  $T_c > 374$  °C) for hydrogen production was widely reported in previous articles [4–7]. SCW is miscible with organic compounds and gases, which allows for a high reaction rate because of the elimination of

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mass and heat transfer resistance [8]. In addition, SCW serves as both a solvent and a reactant during the gasification process, the need for drying feedstock can be avoided [9]. Thus, the supercritical water gasification (SCWG) was discovered to be a more efficient way to gasify high-moisture materials and the technology has been devoted more and more attentions in recent years.

There are many literatures reporting the conversion lignite in SCW. Hu et al. [10] studied the extraction of lignite with SCW and found the gas yield was 22 wt% at 550 °C and 30 MPa. Cheng et al. [11] also studied the pyrolysis of low-rank coal in SCW and found that about 68% of the carbon centralized as a residue char under 550 °C and water density of 0.21 g/cm<sup>3</sup>. Yamaguchi et al. [12] investigated the non-catalytic gasification of Victorian brown coal in SCW with quartz reactors, and found the carbon gasification efficiency (CGE, expressed as the total carbon in the gaseous product/the total carbon in feed) was only 34.7 wt% under 800 °C and 6.8 wt% feed concentration. Jin et al. [13] studied the gasification kinetics of hydrogen production from lignite in SCW. In the SCWG of lignite, char conversion process is considered as the rate-determining step, thus they also paid special attention to the progress of char conversion in the process of lignite gasification [14].

It remains a great obstacle for the commercial development of SCWG as lignite is difficult to be gasified in SCW even at a relatively high temperature. In order to achieve complete gasification of lignite, Ge and Guo et al. [5] conducted gasification of lignite in SCW by non-catalytic partial oxidation with H<sub>2</sub>O<sub>2</sub>, and found that complete gasification of lignite can be obtained at 950 °C. However, the operation condition was so severe that they subsequently studied catalytic gasification of lignite in SCW with alkaline catalysts [6]. And the results showed that coal was completely gasified at 700 °C when the weight ratio of K<sub>2</sub>CO<sub>3</sub> to coal was 1. However, alkaline catalysts have problems in the recovery and corrosion of the reactor [15]. On the other hand, the temperature required for complete gasification of coal is still relatively high (700 °C). To overcome the disadvantages, we previously studied the lignite gasification in SCW with Ru/CeO<sub>2</sub>-ZrO<sub>2</sub> as a heterogeneous catalyst and higher than 85 wt% CGE was obtained at a moderate temperature 500 °C [16].

The above researchers mainly focused on the conversion rate of coal in SCW and very few paid full attention to the liquid intermediates generated from the process of gasification. However, the liquid intermediates formed during the supercritical water conversion of coal may have a significant influence on the process. Therefore, it is beneficial to investigate the conversion of liquid intermediates for further understand the gasification routes of lignite in SCW. But unfortunately, to our knowledge, there are only two articles briefly referred to the analysis of liquid products from conversion of coal in SCW. One is that Vostrikov et al. [17] analyzed the extracted substances (butanol and chloroform) from conversion of brown coal at low temperature (<400 °C) by infrared spectroscopy (IR-spectra) and found the hydrocarbon component of substances from water emulsion contained aromatic and aliphatic fragments. The other is that Wu et al. [18] analyzed the hydrogen distributions of liquid fraction (cyclohexane soluble) from extraction of coal with <sup>1</sup>H nuclear magnetic resonance and found that the extraction from SD

coal (a weakly reductive coal) contained a lower content of aliphatic H than that from PS coal (a reductive coal). Their studies provide some information on the liquid products, but that is hardly enough for well understanding the SCWG of lignite.

These gaps motivate our present research. The aim of the present study is to characterize the components and their distribution in liquid intermediates obtained by SCWG of lignite under different conditions. The effect of time, temperature and Ru catalyst on the liquid products were investigated. Based on the results and previous studies, the possible reaction pathways for gasification of lignite in supercritical water were also proposed.

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## Materials and methods

### Materials

Zhaotong lignite was used as feedstock, the characteristics of coal can be found in our previous report [1]. The Ru/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst used was prepared as our previous study [16]. The solvent dichloromethane was purchased from Sigma-Aldrich.

316-stainless steel mini-batch reactors with an internal volume of 4 cm<sup>3</sup> were used in this study. The reactor had a Swagelok cap on one end and a HiP high pressure valve assembly on the other, which have been described in detail in our previous work [16,19].

### Sample preparation

In the present study, we conducted the catalytic and non-catalytic gasification of lignite under different conditions: 390–500 °C and reaction time of 3–32 min with a constant water density of 0.23 g/cm<sup>3</sup> and a constant lignite concentration of 5 wt%. In a typical experiment, the given 0.049 g lignite and 0.098 g catalyst were loaded into a reactor, and then 0.925 mL of freshly deionized water was added. The cap assembly was connected and securely tightened to seal the reactor. The air inside the reactor was replaced with helium by repeated cycles of evacuation and charging with He (0.2 MPa, gauge). Reactions were carried out by placing the reactors vertically in a Techne fluidized sand bath (model SBL-2) maintained at the desired temperature by a Techne TC-8D temperature controller. After the desired reaction time, the reactors were removed and cooled to room temperature by a fan for gas phase analysis. It is worthy to note that the potential catalytic effect of reactor wall was difficult to be eliminated due to the fact that 316-stainless steel reactors were employed. Therefore, the non-catalytic gasification indicated that any additive was not added in the SCWG of lignite. The catalytic effect of reactor wall was neglected under non-catalytic condition, and only the effect of Ru/CeO<sub>2</sub>-ZrO<sub>2</sub> was considered in the catalytic cases in the present study.

After the gas phase was analyzed, the reactors were opened to recover the liquid fraction. 2 mL dichloromethane was added to the reactor, which was then capped and shaken vigorously by hand. The reactor was washed twice more with

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