



Supercritical water gasification of ethanol production waste over graphite supported ruthenium catalyst



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ABSTRACT

Supercritical water gasification of ethanol production residue from eucalyptus powder was studied over a graphite-supported 5 wt% ruthenium catalyst (Ru/G) in a batch reaction system. The complete gasification of 0.1 g of the residue proceeded over 0.05 g of Ru/G at 673 K in supercritical water with 0.5 g cm^{-3} water density. The gasification behavior of the residue from eucalyptus was compared with that from Japanese cedar to evaluate the potential of fuel gas production from bioethanol production residue. The gasification profiles (gaseous yield and selectivity) of the residues were well reproduced by the linear combination of those of woody biomass fractions (lignin and cellulose).

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1. Introduction

The development of catalytic partial decomposition of plant biomass and the subsequent catalytic transformation of the decomposed chemical blocks for the production of useful platform chemicals, which are currently synthesized by chemical processing of the fossil fuel, would contribute to the establishment of sustainable way of production of chemicals. Ideally, catalytic processes that utilize all the constituents of plant biomass are desirable; however, only the partial usage of constituents of biomass, e.g. cellulose, is until now in progress and other waste fractions, e.g. lignin, are incineration and/or disposal in land filling. The disposal of biomass waste by incineration does not cause much of carbon dioxide emission, because most of the carbon dioxide is utilized for the regrowth of the plant via photosynthesis. However, the thermal recovery by incineration of waste plant biomass is not so efficient as it contains water and drying processes of wet biomass needs energy.

Ethanol production from food resources, such as starch and sucrose, has been commercialized to provide alternative or additives to gasoline [1–6]. The development of manufacturing processes for the production of ethanol from wood-derived cellulose is desirable not only because the competition between energy and food could be eliminated, but also larger amounts of cellulose can be available from woody biomass than those from herbaceous biomass per unit area of land [7–10]. The problem

for the utilization of woody biomass for ethanol production is the treatment of the residue which is mainly a lignin fraction. The residue contains moisture and a drying pretreatment is needed for the thermal recovery by its incineration. Synthetic gas (carbon monoxide and hydrogen) can be obtained by steam reforming of the dried woody powder using nickel catalysts; however, high temperature more than 1000 K is needed and this process suffers from fast deactivation of the catalyst by coking.

Supercritical water gasification technique (critical point of water: 647.3 K and 22.1 MPa) is a prospective way to utilize low-quality wastes and provides fuel gases (methane and hydrogen) from woody biomass using supported metal catalysts [11–16]. The structural stability of the catalyst in supercritical water is important for the development of gasification catalysts, and ruthenium is the most effective metal species while supports like carbon (charcoal [17–19], carbon nanotube [20], and graphite [21]), titania [16,17,22], zirconia [23], and α -alumina [24] are most suitable in supercritical water media. There are several reports for the development of catalytic gasification of organosolv lignin [17–19] and real biomass containing lignin, such as sawdust [24], bagasse [25], bark [26], and a residue from a saccharification process in a bioethanol production system from Japanese cedar, which is a softwood, over supported ruthenium catalysts in supercritical water [27].

We have reported that complete gasification of organosolv lignin proceeded over a graphite supported ruthenium catalyst, having 1.5 wt% ruthenium metal loading, in supercritical water [21]. The supercritical gasification also proceeded over a charcoal supported ruthenium catalyst with 1.5 wt% of ruthenium loading;

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however, the complete gasification could not be obtained under the same reaction condition. Different gasification yields were obtained between the graphite supported and charcoal supported ruthenium catalysts, which could be explained by the gasification mechanism of organosolv lignin and the structure of supported ruthenium catalysts. Organosolv lignin was hydrolyzed to small molecules, such as alkylphenols, formaldehyde, and glycerin and the small molecules are gasified over ruthenium metal particles in supercritical water [12]. The size of ruthenium metal particles in the graphite supported catalyst are almost the same as that of the charcoal supported catalyst; however most of ruthenium metal particles are located on flat plate-like graphite particles with few micropore and parts of ruthenium metal particles in micropores in the charcoal-supported catalyst. Easy accessibility of hydrolyzed small molecules from organosolv lignin in supercritical water to ruthenium metal particles on the flat graphite surfaces enables the complete gasification [21].

In this study, we report the gasification of an ethanol production residue from eucalyptus, which is a hard wood, in supercritical water with the graphite supported ruthenium metal catalyst. Based on comparative study with the gasification behavior (in terms of yield, TOF, and gaseous selectivity) of organosolv lignin and cellulose, which are model fractions of woody biomass, and also the saccharification residue from cedar powder, we discuss (i) the potential of the graphite supported ruthenium metal catalyst for the gasification of residue, and (ii) the effect of kind of wood type and cellulose fraction on the catalytic gasification of residue from woody biomass in supercritical water media.

2. Experimental

The sample preparation of sulfuric acid free solid residue from eucalyptus for ethanol production process is described as follows [28]. Eucalyptus powder pulverized in a disk mill was treated with cellulase and yeast for simultaneous saccharification and fermentation. Following to the separation of the prepared slurry by filtration, the solid residue was washed with distilled water, and then the residue was dried at 378 K for 12 h.

The solid residue from Japanese cedar powder was obtained as follows. Following the saccharification of Japanese cedar already pulverized in a tandem-ring mill, the solid fraction was filtered, washed with distilled water, and then, dried at 378 K for 12 h [29,30].

Reference samples, organosolv lignin and cellulose powder were purchased from Sigma–Aldrich Cooperation. All the chemicals were used without further purification.

The elementary composition was determined by ultimate CHNS analyzer (CE Instruments EA1110) and O analyzer (CE Instruments EA1112). For the composition analysis, the lignin content in the residue samples was determined as insoluble in aqueous 72% sulfuric acid solution [31] and the holocellulose (total polysaccharide composed of cellulose and hemicellulose) content was determined as insoluble in hypochlorous acid [32].

The catalysts were prepared with an impregnation method using 1.5% aqueous solution of ruthenium(III) nitrosyl nitrate (STREM Chemicals) and graphite powder (TCI HSAG300, surface area 300 m² g⁻¹), followed by the treatment under flowing hydrogen at 573 K for 2 h [21]. The ruthenium metal loading for the catalyst was 5 wt%.

Catalytic gasification was conducted in a stainless-steel 316 reactor with an internal volume of 6 cm³. Known amounts of catalyst, organic sample (residue, organosolv lignin, and cellulose for the respective gasification), and 3 g of water were charged to the reactor; the amount of water corresponded to a density of 0.5 g cm⁻³. The air inside the reactor was removed by purging with

Table 1
Elemental composition of the residues and reference samples.

	Elemental analysis (wt%)					
	C	H	O	N	S	ash
Residue from eucalyptus	52.7	5.9	36.7	0.9	0.0	1.7
Organosolv lignin	65.4	5.9	28.2	0.2	0.0	0.02
Cellulose	42.0	6.4	49.0	0.0	0.0	0.01

argon gas. The reactor was submerged into a preheated sand bath (ACRAFT, model AT-1B) at 673 K and the internal temperature of the reactor was monitored by a K-type thermocouple. The reaction period reported here includes the heating up period (5 min) also. Although we did not measure the partial pressure of water inside the reactor at 673 K it was estimated to be as high as 37 MPa [33]. After a given reaction time, the reactor was taken out from the sand bath and submerged into a water bath for rapid cooling to room temperature. Gaseous products were collected by a syringe and injected through sampling loops attached to a gas chromatograph for its analysis by a thermal conductivity detector (Shimadzu, model GC-8A) using a Shincarbon ST column. After the gaseous products were sampled, the remaining products in the reactor were recovered with pure water and separated as water-soluble and water-insoluble fractions. Because the water-insoluble solid fraction also contained the catalysts used, we evaluated the amount of water-insoluble products by subtracting the weight of the catalyst charged from the former.

The amounts of organic carbon in the water-soluble fractions were evaluated using a total organic carbon analyzer (Shimadzu, model TOC-V).

The product yield based on the amount of carbon and the gas composition are defined as given below,

product yield based on carbon(C%)

$$= \frac{\text{moles of carbon in the product}}{\text{moles of carbon in the reactant sample}} \times 100 \quad (1)$$

$$\text{gas composition(\%)} = \frac{\text{moles of gaseous product}}{\text{sum of moles of gaseous product}} \times 100 \quad (2)$$

The turnover number of Ru/G is defined as given below,

turnover number(TON)

$$= \frac{\text{moles of carbon in the gaseous product}}{\text{moles of surface ruthenium atoms in Ru/G}} \quad (3)$$

Some experiments were repeated three times to quantify run to run variability. The average of these trials was included in the figures along with the standard deviations.

3. Results and discussion

3.1. Residue sample

The elemental analysis of the eucalyptus residue, organosolv lignin and cellulose is shown in Table 1.

The carbon content value of the residue from eucalyptus was lower than that of the organosolv lignin sample but higher than that of the cellulose sample. On the other hand, the oxygen content in the residue sample was higher than that of the organosolv lignin sample but lower than that of the cellulose sample. The residue sample contained 0.9% nitrogen, which would be derived from cellulase and/or yeast used for saccharification and/or fermentation; however, it should be emphasized that the residue sample did not contain any sulfur.

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