

Exhaustive solvolysis of lignocellulosic waste for preparing useful chemicals

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Utilization of biomass resources will be one of the most important factor for environmental protection in the 21st century. Solvolysis has been recognized as a useful fractionation technology of lignocellulosics. This technique has been studied as a kind of pulping method for preparing proper cellulose such as paper. Recently, the complete recycling of lignocellulosic waste has attracted a great deal of attention. Some lignocellulosic waste does not contain proper cellulose chains for preparing paper. However, we expect to recycle whole lignocellulosic waste, even if the quality is poor. We have proposed a new solvolysis technique that can be applied to such poor waste. The technique is a chemical recycling system for lignocellulosic waste through exhaustive solvolysis (e-solvolysis)¹. Cyclic carbonates are used as accelerating reagents for exhaustively producing solvolysis reaction in the e-solvolysis. We have found that cyclic carbonates such as ethylene carbonate (EC) and propylene carbonate (PC) provide quite rapid degradation of cellulosic materials². In particular, cyclic carbonates accelerate the acid solvolysis of cellulose and rapidly lead cellulose to levulinates³. Levulinic acid is known as a starting material for some useful chemical products such as methyltetrahydrofuran, aminolevulinic acid, diphenolic acid and succinic acid. In this study we are trying to produce useful chemicals such as levulinic acid through solvolytic reaction. Generally, levulinic acid is produced through thermo hydrolysis of biomass. Hydrolysis will produce a large quantity of residual lignin fraction. On the other hand, e-solvolysis will not make any residual fraction. Lignin fraction (ES-lignin) can be used as raw materials for plastics such as polyurethane resin. The essential objective of e-solvolysis is to produce useful chemicals from lignocellulosic waste without producing any humic residue. This paper describes the features of e-solvolysis in the presence of cyclic carbonates.

Experimental

The flask, charged with 1g of lignocellulosics, was immersed in an oil bath preheated at 120-150 °C. The mixture of 5g of solvolysis reagents (EC, PC, EG, PEG etc.) and 0.15g (3 wt % for the solvolysis reagent) of 97 % sulfuric acid was then added into the flask. After the preset time, the flask was immersed in cold water to quench the reaction.

The resultant was diluted by an excessive amount of distilled water, and then separated into water soluble and insoluble parts by using a Toyo GA100 glass filter. Polyurethane film was prepared from the water insoluble part (ES-lignin) in cooperation with isocyanates. The water soluble part was transferred to a 200 ml of Erlenmeyer flask equipped with a reflux condenser and a magnetic stirrer.

The flask was refluxed on a hotplate with stirring. After a preset time, the flask was immersed into cold water to quench the reaction. The water solution was then analyzed by the HPLC.

Results and discussion

Cellulose was completely converted into substances soluble into widely used organic solvents such as dioxane in only 10 minute of solvolysis time in the presence of EC. The reaction rate for cellulose by using EC shows a rate more than 10 times faster than the current reaction using polyhydric alcohols such as polyethyleneglycol (PEG). EC particularly accelerated the acid catalyzed solvolysis of cellulose and rapidly led cellulose to levulinates.

The water soluble fraction was treated in hydrolysis to isolate levulinic acid and formic acid. The levulinic acid and formic acid content was determined by using HPLC. Levulinic acid content was increased with the passing of hydrolysis time from 0 to 60 min. However, further hydrolysis did not increase the levulinic acid content. The produced rate of levulinic acid was not very high. However, the most important objective of this system is to produce levulinic acid from lignocellulosic waste without producing humic residue. The water insoluble fraction was used as raw materials for resins, and solvolysis reagents could be recovered from the hydrolysate.

It is known that EC is transformed into EG by releasing carbon dioxide at elevated temperature in the presence of acid catalysts. Furthermore, EC will be polymerized in the reaction. These reactions may occur during the solvolysis in this study. At the end of the reaction, some part of EC would be transformed into polyhydric alcohols.

Through e-solvolysis, degraded lignin derivatives are modified with the solvolysis reagent. In fact, the functional hydroxyl group from solvolysis reagents such as EC is introduced to the product. Polyurethane film could be prepared from the water insoluble fraction (ES-lignin) in cooperation with isocyanates. We prepared a trial piece of polyurethane film from the ES-lignin of the Japanese cedar wood meal and polymeric MDI. The biomass content in the film was estimated at approximately 50 %. Further study about the mechanical property of the film is in progress.

References

- [1] Yamada T, Ono H, Abstracts of the 51st annual meeting of the Japan wood research society 2001.
- [2] Yamada T, Toyota S, Shimizu K, Ono H, Japanese Pat. Appl. 80367, 1999.
- [3] Yamada T, Ono H, *Bioresource Technology*, 1999, 70(1), 61-67.