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Selective production of ketones from biomass waste containing a large amount of water using an iron oxide catalyst

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ABSTRACT

The disposal of biomass waste containing large amounts of water by burial in the ground or burning causes environmental problems. Therefore, efficient methods for the treatment of biomass waste are required. In this study, conversion of livestock manure, a significant biomass waste, to useful chemicals such as ketones was carried out using a new conversion process consisting of hydrothermal treatment and reaction in the presence of an iron oxide. We succeeded in the selective production of acetone from a livestock manure-derived slurry liquid using the iron oxide catalyst. Moreover, the acetone yield in the product liquid was increased with increasing concentration of acetic acid in the slurry liquid.

1. Introduction

In dairy regions, a large quantity of livestock manure is produced every day. Livestock manure is a biomass waste that contains large amounts of water and is generally used as a fertilizer. However, surplus amounts of livestock manure are disposed of by burying the material in the ground or burning it, which contributes to ground pollution and water contamination. Therefore, efficient methods for the disposal and treatment of livestock manure are required. Previously, several processes were described that used manure as an energy resource, for example in the production of methane and hydrogen [1] and treatment of biomass slurry as a microbial fuel cell [2]. Because biomass waste contains an abundance of organic compounds, it is also expected to be a valuable feed material for chemical resources.

We propose herein a new conversion process to convert high water content biomass into useful chemicals. The outline of the new conversion process is shown in Fig. 1. The water content in the livestock manure is approximately 95 wt%. Accordingly, the liquid component is simply separated from the livestock manure by filtration to obtain the solid component with a lower water content of 70 wt%. The solid component is decomposed to lower molecular weight organics by hydrothermal treatment in sub- or supercritical water [3,4], and a water soluble organics solution (slurry liquid) is obtained. Next, a catalytic reaction is carried out using the obtained slurry liquid as a feedstock, thus converting the low molecular weight organics into useful chemicals [5–7]. In addition, NH_3 or urea is recovered from the liquid component of the livestock manure by adsorption on magnesium phosphate ($MgHPO_4 \cdot 6H_2O$) [8].

Because biomass waste, including livestock manure, contains a large amount of water, stable activity in a steam atmosphere is required for the catalytic conversion process. We developed an iron oxide catalyst as an efficient catalyst for the conversion of chemicals in high water content biomass [9]. Moreover, we previously reported that addition of zirconia to the iron oxide catalyst enhanced the catalytic activity [10] and have succeeded in selectively producing ketones and phenol from palm oil waste [5], sewage sludge [6] and coliform-fermented residue [7] in a steam atmosphere using the catalyst. Because the iron oxide catalyst possesses oxidation activity, it is only minimally deactivated by coke deposition [11]. Therefore, this catalyst was expected to also be suitable for reactions with the livestock manure-derived slurry liquid.

In this study, livestock manure was hydrothermally decomposed to obtain a slurry liquid, and a catalytic reaction with the slurry liquid to produce useful chemicals such as acetone was carried out using iron oxide catalysts. First, catalytic reactions using differently prepared iron oxide catalysts were carried out. Next, the effect of the composition of the slurry liquid on the production of acetone was investigated.

2. Experimental

2.1. Preparation of iron oxide catalysts

All reagents were purchased from Wako Pure Chemical Industries (Japan). The composite metal oxide catalyst of Fe and Zr (abbreviated ZrO_2–FeO_X) was prepared by a coprecipitation

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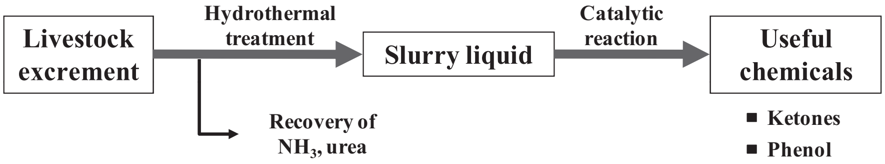

Fig. 1. Outline of efficient livestock manure conversion process.

method, where ferri-hydroxide precipitates were prepared by addition of aqueous NH_3 into an aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ and $ZrO(NO_3)_2$. The ZrO_2 composition of the catalysts was 8.9 wt%. The obtained catalysts were calcined at 773 K for 2 h in an air atmosphere. The Fe_2O_3 catalyst was also prepared by the precipitation method, and the iron oxide supported zirconia catalyst (abbreviated ZrO_2/FeO_X) was prepared by an incipient wetness impregnation method using the thus obtained Fe_2O_3 catalyst and aqueous $ZrO(NO_3)_2$.

2.2. Hydrothermal treatment of livestock manure

The hydrothermal treatment of livestock manure was carried out in an autoclave reactor made of stainless steel with a volume of 250 cm^3. Raw livestock manure and livestock manure after methane fermentation (abbreviated fermentation residue) were used as reactants. One hundred grams of the reactants was loaded into the autoclave reactor and the hydrothermal treatment carried out at 573 K for 2–24 h in a nitrogen atmosphere. After treatment, the liquid component of the products (slurry liquid) was separated from the solids via natural filtration using mixed cellulose ester filter with pore size of 0.2 μm (Advantec MFS, Inc.). The slurry liquid was analyzed using a gas chromatograph with a flame ionization detector (GC-2010; Shimadzu Co. Ltd.) and a CP-Pora PLOT Q capillary column (Varian, Inc.). In addition, because heavy components that cannot be detected by gas chromatography existed in the slurry liquid, the total amount of carbon dissolved in the slurry liquid was analyzed using an elemental analyzer (ECS4010; Costech Co. Ltd.).

2.3. Catalytic reactions using the iron oxide catalysts

Catalytic reactions using the iron oxide catalysts were carried out in a fixed-bed type reactor for 2 h at reaction temperatures of 573–773 K and 0.1 MPa. The scheme for the reactor is shown in Fig. 2. Nitrogen gas was introduced as a carrier gas at a flow rate of 5 cm^3/min. The livestock manure-derived slurry liquid and the model compound (aqueous acetic acid) was used as the feedstock and fed to the reactor with a syringe pump. The time factor W/F was 0.5–1 h, where W is the amount of the iron oxide catalyst and F is the flow rate of the feedstock. The liquid and gaseous products were collected with an ice trap and gas pack, respectively. The liquid products were analyzed by a gas chromatograph with a flame ionization detector and a CP-Pora PLOT Q capillary column. The gaseous products were analyzed by a gas chromatograph with thermal conductivity and flame ionization detectors (GC-8A; Shimadzu Co. Ltd.) using activated charcoal and Porapak Q columns (Shimadzu Co. Ltd.), respectively.

3. Result and discussion

3.1. Hydrothermal treatment of livestock manure

To obtain the slurry liquid from the livestock manure, hydrothermal treatment was carried out at 573 K. Fig. 3 shows the carbon composition of the slurry liquid. Because many components undetectable by the gas chromatograph were contained in the slurry liquid, the amount of carbon analyzed by the elemental analyzer was considered to be the total carbon amount in the slurry liquid. Organic compounds such as carboxylic acids existed in the slurry liquids, and acetic acid was the main component of the organic content. These results were in good agreement with results reported previously [7,12–14]. As shown in Fig. 3, it was found that the raw livestock manure-derived slurry liquid contained a higher amount of acetic acid than that of the fermentation residue-derived slurry liquid. This difference is believed to be due to decomposition of easily degraded organic components in the fermentation residue during the methane fermentation process. The carbon composition in the slurry liquid of the raw livestock manure remained nearly

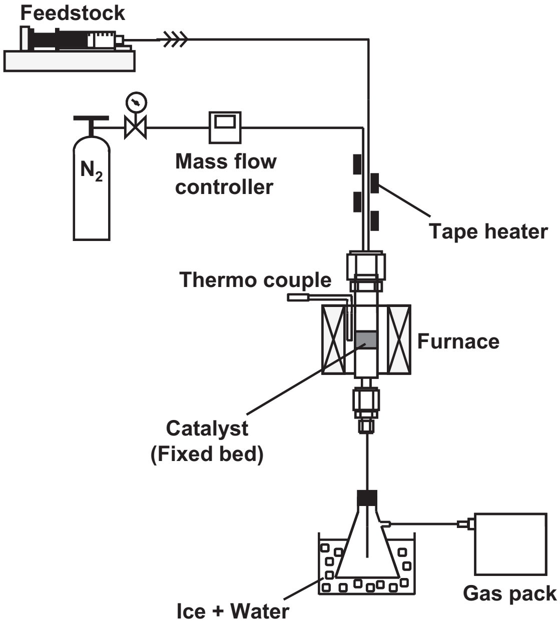

Fig. 2. Schematic diagram of the fixed-bed reactor.

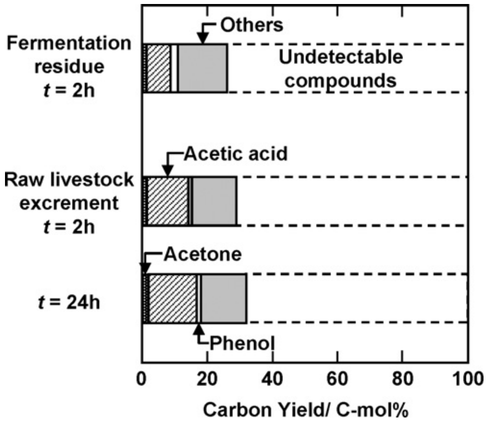

Fig. 3. Carbon composition of livestock manure-derived slurry liquids. Treatment temperature: 573 K, treatment time t = 2–24 h.

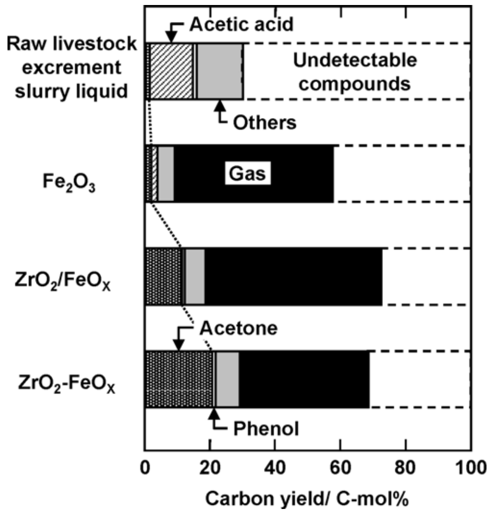

Fig. 4. Carbon yields after reaction of the livestock manure-derived slurry liquid using iron oxide catalysts. Reaction conditions: $T = 723$ K, $W/F = 1$ h, $P = 0.1$ MPa.

unchanged after 2 h and 24 h of hydrothermal treatment. Accordingly, the catalytic reaction was carried out using the livestock manure-derived slurry liquids obtained from the 2 h treatment as the feedstock.

3.2. *Catalytic reactions of the livestock manure-derived slurry liquid*

The catalytic reactions were carried out using Fe_2O_3, ZrO_2/FeO_X and ZrO_2–FeO_X catalysts as the catalysts. The raw livestock manure-derived slurry liquid was used as a feedstock. The carbon yields of the reaction products are shown in Fig. 4. It can be seen that acetone was selectively produced from the livestock manure-derived slurry liquid via a catalytic reaction using these iron oxide catalysts. The main gaseous product of the reactions was CO_2. Moreover, only a small amount of acetone was produced using Fe_2O_3 as the catalyst, whereas more acetone was produced with ZrO_2/FeO_X and ZrO_2–FeO_X. Accordingly, it was confirmed that the catalytic activity of iron oxide was enhanced by the addition of ZrO_2.

The acetone yield was lower and a large amount of CO_2 was produced with the ZrO_2/FeO_X catalyst as compared to the reactions with ZrO_2–FeO_X. The differences in the acetone and CO_2 yields are attributed to the dispersion of ZrO_2 on FeO_X. In the ZrO_2–FeO_X catalyst, a solid solution of ZrO_2 and FeO_X is formed during coprecipitation and calcination, whereas ZrO_2 particles are only dispersed on the surface of FeO_X in the ZrO_2/FeO_X catalyst. The gasification of organic components in the slurry liquid is believed to be mediated by the ZrO_2 particles on the ZrO_2/FeO_X catalyst. Therefore, we decided that ZrO_2–FeO_X was the appropriate catalyst to use for further investigation of the catalytic reactions of the slurry liquid.

3.3. *Effect of reaction temperature on the product yield of the catalytic reaction*

The effect of reaction temperature on product yields was investigated using the fermentation residue-derived slurry liquid. The carbon yields of the slurry liquid and the reaction products are shown in Fig. 5(a). As can be seen, the acetone yield increased with increasing the reaction temperature, with a maximum acetone yield of approximately 10% obtained at a reaction temperature of 723 K. However, at 773 K, the acetone yield decreased while the gas yield increased considerably. We hypothesize that the produced acetone is oxidized at this temperature, establishing that the lower temperature of 723 K is the optimum temperature for the catalytic reaction. Therefore, further catalytic reactions were carried out at 723 K.

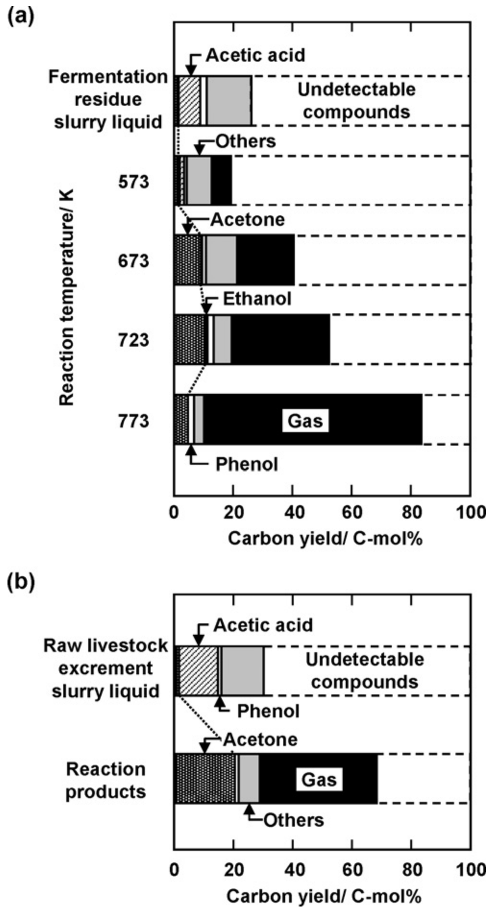

Fig. 5. Carbon yields after reaction over the ZrO_2–FeO_X catalyst. (a) Fermentation residue-derived slurry liquid, $T = 573$–773 K, $W/F = 1$ h, $P = 0.1$ MPa, and (b) raw livestock manure-derived slurry liquid, $T = 723$ K, $W/F = 1$ h, $P = 0.1$ MPa.

The catalytic reaction using the raw livestock manure-derived slurry liquid was also carried out at 723 K. The carbon yields of the reaction products are shown in Fig. 5(b). As can be seen, as in the case of fermentation residue-derived slurry liquid, the main product of catalytic reaction was acetone, and the acetone yield was higher than that obtained with fermentation residue-derived slurry liquid. In both reactions, the yield of acetone increased, while the yields of acetic acid and other organic components decreased, indicating that the production of acetone is related to the decrease in these organic compounds.

3.4. *Effect of acetic acid concentration in the slurry liquid on the production of acetone*

To investigate the effect of the acetic acid concentration in the slurry liquid on acetone yield, slurry liquids with different acetic acid concentrations were produced from livestock manures discharged from several farms. Catalytic reactions were carried out using these slurry liquids at 723 K. The relationship between the concentration of acetic acid in the slurry liquid and the concentration of acetone in the product liquid is shown in Fig. 6. As can be seen, the concentration of acetone increased with the concentration of acetic acid increased. Moreover, catalytic reactions were carried out using aqueous acetic acid as a model compound at 648 K. The carbon yields of reaction products were shown in Fig. 7. As shown in this figure, in the reaction of pure acetic acid, only ace-

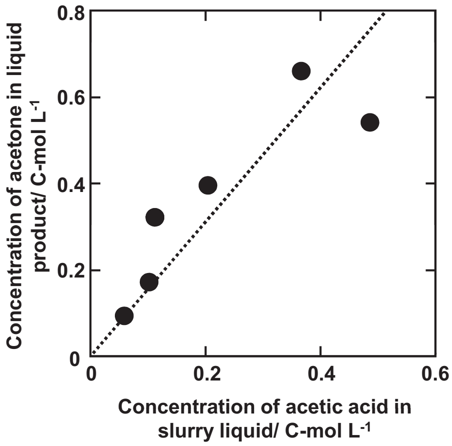

Fig. 6. Relationship between the concentration of acetic acid in the slurry liquid and the concentration of acetone in the product liquid. Reaction conditions: $T = 723$ K, $W/F = 1$ h, $P = 0.1$ MPa.

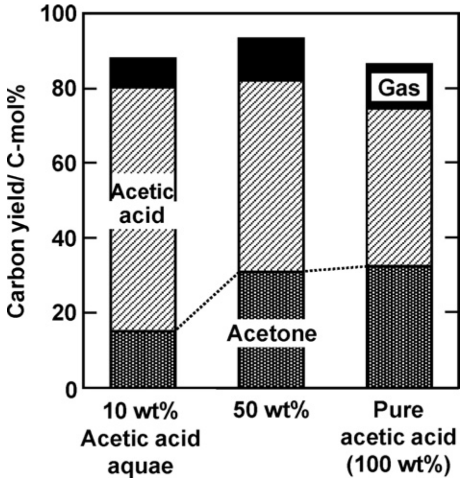

Fig. 7. Carbon yields after reaction of aqueous acetic acid using ZrO_2–FeO_X catalyst. Reaction conditions: $T = 648$ K, $W/F = 0.5$ h, $P = 0.1$ MPa.

tone and CO_2 were produced and similar results were obtained in the reaction of aqueous acetic acid (in a steam atmosphere). These results indicate that the acetone was produced from the acetic acid in the slurry liquid. Previously, it was reported that one molecule of ketone is produced from two molecules of carboxylic acid in ketone formation reactions using catalysts as shown by the following reaction formula [15,16]:

$$2RCOOH \rightarrow RCOR + CO_2 + H_2O$$

As shown in Figs. 5 and 6, the acetone yield was much higher than that expected from the acetic acid concentration in the slurry liquid. Previously, we reported that model compounds (alcohols or aldehydes) of biomass-derived slurry liquids are converted to ketones in consecutive oxidation reactions over the iron oxide catalyst [7]. In these cases, it is believed that decomposition of other undetectable compounds in the slurry liquid into acetic acid occurred over the catalyst, leading to the production of acetone from newly produced acetic acid as shown in Fig. 8. Therefore, the acetone was produced not only from acetic acid but also other organic compounds in the slurry liquid via consecutive reactions over the ZrO_2–FeO_X catalyst.

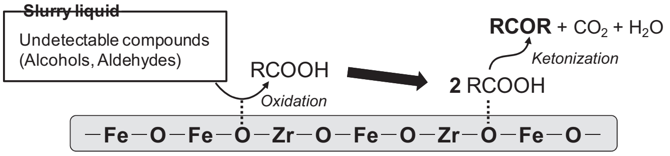

Fig. 8. Reaction scheme of ketone formation from organic compounds over the ZrO_2–FeO_X catalyst.

4. Conclusion

Catalytic reaction of livestock manure-derived slurry liquid using an iron oxide catalyst successfully resulted in the selective production of acetone. The acetone yield in the product liquid increased as the concentration of acetic acid in the slurry liquid increases. Moreover, the acetone was produced not only from acetic acid in the slurry liquid but also other organic compounds (alcohols or aldehydes) via consecutive reactions over the ZrO_2–FeO_X catalyst.

Acknowledgments

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