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Kinetics of Microwave-based Ionic Liquid-mediated Catalytic Conversion of Ricinus Communis to Biofuel Products

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The main objective of this work is to determine the kinetics of a fast, economically viable process for the conversion of lignocellulose (Ricinus communis) to fuel products such as 5-hydroxymethylfurfural (HMF) – the platform chemical, along with the production of glucose for bioethanol production. Here, we perform ionic liquid ([BMIM]Cl) based catalytic conversion of Ricinus communis (Castor leaves/tree mixtures) under the influence of microwave radiations with $CuCl_2$ as a catalyst in a microwave reactor. The lignocellulosic substrate is first depolymerized into glucose, which then converts to HMF that further dissociates into levulinc acid (LA) and formic acid (FA). We focus on experimental determination of the optimal water addition and microwave heating profile (temperature and pressure) for maximizing the HMF yield from Ricinus communis in [BMIM]Cl aided with $CuCl_2$ catalyst. Our kinetic model along with a Power Law model (for the dehydration of HMF and conversion of HMF to LA) and Biphasic Model (for lignocellulose hydrolysis) for quantifying the temporal dynamics of glucose and HMF production uses our understanding of the crucial role that water plays in determining the product distribution. The effect of pre-treatment on the lignocellulosic substrate has also been analyzed using FESEM (pore structure, size and density), BET (pore-surface analysis), Particle Size Analyser and XRD (extent of crystallinity). The microwave reactor helps align the dipoles in the electromagnetic field created by the combination of ionic liquid and microwave radiation, thus reducing the total reaction time drastically to 35 - 50 min, while our novel water addition strategy allows us to manipulate the production distribution for maximizing the conversion of lignocelluloses to HMF via glucose.

1. Introduction

Lignocellulosic fuels are an important class of second generation biofuels for the future, particularly because they, unlike the first generation cellulosic fuels, do not engender any food vs. fuel debate. Lignocellulosic agricultural residues such as wheat straw, Jatropha, sugarcane, castor plant, corn starch, wheat straw, etc. represent a promising resource to serve as a sustainable feedstock for the production of second generation biofuels. The major chemical components of lignocellulosic biomass are cellulose, hemicelluloses and lignin. Cellulose is a linear polymer of β-1,4-glycosidic bonds units linked by hydrogen-bonding (Nishiyama et al., 2003) and van der Waals forces (Notley et al., 2004). Hemicelluloses are polymers composed of pentose and hexose sugars. They differ from cellulose by being smaller and have branched polymer chains (Carrier et al., 2011), usually containing more than one sugar type; they are also amorphous polysaccharides. Lignin is a complex, cross-linked, three-dimensional polymer formed with phenyl-propane units. The chemical differences between these components directly influence their chemical relativities.

Lignocellulose feedstocks can be converted into fuel products or fuel precursors via pyrolysis, gasification or by hydrolysis. HMF is one of the leading fuel precursors, used for formation of 2,5-dimethylfuran and 2-methylfuran, which are promising liquid transportation fuels (Zhong et al., 2010). HMF has been considered as feedstock of bioenergy, building-block chemical, and medicine. However, pyrolysis is limited due to the complexity of high temperature thermochemical conversion, low yield and purity of product (Bridgwater, 2003). Gasification requires precise metal catalyst and alkali concentration (Tavasoli et al., 2015). Moreover, lignin and cellulose render the substrate recalcitrant to hydrolysis, reducing yields (Mosier, 2005).

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Ionic liquids (IL) are good biopolymer solvents for celluloses and lignocelluloses, which are easy to recycle, and are capable of accelerating the grafting reaction rate as a reaction medium (Chang et al., 2015). Swatloski et al., 2002, compared the solubility and the decomposition effect of Ionic liquids with that of water, and showed that the reactions are more rapid and stable in IL medium. Up to 25 wt.% of cellulose can be dissolved in $[C_4mim]Cl$ to form a homogeneous solution. Chloride-containing Ionic Liquids have shown to be more effective in substrate solubilation than $[BF4]^-$ and $[PF6]^-$. High activity and chloride concentration of IL enhance its ability to break the extensive hydrogen bonding present in the substrate. Studies by Pinkert et al., 2009, also showed that ILs are highly polar due to their ionic character, resulting in their enhanced biopolymer dissolving capacity engendered by their effective polarity and hydrogen bonding capacity, and also their melting temperature and the viscosity. Using $[C_4mim]Cl$ as IL and $CrCl_3$ as catalyst, Li et al., 2009, showed that β-1,4-glucosidic bonds of cellulose were weakened partially because of coordination with $[CrCl^{3+}n]_n$, enhancing the possibility of water attack during hydrolysis. Glucose undergoes complex muta-rotation, forming α and β glucopyranose anomer with Chloride ion. The α and β anomers undergo a series of rearrangement to form HMF, that further dissociates into levulinc acid and formic acid.

The dissolution rates of the substrate can be significantly improved by heating in a microwave oven (Swatloski et al., 2002). Pinkert et al., 2009, showed microwave heating to be an internal heating process due to the direct absorption of energy by polar molecules. This internal heating leads to more effective breakdown of the H-bond network causing rapid and easy depolymerisation of biopolymers. de la Hoz et al., 2005, showed that cellulose and IL combination has the ability to absorb microwave energy and effectively convert the electromagnetic energy to heat. According to Beszedes et al., 2012, alternating electric field induces vibrational motion of ions but the dipoles present attempt to align themselves with the oscillating electric field of the microwave irradiation, leading to their rotation. This vibrational motion of ions and the resistance of the reaction mixture to ion flux leads to heat generation that increases the temperature (Li et al., 2009). Microwaves also lower the reaction’s activation energy by decreasing the pre-exponential factor in the Arrhenius equation due to the orientation effect of the polar species (IL and substrate) in an electromagnetic environment (Hosseini et al., 2007). A fast, economically viable process for conversion of lignocelluloses to bioethanol has been innovated by Chakraborty and Paul, 2016, using Sunn hemp as the lignocellulosic biomass substrate, which reduces the total reaction time drastically to 35 - 50 min. We use the same process (Chakraborty and Paul, 2016) to convert Ricinus communis (castor plant residues) to fuel precursors such as HMF and glucose, and quantify the kinetics of the process.

2. Experimental

In this work, the effect of microwave is studied on catalytic conversion of Ricinus communis (50 % cellulose, 29.46 % Hemicellulose and 17.34 % Lignin by weight) in IL medium by quantifying the yields of the fuel precursors (glucose and HMF), morphological characteristics of substrate during 5 – 20 min of pre-treatment. The detailed experimental strategy and the analytical methods used are explained below.

2.1 Materials and chemicals

Ricinus communis (finely crushed and dried Castor Plant residues such as stems and leaves), 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 %) are supplied by Himedia Lab Mumbai, India. $CuCl_2$ with (99.7 %) is obtained from S.D. Fine Chemicals Limited, Mumbai, India.

2.2 Microwave Reactor

Titan MPS™ 16 Position Microwave Sample Preparation System: Incorporates Standard 75mL (40 Bar) TFM digestion vessels, DTC™ Direct Temperature Control™ and DPC™ Direct Pressure Control™.

2.3 Experimental technique

The reactions are performed in Standard Microwave Vessel (75 mL) at 35 atm and 190°C, in which a mixture of 2 g of [BMIM]Cl and 4 mg of copper chloride catalyst ($CuCl_2$) and 100 mg of Ricinus communis are mixed. Samples are added with different water percentages varying from 5 % to 50 % of IL and exposed to microwave radiation for different amounts of time (5 - 20 min). After the reaction, the setup is cooled down for 10 min before samples are taken out for analysis. Glucose is measured using UV spectrometer whereas HMF and LA are determined using a HPLC system. Surface analysis is done using FESEM and the particle size distribution is measured using the Particle Size Analyser.

2.4 Kinetic Model

We use the kinetic model proposed by Gaikwad and Chakraborty, 2014, for the decomposition of cellulose to glucose, which further converts to 5-hydroxymethylfurfural (HMF), levulinic acid (LA) and formic acid (FA).

$$\underset{Cellulose}{(C_6H_{10}O_5)_n} \overset{k_1}{\rightarrow} \underset{Glucose}{C_6H_{12}O_6} \overset{k_2}{\rightarrow} \underset{HMF}{C_6H_6O_3} \overset{k_3}{\rightarrow} \underset{LA}{C_5H_8O_3} + \underset{FA}{C_2H_2O} \tag{1}$$

$$C_{Cel} = C_{Cel0}\exp(-k_1 t) \tag{2}$$

$$C_{Glu} = \frac{k_1 C_{Cel0}}{(k_2-k_1)}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{3}$$

$$C_{HMF} = k_1 k_2 [\frac{\exp(-k_1 t)}{(k_2-k_3)(k_3-k_1)} - \frac{\exp(-k_2 t)}{(k_2-k_1)(k_3-k_2)} + \frac{\exp(-k_3 t)}{(k_3-k_1)(k_3-k_2)}] \tag{4}$$

$$C_{LA} = C_{Cel0} - C_{Cel} - C_{Glu} - C_{HMF} \tag{5}$$

where C_{Cel}, C_{Glu}, C_{HMF}, C_{LA} are the concentrations of cellulose, glucose, HMF, and LA, respectively, and k_1, k_2 and k_3 are the pseudo-first order reaction rate constants for the three reactions. In this paper, these reactions are taken as the basis for the kinetic analysis of our process.

3. Results and Discussions

3.1 Effect of Water Concentration on Glucose and HMF yield

The reaction between Ricinus Communis and IL is accelerated by the continuous dipole rotation in the presence of microwave field, which helps in reducing both the mass transfer and reaction resistances. Figure 1 and Figure 2 show a maximum glucose concentration of 15.28 mg/mL, with a yield of 75.71 % for 30 % of water addition and a reaction time of 15 min. The decrease in glucose on further water addition may be attributed to the fact that the cellulose is insoluble in water and precipitates even before the reaction can start. A maximum HMF concentration of 1.292 mg/mL, with a yield of 5.63 %, is observed at 15 % water addition. Since the formation of HMF from glucose is a dehydration reaction, lower water concentration ensures higher HMF production and the HMF yield decreases continuously with higher water addition. However, at 5 % water addition, the HMF yield was lower since the glucose formed is significantly lower. A maximum LA concentration of 6.80 mg/mL, with a yield of 16.37 %, is observed at 30 - 35 % water addition. Since the formation of LA from HMF is much faster reaction than the formation of HMF from glucose, high glucose concentrations correspond to high LA concentration. The maximum overall conversion of 95.2 % is observed at 30 % water addition with three fuel precursors (glucose, HMF and LA) being formed.

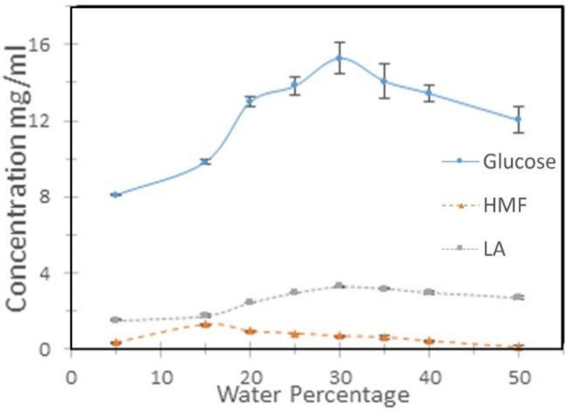

Figure 1: Dynamics of Glucose, HMF and LA for different amounts of water addition

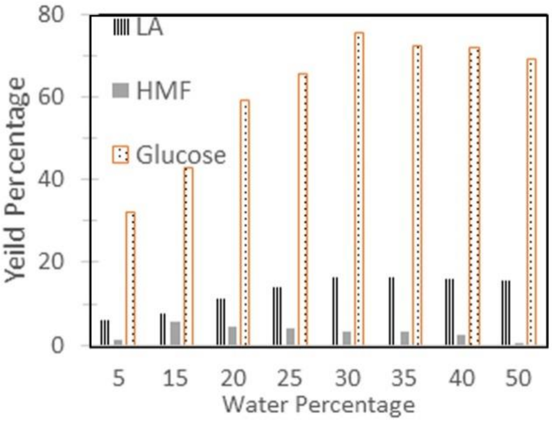

Figure 2: Yield Analysis of Glucose, HMF and LA Yield for different amount of water addition

3.2 Effect of water over Rate Constants

Using Eq(2), (3), (4) and (5), the kinetic constants k_1, k_2 and k_3 are calculated and plotted against the % water addition (Figure 3 and Figure 4). These were fitted using a MATLAB curve-fitting tool to generate a kinetic model that quantifies the effect of water addition on the kinetic constants. Figure 3 shows that the hydrolysis of cellulose to glucose follow a biphasic response, since at lower water concentrations (up to 30 %), the glucose concentration increases whereas above 30 % water addition, there is a decrease in glucose concentration, whereas, the formation of LA follows Power Law model (Figure 3).

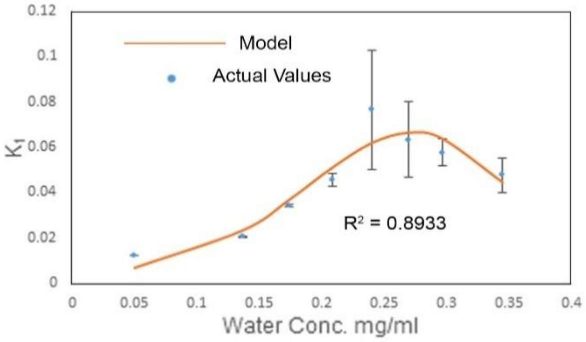

Figure 3: Curve Fitting for K_1 (sec^{-1}) v/s water: Biphasic Model

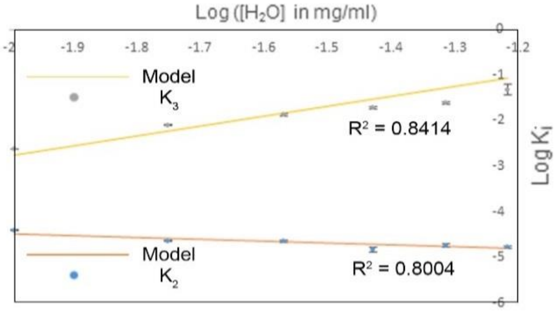

Figure 4: Curve Fitting for Log K_2 (sec^{-1}) and Log K_3(sec^{-1}) v/s Log water (mg/ml): Power Law Model

The effect of water on the observed rate constants may be quantified as

$$K_1(sec^{-1}) = 0.00414 * exp(33.37\left[H_2O\left(\frac{mg}{ml}\right)\right]^{1.379}) * exp(-97.93\left[H_2O\left(\frac{mg}{ml}\right)\right]^{2.723}) \quad (6)$$

$$K_2(sec^{-1}) = 0.0051 * \left[H_2O\left(\frac{mg}{ml}\right)\right]^{-0.4057} \quad (7)$$

$$K_3\ (sec^{-1}) = 4.8453 * \left[H_2O\left(\frac{mg}{ml}\right)\right]^{2.173} \quad (8)$$

3.3 Effect of reaction time on glucose and HMF yields

The concentrations of Glucose (Figure 5) and HMF (Figure 6) gradually increase with the increase in reaction time from 5 min to 15 min, and decreases with subsequent increase of reaction time. This is probably because of spontaneous decomposition of cellulose to lower chain length polymers rather than to its monomer glucose, due to prolonged exposure to microwaves. However, both the concentrations are out of phase w.r.t water addition as higher water concentration restricts the dehydration reaction leading to HMF production.

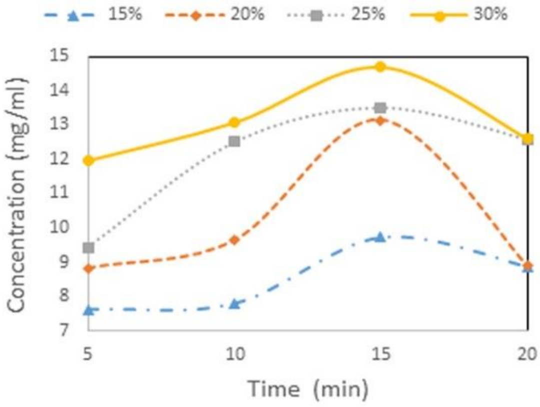

Figure 5: Glucose Conc.(mg/mL) with time (min)

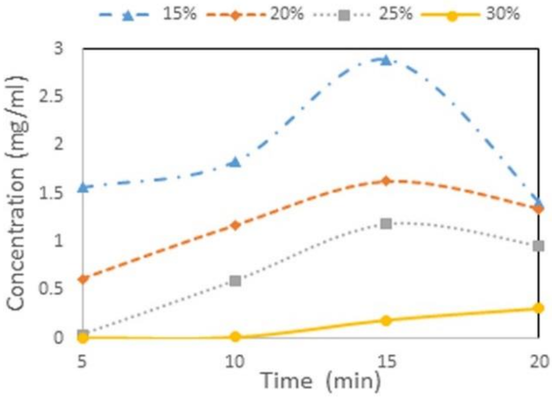

Figure 6: HMF Conc.(mg/mL) with time (min)

3.4 Substrate Surface Analysis

Figure 7 shows a significant decrement in both pore size and density with both longer reaction times and water addition. As extent of the reaction increases, the surface of the substrate dissolves due to hydrolysis, allowing the chlorine ions from the IL to fill the pores; hence reduction is size observed with increase in time. (At t = 20 min, the sample is almost burned due to prolonged exposure to microwave radiation.)

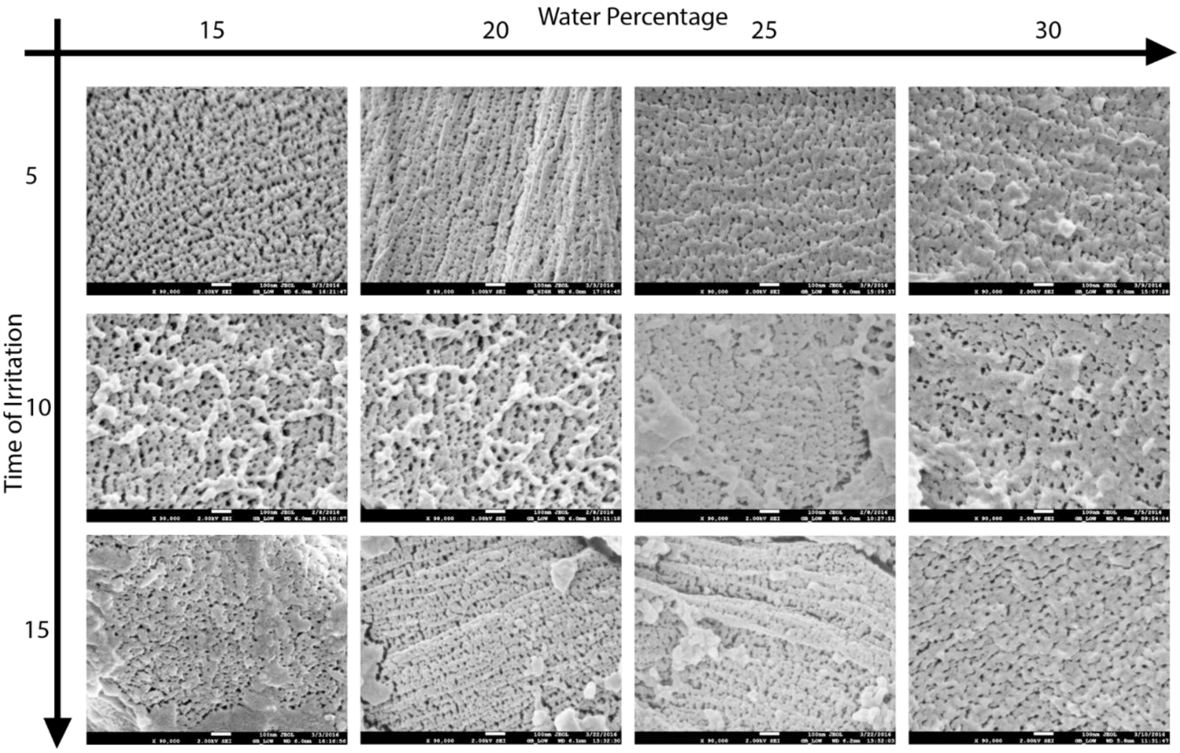

Figure 7: Variation of Pore density of treated sample with increasing time and water addition (%)

3.5 Particle Size Analysis

Figure 8 shows a shift in mean pore size and peak density (measured by Particle Size Analyzer) as the reaction time increases from 0 to 10 min. The particle size of 120 μm appears to be a crucial point for determining the extent of reaction and potential of the sample to convert to the desired fuel products.

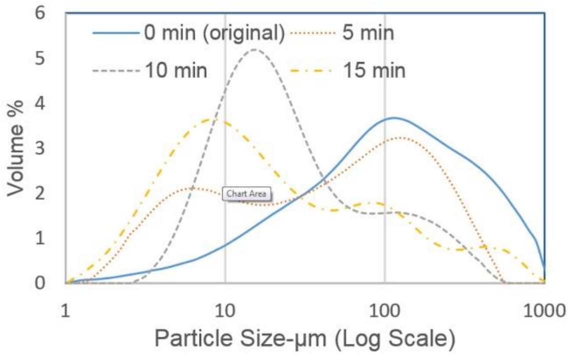

Figure 8: Particle Size variation (μm) with time

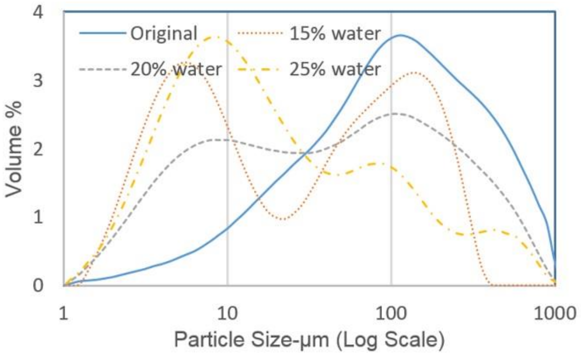

Figure 9: Particle Size variation (μm) with water added

4. Conclusion

This experimental study for the catalytic conversion of Ricinus Communis under the microwave-ionic liquid medium turns out to be a fast and efficient process for the production of fuel precursors such as glucose and HMF. A microwave radiation mediated reaction at 190 °C for 15 min results in maximum conversion of the lignocellulosic biomass. However, based on the desired product distribution, one may switch to 30 % water addition for maximizing glucose yield to about 76 % or 15 % water addition for maximizing HMF yield to about 6 %. Our morphological studies reveal that the microwave-ionic liquid combination decreases the pore size decrease as the reaction progresses. We quantify the three kinetic constants for the process, as well as model how the water addition affects these rate constants, thus accelerating the hydrolysis of cellulose to glucose as well as Levulinc Acid production from HMF but inhibiting the dehydration reaction for the formation of HMF.

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