

Successive Conversion of Lignocellulose to Bio-ethanol Using Zwitterions

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| journal or publication title | 博士論文要旨Abstractおよび要旨Outline |
| 学位授与番号 | 13301甲第4636号 |
| 学位名 | 博士(工学) |
| 学位授与年月日 | 2017-09-26 |
| URL | http://hdl.handle.net/2297/00049559 |

doi: 10.1021/acssuschemeng.6b02055



学位論文概要

Dissertation Summary

学位請求論文 (Dissertation)

題名 (Title) Successive Conversion of Lignocellulose to Bio-ethanol Using Zwitterions

双性イオン液体を用いたリグノセルロースからバイオエタノールへの逐次変換

専攻 (Division) : Natural System

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Utilization of lignocellulosic feedstock in bioethanol production is demanded. To convert biomass into ethanol, three main processes consist of biomass dissolution, hydrolysis, and fermentation are required. Recently, ionic liquids (ILs) have demonstrated to be promising pretreatment solvents or hydrolytic catalysts for lignocellulose. On the other hand, successive efficient process on conversion of lignocellulosic biomass into ethanol is needed from a viewpoint of efficiency of cost and energy. However, the application of ILs has been limited due to their inhibition effect on fermentable microorganisms, and this condition critically prevents the successive process on lignocellulosic biomass conversion. In this study, we realized the successive process avoiding the toxicity of ILs while exploiting ILs as cellulose solvents or hydrolytic catalysts.

ILs show toxicity to microorganisms by destruction of cell membranes. The cation part first approaches to anionic phospholipid in membranes, followed by insertion of alkyl chain of the cation into hydrophobic part of the membranes. We introduced the anion part of ILs to the end of the cation, namely zwitterions (ZIs), and the ZIs are expected to be effective to prevent the insertion of the alkyl chain of the cation to the membranes because ZIs no longer have the hydrophobic cation tail. As a result, the ZIs were not toxic to the growth of *E. coli*. We investigated the toxicity of ILs to fermentation, and the ILs which act as hydrolytic catalysts or cellulose solvents were highly toxic. On the other hand, ZIs were low-toxic regardless of the structure. By exploiting the low toxic of ZIs, we developed the two successive processes.

We developed a successive process with an IL as a hydrolysis catalyst. The catalytic IL, 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ($[C_1\text{imC}_4\text{SH}]\text{HSO}_4$) is composed of sulfuric acid and a ZI, 1-(4-sulfobutyl)-3-methylimidazolium ($C_1\text{imC}_4\text{S}$). Sulfuric acid has pretreatment ability and $[C_1\text{imC}_4\text{SH}]\text{HSO}_4$ has high catalytic activity. Bagasse was pretreated by using sulfuric acid that included in IL, for pretreatment. Following the pretreatment, the ZI has added for *in situ* synthesis of $[C_1\text{imC}_4\text{SH}]\text{HSO}_4$. This process improved the glucose yield at 77% for 40 minutes hydrolysis at 100 °C. Subsequent to hydrolysis, the $[C_1\text{imC}_4\text{SH}]\text{HSO}_4$ then separated into $C_1\text{imC}_4\text{S}$ and H_2SO_4 by electrodialysis to decrease the toxicity of IL because the remaining ZI no longer toxic. In addition, electrodialysis successfully separated H_2SO_4 from $[C_1\text{imC}_4\text{SH}]\text{HSO}_4$ by the recovery at 97%; the separation enabled the successive fermentation. This successive conversion of bagasse into ethanol has the ethanol yield at 71%.

We also developed a successive process with a ZI as a pretreatment solvent. In this strategy, we come up an idea to replace ILs with ZIs that have ability to dissolve cellulose as a pretreatment solvent; consequently one-pot conversion of bagasse into ethanol would be allowed. A novel carboxylate-type zwitterion (1-(3-carboxypropyl)-3-(methoxyethoxyethyl)imidazolium, $\text{OE}_2\text{imC}_3\text{C}$) was synthesized. $\text{OE}_2\text{imC}_3\text{C}$ dissolved 6 wt% of cellulose at 100 °C. Since $\text{OE}_2\text{imC}_3\text{C}$ does not show toxicity to *E. coli*, the one-pot process using 0.5 M of $\text{OE}_2\text{imC}_3\text{C}$ obtained ethanol yield at 41%, while when using ILs no ethanol was obtained due to the toxicity. The viscosity of $\text{OE}_2\text{imC}_3\text{C}$ was noted as a critical inhibition factor in this one-pot process. Dimethyl sulfoxide (DMSO) was added as a co-solvent to improve the efficiency of conversion. The addition DMSO into $\text{OE}_2\text{imC}_3\text{C}$ accelerated dissolution of cellulose. Furthermore, $\text{OE}_2\text{imC}_3\text{C}/\text{DMSO}$ (8/2) at 150 gL^{-1} was chosen as a solvent to conduct the one-pot conversion and the ethanol yield was increasing at 67%.

This study successfully developed successive processes by exploiting ZIs to avoid the high toxicity of ILs while the superior ability of ILs maintained.