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Gasification of guaiacol in supercritical water: Detailed reaction pathway and mechanisms

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ABSTRACT

Supercritical water gasification of guaiacol as a model compound for lignin was conducted in quartz reactors. The formation and degradation pathways of intermediates were discussed. The results show that the gasification efficiency of guaiacol in supercritical water increased as the reaction time increased. The intermediates in the residual liquid consisted mainly of phenols, arenes, cyclopentanones, alcohols and organic acids. Phenols and arenes were difficult to be gasified in supercritical water and easily turned into char and tar while cyclopentanones, alcohols and organic acids could be easily gasified and turn into hydrogen-rich gas. The Ru/Al₂O₃ catalyst promoted the degradation of phenols and arenes and thus inhibited the formation of char and tar.

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Introduction

Biomass is mainly composed of cellulose, lignin and hemicellulose together with small amounts of other components like minerals, phenolic substituents and acetyl groups [1]. Lignin is a three-dimensional polymer which is synthesized by polymerization of phenolic monomers. Supercritical water is a very promising reaction medium for converting biomass to gas owing to its peculiar physicochemical property [2,3]. Lignin could be gasified to hydrogen-rich gas in supercritical water [4–7]. The metal and alkaline catalysts could further improve the gasification efficiency of lignin, shorten the reaction time and inhibit the formation of tar and char [8–10].

Owing to the complexity of lignin macromolecules, many studies have used monomeric model compounds such as guaiacol, benzene and phenol as a model compound of lignin for gasification in supercritical water [11–13]. Guaiacol (o-methoxyphenol) contains an aromatic ring with hydroxyl and methoxyl substituents, which is a simple model compound for lignin with important structural features similar to lignin. Several studies have been conducted to look for the reaction pathways of supercritical water gasification (SCWG) of guaiacol [14,15]. SCWG of guaiacol is a complicated reacting process and the gasification production mainly contains hydrogen, methane, carbon dioxide and carbon monoxide. The residual liquid of SCWG of guaiacol contain catechol, phenol, o-cresol and so on [14]. Unlike SCWG of glucose, char formation from guaiacol was promoted in supercritical water

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[15]. Nickel and ruthenium catalysts could significantly promote the hydrodeoxygenation of guaiacol and thus greatly increase the gas yields of SCWG of guaiacol [16–19].

In our previous studies, the degradation pathway of glucose in supercritical water was investigated. The results show that the intermediate products of SCWG of glucose consisted mainly of furans, phenols, arenes, organic acids, alcohols and ketones. The detailed formation and degradation pathways of these intermediates were discussed [20]. Phenols, furans and arenes were hard to be gasified once generated in supercritical water and played an important role in the formation of tar and char.

SCWG of guaiacol has been conducted in some studies and the effects of the heating rate, catalyst and temperature on SCWG of guaiacol have been reported. However, most of these studies were conducted in metal reactors containing significant amounts of Ni and Fe. These metal reactor walls have dramatically catalytic effect on gasification of guaiacol and could disturb the reaction mechanisms analysis of SCWG process [21–23]. Besides, the heating and cooling rate of these metal reactors were slower than quartz reactors. Low heating and cooling rate lead to an increase yield of unwanted intermediates and thus decreased the yields of hydrogen-rich gas [24–26]. In this work, SCWG of guaiacol as a model compound for lignin was conducted in a quartz tube reactor to investigate its conversion pathway and mechanisms. The effects of reaction time and catalyst on SCWG of guaiacol were studied. The catalytic mechanism of Ru/Al₂O₃ catalyst was proposed and the formation process and inhibition mechanism of char was carried out.

Materials and methods

The quartz reactors packed with catalyst and feedstock were prepared using the following procedure. Firstly, the Al₂O₃ catalyst could be measured by a millionth balance and then

put into the quartz reactor by a micro spoon. The guaiacol solution was then withdrawn from a brown bottle and injected into the quartz tube. Secondly, the quartz tube was put into a filtering flask and the filtering flask was evacuated with a vacuum pump. The filtering flask was filled with Ar to ensure that O₂ in the air didn't participate in chemical reactions. Lastly, the quartz tube was sealed by hydro-oxygen flame. So far the quartz reactor was completed.

After the tube furnace was heated to the set temperature, the premade quartz reactor was put into the furnace and it could be heated to the set temperature quickly. After a period of time, the quartz reactor was removed from the tube furnace and cooled in the air. The gas in the reactor was analyzed by gas chromatography while the organics in the residual liquid were extracted by liquid-liquid microextraction method and detected by gas chromatography/mass spectrometry (GC/MS) [20]. The liquid-liquid microextraction method was shown in Fig. 1. A measured amount of ethyl acetate was injected into the bottom of the quartz tube. The tube was then put in a centrifuge tube which was centrifuged in a centrifugal machine to extract organics to ethyl acetate. The ethyl acetate was then withdrawn from the quartz tube and analyzed by GC/MS. The detailed steps were described in our earlier researches [20]. The chemical oxygen demand (COD) of residual liquid was detected by a spectrophotometer. The hydrogen gasification efficiency (HGE), carbon gasification efficiency (CGE) and gas composition are defined as follows:

$$\text{CGE} = \frac{\text{mol of carbon atom in gas product}}{\text{mol of carbon atom in the feed}} \times 100\% \quad (1)$$

$$\text{HGE} = \frac{\text{mol of hydrogen atom in gas product}}{\text{mol of hydrogen atom in the feed}} \times 100\% \quad (2)$$

$$\text{Gas compositions} = \frac{\text{mol of gas product}}{\text{sum of mol of gas product}} \times 100\% \quad (3)$$

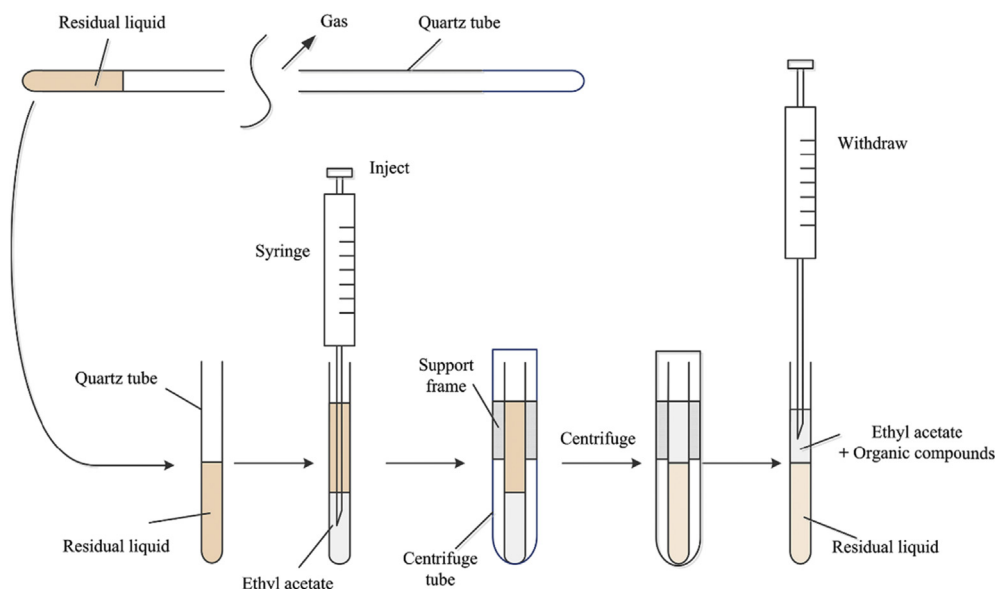


Fig. 1 – The liquid-liquid microextraction method for component analysis [20].

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