γ-Valerolactone from pyrolysis of calcium salts of levulinic-formic acid mixtures derived from solid cellulosic biomass waste

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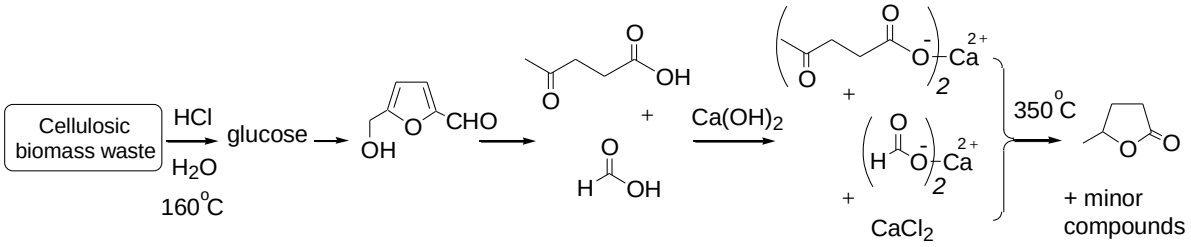
The inevitable decline in fossil fuel resources and the global climate change concerns have contributed to the current interest in conversion of renewable lignocellulosic biomass to renewable liquid transportation fuels and feedstock chemicals. Since there are certain disadvantages in first generation fuels like corn and sugar cane ethanol, the research efforts are gradually shifting to more advanced 2nd generation cellulosic ethanol and 3rd generation fuels (Amarasekara, 2013). The third generation biofuel would be the direct or indirect conversion of highly oxygenated polysaccharides and lignin in biomass to hydrocarbons compatible to gasoline, diesel, and kerosene. The agricultural biomass wastes such as corn stover, wheat, rice straw and cellulosic municipal waste are excellent feedstock to produce 3rd generation renewable fuel precursors. The five carbon γ-valerolactone is one of these promising renewable resources based intermediates that can be converted to new generation liquid transportation fuels and feedstock chemicals. As a continuation of our studies on development of biomass processing technologies to produce renewable transportation fuels and feedstocks, we have studied the pyrolysis of calcium levulinate - formate mixtures derived from acid hydrolysis of a variety of solid cellulosic biomass waste forms: corn stover, wheat straw and forest residues (Amarasekara & Wiredu, 2013), (Amarasekara & Ebede, 2009), (Amarasekara & Owereh, 2009). In this presentation we report the preparation, characterization of calcium salts of solid cellulosic biomass waste derived carboxylic acids and analysis of the pyrolysis oils produced from these crude salt mixtures.



The cellulosic biomass waste was converted γ-valerolactone in a two step process as shown in the figure. In the first step dilute aqueous acid catalyzed hydrothermal degradation of biomass gives a mixture of levulinic and formic acids, which was neutralized to pH ~ 7.0 by adding solid $Ca(OH)_2$. The neutralized solution was then evaporated to dryness to give a solid composed of calcium salts of levulinic and formic acids. Pyrolysis of this crude mixture at 350 °C for 3.0 min. and condensation of the vapors produces a colorless liquid pyrolyzate with ~ 97% γ-valerolactone in 130-202 g/kg biomass yield. The minor products in the pyrolyzate are levulinic acid, 3-methyl-2-cyclopentenone, and 2,3-dimethyl-2-cyclopentenone. This technique can be developed in to a simple two step process for the production of γ-valerolactone from solid cellulosic biomass waste. Currently known methods for the conversion of levulinic acid to γ-valerolactone are catalytic reduction using hydrogen gas with Pd, Pt or Ru as the catalyst or using formic acid as the hydrogen source with Ru catalyst. In contrast, the new two step process allows the production of γ-valerolactone from abundant cellulosic biomass waste without isolation of levulinic acid, using catalytic amount of HCl and equivalent amount of $Ca(OH)_2$ as the reagents. Therefore, new method has certain advantages such as; no external hydrogen source or expensive noble metal catalysts are required and Ca byproducts formed in the pyrolysis step can be recycled and used to regenerate $Ca(OH)_2$ required in the neutralization of the biomass derived acids.

References

Amarasekara, A. S, & Wiredu, B. (2014). Single reactor conversion of corn stover biomass to C5–C20 furanic biocrude oil using sulfonic acid functionalized Brönsted acidic ionic liquid catalysts. *Biomass Conversion and Biorefinery, 4*(2), 149-155.

Amarasekara, A. S. (2013). *Handbook of Cellulosic Ethanol*. John Wiley & Sons, NewYork.

Amarasekara, A. S., & Ebede, C. C. (2009). Zinc chloride mediated degradation of cellulose at 200 °C and identification of the products. *Bioresource Technology, 100*(21), 5301-5304.

Amarasekara, A. S., & Owereh, O. S. (2009). Hydrolysis and decomposition of cellulose in brønsted acidic ionic liquids under mild conditions. *Industrial and Engineering Chemistry Research, 48*(22), 10152-10155.