



# Kinetic analysis and process modeling for cellulose valorization in cooperative ionic liquid pairs



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## ABSTRACT

Studies on kinetic analysis and process modeling are important and necessary for the development of novel and efficient technology for cellulose utilization. In this study, a kinetic model for the batch reactor was described for catalytic cellulose degradation in cooperative ionic liquid pairs based on an intensive analysis of the experimental parameters. Our fitting results show that the proposed model agrees well with the experimental data. The kinetic parameters obtained from the above model were subsequently applied to the continuous stirred tank reactor (CSTR) by constructing a mathematical process model for the continuous operation of cellulose degradation combined with product separation. The effects of reaction temperature, retention time, extract flow rate and distribution coefficients were intensively investigated. The numerical results demonstrate that relatively high temperature and larger retention time are favorable in cellulose conversion, whereas the product distribution coefficient and extract flow rate mainly affect the concentration of the hexane-soluble fraction (volatile chemicals). The findings presented in this work will serve as a beneficial reference for further biomass transformation of industrial purpose.

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## 1. Introduction

Conversion of biomass substance to bio-fuel or chemicals is being actively pursued because of its great potential for relieving the environmental pollution and energy crisis [1]. However, typical transformation methods for this process are generally cost-ineffective due to the complex and highly recalcitrant property of the biomass composition caused by the robust 3D hydrogen bond network, so the current technologies are unable to meet the requirement of large scale commercialization [2,3]. Therefore, efficient biomass valorization technology at mild conditions is crucial and highly desirable. Catalytic liquefaction is regarded as a useful technique for biomass valorization because of its comparatively mild reaction condition (low temperature and pressure) and concentrated production distribution [4]. In general, both chemical and biochemical catalytic processes are considered to be efficient strategies for biomass liquefaction [5–8]. However, the liquefaction efficiencies are still improvable because the lignocellulosic biomass is normally non-dissolvable in both water and traditional organic solvents. Various process intensification techniques thereby have

been extensively explored for promoting the liquefaction degree, product yield and selectivity, and reducing the reaction temperature and time [9–11].

In 2002, Rogers and coworkers found that cellulose can be directly dissolved in alkyl-imidazolium ionic liquids (ILs) under a moderate condition with 10 wt% solubility [12], which opens up a new perspective for the homogeneous liquefaction of biomass and its components. ILs as a novel solvent or efficient catalyst for biomass disposition has thereby received increasing attention [13–16] and it is regarded as a useful solvent to achieve biomass valorization. For example, the efficient hydrolysis of cellulose was reported with more than 77% yield of reducing sugar over the ILs [bmim]Cl and proton acid catalyst [17]. The conversion of cellulose and real lignocellulosic biomass to fine chemicals, such as 5-hydroxymethylfurfural (HMF) and levulinic acid, were also extensively examined [18–20]. However, in most of the above-mentioned processes, cellulose should be pre-dissolved in the ILs. Therefore, the liquefaction efficiency in these processes is still an issue due to the limited solubility of biomass in ILs. In order to solve this problem, we previously proposed a dissolution and *in-situ* degradation mode for cellulose and lignocellulosic biomass liquefaction at mild conditions using cooperative IL pairs [21–23]. In a typical approach [21], the cellulose was first partially dissolved by the IL solvent to give a homogeneous medium, and then this

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### Nomenclature

$C_0$	initial cellulose concentration in reactor (g/L)
$C_c$	catalyst concentration (g/L)
$C_f$	fast-reaction part concentration (g/L)
$C_h$	hexane-soluble products concentration (g/L)
$C_m$	methanol-soluble products concentration (g/L)
$C_m^E$	methanol-soluble products concentration in extract (g/L)
$C_h^E$	hexane-soluble products concentration in extract (g/L)
$C_{rf}$	active concentration of fast-reaction part (g/L)
$C_{rs}$	active concentration of slow-reaction part (g/L)
$C_s$	slow-reaction part concentration (g/L)
$k$	rate constant
$k'$	reaction constant correlated with catalyst concentration ( $s^{-1}$ )
$m_0$	initially total cellulose mass (g)
$m_{s0}$	initial slow-reaction part mass (g)
$R_1$	distribution coefficient of methanol-soluble products
$R_2$	distribution coefficient of hexane-soluble products
$r$	reaction rate (g/sL)
$r_c$	cellulose degradation rate (g/sL)
$S$	solubility of cellulose in ILs (g/100 g ILs)
$T$	temperature (K)
$t$	time (s)
$t_R$	average retention time of feedstock (s)
$V$	volume (L)
$v$	mass flow rate (g/s)
$\Phi$	ratio of slow-reaction part
$\rho$	density (g/L)
<b>Subscripts</b>	
$f$	fast-reaction
$IL$	ionic liquid
$m$	methanol-soluble products
$h$	hexane-soluble products
$s$	slow-reaction
1	methanol-soluble products conversion to hexane-soluble products
-1	hexane-soluble products conversion to methanol-soluble products

IL/cellulose homogenous medium was catalytically degraded to useful chemical while a coordinated acidic IL was used as catalyst simultaneously. With the synergic effect of the cooperative IL pairs (one IL serving as the solvent for cellulose dissolution and the other as the catalyst for the degradation), cellulose can be completely converted to useful industrial chemical in a single batch reaction at mild conditions (473 K for 15 min). The dragging of the dissolution equilibrium, combined with the rapid, *in situ* acid-catalyzed degradation of bulk insoluble cellulose, overcame the long intrinsic problem of cellulose insolubility encountered in the conversion of biomass to biochemical. However, as the most prominent problems in current biomass conversion processes, complex combination and optimization of process factors, such as product separation, comprehensive energy utilization, solvent recycling and realization of continuous operation are far from being resolved [3] and thus should be comprehensively understood and intensively investigated. In contrary to catalysis chemistry studies, kinetic modeling and whole process simulation are able to provide deep understanding about the optimal design of the process. Such efforts are currently still in great need [24]. Our previous dissolution

and *in situ* degradation method for the transformation of cellulose and lignocellulosic biomass was originally focused on the biomass valorization in batch reactor. Its effectiveness and efficiency in comprehensive utilization of energy, convenient separation of products and mass production of biomass need to be examined and evaluated in the industrial scope.

In this work, we proposed a reaction kinetic model for the cellulose catalytic liquefaction based on the cooperative IL pairs system. The kinetic property of the cellulose degradation in a batch reactor was first investigated and analyzed. And then, based on the parameters obtained from the batch reactor, an intensive process simulation of the continuous process for cellulose depolymerization plus the product separation in an integrated reactor was put forward to provide an insight into the industrial valorization of lignocellulosic biomass and its components.

## 2. Experimental

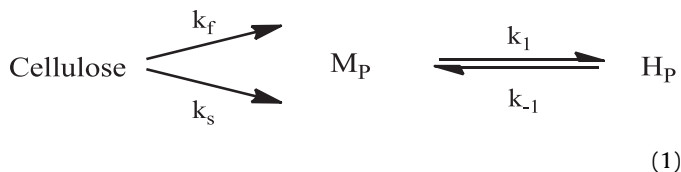
Cellulose degradation is carried out in a 150 mL stainless autoclave as a batch reactor. Typically, 5 g cellulose, designated amount of cooperative ILs (20 g bmimCl and 3.5 mmol  $C_4H_8SO_3HmimHSO_4$ ), 10 mL methanol and 80 mL hexane are added to the reactor. After displacing the air in the reactor with nitrogen, the reactor is heated and kept at designated temperature for 15 min, and then the mixture of IL and products are cooled to room temperature for separation.

The product from the cellulose degradation forms two phases in a separating funnel, and is first separated. The heavy component fraction is then extracted by hexane for three times to remove the residual volatile chemical in the IL. By collecting the extract and the upper phase product, the hexane-soluble fraction is obtained. After a sequence of IL removal operations (extracted by  $CH_2Cl_2$ ) and dilution with methanol, the nonvolatile product from the cellulose dissolution and degradation process is obtained as the methanol-soluble fraction. The volatile components are determined with a gas chromatography mass spectrometry (GC-MS). The molecular weight distribution of the methanol-soluble fraction is measured with a gel permeation chromatography (GPC) and the particle size of this fraction was measured with the Malvern analysis [21].

## 3. Modeling

### 3.1. Kinetic model in batch reactor

The dissolution and *in situ* catalytic degradation of cellulose by cooperative IL pairs are a complex process [21], in which part of the feed cellulose is dissolved by the IL solvent to yield a homogeneous solution at first, and then it can sufficiently contact with another acidic IL catalyst to form an efficient process. At the same time, the depolymerization of cellulose in the first step can be divided into two fractions: fast-reaction and slow-reaction parts to obtain the methanol-soluble products. Then, the second step about further degradation of the methanol-soluble products, as a homogeneous reaction, can be simplified as a reversible first order process. This two-step reaction model in a batch reactor is described as Eq. (1):



where  $M_p$  and  $H_p$  represent the methanol-soluble and hexane-soluble products, respectively. The rate constants  $k_f$  and  $k_s$  are for the fast reaction and slow reaction, whereas  $k_1$  and  $k_{-1}$  denote the

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