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# Catalytic supercritical water gasification of proteinaceous biomass: Catalyst performances in gasification of ethanol fermentation stillage with batch and flow reactors



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## HIGHLIGHTS

- Highly active catalysts for low temperature SCWG of ethanol fermentation stillage were found.
- The reaction was structure-insensitive over supported Ru catalysts.
- Catalyst durability in batch reactors was not the same in flow reactors.
- The SCWG reaction mechanism is similar to steam reforming but differs in  $C_2+$  behaviors.

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## ABSTRACT

The catalytic supercritical water gasification (SCWG) characteristics of ethanol fermentation stillage as a model for proteinaceous biomass were examined using batch and flow reactors. Batch reactions conducted at 385 °C and 26 MPa found that certain Ni and Ru catalysts gave almost 100% carbon conversion within 60 min of reaction time, while non-catalyzed reactions gave only 10% conversion for the same duration. Ru generally showed higher catalytic activity per mass of catalyst metal than Ni. Control of the extent of reaction by changing the reaction time and catalyst amount showed that in the case of supported Ru catalysts, major gas component yields ( $CH_4$  and  $CO_2$ ) exhibited respective universal dependence against total carbon yield, despite the varied support materials and Ru particle sizes used. This is an indication that the present reaction system is structure-insensitive with respect to supported Ru catalysts. For repetitive batch reactions, Raney-type Ni catalysts were more stable than supported Ni or Ru catalysts. A modified Raney Ni catalyst that showed better durability than non-modified one in batch reactions did not show advantages in flow reactions, which could be explained by the differences in reaction environment with respect to the two types of reactors. The SCWG reaction pathways of ethanol stillage are discussed in relation to the steam reforming mechanism; the reason for the appearance of minor amounts of  $C_2+$  species in the product gas stream, which is not expected from the steam reforming mechanism, is discussed.

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## 1. Introduction

Hydrothermal gasification of wet organic wastes and biomass, with sub- or super-critical water as a reaction medium, has attracted wide attention as a means of both disposal and conversion to fuel gas (for recent reviews see: [Matsumura et al., 2005, 2013](#); [Elliott, 2008](#); [Peterson et al., 2008](#); [van Rossum et al., 2009](#); [Kruse, 2009](#); [Guo et al., 2010](#); [Azadi and Farnood, 2011](#)). Various

biomass sources including cellulose ([Minowa and Ogi, 1998](#); [Watanabe et al., 2002](#); [Yoshida et al., 2004](#); [Hao et al., 2005](#)), lignin ([Yoshida et al., 2004](#); [Osada et al., 2006a, 2006b](#); [Furusawa et al., 2007](#); [Yamaguchi et al., 2009](#)) and glucose ([Xu et al., 1996](#); [Watanabe et al., 2002](#); [Sinağ et al., 2004](#); [Azadi et al., 2009](#); [Lu et al., 2010](#)) have been examined with respect to their reactivity in gasification with various catalysts. Despite the intensive interest in hydrothermal gasification of biomass, it should be noted that the corresponding reaction of protein-rich biomass has been scarcely examined. Only a few reports are known to the authors: [Elliott et al. \(2004\)](#) gasified two types of dried distiller's grains and solubles (DDG&S) under subcritical hydrothermal conditions with

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a Ru-based catalyst, and Kruse et al. (2005, 2007) examined the addition of meat or amino acids to plant materials for their reactivity in non-catalytic supercritical water gasification (SCWG). The reason for the scarcity may be obvious: the amount of ligno-cellulosic and carbohydrate biomass on the earth far exceeds that of proteinaceous biomass in amount. Also protein has higher value as food rather than as fuel feedstock. Nevertheless, studies on hydrothermal gasification behaviors of protein-rich biomass are of importance, and may be critical in some cases, considering the necessity of disposal and conversion of food- and/or bioprocess-related wastes such as fermentation stillage and sewer sludge, as well as in view of anticipated energy production from protein-containing microalgae by hydrothermal gasification.

The catalytic gasification pathway of biomass in general can be provisionally divided into two stages: in the early stage the reactant macromolecules such as cellulose or protein are decomposed and/or hydrolyzed to smaller molecules, and in the following stage these smaller molecules are converted into gaseous molecules. These processes can be expressed by the following:

Early stage: breakdown of macromolecules to smaller molecules  
 Biomass (cellulose, lignin, protein, etc.) → smaller molecules (1)

Latter stage: similar to hydrocarbon steam reforming  
 $C_xH_yO_z + (x-z)H_2O \rightarrow xCO + (y/2 + x-z)H_2$  “oxygenolysis” (2)

$CO + H_2O \rightleftharpoons CO_2 + H_2$  “water – gas shift” (3)

$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$  “methanation” (4)

The early stage of hydrothermal gasification can be quite complicated, involving a large number of reactions leading to molecular breakdowns as well as possible condensations; as such, it is still far from being understood in detail, with the exception of cellulose feedstock gasification (Sasaki et al., 1998; Kruse et al., 2005). On the other hand, the latter stage of hydrothermal gasification is easier to understand with the analogy to the well-established steam reforming mechanism (Reactions (2)–(4)) (Sealock et al., 1993; Minowa and Ogi, 1998; van Rossum et al., 2009). In this steam reforming mechanism, slow “oxygenolysis” occurs first to breakdown hydrocarbons or carbohydrates into CO and H<sub>2</sub> (Reaction (2)), followed by a fast “water–gas shift” reaction (Reaction (3)) and “methanation” (Reaction (4)). Kruse and Dinjus (2005) have emphasized the importance of the water–gas shift reaction in SCWG of cellulosic biomass. Since the Reactions (3) and (4) are very fast in the presence of active catalysts, the resulting gas phase composition would approach that of equilibrium, which is heavily shifted toward product side at low temperatures (Rostrup-Nielsen, 1984).

This analogy to the hydrocarbon steam reforming mechanism, however, may not be unequivocally accepted as an explanation of the latter stage of hydrothermal gasification. For instance, Osada et al. (2006a) have postulated that CO<sub>2</sub> and H<sub>2</sub> are the initial products appearing in the gas phase in their Ru-catalyzed SCWG of lignin. In the present study, using a rice liquor stillage as a model of protein-rich biomass, we argue that the major part of the latter stage of SCWG could be understood by the above steam reforming mechanism.

Another point noted in the catalytic hydrothermal gasification of biomass is that the catalyst structure–activity relationship as well as catalyst life and deactivation have scarcely been addressed. No systematic studies on catalyst structure–activity relationships such as particle-size effects on the hydrothermal gasification of biomass are known to the authors. As for examinations of catalyst life and deactivation, a detailed study on catalytic wastewater

(*p*-cresol or phenol) gasification has been reported (Elliott, et al., 1994) but only a few reports (Furusawa et al., 2007; Azadi et al., 2009; Lu et al., 2010) have addressed the issue of catalyst deactivation for the hydrothermal gasification of biomass. Herein, we examine the effects of catalyst metal particle size on its SCWG over supported Ru catalysts, concluding that the present reaction system is structure-insensitive with respect to the catalyst. The present study also provides a comparison of the catalyst deactivation behaviors between batch and flow reactors; the results indicate that there are certain differences between the two types, which may be important in view of the fact that very often initial studies on hydrothermal gasification of biomass (catalytic or non-catalytic) are performed using batch reactors.

## 2. Experimental

### 2.1. Materials

For experiments comparing catalyst activities, five commercial catalysts, Ru/Al<sub>2</sub>O<sub>3</sub>(s) (Süd-Chemie, sphere, 2.1 wt% Ru), Ru/Al<sub>2</sub>O<sub>3</sub>(p) (Wako, powder, 5 wt% Ru), Ru/C (Wako, powder, 5 wt% Ru), Ni/Al<sub>2</sub>O<sub>3</sub>(s) (Süd-Chemie, sphere, 12 wt% Ni) and Raney Nickel (Wako, ca. 50% Ni) were employed. For the structure–activity study using Ru catalyst, Ru/charcoal (Johnson-Matthey, particle, 3 wt% Ru) was added to the above catalyst list. All catalysts were used as received, except for Raney Nickel which was treated with a standard leaching procedure and Ni/Al<sub>2</sub>O<sub>3</sub>(s) which was reduced at 500 °C for 2 h under hydrogen atmosphere. For the catalyst deactivation study, an industry-grade Raney Nickel (Nikko Rika, 68.2% Ni) was used as received or with in-house surface modification. Reactant rice liquor stillage was supplied courtesy of Kurosawa Shuzo, Nagano, Japan. The organic content of the stillage comprised 6.9 wt% of solids and 1.5 wt% of ethanol. Elemental N, C and H compositions of the organic matter were 7.1, 42.5 and 7.6 wt %, respectively, as measured by elemental analysis (Flash EA1112, ThermoFinnigan). No sulfur was detected in the reactant.

### 2.2. Equipment and reaction procedures

A stainless steel tube (SUS316, OD=1/2 in., length=150.0 mm) was employed as a batch reactor. One end of the reactor was connected to a needle valve through a stainless steel tube (SUS316, OD=1/8 in.) for retrieval of generated gas. Total volume of the reactor was 8.5 mL. The reaction tube was charged with an appropriate amount of each catalyst (see caption of Fig. 1) and 3.0 mL of rice liquor stillage; gasification was then performed by immersing the charged reaction tube into a molten salt bath kept at 400 °C or 465 °C. The reactor temperature inside quickly rose to 385 °C or 450 °C within 5 min of its immersion into the baths held at 400 °C or 465 °C, respectively, and stayed at that temperature thereafter. These lower reactor temperatures compared to that of the molten salt bath are thought to arise from the heat loss through the valve-connecting pipe. After a predetermined time, the reactor was withdrawn from the bath and flush-cooled under running water to below 40 °C within 5 min. The pressure in the reactor during the reaction held at a 400 °C bath temperature setting was estimated to be 26.2 MPa from a separate experiment. Gases generated by the reaction were collected in a gas bag and its volume was measured by a displacement method. Collected gases were then analyzed by gas chromatography using a thermal conductivity detector (for methane and other inorganic gases) or a flame ionization detector (from C<sub>2</sub> to C<sub>4</sub> components including unsaturated species). Preliminary N analysis was performed using detector tubes (for gas phase) and pack tests (for aqueous phase).

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