



## Production of ketones from pyrolygneous acid of woody biomass pyrolysis over an iron-oxide catalyst <sup>☆</sup>

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### ABSTRACT

Catalytic upgrading of pyrolygneous acid, by-product from slow pyrolysis of woody biomass for char production, was carried out using zirconia-supported iron-oxide catalysts under a steam atmosphere at temperatures ranging from 623 to 723 K, and the effect of ZrO<sub>2</sub> content in the ZrO<sub>2</sub>–FeO<sub>x</sub> catalysts on catalytic activity and ketone yields was investigated. It was demonstrated that hydroxyacetone and carboxylic acids (acetic and propionic acids) in the pyrolygneous acid were converted into aliphatic ketones (acetone and 2-butanone) via a ketonization reaction over the ZrO<sub>2</sub>–FeO<sub>x</sub> catalyst. However, reaction inhibition by metal impurities in the pyrolygneous acid such as potassium (K) and magnesium (Mg) was also observed. These metal impurities could be removed from the pyrolygneous acid without changing the organic composition by using an ion-exchange resin. The removal of the metal impurities was effective in increasing the ketone yields. Moreover, as the W/F value (W: Amount of catalyst, and F: Flow rate of the pyrolygneous acid in the feed) increased, the ketone yield increased up to approximately 30 C mol%, and the ketone fraction in the liquid product reached 55 C mol%.

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### 1. Introduction

In response to the need for alternatives to petroleum-based energy and the desire to use renewable resources for chemical production, many efforts have recently been concentrated on conversion of biomass into energy and useful chemicals. Sustainability in energy recovery from biomass such as steam gasification of char is becoming attractive because biomass to energy conversion adds no additional greenhouse gases to the atmosphere [1,2]. The char as high-quality solid fuel is produced from pyrolysis and its higher yield can be recovered by slow pyrolysis than fast or flash ones [3,4]. During slow pyrolysis (low-moderate temperature and slow heating rate process), volatile matters are condensed into two liquid fractions, an aqueous and an organic liquid fractions. The organic liquid fraction has higher carbon concentration and heating value than the aqueous one because the aqueous fraction is characterized by high water content, relative low carbon concentration, and very low heating value [5]. Therefore, the organic liquid fraction has potentiality for fuel application [6]. The aqueous fraction,

also known as pyrolygneous acid, will create waste-water disposal problems, although this could be incinerated [3,5].

The pyrolygneous acid, a by-product from slow pyrolysis of woody biomass for char production, dissolves organics (such as acetic acid, methanol, and phenolic compounds) in water. Therefore, the possible wet utilization basis and catalytic upgrading is required for its conversion to higher value chemicals. In the previous study, we have developed ZrO<sub>2</sub>–FeO<sub>x</sub> catalysts to selectively produce valuable chemicals such as phenol and ketones from palm waste, sewage sludge, and coliform-fermented residue-derived tars [7–9]. Because the ZrO<sub>2</sub>–FeO<sub>x</sub> catalyst possesses oxidation activity towards hydrocarbons, it is possible to reduce the amount of deposited carbonaceous residue on the catalyst [10].

In aqueous solution of pyrolygneous acid, many organics such as carboxylic acid and alcohol were contained. Because the ZrO<sub>2</sub>–FeO<sub>x</sub> catalysts possess ketonization activities from carboxylic acid and alcohol, we examined the catalytic upgrading of the pyrolygneous acid derived from woody biomass over ZrO<sub>2</sub>–FeO<sub>x</sub> catalysts to produce useful chemicals. Here, the catalytic upgrading is the process integration of slow pyrolysis for biomass utilization. The effects of the reaction temperature, catalyst composition, metal impurities in the pyrolygneous acid, and W/F values on the catalytic activity and product yields were investigated. Moreover, catalytic reactions using model compounds were also carried out in order to clarify the reaction routes.

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## 2. Experimental

### 2.1. Material

The pyrolygneous acid was produced from slow pyrolysis of dried Japanese cedar woodchips for char production using a horizontal screw-conveyor reactor. The chips have an average size of  $10 \times 10 \times 2$  mm, 50.9 wt.% carbon and 3 wt.% moisture content. The pyrolysis was carried out with a feeding rate, an average residence time, a heating rate, a peak temperature, and a gas pressure inside the reactor of  $270 \text{ g h}^{-1}$ , 47 s,  $5.0\text{--}5.5 \text{ }^\circ\text{C s}^{-1}$ ,  $500 \text{ }^\circ\text{C}$ , and 1.0 atm, respectively [2]. The slow pyrolysis produces char, heavy tar, light tar which consist of two separate phases: organic liquid (water-insoluble fraction) and pyrolygneous acid (water-soluble fraction), and gaseous products. Carbon concentration of feed for the pyrolysis (woodchips) and the products (char, heavy tar, organic liquid, pyrolygneous acid) was analyzed by elemental analysis (Costech, ECS 4010 CHNS-O) and the weights of used feed and the products were measured and then, each of them was calculated in C mol. During the pyrolysis, gas and non-condensable volatile (gaseous products) were collected in gas pack and then analyzed by gas chromatography with TCD and FID detectors. Total gas produced was also calculated in C mol. All the products after the pyrolysis were divided by C mol used feed to determine the yield in C mol%.

Furthermore, the chemical compositions of pyrolygneous acid (feed for the catalytic reaction) were analyzed using a GC-17A (Shimadzu, CP-Pora PLOT Q capillary column) for identification of volatile chemical compounds such as acetaldehyde, methanol, acetone, and 2-butanone using ethanol as an internal standard. Then, higher vapor pressure chemicals such as hydroxyacetone, acetic acid, phenol were analyzed by a GC-2014 (Shimadzu, DB-WX capillary column), and a GC/MS-QP5050 (Shimadzu, CP-Pora PLOT Q\_DB-WX capillary columns) with n-butanol as an internal standard. Because heavy components undetectable by gas chromatography were contained in the pyrolygneous acid, the amount of carbon measured by elemental analysis was considered to be the total amount of carbon in the pyrolygneous acid. The yield of pyrolygneous acid was shown as C mol% by divided C mol pyrolygneous acid based on GC analysis with its C mol based on elemental analysis. Moreover, the GC/MS analysis was used for the quantitative identification of chemical compounds in the pyrolygneous acid. Then, the amount of metal impurities in the pyrolygneous acid was determined by X-ray fluorescence (XRF, Rigaku Corporation, Supermini-GR16008).

### 2.2. Catalyst preparation and characterization

All reagents were purchased from Wako Pure Chemical Industries, Ltd (Japan). The zirconia-supported iron-oxide ( $\text{ZrO}_2(\text{Y})\text{-FeO}_x$ : Y = wt.%  $\text{ZrO}_2$ ) catalysts were prepared using a co-precipitation method in an aqueous solution of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  using aqueous ammonia. The obtained catalysts were calcined at 773 K for 2 h in an air atmosphere [9]. Catalysts with  $\text{ZrO}_2$  content of 8.9, 50, and 70 wt.% were prepared, and their crystallinity characterized by X-ray diffraction (XRD, JEOL, JDX-8020).

### 2.3. Cation-exchange treatment for the pyrolygneous acid

XRF analysis revealed that the pyrolygneous acid contained potassium (K) and magnesium (Mg) as metal impurities. A cation-exchange resin [MP Biomedicals, LLC: Amberlite®IR-120 plus (H)] was used to remove alkali and alkaline earth metals such as K and Mg from the pyrolygneous acid. The treatment was carried

out in standard glass bottle (25 ml) by placing 5 ml of pyrolygneous acid into 2 g of the resin for 24 h at 275 K with occasional shaking.

### 2.4. Catalytic reaction

Catalytic reactions were carried out in a fixed bed flow reactor for 2 h at 623–723 K under atmospheric pressure. Fig. 1 shows a schematic of the experimental apparatus.  $\text{ZrO}_2\text{-FeO}_x$  catalysts were pelletized without any binders, then crushed and sieved to provide pieces 300–850  $\mu\text{m}$  in diameter. The pyrolygneous acids prior to and after cation-exchange treatment were used as feedstocks. Nitrogen gas ( $10 \text{ cm}^3 \text{ min}^{-1}$ ) was introduced as the carrier gas. The pyrolygneous acids and  $\text{H}_2\text{O}$  were mixed in a 1:1 weight ratio and fed into the reactor at  $2 \text{ ml h}^{-1}$  using a syringe pump. The time-factors, W/F, were 1–4 h. The liquid and gaseous products were collected in an ice/water trap and gas pack, respectively. The liquid product and catalyst crystallinity after each reaction were analyzed using the same gas chromatographs, elemental analyzer, and XRD as mentioned above. Gaseous products were analyzed by gas chromatography [GS-20B (Shimadzu, FID detector) and GC-8A (Shimadzu, TCD detector)].

## 3. Results and discussion

### 3.1. Chemical composition of the pyrolygneous acid

During pyrolysis of the woodchips biomass, organic chemical bonds such as C–C and C–O bonds were decomposed by dehydration, hydrolysis, oxidation, decarboxylation, and depolymerization to produce gaseous products, water vapor, tar, and volatiles. The water vapor, tar, and volatiles generated from the biomass were condensed and collected by filter and cold traps of different temperatures (393, 278, and 233 K, respectively), and three types of tar (heavy tar, an organic liquid fraction and pyrolygneous acid) were obtained. Incondensable volatiles and gaseous products were recovered as gas products. The remaining residue of the pyrolysis process was recovered as char. Yields of the pyrolygneous acid, the organic liquid and heavy tar on the basis of carbon concentration in the woodchips were 14.0, 3.3, and 39.8 C mol%, respectively, and the yields of all of pyrolysis products including gas and char are listed in Table 1.

Since the chemicals contained in the pyrolygneous acid dissolved in water, it was considered that they consisted of polar compounds of low molecular weight, and thus the pyrolygneous acid was mainly derived from the pyrolysis of cellulose and hemicellulose. On the other hand, the portion of the organic liquid that was

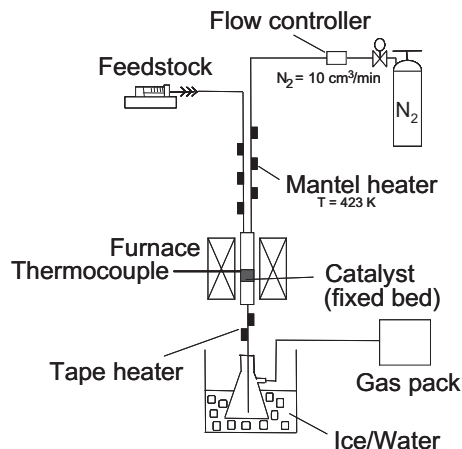


Fig. 1. Schematic of experimental apparatus.

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