Protic Ionic liquid mediated catalytic conversion of lignocelluloses to biofuel precursors

Subhrajit Roy
Roll No. 17CH91R13
Department of Chemical Engineering, Indian Institute of Technology Kharagpur
Supervisor: Prof. Saikat Chakraborty

Abstract

Non-edible lignocellulosic biomass has emerged as a potential biofuel feedstock because it is abundantly available and does not compete with food sources. While their high cellulose content makes them viable candidates for large-scale biofuel production, their high crystallinity and low porosity make them recalcitrant to enzymatic treatment. Here, we employ Protic (PIL) and Aprotic (APIL) Ionic Liquids to accelerate the microwave-irradiated and oil-bath mediated catalytic conversion of two lignocelluloses (Sunn hemp and June grass) to biofuel precursors such as glucose, 5-Hydroxmethylfurfural (HMF), Levulinic (LA), and Formic acid (FA).

The microwave-irradiated conversion is rapid (taking less than an hour), cost-effective, produces high-value products from low-cost PIL, is feedstock agnostic, requires no pre-treatment and can convert raw lignocelluloses to biofuel precursors in a one-pot synthesis system. Reactor-scale parameters such as catalyst, substrate and ionic liquid loading, water, temperature, and time are optimized in order to regulate the product distribution and maximize yields of specific biofuel precursors. The APIL gives a maximum glucose yield of 88.2% at 180ºC and 40% water, while the PIL produces a maximum HMF yield of 34.8% at 180ºC with no added water, and maximum LA and FA yields of 19.2% and 7.6%, respectively, at 200ºC from June grass. The PIL-based conversion targeting HMF as the biofuel precursor from June grass, with glucose, LA, and FA as co-products, gives a product-reactant cost ratio of 194.

Our oil-bath experiments in PIL medium, shows that the water, being a substrate in cellulose hydrolysis to glucose (isomerized to fructose), and an inhibitor in fructose dehydration to HMF, regulates product yields through interactions between transport (heat conduction and viscosity) and reaction (non-linear kinetics and activation energy). The yields of glucose and HMF peak at 6 h to 60.2% and 10.2%, respectively, from Sunn hemp, and at 4 h to 62.7% and 12.8%, respectively, from June grass, while those of LA and FA peak at 8 h to 23% and 9.1%, respectively, from Sunn hemp, and at 5 h from 19.3% and 7.7%, respectively, from June grass. The regulatory effects of water on cellulose hydrolysis are quantified (R^2>0.92) by a linear superposition of two Gaussian distributions representing the 'ignited' and 'extinguished' reaction states that delineate the three water-regulated regimes, and allow us to quantify the water-sufficient regime for maximizing product yields. PIL recovery (91.4%) and product separation (75% glucose, 54% HMF) are performed to improve the process-economics.

Keywords: Lignocellulose; June grass; Sunn hemp; Catalytic hydrolysis; Microwave-irradiation; Oil-bath; Protic Ionic Liquids; Biofuel Precursors; Temporal Dynamics; Regulatory Effects; Product Distribution; Low-cost process; Ionic Liquid Recycling; Product Separation; Non-linear Kinetics; Gaussian Distribution