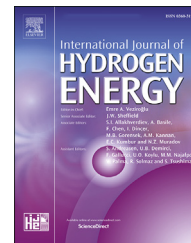


Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/ijhydene

Investigation of the interaction between intermediates from gasification of biomass in supercritical water: Formaldehyde/formic acid mixtures

Y.J. Fan ^{a,b,*}, W. Zhu ^{b,**}, M. Gong ^c, Y. Su ^d, C.Y. Wang ^b

^a Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, Hermann-von-Helmholtz-Platz, 1, 76344, Eggenstein-Leopoldshafen, Germany

^b College of Environment, Hohai University, Nanjing, 210098, PR China

^c School of Civil and Hydraulic Engineering, Hefei University of Technology, Hefei, 230009, PR China

^d College of Civil Engineering, Yancheng Institute of Technology, YanCheng, Jiangsu, 224051, PR China

ARTICLE INFO

Article history:

Received 22 March 2018

Received in revised form

6 May 2018

Accepted 18 May 2018

Available online 19 June 2018

Keywords:

Supercritical water gasification

Hydrogen

Formaldehyde

Formic acid

ABSTRACT

Supercritical water gasification (SCWG) is a promising technology for converting wet biomass and waste into renewable energy. While the fundamental mechanism involved in SCWG of biomass is not completely understood, especially hydrogen (H₂) production produced from the interaction among key intermediates. In the present study, formaldehyde mixed with formic acid as model intermediates were tested in a batch reactor at 400 °C and 25 MPa for 30 min. The gas and liquid phases were collected and analyzed to determine a possible mechanism for H₂ production. Results clearly showed that both gasification efficiency (GE) and hydrogen efficiency (HE) increased with addition of formic acid, and the maximum H₂ yield reached 17.92 mol/kg with a relative formic acid content of 66.67% in the mixtures. The total organic carbon removal rate and formaldehyde conversion rate also increased to 67.33% and 89.81% respectively. The reaction pathways for H₂ formation from mixtures was proposed and evaluated, formic acid promoted self-decomposition of formaldehyde to generate H₂, and induced a radical reaction of generated methanol to produce more H₂.

© 2018 Published by Elsevier Ltd on behalf of Hydrogen Energy Publications LLC.

Introduction

With the traditional fossil energy resources dwindling, as well as strengthening efforts to control carbon emissions, development and utilization of biomass and other renewable

energy are seen as a greener process and has become increasingly more attractive to researchers. In this regard, different thermochemical methods of depolymerizing biomass into high-value energy are being investigated, including fast pyrolysis, wet oxidation and hydrothermal processing, wherein the supercritical water gasification

* Corresponding author. Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, Hermann-von-Helmholtz-Platz, 1, 76344, Eggenstein-Leopoldshafen, Germany.

** Corresponding author.

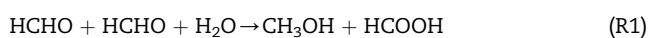
E-mail addresses: yujie.fan@partner.kit.edu (Y.J. Fan), zhuweiteam.hhu@gmail.com (W. Zhu).

<https://doi.org/10.1016/j.ijhydene.2018.05.118>

0360-3199/© 2018 Published by Elsevier Ltd on behalf of Hydrogen Energy Publications LLC.

(SCWG) technology can directly feed wet biomass without pre-drying, and produce hydrogen (H_2) as a clean energy source has been widespread concerned [1–3]. A deep understanding of the mechanism of H_2 formation is required to optimize H_2 production and promote industrialization of this technology.

The SCWG reaction process is considered as complex because of various coupled reactions between organic fractions in the real feedstocks, which makes it difficult to determine the specific reaction processes and transformation pathways [4,5]. The study of model compounds with known compositions can provide deep understanding into the reaction products, pathways, kinetics, and mechanisms of H_2 production from actual biomass. There are numbers of reports on the SCWG of model compounds such as glucose [6–9], cellulose [10–12] and glycerol [13–15], almost unanimously finding that alcohols, aldehydes, acids and other small molecular substances generated during the gasification process are key intermediates and closely related to H_2 production. Therefore, to evaluate the contribution of H_2 from key intermediates, theoretically, the study of formaldehyde and formic acid have the lowest molecular weights and the simplest structures of the aldehydes and organic acids produced during SCWG [16,17], which may render the these more attractive to be used as model compounds. Akgül et al. [18] reported that formaldehyde was involved in two competing disproportionation reactions in hot water. The first of these is self-disproportionation (R1), and second is cross-disproportionation (R2), simultaneously, the generated formic acid decomposes into H_2 , CO and CO_2 through decarboxylation (R3) and dehydration (R4).



Osada et al. [19] investigated the water density dependence of the formaldehyde reactions in SCWG with batch experiments, and found that the gasification efficiency (GE) was very low at temperatures below 400 °C. Kruse's group [20–22] presented that small molecule aldehydes are the main intermediates, which also forms undesired macromolecular pollutants through polymerization reactions instead of gasifying H_2 under moderate conditions. SuSanti et al. [14] demonstrated that conversion of formaldehyde and improved the H_2 production were remarkably increased with reaction temperature (650–750 °C). Furthermore, Watanabe et al. [23] found that acid and base metal oxide catalysts promoted the decomposition of formaldehyde, and acid metal oxide catalysts particularly improved H_2 production. These studies above suggest that formaldehyde is a relatively stable compound in hot water, and generally requires a high temperature or suitable catalyst to achieve desirable gasification.

Formic acid, which is another common intermediate, reacts via reaction (3–4) to generate syngas in supercritical water [18,24]. Moreover, Yasaka et al. [25] and Yoshida et al. [26] explored the relationship between formic acid and the

water-gas shift reaction, revealing that formic acid was the key intermediate in the water-gas shift reaction. More interestingly, the use of formic acid for promoting hydrothermal hydrolysis of organic chemicals has increased in recent years. Yemiş et al. [27] found that formic acid could effectively catalyze conversion of xylose and xylan to furfural by microwave-assisted reaction. Watanabe et al. [28] reported that a high concentration of formic acid and a low temperature favored the formation of levulinic acid from glucose. Onwudili [29] investigated the effects of formic acid on the composition of liquid products during two-stage hydrothermal conversion of alkali lignin in a batch reactor, and found that the mass fraction of liquid products reached up to 40% in the presence of formic acid. Our former study focused on the catalytic efficiency of formic acid on the SCWG of sewage sludge, results revealed that formic acid acted as an active agent to improve gasification and suppress the polymerization to produce undesirable by-products like phenols and char [9,30]. All these studies imply that formic acid is an effective catalyst on decomposition of organic compounds. Meanwhile, Kruse et al. [20] indicated that what was thought to be an effect of the heating rate on the hydrogen production was actually caused by interaction of key intermediates with unequal reactivity.

To our best knowledge, regarding the study of intermediate products whether from SCWG of real feedstock or model compounds, most were concentrated on the characteristics and compositions, proposed reaction pathways were further revealed based on single intermediates or binary mixtures. However, as we mentioned above, formic acid and formaldehyde are the simple but significant key intermediates, especially involved in the H_2 production, only several reports [17,18,24] have reported the reaction pathways of hydrothermal gasification of separate formaldehyde or formic acid, limited information is available on the possible mutual effects between formaldehyde and formic acid in mixtures, as mentioned before, formic acid is not only a simple intermediate, also a promising effective catalyst to improve hydrolysis and decomposition of organic chemicals. It is a great potential to determine the influence of formic acid on gasification of mixtures. Thus, to elucidate the mechanism of the hydrogen production, more detailed information on gas reaction from the mixtures of formic and formaldehyde is required.

The objective of this study is to investigate the gasification efficiency of formaldehyde and formic acid mixtures in SCWG, and further elucidate the impact of formic acid on H_2 production. A possible mechanism was determined and evaluated for H_2 production by analyzing the compositions of the products. The knowledge from these relatively simple reactions could then be applied to the more complex reactions in SCWG of biomass.

Materials and methods

Materials

Formaldehyde (monomeric, 37–38%) and formic acid (88% with 12% water) were purchased from Sinopharm Chemical Reagent Co., Ltd. Aqueous solutions of these reagents were

Download English Version:

<https://daneshyari.com/en/article/7705442>

Download Persian Version:

<https://daneshyari.com/article/7705442>

[Daneshyari.com](https://daneshyari.com)