Mixing Effects on Enzymatic and Catalytic Conversion of Cellulose to Fuel Products

Abstract

Mixing plays an important role in determining the product yield in the enzymatic and catalytic conversion of cellulose to fuel products. This thesis explores the effects of mixing on the production of cellulosic fuels by attempting to understand the complex interlocked dynamics between mass-transfer and reactions. Our major objectives are to investigate and quantify (i) the effects of mixing on the kinetics of enzymatic hydrolysis of Avicel for batch production of cellulosic ethanol, (ii) the mixing effects in cellulase-mediated hydrolysis of cellulose in CSTR,(iii) the mixing and temperature effects on the kinetics of alkali metal catalyzed, ionic liquid based batch conversion of cellulose to glucose, 5-Hydroxymethylfurfural (HMF) and Levulinic Acid, and (iv) the mixing effects on the kinetics of *S. cerevisiae* mediated batch fermentation of glucose to bioethanol.

For enzymatic hydrolysis of cellulose, we present a strategy for optimizing the reactor mixing that maximizes glucose and reducing sugar yields. The kinetic parameters for the three enzymes (endoglucanase, exoglucanase, β-glucosidase) that constitute cellulase are experimentally quantified as functions of the mixing speed and are fitted to algebraic expressions that– in the asymptotic limit of complete mixing– give their pure kinetic values in the reaction limited regime. An unsteady-state multi-step three-enzyme kinetic model incorporating product inhibition is simulated using the experimentally obtained kinetic parameters at various mixing speeds, and the model simulations are validated with our experiments. We also simulate a mixing model to predict the optimal mixing and reactor configuration that would maximize glucose yield in enzymatic hydrolysis in CSTRs.

For the catalytic process, we perform a tightly-coupled experimental–modeling study to quantify the effects of temperature and mixing on the kinetics of batch conversion of cellulose to glucose and HMF using $CuCl_2$catalysts in ionic liquid ([BMIM]Cl) medium. While glucose is fermented to bioethanol, HMF can be selectively hydrogenated to produce a gasoline derivative 2,5-dimethylfuran (DMF), which, post treatment, can be used as gasoline. The algebraic expressions we obtain allow us to quantify the variation of the kinetic constants with mixing speed from the mass transfer limited regime through a transition zone to the reaction limited regime. We predict the optimal mixing speed and temperature that eliminate all mass transfer limitations and maximize glucose and HMF yields, and calculate the activation energies of the reactions.

We also quantify the effect of mixing on the yield of bioethanol by performing *S. cerevisiae* mediated batch fermentation of glucose at various mixing speeds. We find that the rate of cell growth (and the parameters $\mu_{\max}$ and K_S) increases with increasing mixing speed, and the maximum ethanol production (89% of the theoretical) is attained for the case of moderate mixing at 80 rpm (intermediate regime).

We conclude that no (or minimal) mixing maximizes glucose and reducing sugar yields in enzymatic hydrolysis of cellulose, high mixing maximizes glucose and HMF production in catalytic conversion of cellulose in IL media, whereas moderate mixing helps in maximizing the *S. cerevisiae* mediated fermentation of glucose to bioethanol.In other words,operating the reactor in the mass transfer limited regime during enzymatic hydrolysis of cellulose, in the reaction limited regime during catalytic production of cellulosic fuels, and in the intermediate regime during the fermentation of glucose maximize the corresponding product yields. This study, which is based on our understanding of the complex coupled dynamics of mixing and chemical and biochemical reactions, hopes to provide a framework for quantifying the extent of mixing needed in biofuel plants to maximize the product yields at each step of the process during the production of cellulosic fuels.

Keywords: Mixing; Enzymatic Hydrolysis; Cellulose; Avicel; HMF; Fermentation; Biofuel; Bioethanol; Mass transfer; Ionic liquid