1. Introduction

Biomass, especially lignocellulose, is well known as an abundant renewable energy resource. The use of lignocellulose for biofuel production has been highlighted over the past two decades. Conventionally, bioethanol production from lignocellulose proceeds through a multi-step process, including saccharification, alcohol fermentation and distillation. However, not only fermentable saccharides, such as glucose, but also unfermentable products, such as pentoses, various saccharide-derived and lignin-derived products, are obtained simultaneously. Besides, carbon dioxide (CO₂) is emitted as a by-product during the fermentation by yeast. Therefore, the use of all compounds produced in the saccharification step with reducing the CO₂ emission seems to be a promising way in order to establish an efficient and environmentally friendly bioethanol production.

Our research group has proposed a highly efficient process of bioethanol production from lignocellulose as shown in Fig. 1. First, the two-step, semi-flow, hot-compressed water treatment is applied to produce various water-soluble products from lignocellulose. In the next step, the obtained products are anaerobically fermented to acetic acid. Then, acetic acid is esterified into ethyl acetate, followed by catalytic hydrogenolysis to produce ethanol. This study focused on the esterification and hydrogenolysis step, which involves the following reactions:

\[
\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOCH}_2\text{H}_5 + \text{H}_2\text{O} \quad \text{(esterification)}
\]

\[
\text{CH}_3\text{COOC}_2\text{H}_5 + 2\text{H}_2 \rightarrow 2\text{C}_2\text{H}_5\text{OH} \quad \text{(hydrogenolysis)}
\]

The net result can be described as follows:

\[
\text{CH}_3\text{COOH} + 2\text{H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \quad \text{(net reaction)}
\]

Therefore, one mole of ethanol is produced from one mole of acetic acid even though ethanol is used as a reactant. Although we have also developed direct hydrogenolysis of acetic acid to ethanol using a Lewis acid catalyst, this two-step method is still a good candidate for ethanol production owing to the fast reaction rate of Eq. (2). In industry, this two-step reaction is applied to produce alcohols from carboxylic acids to overcome the problem of low reactivity of direct
Several methods are available for the esterification step, as reviewed by Yadav and Mehta\(^{18}\), and the most common method uses acid catalysts\(^{18,19}\). However, to avoid the use of acid catalysts and to invent a more environmentally benign technology, we studied a catalyst-free process with supercritical ethanol (critical temperature and pressure = 243 °C/6.4 MPa). We have already demonstrated that the esterification reaction of fatty acids proceeds without catalyst in supercritical methanol\(^{20,23}\).

For the hydrogenolysis of organic esters, copper (Cu) metal has been widely used\(^{24-32}\), and various catalysts are known, such as Cu-Zn\(^{24-26}\) and Cu-Cr\(^{24,27-29}\). Although significant efforts have been conducted for developing the hydrogenolysis catalysts\(^{24-32}\), the hydrogenolysis of ethyl acetate into ethanol has not been fully elucidated. Besides, the separation of ethyl acetate and ethanol by distillation is difficult because their boiling points are almost the same. Therefore, complete hydrogenolysis to ethanol would be more critical for bioethanol production.

In this study, ethyl esterification of acetic acid was first investigated in supercritical or subcritical ethanol to obtain ethyl acetate. The effects of temperature and molar ratio of the reactant on the yield of ethyl acetate were reported. Subsequently, catalytic activities of Cu-Zn- and Cu-Cr-type catalysts for hydrogenolysis of ethyl acetate were evaluated with a flow-type reactor. The effects of temperature and hydrogen pressure were also studied. Based on the obtained results, appropriate reaction conditions for esterification and hydrogenolysis were discussed in order to establish an actual bioethanol production process.

### 2. Experimental Methods

#### 2.1. Esterification of Acetic Acid into Ethyl Acetate

Acetic acid (extra pure reagent (EP), > 99 %, Nacalai Tesque, Inc., Kyoto, Japan) was treated with ethanol (specially prepared reagent (SP), > 99.5 %, Nacalai Tesque) in its supercritical or subcritical state to produce ethyl acetate by using a flow-type reactor shown in Fig. 2(a). Ethanol and acetic acid were supplied by high-pressure pumps into a coiled tubular reactor, which was made from Hastelloy HC-276 steel (outer diameter, 3.2 mm; inner diameter, 1.2 mm; length, 84 m). The reactor was placed in a salt bath, heated at designated temperatures. After cooled by a cooling jacket, the product was collected in glass bottles. The pressure inside the reactor was controlled by a back-pressure regulator to be 20 MPa.

The residence time (reaction time, \(t\)) was calculated by dividing the inner volume \(V\) of the reactor (95 mL) by the total volumetric flow-rate of the reaction mixture as the following equation:

\[
\frac{\text{Density of Acetic Acid}}{\text{Density of Ethanol}} = \frac{F}{\rho'} (4)
\]

where \(F\) is the total flow-rate of acetic acid and ethanol.
at ordinary condition (20 °C/0.1 MPa), while \( \rho \) and \( \rho' \) are densities of the mixture at ordinary (20 °C/0.1 MPa) and reaction conditions (190-310 °C/20 MPa), respectively. The densities were estimated by using a steady-state process simulator, PRO/II ver. 9.1 (Schneider Electric, Rueil-Malmaison, France) on the Non-random two-liquid (NRTL) model.

The product was diluted by methanol (SP, 99.8 %, Nacalai Tesque) and analyzed by high-performance liquid chromatography (HPLC) with an LC-10A system (Shimadzu Corp., Kyoto, Japan) under the following conditions: column, cadenza CD-C18 (250 x 4.6 mm, Imtakt Corp., Kyoto, Japan); flow-rate, 1.0 mL/min; eluent, methanol; detector, UV at 205 nm wavelength; oven temperature, 40 °C. Based on the HPLC chart, the yield of ethyl acetate was determined in mol% upon the fed acetic acid.

2.2 Hydrogenolysis of Ethyl Acetate into Ethanol

A flow-type experimental set-up, as illustrated in Fig. 2(b), was used for the vapor-phase catalytic hydrogenolysis of ethyl acetate. The reactor was made from Incoloy NCF800 steel (inner diameter, 13.8 mm; length, 300 mm) with an inner tube (outer diameter, 3.2 mm), in which a thermocouple was inserted. A vaporizer filled with glass beads (diameter, 2 mm) was placed at the top of the reactor. A Cu-type catalyst was placed in the middle of the reactor (bed height: 10 mm), and the rest space was filled with glass wool. As the catalyst, Cu-Zn (N211, Cu-Zn = 48/44, w/w), Cu-Cr-Mn (N202E, Cu-Cr-Mn = 38/37/2, w/w) and Cu-Cr-Ba-Si (N201H, Cu/Cr/Ba/Si = 38/36/11/8, w/w) were purchased from Nikki Chemical Co., Ltd., Kawasaki, Japan, and used as a powder (30-100 mesh).

Before each experiment, the catalyst was activated under N\(_2\) flow (250 mL/min, 0.1 MPa) and then H\(_2\) flow (250 mL/min, 2.0 MPa) at 250 °C for 2 h each. The reactor was heated with a cylindrical electric furnace. The gas flow-rates were controlled with mass flow controllers, and the pressure was maintained with a back-pressure regulator. The N\(_2\) (99.99 %) and H\(_2\) gases (99.9 %) were purchased from Imamura Sanso K.K., Ohtsu, Japan. During the above H\(_2\) treatment for 2 h, the water generation was confirmed and completed in time sufficiently shorter than 2 h for all catalysts. Therefore, the reduction treatment of all catalysts was thought to be sufficient.

After the activation, the H\(_2\) flow-rate, temperature and pressure were adjusted at designated values. Ethyl acetate (EP, > 99 %, Nacalai Tesque) was then injected into the vaporizer with a high-pressure pump at designated flow rates, and the resulting vapor mixed with H\(_2\) was introduced into the reactor. Since the bulk volume of the catalyst was only approximately 1.4 mL, the residence time of ethyl acetate in the catalyst region was very short. After passing through the reactor, the liquid products were recovered in a cold trap at −20 °C, and the gaseous products were collected in a gasbag.

Ethanol and ethyl acetate in the liquid products were determined by gas chromatography (GC) with a GC-14B system (Shimadzu) under the following conditions; column, CBP-5 (25 m x 0.25 mm in diameter, Shimadzu); injector temperature, 250 °C; column temperature, 40 °C (0-12 min), 40-150 °C (12-15 min); carrier gas, He (1.5 mL/min). Based on the GC chart, the yield of ethanol was determined in mol% upon the fed ethyl acetate. However, since one mole of ethyl acetate produces two moles of ethanol, this case was defined as 100 mol%. The gaseous products were analyzed with a Varian CP-4900 micro GC (Agilent Technologies, CA, USA) under the following conditions: Channel 1, column, MS5A 10 m; carrier gas, Ar; column temperature, 100 °C; column pressure, 170 kPa; detector, thermal conductivity detector (TCD); Channel 2, column, PoraPLOT Q 10 m; carrier gas, He; column temperature, 80 °C; column pressure, 190 kPa; detector, TCD.

3. Results and Discussion

3.1. Esterification of Acetic Acid into Ethyl Acetate

The effect of temperature on esterification was first investigated. Figure 3 shows the yield of ethyl acetate when acetic acid was treated with ethanol at various temperatures under the pressure of 20 MPa (acetic acid/ethanol = 1 : 5 mol/mol). It was confirmed that the esterification reaction of acetic acid to ethyl acetate proceeded without catalyst in supercritical or subcritical ethanol. Higher temperatures resulted in faster reaction rates for ethyl acetate formation. In addition, the

![Figure 3](https://example.com/figure3.png)

**Fig. 3** Effect of Reaction Temperature on Esterification of Acetic Acid in Sub- and Supercritical Ethanol at 190-310 °C/20 MPa. Acetic Acid/Ethanol = 1 : 5 mol/mol (1 : 5.1 vol/vol), Total Flow-rate = 1.7-13.7 mL/min
yield of ethyl acetate tended to increase quickly in the early stage of the reaction, but the formation rate became slow when the reaction time was prolonged. At the given reaction temperatures (190-310 °C), there was no side reaction because only acetic acid and ethyl acetate were found in HPLC analysis (i.e., yield of ethyl acetate = conversion (consumption) of acetic acid, mol%).

The yield of ethyl acetate was relatively low (63.5 mol%) at 190 °C, even after the treatment for 48 min. The yield was improved as the temperature was increased, and seemed to reach equilibrium at about 70 mol% at 250 °C. When the temperature was further increased to 270, 290 and 310 °C, the yield of ethyl acetate was increased and equilibrated at about 80 mol% even though the yield was slightly different. Therefore, the reaction was considered to reach equilibrium at about 80 mol% under the given molar ratio of acetic acid and ethanol (1 : 5) and reaction temperatures around 300 °C.

In terms of energy consumption, lower reaction temperatures are more preferred; therefore, 270 °C is sufficient for ethyl esterification of acetic acid. With regard to pressure, lower pressures are more desirable because of safety reasons. However, low pressure reduces the density of the reaction mixture and shortens the residence time in the reactor. Therefore, a more extended reactor is necessary. Thus, although this study was conducted at 20 MPa, the optimum reaction pressure will depend on the situation.

As noted above, since the yield of ethyl acetate relates to the molar ratio of acetic acid and ethanol, the effect of the molar ratio was investigated at 270 °C/20 MPa as shown in Fig. 4. The high yield is expected if the ethanol ratio is high because the forward reaction will become dominant, while the reverse reaction of ethyl acetate to regenerate acetic acid is suppressed. When the ethanol ratio was increased from 1 : 1 to 1 : 10, the yield of ethyl ester was improved to be about 90 mol%. However, as the ethanol ratio was further increased (1 : 20, 1 : 30, and 1 : 50), the esterification reaction proceeded very slowly and the ester yield remained low.

These behaviors can be explained by an autocatalytic effect of acetic acid. Because acetic acid can act as an acid catalyst, it will enhance the esterification reaction. However, a large amount of ethanol diluted acetic acid, weakened the autocatalytic effect of acetic acid, and led to a slow reaction. Besides, we can also explain the fast reaction rate in the early stage of the reaction, because the concentration of acetic acid is high at the beginning. A similar phenomenon has been reported in our previous study on methyl esterification of fatty acids in supercritical methanol.

In this study, the maximum ethyl acetate yield was achieved to be 89 mol% under the conditions of 270 °C/20 MPa for 60 min and the molar ratio of 1 : 10 (acetic acid/ethanol). However, a lower ethanol ratio may be desirable. More applicable operating conditions will be discussed later, along with the conditions of hydrogenolysis.

3.2 Hydrogenolysis of Ethyl Acetate into Ethanol

Figure 5 shows the catalytic activities of several Cu-type catalysts evaluated as the ethanol yield after the hydrogenolysis of ethyl acetate at 200-350 °C/2.0 MPa.
The molar ratio of ethyl acetate/H$_2$ was 1 : 8. Since one mole of ethyl acetate requires two moles of H$_2$ for hydrogenolysis as shown in Eq. (2), this ratio corresponds to four times the required amount.

All catalysts used in this study were not so active at 200 °C, while the ethanol yield increased with increasing the reaction temperature. Among these catalysts, only Cu-Zn exhibited a high activity at 250 °C, but Cu-Cr-Mn and Cu-Cr-Ba-Si showed high activity at 300 °C. There was almost no side reaction for all catalysts (i.e., yield of ethanol $\equiv$ conversion of ethyl acetate, mol%) at the temperatures between 200 to 300 °C because only trace amounts of by-products were found in GC analysis. The ethanol yield continued to increase even at 350 °C for Cu-Zn, but the yield decreased for the other two catalysts. In the cases of Cu-Cr-Mn and Cu-Cr-Ba-Si, the raw material (ethyl acetate) did not remain in the reaction mixture at 350 °C; therefore, the decrease in ethanol yield was due to side reactions other than hydrogenolysis. Actually, unidentified by-products were found to some extent in GC analysis. On the other hand, no side reaction was observed for Cu-Zn even at 350 °C.

The reaction conditions were further evaluated for the Cu-Zn catalyst in the temperature range of 180-270 °C as shown in Fig. 6. The catalytic hydrogenolysis became effective around at 200 °C and the reactivity increased linearly with increasing the reaction temperature. In the micro GC analysis, ethane and a trace amount of methane were detected as gas products at 240 °C (0.15 wt% upon the fed ethyl acetate) and they increased with the reaction temperature, but their combined yield was only 0.89 wt% even at 270 °C. Therefore, it was suggested that the hydrogenolysis of ethyl acetate to ethanol with Cu-Zn proceeded quite selectively in the temperature range of 210-270 °C. In the following experiments, the selectivity of hydrogenolysis was also high except for a very small amount of gaseous products, and thus the ethanol yield was almost equal to the conversion of ethyl acetate.

The effect of reaction pressure on the hydrogenolysis with Cu-Zn was investigated as shown in Fig. 7. The ethanol yield was improved as the pressure was increased. When the hydrogenolysis was conducted at 4 MPa, the ethanol yields became about 1.7 times higher than that at 1.0 MPa. This might be owing to the increase in residence time in the reactor, because the density of vapor ethyl acetate and H$_2$ mixture was increased when the pressure was increased. Moreover, the increase in density will enhance the reaction between ethyl acetate and H$_2$.

Figure 8 shows the effect of the molar ratio of H$_2$ and ethyl acetate on the ethanol yield. By using a large excess amount of H$_2$ (ethyl acetate/H$_2$, 1 : 32), ethyl acetate was converted to ethanol almost quantitatively (98.7 mol% yield). Such complete hydrogenolysis would be essential for bioethanol production due to the separation problem as described earlier. Although an excess amount of H$_2$ is required for the hydrogenolysis, we can reuse the recovered H$_2$ after the reaction, which still has high purity because the gaseous by-product is quite small in this reaction.

The above experiments were conducted by using pure ethyl acetate as a reactant to reveal fundamental
reaction behaviors. However, actual products from the esterification stage include unreacted acetic acid and ethanol as well as ethyl acetate and water produced. Therefore, the effects of ethanol and acetic acid on the hydrogenolysis with Cu-Zn were studied at 250 °C/2.0 MPa as shown in Fig. 9, where white bars show the ethanol yield from pure ethyl acetate. The ethanol yield was evaluated by subtracting the added ethanol from the total amount of ethanol in the GC analysis. The addition of 10 mol% ethanol in ethyl acetate did not affect the ethanol yield from ethyl acetate. However, a more excessive amount of ethanol, 100 mol% in ethyl acetate, reduced the ethanol yield to about 56% level of that from pure ethyl acetate. A dilution effect by ethanol is considered as the main reason. On the other hand, the effect of acetic acid was more evident than ethanol; the ethanol yield was reduced by half when 10 mol% acetic acid was added. These results indicate that acetic acid should be converted to ethyl acetate in high yield by the esterification stage to achieve efficient hydrogenolysis.

### 3.3 Discussion to Establish the Actual Process

Although the Cu-Zn catalyst exhibited excellent reactivity and selectivity in the hydrogenolysis of ethyl acetate to ethanol, it was found that unreacted ethanol and acetic acid should be reduced as much as possible in the esterification stage for the following hydrogenolysis. In the esterification reaction of acetic acid, the yield of ethyl acetate was improved by using a large excess amount of ethanol. However, when the ethanol ratio was increased, the rate of esterification reaction became slower due to the dilution effect, and more ethanol remained after the reaction. Besides, a large amount of ethanol will increase the energy consumption of the process.

Therefore, the two-step reaction method proposed in this study still has challenges, especially in the esterification step. An appropriate design would be to employ a low ethanol ratio to acetic acid (e.g., 1:1) in the esterification reaction, which makes the reaction rate high owing to the autocatalytic effect of acetic acid. We can remove the produced water after a certain treatment time and then repeat the esterification reaction. For example, the pervaporation technique is available to remove water from the reaction mixture (33), and the water removal will favor the reaction to form ethyl acetate. Ideally, it is better to remove water simultaneously with the esterification reaction. For that, the reactive distillation may also be a candidate (34). In this way, if high purity ethyl acetate can be obtained from acetic acid, the subsequent hydrogenolysis will be carried out efficiently, and the bioethanol production from acetic acid will be established.

### 4. Conclusion

The two-step reaction for bioethanol production from acetic acid was proposed; ethyl esterification of acetic acid to ethyl acetate, followed by hydrogenolysis to ethanol. The catalyst-free esterification of acetic acid was performed well in subcritical and supercritical ethanols and the autocatalytic effect of acetic acid was found. Therefore, a low ethanol ratio to acetic acid led to a fast reaction rate but caused a low ethyl acetate...
yield due to the reverse reaction of ethyl acetate with water. Although an appropriate reaction condition was found to be 270 °C/20 MPa, the water removal during the esterification reaction, for example by pervaporation or reactive distillation, will be necessary to achieve a high ethyl acetate yield without a large excess amount of ethanol.

As for the hydrogenolysis, the Cu-Zn catalyst performed excellent reactivity and selectivity in the temperature range of 210-270 °C, where only very small amounts of ethane and methane were formed as by-products. With an excess amount of H₂, ethyl acetate was wholly converted to ethanol. However, if unreacted acetic acid or ethanol included in the reactant, the ethanol yield was worsened. An excellent conversion in the esterification stage is also essential for the hydrogenolysis.

These findings will contribute to developing efficient and practical conversion process of acetic acid to ethanol by this two-step method, even though some challenges remained. This is also a part of the establishment of the highly efficient bioethanol production from lignocellulose through acetic acid fermentation developed by our research group.

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要  旨

エチルエステル化と接触水素化分解の二段階反応による酢酸のバイオエタノールへの変換

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酢酸発酵を経由したリグノセルロースからの高効率バイオエタノール生産のため、エステル化と接触水素化分解の二段階反応による酢酸からのエタノール生産を検討した。酢酸のエステル化反応には無触媒の超臨界エタノール処理を採用し、270 ℃/20 MPa で良好に酢酸エチルが生成することを示した。また、酢酸の自触媒効果によりエタノールが少ないほど反応速度が向上するが、逆反応のため酢酸エチル収率は減少した。そのため、反応で生成した水を除去する方策を探り、少量のエタノールで高い酢酸エチル収率を実現することが望ましい。一方、酢酸エチルの水素化分解のため、Cu 系触媒を流通式反応器で評価した。Cu-Zn 触媒は 210 ～ 270 ℃の範囲で他の Cu-Cr 系触媒よりも触媒活性が高く、副産物であるメタンおよびエタンは計 0.89 wt%（270 ℃、供給酢酸エチルベース）とわずかであった。以上の成果は、提案した二段階反応による酢酸からの効率的なバイオエタノール生産プロセスの設計に資する知見である。