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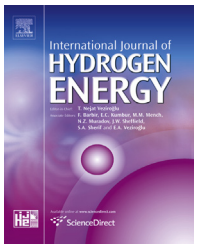

Effects of reaction time and catalyst on gasification of glucose in supercritical water: Detailed reaction pathway and mechanisms

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ABSTRACT

Supercritical water gasification of glucose as a model compound for biomass was conducted in quartz reactors at 500 °C. The concentration of glucose solution was 5 wt.% and the reaction time was adjusted within the range of 10–1800 s. The effects of reaction time and catalyst on the product distribution were investigated and the formation and degradation pathways of intermediate products with and without catalyst were discussed. The results show that the gas yields increased while the yields of organic intermediates in residual liquid decreased with the reaction time. The organic intermediates in residual liquid were mainly composed of phenols, furans, organic acids, alcohols, arenes and ketones. The Ru/Al_2O_3 catalyst had a significant influence on the gasification of glucose, which promoted the degradation of intermediates to gaseous products, increased the yield of hydrogen and inhibited the formation of char.

Introduction

The conversion of biomass to hydrogen-rich gas is a promising technology due to its advantage of being friendly to the environment and reducing the dependence on petroleum. Supercritical water gasification (SCWG) of biomass is an efficient and clean approach for providing hydrogen-rich gas. The gas is produced under higher pressure, leading to a smaller reactor volume and lower energy expenditure to pressurize the gas [1,2]. Supercritical water (SCW) can directly deal with wet feedstocks, thus avoiding the energy requirement of dewatering or drying [2]. Adding catalyst in supercritical water gasification could reduce the reaction temperature, shorten the reaction time, improve the gas yields and decrease the yields of tar and char [3–7].

Supercritical water gasification in a continuous tubular reactor or in a batch cylindrical autoclave could be catalyzed by the reactor metal walls [8]. The metal reactors are made of stainless steel or nickel-based alloy. In order to avoid the interference from the catalytic metal walls, quartz tubes could be used as reactors. The walls of quartz tubes are made of SiO_2 and have no catalytic activity on SCWG, thus the catalytic effect of catalysts in quartz reactors could be evaluated accurately. Resende et al. [9] conducted a series of experiments on cellulose and lignin gasification in quartz reactors with nickel wire, copper wire and iron wire as catalysts. DiLeo & Savage [10] used nickel wire as catalyst to gasify methanol in

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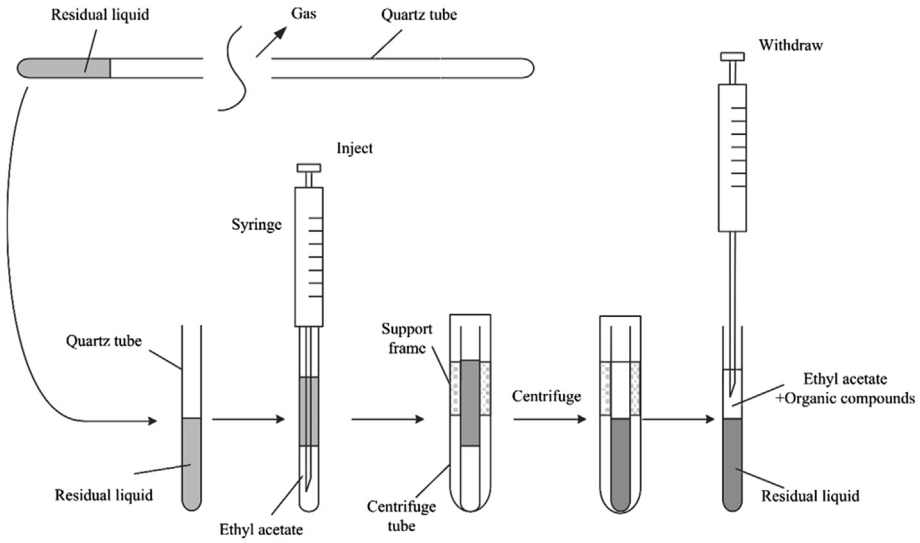

Fig. 1 – The method of liquid–liquid microextraction of organic compounds in the quartz tubes.

quartz reactor and found that nickel wire could obviously improve the hydrogen yield. Another feature of the quartz tube is its small volume. Thus it could be heated to the set temperature rapidly. The hydrothermal gasification of glucose could be enhanced with a high heating rate [11].

Biomass is a renewable resource and mainly consists of cellulose, hemicellulose and lignin. Glucose and cellulose are always selected as model compounds to study the route of biomass degradation [12]. SCWG of glucose is a complicated biochemical reaction process, and the main gasification products are hydrogen, methane, carbon monoxide and carbon dioxide. The organic compounds in residual liquid are mainly composed of phenols, furans, organic acids, aldehydes and ketones [13–15]. Organic acids, aldehydes, and ketones are the intermediates in the formation of gaseous products, while phenols and furans are responsible for the polymerization reaction and the formation of solid char particles [16]. SCWG could be promoted by adding catalysts or increasing reaction temperature. The C–C bond breaking for CO formation could be enhanced at higher temperature [11]. Nickel catalysts could catalyze the water-gas shift reaction ($CO + H_2O \leftrightarrow H_2 + CO_2$) to increase the hydrogen yield of SCWG of glucose [17,18]. NaOH catalyst could increase hydrogen yield by promoting the water–gas shift reaction and capturing CO_2 in the gaseous products [19]. Raney nickel could catalyze the hydrogenation of phenols or phenol precursors, thus inhibiting the formation of char [20]. Alkylphenols were used as lignin model compounds and gasified with supported noble metal catalysts in supercritical water at 673 K and the results show that the activity of the catalyst was in the order of Ru/alumina > Ru/carbon, Rh/carbon > Pt/alumina, Pd/carbon, and Pd/alumina [36].

SCWG of glucose has been doing extensive researches and many mechanism studies on SCWG of glucose have been

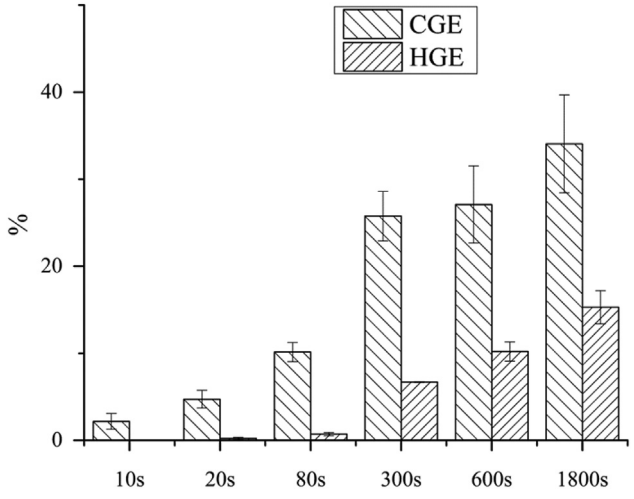

Fig. 2 – The CGE and HGE of SCWG of glucose at different time without catalyst (500 °C, 5.0wt.%, 0.11 g/cm³).

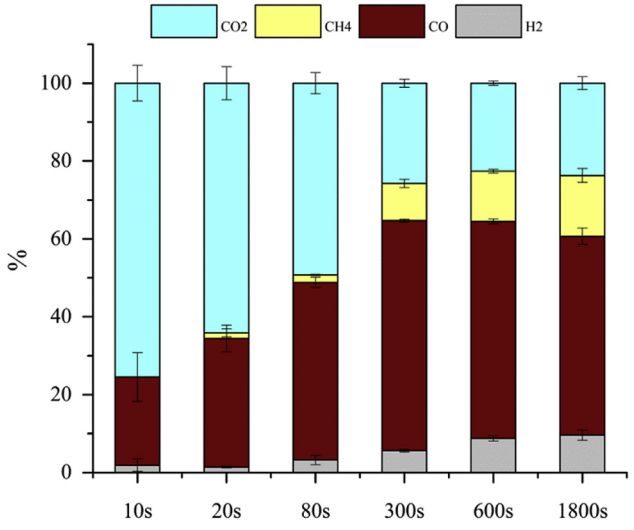

Fig. 3 – The gas compositions of SCWG of glucose at different time without catalyst (500 °C, 5.0wt %, 0.11 g/cm³).