# Mixing and temperature effects on the kinetics of alkali metal catalyzed, ionic liquid based batch conversion of cellulose to fuel products

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## HIGHLIGHTS

- We quantify kinetics of ionic liquid-based catalytic conversion of cellulose to fuel products.
- Effects of mixing (150–1200 rpm) and temperature (120–160 °C) on the kinetics are quantified.
- We measure variation of observed kinetics from mass-transfer limited asymptote to reaction limited one.
- We recommend 700 rpm (or above) and 120 °C as the optimum mixing speed and temperature.
- We report huge increase in glucose and HMF yields above 700 rpm (reaction limited regime) at 120 °C.

## ARTICLE INFO

## ABSTRACT

This paper explores the effects of mixing and temperature on ionic liquid-based catalytic conversion of cellulose to fuel products and suggests the optimal mixing speed and temperature for maximizing the production of cellulosic fuels. We perform a tightly-coupled experimental-modeling study to quantify the effects of mixing (150–1200 rpm) and temperature (120–160 °C) on the kinetics of batch conversion of cellulose (Avicel) to glucose and 5-hydroxymethylfurfural (HMF) using alkali metal ($CuCl_2$) catalysts in ionic liquid ([Bmim]Cl) medium. While glucose could be fermented to produce 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 asymptote through the intermediate regime to the reaction limited regime. We identify the rate-limiting step in the three-step reaction network and recommend 700 rpm or above (in the reaction limited regime) and 120 °C as the optimum mixing speed and temperature, respectively, which eliminate mass transfer resistances from the system and maximize glucose and HMF yields while minimizing energy expenditure. We report very significant increase in glucose and HMF yields when these batch reactions in series are conducted in the reaction limited regime rather than in the mass-transfer limited regime.

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## 1. Introduction

Catalytic conversion of cellulosic biomass in ionic liquid medium has turned out to be one of the faster routes to cellulosic fuels. The β-glucosidic bonds of cellulosic substrates are first cleaved to produce glucose which can be further converted to bulk chemicals. Dehydration of glucose in presence of $CrCl_2$, $CrCl_3$ or $CuCl_2$ catalysts in ionic liquids directly produces the platform chemical 5-hydroxymethylfurfural (HMF) through the loss of three water molecules. HMF, on selective hydrogenation in the presence of palladium catalyst and hydrogen in ionic liquid, loses two water molecules to produce a gasoline derivative 2, 5-dimethylfuran (DMF) [1,2]. DMF, after treatment, can be used as gasoline.

On thermal degradation, HMF undergoes dehydration and ring cleavage under severe conditions to a linear molecule, levulinic acid (LA) along with formic acid (in 1:1 M ratio) and fractions of humic acid [3,4]. LA – a short chain fatty acid containing both carbonyl and carboxyl groups – is an important building block for fuel additives [5–7], and when produced from hexose sugar on degradation by mineral acids, gives a maximum theoretical yield of 64.5% [8]. The rate of cellulose hydrolysis in pure water is very slow because of the lower solubility of cellulose. The hydrolysis rate can be enhanced by using high temperatures (>150 °C) [9] and pressures [6] or by using acid catalysts or highly specific enzymes such as cellulases [10]. Cellulose is a carbohydrate based polymer (MW: $10^4$ to $10^6$) that can be broken down to low molecular weight fractions (i.e., glucose and fructose) using acid catalysts or enzymes. The acid-catalyzed reaction of the hexose sugar yields HMF as an intermediate product, which is further

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rehydrated to produce LA and formic acid as the final products [11].

A first systematic study of the kinetics of biomass hydrolysis to glucose was performed by Saeman in 1945 [12], who investigated the acid-catalyzed reaction of Douglas fir in batch reactors. Studies on the kinetics of hydrolysis of Kraft pulp, Solka-Floc and filter paper in a dilute sulphuric acid in a plug flow reactor have also been performed [13,14]. It has been observed that the catalytic activity of acids increases in sub/super-critical water, leading to increase in the selectivity of HMF formation through dehydration of both glucose and fructose [15,16]. Extensive work has been done to investigate the catalytic activities of acids alone or acid dissolved in solvents to achieve a high HMF yield [17–19].

Metal ion catalysts in ionic liquids (ILs) were shown to efficiently convert cellulose into HMF and LA [20]. Negligible vapor pressure, multiple solvation interactions, high ionic conductivity, and excellent chemical and thermal stability are among the many unique physicochemical properties that ILs possess [21,22]. Depending on the chemical structures of cations and anions, ILs can be made hydrophobic or hydrophilic [23]. de Bellefon et al. [24] have investigated the biphasic Trost–Tsuji coupling reactions in [BMIM]Cl to convert ethyl cinnamyl carbonate with ethyl aceto-acetate, and compared the results to the identical reaction in butyronitrile/water system. The reaction yield in [BMIM]Cl rises up to 90%, which was more than the yield (65%) achieved in the aqueous biphasic system, mainly because of the increased catalytic activity (by a factor of ten) in [BMIM]Cl resulting from the greater solubility of the substrate in the ILs [21]. Similarly, Dupont et al. [25] has studied the hydrodimerization of 1,3-butadiene with palladium(II) compounds in [BMIM]BF$_4$, wherein on the addition of 1,3,6 octatriene, the telomer octa-2,7-dien-1-ol was obtained. A turnover frequency (TOF) of 118 h$^{-1}$ was reported which could be further increased to 204 h$^{-1}$ by operating under CO$_2$ pressure. Chou et al. [26] have studied the conversion of MCC (84%) to furans using CoSO$_4$ in 1-(4-sulphonic acid) butyl-3-methylimidazolium hydrogen sulphate with a yield of up to 24% and 17% for HMF and furfural, respectively. Much improved, highly efficient, single-step processes involving paired metal chloride catalysts (CuCl$_2$ and CrCl$_3$) in [EMIM]Cl with 55% HMF yield were also reported in the literature [20,27].

Operating parameters such as residence time, temperature and mixing speed significantly influence the reaction kinetics and product yield. Lin et al. [9] has studied the effects of temperature and mixing speed on CrCl$_3$, FeCl$_3$ and CuCl$_2$ catalyzed cellulose depolymerization in water, where they showed that the increase in mixing speed increases the yield of LA up to a speed of 200 rpm, and attains a constant value thereafter. With the increase in temperature from 180 to 200 °C, the yield of LA increases whereas those of glucose and HMF decrease gradually. In order to investigate the effects of temperature and catalyst concentration on reaction kinetics, Saeman [12] presented a kinetic model on the acid-catalyzed wood saccharification, where the decomposition of sugars was represented by first order reaction kinetics along with the empirical equations for rate constants [12]. McParland et al. [28] have also discussed a kinetic model for acid hydrolysis of cellulose using homogeneous first-order reaction kinetics and the rate expression for glucose formation was presented. Most recently, Shen and Wyman [17] have presented a kinetic model and its analytical solution to determine the LA and FA through glucose and HMF, based on irreversible pseudo-first order reaction kinetics.

Since acid-catalyzed hydrolysis involves solid–liquid interactions, no simplified model can accurately predict the behaviour and the physical changes of the complex structure of raw cellulose during the course of the reaction. Previous studies have shown ILs as exceptional solvents for cellulosic substrates as they can dissolve both refined and natural cellulose to high concentrations [29–31]. It has been shown that ILs are suitable solvents for the acidic hydrolysis of lignocellulosic biomass [30,31]. Vanoye et al. [32] used a first order chain scission model to quantify the kinetics of acid-catalyzed cellulose depolymerisation, followed by a first order glucose degradation to HMF [32]. Specific studies on the effect of ionic liquid pre-treatment on enzymatic hydrolysis of biomass [33] and the adsorption based recovery of the glucose from the ionic liquid [34] have also been recently reported.

Previous studies on cellulosic depolymerization in ILs are mainly concerned with the effect of temperature and catalyst activities and have not explored the effects of mass transfer/mixing on reaction kinetics. While our previous works have captured the effect of mixing on the enzymatic production of cellulosic fuels in continuous [35] and batch [36,37] systems, here we attempt to quantify the effect of mixing (i.e., mass transfer) and temperature on the CuCl$_2$-catalyzed reaction kinetics in ILs. The primary objectives of this paper are (i) to quantify the effect of mixing speed (rpm) on reaction kinetics by developing a relationship between mixing speed and rate constants on product yield, (ii) to study the effect of temperature on the reaction kinetics of Avicel degradation to glucose, HMF and LA in a batch reactor; (iii) to develop a kinetic model based on the proposed reaction scheme and validate the analytical solution of the model with our experimental data, (iv) to determine the model parameters (kinetic constants and activation energies) for each reaction using our experimental data, (v) to obtain algebraic expressions for variation of the rate constants with mixing speed and temperature, (vi) to predict the mass-transfer controlled asymptote and the kinetic asymptote from the expression obtained in (v), and (vii) to recommend the optimal mixing speed and temperature for best conversion and product distribution.

## 2. Experimental

In this work, the effect of temperature on catalytic conversion of cellulose is captured in the range of 120–160 °C, whereas mixing characteristics are studied in the range of 0 rpm (no mixing) to 150 rpm (high mixing). The detailed experimental strategy and the analytical methods used are explained below.

### 2.1. Materials and chemicals

Microcrystalline cellulose (MCC), Avicel PH101 with an average particle size of 50 μm and particle density of 0.6 g/cm$^3$, purchased from Sigma Aldrich Co., USA, was used as substrate. d-(+)-Glucose (99.7%) was obtained from Merck, India. Ionic Liquid (IL) 1-butyl-3-methylimidazolium chloride [BMIM]Cl (98%), HMF (99.7%) and levulinic acid (LA) (99.7%) were supplied by Himedia Lab Mumbai, India. CuCl$_2$ with (99.7%) was obtained from S.D. Fine Chemicals Limited, Mumbai, India.

### 2.2. Experimental technique

The reaction was performed in 10 ml glass vials, in which a mixture of 3 g of [BMIM]Cl and 18.9 mg of copper chloride catalyst (CuCl$_2$) was taken and premixed at 150 °C and 600 rpm for 30 min to completely dissolve the catalyst in the ionic liquid. The homogenous mixture was then cooled to room temperature. 300 mg of Avicel was added into the reaction vial and kept at the desired temperature and mixing speed for 1 h, following which the reaction mixture was cooled and samples were taken out for analysis. 300 μl of HPLC water was added and the reaction was continued for 20 h. Sampling was done every half an hour for the first 3–4 h and then every one hour up to 20 h of the reaction period. Samples were properly diluted and centrifuged for further