

OPTICAL AND CONFOCAL MICROSCOPIC STUDIES ON DISSOLUTION OF RICE STRAW PARTICLES IN 1-ETHYL-3-METHYLIMIDAZOLIUM ACETATE

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Abstract

Abundant agriculture residue such as rice straw needs an effective pretreatment method in order to efficiently and economically process it into biofuels and chemicals. In order to develop an economical liquefaction process for pretreatment of rice straw, a 3D particle based-dissolution process model needs to be investigated. As a result, this study was undertaken to develop a dissolution model of ball milled rice straw (RS) particles in 1-Ethyl-3-Methylimidazolium Acetate [Emim][OAc], at 120°, 140° and 160°C using optical and confocal microscopes. These results showed the rectangular particle swelled in-plane during the heat treatment in [Emim][OAc] but the thickness and volume decreased with heating time. As the particle swelling progressed, the particle light intensity ratio increased which was confirmed by confocal and optical microscopy. Both the particle light intensity ratio and volume ratio measurement were used to estimate the particle dissolution end point. Heating at 160°C accelerated particle dissolution and swelling significantly. Decreasing the temperature from 160°C to 120°C extended the dissolving time changing from 10 min to 1 h. This new imaging analysis process model utilizing particle light intensity and volume ratios allows significant improvement in dissolution process modeling for endpoint determination and prediction. The dissolution process also has applications to other types of biomass.

Keywords: 1-Ethyl-3-methylimidazolium acetate, Ball-milled rice straw particle, Confocal microscopy, Dissolution, Ionic liquid, Optical microscopy

Introduction

Lignocellulosic biomass such as rice straw is a sustainable and underutilized renewable potential feedstock to produce biofuels that is an alternative to petroleum derived fuels. Lignocellulosic biomass is composed of cellulose, hemicellulose and lignin. Cellulose is insoluble in water and many organic solvents because of the rigid long chains and strong hydrogen bonds within. Moreover, crystalline cellulose in biomass is more difficult to dissolve than its amorphous phase [1]. Previously, crystalline to amorphous transformation of cellulose was investigated at higher temperatures and pressures by *in-situ* microscopic observation that showed complete dissolution in water where cellulose's relative brightness was monitored by micrographs [2]. Therefore, dissolution process models of lignocellulosic biomass are needed in order to promote economic process development [3]. The group of Rogers discovered that several imidazolium-based ILs can dissolve large amounts of cellulose [4]. Zavrel et al. observed that among the ionic liquids tested [Emim][OAc] is the most efficient for dissolving cellulose [5]. Sun et al. reported that [Emim][OAc] is a better solvent for wood treatment than 1-butyl-3-methylimidazolium chloride [C₄mim][Cl] because [C₂mim][OAc] dissolved approximately 98.5% of the wood

sample during the treatment, whereas [C4mim][Cl] dissolved only 52.6% of the wood sample treated under the same conditions [6]. In addition, Nguyen et al. (2010) concluded that [Emim][OAc] is a better solvent for rice straw treatment than 1-butyl-3-methyl imidazolium chloride [Bmim][Cl] [7]. Ionic Liquid (IL) pretreatment of biomass is a relatively new technology and it can decrease lignin content of biomass and also dissolve microcrystalline cellulose in lignocellulosic biomass [8].

In first published paper of this study, we proposed the dissolution model based on dissolution of ball milled rice straw particles at different milling temperatures of 60°C, 25°C, and -196°C (cryogenically) in [Emim][OAc] at three different temperatures (120°C-160°C) and applied this model to the optical microscope [9]. We departed from our earlier proposed the basic characterization of rice straw powder of different milling temperatures. In doing so successfully predicted the particle dissolution time and changes particle swelling behavior using optical image analysis. In this study, to better understand the dissolution process model, the three dimensions (3D) image analysis is needed at the microscopic particle level. Previously, a published observation on the dissolution mechanism of lignocellulosic biomass in IL has shown particle swelling using optical microscopy [10]. Zavrel et al. noted that scattered light intensities are sufficient to follow physical changes during dissolution using *in-situ* image monitoring of cellulose by using optical microscope but did not model the dissolution endpoint [5].

Confocal laser microscopy provides greater insight into the structure of biomass during pretreatment because it allows for physical and chemical related measurements. On the other hand, optical microscopes are widely used for mapping RS particle surface features and there are numerous literature publications on this topic [2, 10]. Previous studies showed that thin specimen sample preparation of switchgrass can destroy and alter the sample features which makes sample or particle dissolution studies using this technique impractical [11]. Luterbacher et al. investigated auto fluorescence intensity behavior effect on the hydrolysis by using the fluorescence imaging [12]. However, they did not measure localized light intensity change and compare systematically the relationship between the biomass particle structure and background's light intensity changes. What is currently lacking in the literature is a comprehensive and quantitative study that evaluates the dissolution of RS particles using both optical microscopy and confocal laser microscopy. Furthermore, how to estimate the end point of particle dissolution of lignocellulosic biomass based upon particle thickness, light intensity and particle volume has not yet been investigated in detail.

Therefore, in this study the objective was to measure rice straw particle light intensity ratio, volume ratio, and area ratio during dissolution in [Emim][OAc] by ex-situ heating at 120°, 140° and 160°C utilizing both optical and confocal microscopy. This allowed us to develop two new particle light intensity ratio model and volume ratio model of the rice straw particle dissolution process and end point determination which we believe can be extended to other temperatures and applicable to other types of biomass.

Material and Methods

Preparation of Milled Rice Straw powder

Dried rice straw (RS) stalks were obtained from a Machida City, Tokyo, Japan Tatami mat vendor in the *Naruse* district. Dried rice straw stalks were cut into a length of 1 cm. A stainless steel milling jar containing 3 g of 1 cm cut rice straw strips with a 25 mm stainless steel ball was kept in an oven at room temperature for 2 h prior to grinding. The RS pieces were milled with a Mill Mixer (Retsch MM400, Germany) at a frequency of 28 Hz with a 25 mm stainless steel ball for 2 min followed by screening to achieve powder particle size

ranges from 75 to 100 μm using a Vibratory Sieve-Shaker (ANALYSETTE3, Germany).

Dissolution Procedure of Rice Straw Particle in [Emim][OAc]

Ionic liquid 1-ethyl-3-methylimidazoliumacetate [Emim][OAc] (97% purity) was purchased from Sigma Aldrich and used without further purification. Ball milled RS particles having dimensions between 75-100 μm were put on a hot plate and dried at 140°C for 5 min in air on a glass slide to desorb moisture prior to adding [Emim][OAc]. In a typical dissolution trial, 0.01 mg of rice straw was added to 10 μL [Emim][OAc] on a 1.0 mm thick glass slide and heated on a hot plate (HP-1S, As One, Japan) at 120°C. The glass slide containing the RS particles in the [Emim][OAc] drop was removed from the hot plate and observed periodically by an optical microscope (Olympus BX41, Japan) with a Olympus E330 Hyper Crystal LCD digital camera (Japan) as well as using a Confocal Laser Scanning Microscope (CLSM) (Olympus FLUOVIEW, FV 1200, Japan) after fixed intervals of time. For the comparison of quantitative measurement of dissolution mechanism, the RS particles heated in [Emim][OAc] at 120°, 140°, and 160°C were also observed with both microscopes. In addition, heating at 160°C was done in triplicate on particles to confirm microscopic reproducibility. Therefore, we only report the triplicate results since they were done precisely using the same conditions.

Advanced Imaging Analysis for Rice Straw Particle Dissolution

For optical microscopy imaging, dissolution of RS particle was monitored using the above noted optical microscope for measurements of particle dimensions a Dino-Lite calibration grid was used and the magnification was 60 times in microphotographs using a 20 X objective lens. In confocal laser scanning microscopy imaging system, fluorescence of the RS particles in [Emim][OAc] were imaged without inverting the glass slide with fixed excitation laser power at 2% (transmissivity). Alexa Fluor 488 dye was used with an excitation wavelength of 473 nm and the emission spectra wavelength of 520 nm was detected with a meta-detector scan range of 405-700 nm. Olympus image analysis software (FV10-ASW; Ver. 04.00) was employed for controlling the confocal microscope and image acquisition and area/volume measurements.

Particle Volume Measurement with Confocal Laser Scanning Microscopy

For the acquisition of 3D images and for calculating the particle volume, multiple 2D images were taken after which the stage was raised (z dimension) with a stepping motor under computer control [13]. The particle height or thickness was determined from imaging the top and bottom of the particle while in focus. The stage was moved by dividing the thickness into 11 steps or slices and scanning at each of the intermediate steps. The particle area was determined by measuring the particle perimeter outline from the 2D images and calculating the area. The measured thickness of the particle was multiplied together by the particle area to estimate the particle volume in the case of manual volume measurements.

Figures of Merit - Ratios

The optical microscope particle images were analyzed using ImageJ software to measure the area and confocal microscope images were also analyzed to determine the particle areas and light intensity ratios. The cross-sectional area ratio of particle was calculated using the particle areas as a function of heating time (t) versus the initial area prior to heating (t=0) by Equation 1.

$$\text{Particle Area ratio } (t) = \frac{\text{RS Particle Area } (t)}{\text{RS Particle Area } (t=0)} \quad (1)$$

The particle light intensity ratio was calculated based upon integrating the average color intensity of the particle over the selected area defined above with optical and confocal microscopy compared to [Emim][OAc] background intensity as shown in Equation 2,

$$\text{Particle Light intensity ratio } (t) = \frac{\text{RS Particle Light intensity } (t)}{[\text{Emim}][\text{OAc}] \text{ Light intensity } (t)} \quad (2)$$

The RS particle volume ratio as a function of heating time was calculated using equation 3 below from the confocal microscope image results where volume was calculated from the particle area that was multiplied by the particle thickness,

$$\text{Particle volume ratio} = \frac{\text{RS Particle volume } (t)}{\text{RS Particle volume } (t=0)} \quad (3)$$

Inorganic Material Analysis by ICP-AES

The RS powder was heated with an electric furnace at 500°C for 5 hr, dissolved in concentrated Hydrogen Fluoride (HF) and analyzed by ICP-AES using standards (SPS 7800, Plasma Spectrometer, SII Seiko instruments Inc. Japan).

Results and Discussion

RS particle dissolution experiments were carried out separately in [Emim][OAc] at temperatures of 120°, 140° and 160°C shown in (Figure 1, 2 and 3).

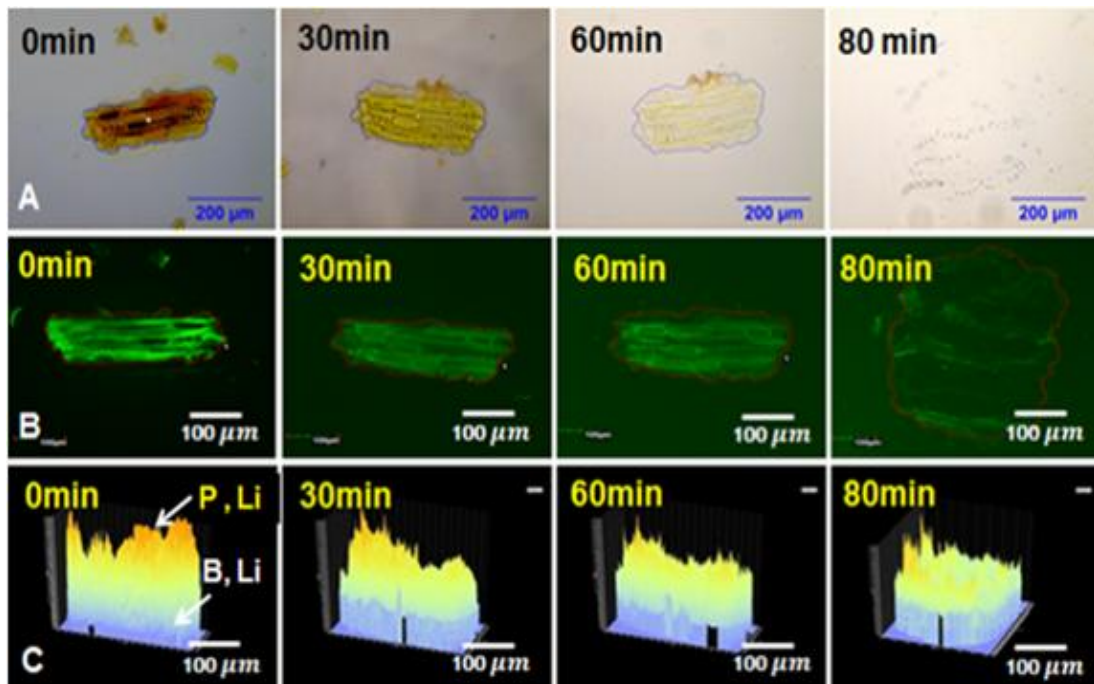


Figure 1. RS particle dissolution in [Emim][OAc] at 120°C as a function of elapsed time from 0 to 80 min. row a) optical microscope images, row b) confocal microscope fluorescence images, row c) Maps of particle fluorescence light intensity change vs time and its position (“P, Li” represents particle light intensity “B, Li” is the background light intensity shown in row c, arrowheads)

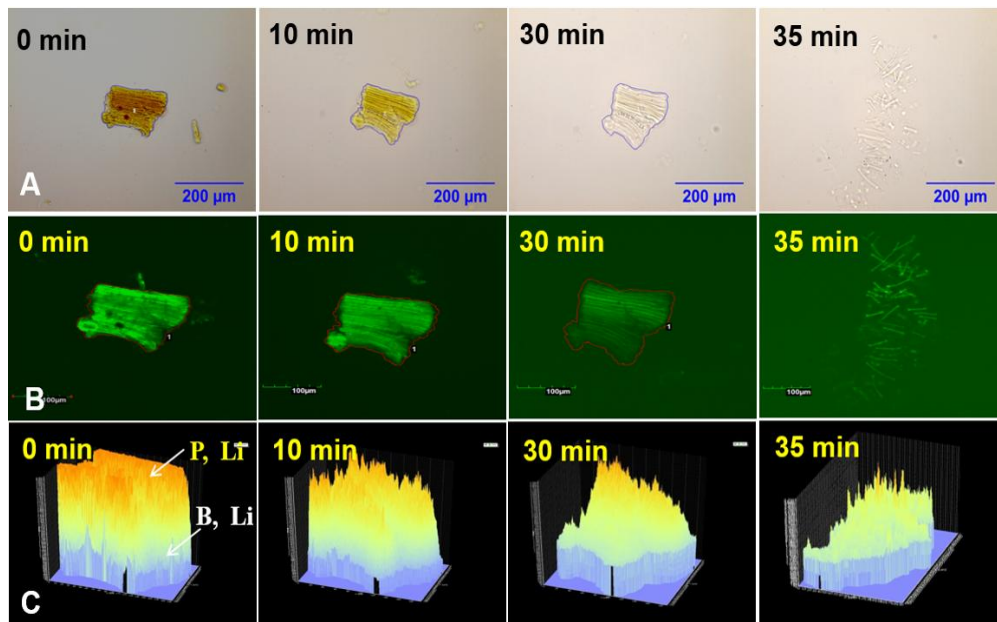


Figure 2. RS particle dissolution in [Emim][OAc] at 140°C as a function of time. row a) optical microscope images. row b) confocal microscope fluorescence images, row C) Maps of particle fluorescence light intensity change vs time and its position. (“P, Li” represents particle light intensity “B, Li” is the background light intensity shown in row C, arrowheads).

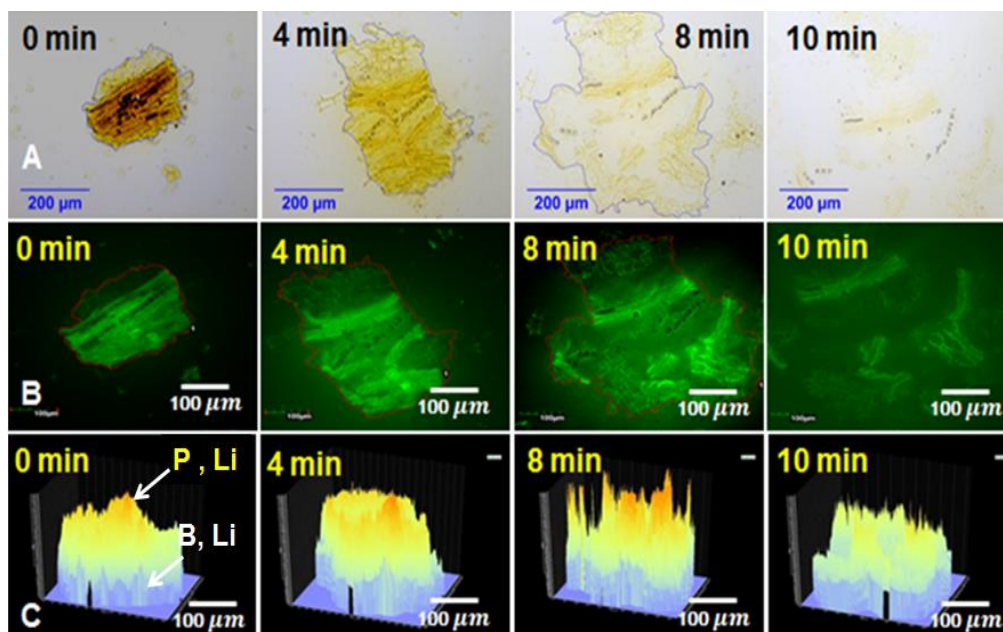


Figure 3. RS particle dissolution in [Emim][OAc] at 160°C as a function of elapsed heating time from 0 to 10 min. row a) optical microscope images, row b) confocal microscope fluorescence images row c) maps of particle fluorescence light intensity change vs time and its position. (“P, Li” represents particle light intensity “B, Li” is the background light intensity shown in row c, arrowheads).

The confocal image shows the same particle with similar texture clearly as optical microscopic images but in green light due to the laser wavelength. The RS particle cross-sectional area was monitored periodically starting from initial heating time (0 min) up to the point at which the particle became so transparent that it was considered to be literally dissolved. In general, upon heating the rectangular-shaped wafer-like RS particles in

[Emim][OAc], the circumference gradually increased with an expanding cross-sectional area as the heating time progressed. It was observed that the rectangular particle surface gradually dissolved, becoming thinner and the particle circumference became larger as noted from left to right in Figure 1, 2 and 3. Therefore, our dissolution model may be applied for use to the other type of biomass that consist of flat particles. However, for fibrous materials, the dissolution is accompanied by swelling also known as ballooning (Navard et al., 2011) [14]. In view of this image analysis, and the fact that published work has not investigated such matters, i.e. measuring composition of dissolved RS particles are difficult. The particle heated at 120°C dissolved in about 60 min, whereas the particle heated at 160°C dissolved in 10 min. Actually, the end point dissolution time of rice straw particle at 120°C occurred at 80 min. Mantanis and coauthor pointed out that two stages are involved in dissolution process: first, the particle (polymer) swelling followed by the dissolution step [15].

The optical microscope image shows a yellowish particle with a mosaic appearance in liquid [Emim][OAc] where the black circular matter consists of SiO₂ particles. In general, dried rice straw contains about 11% SiO₂ and it does not dissolve in the solution and remains [16]. Van Soest et al. stated that silicon cannot be dissolved by solvent in contrast to the action of sodium hydroxide [17]. In addition, as discussed in our first publication on this topic, we measured ICP-AES analysis of rice straw ash composition as shown in Table 1. We also observed that rice straw contains inorganic elements.

Table 1. ICP-AES Analysis of Rice Straw Powder Ash Composition

Inorganic material in RS sample	Si	K	Fe	B	Mn	Mg	Ca	Ti
(ppm)	1666	930	111	105	75	55	39	33

Changes in Particle Light Intensity

In this study, we used 488 Alexa Fluor dye and 473 nm laser for measuring the particle fluorescence intensity in order to compare it to conventional light contrast optical images on the milled particles to track the dissolution. With this approach the need for background subtraction procedures was avoided. Quantitative measurement of the particle and background light intensity from optical images were obtained for particle dissolution in [Emim][OAc]. As the color intensity of dissolving particle gradually grew faint and disappeared, the fluorescence of solution background intensity increased in Figure 1B and 2B. Figure 1C, 2C and 3C (indicated by arrowheads) show the auto-scaled light intensity changes during particle dissolution and of the surrounding solution. The above results are similar to those on poplar, where the cells swell but the cell boundaries became less bright during [Emim][OAc] treatment versus time [18]. As the particle thickness decreased with heating time, the light intensity in the optical micrographs increased in Figure 1C, 2C and 3C. Therefore, tracking the dissolution by microscopy allowed for process model development and is also related to the overall dissolved RS concentration in the [Emim][OAc]. As noted above, the [Emim][OAc] color intensity gradually changed during the particle dissolution. This color change was measured by UV-Vis spectrophotometer (UV-1800, Shimadzu, Japan). The same amount solution of 0.01(w/v %) rice straw in IL described the previous section of dissolution procedure and transferred after heated at 120°C, 140°C and 160°C on hot plate to small-volume (0.5 ml) 1cm path length quartz cuvettes and allowed to cool to room temperature. Absorbance within the 190-1100 nm spectral range was measured using a 1 nm spectral resolution. [Emim][OAc] was referenced for all of the samples and heated

at function times in order to know color changes of pure IL. Both UV-VIS absorption and transmittance spectra of the reaction solution recorded during the several minutes of heating temperature at 140°C accompanied by color darkening and simultaneously increased in intensity (within five minutes) with the liquid color becoming darker (changing from amber to reddish-brown) as the dissolution progressed in Figure 4. The UV spectra region was observed at 400-550 nm for absorbance and 320-900 nm for transmittance. For example, when heated at 140°C, the RS particle absorbance, and transmittance spectra showed significant changes compared to the reference. Similarly increasing dissolution progressed until 30 min. After reaching the particle dissolution end point at 35 min, there is a slight decrease. Therefore, complete dissolution was achieved within 35 min which is also a measurement method of end point dissolution of RS in IL. It was clear that the end point dissolution time can be followed by monitoring the color change during dissolution as shown in Figure 4. The solubility of lignin in IL have been reported and its dissolved concentration strongly affects the solution color without similar to what we have observed [19].

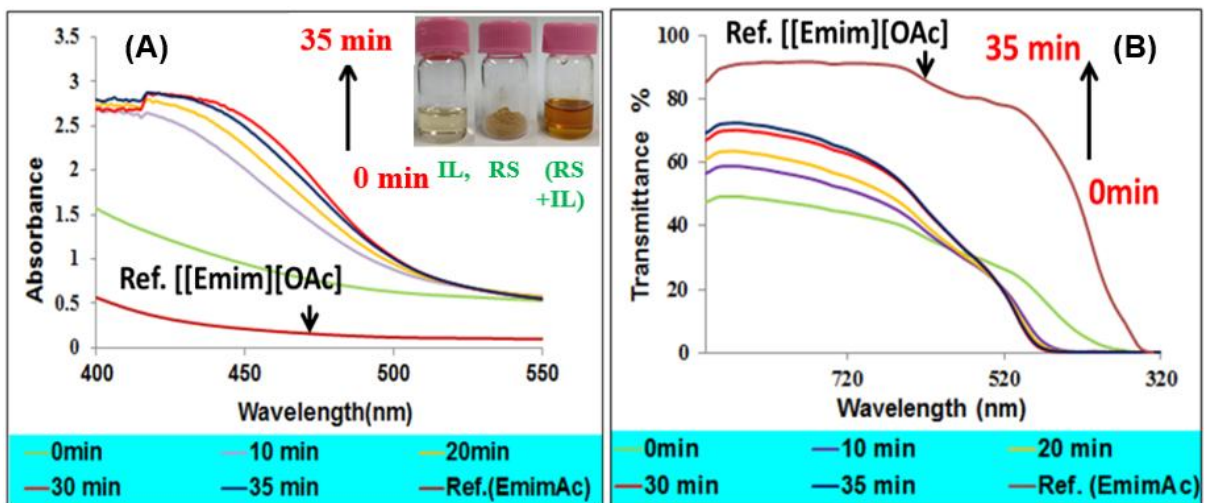


Figure 4. UV-VIS analysis of rice straw dissolution in [Emim][OAc] at heating temperature 140°C as a function of time. a) absorption spectra and b) transmittance spectra of rendering the end point dissolution corresponding color evolution of the solution sample

The particle light intensity ratios were plotted against heating time (min) in Figure 5 (A-B). The data points were fitted by linear regression. Although the ratios initially are quite different comparing the two microscopes, they both show positive slopes with the different temperatures versus time and converge to 1.0 at the point of dissolution. These results indicated that light intensity ratios can be used as a figure of merit to estimate the particle dissolution endpoint due to the high correlation coefficient regardless of the microscope type.

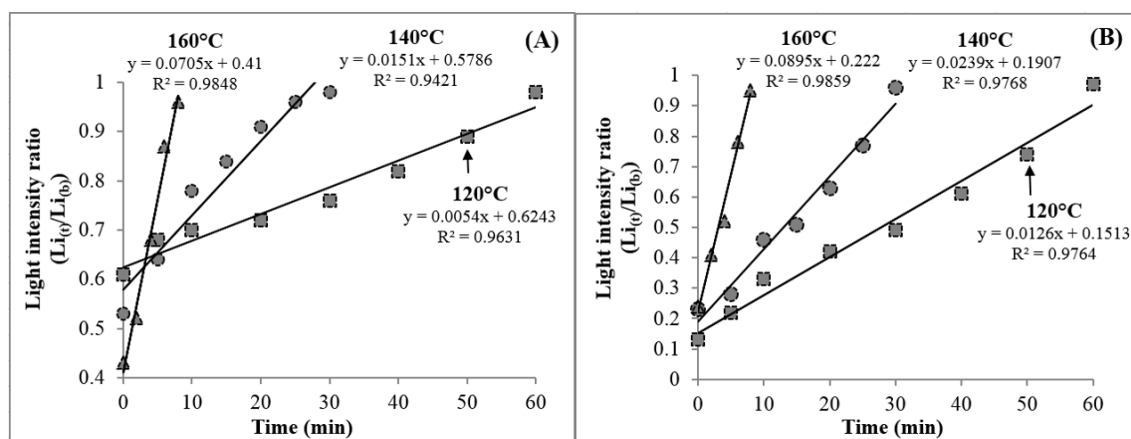


Figure 5. Comparison between measured light intensity ratios of rice straw particle during dissolution in [Emim][OAc] at three different temperatures 120-160°C as a function of time. a) Light contrast (light intensity ratio) analyzed by optical microscope
 B) Fluorescence intensity (light intensity ratio) analyzed by confocal microscope

Particle Area Ratios

The area ratios of the RS particles in [Emim][OAc] as a function of heating times were plotted at 120°, 140° and 160°C using optical and confocal image analysis as shown in Figure 6(A-B). The data points were fitted by linear regression based upon Equation 1.

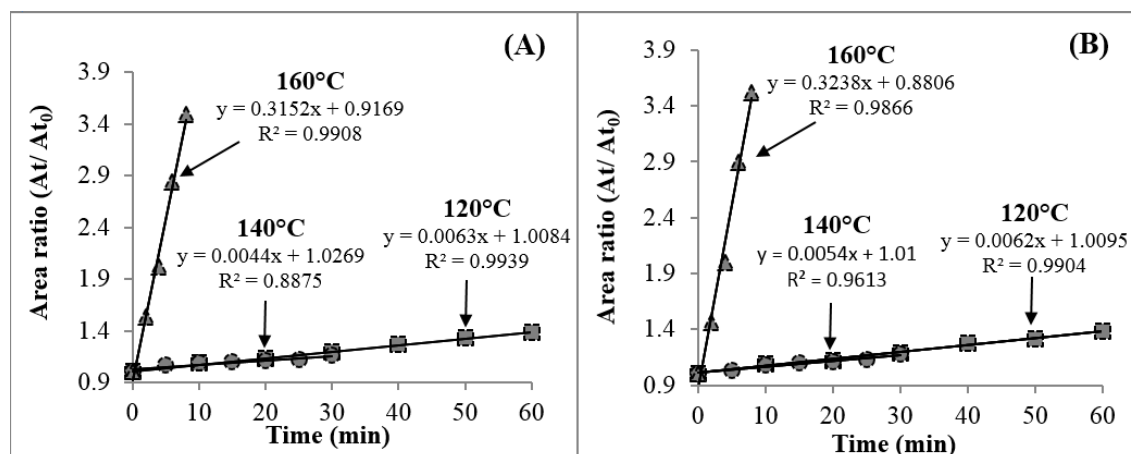


Figure 6. Comparison between measured area ratio of rice straw particle during dissolution in [Emim][OAc] at three different temperatures 120-160°C as a function of time. Area ratio analyzed by using (a) optical microscope and (b) confocal microscope

Similarities in particle swelling or rates of change in the particle's area ratios at 120° and 140°C were observed. Fu et al. noted [Emim][OAc] can extract lignin from triticale (a hybrid of wheat and rye) straw efficiently between 70-150°C with some hemicellulose removal, but little removal of cellulose [20]. In this case, at the highest temperature of 160°C, the particle area increased over three times at the time of dissolution which was confirmed by both microscopes. Previously, significant dissolution is observed at temperatures above 130°C, where the rate of dissolution appears to more than double with every 10°C temperature increment indicating a chemical reaction [21]. The particle swelling is thought to result first in [Emim][OAc] penetration into the particle and subsequent loosening/disruption of intracellular hydrogen bonds. Typically, amorphous material dissolves first followed by crystalline regions of cellulose [22,23]. It is proposed that as the particle swells, intermolecular bonds are broken as a result of the internal

stresses resulting in swelling [24]. Mantanis et al. observed that that mild swelling is confined entirely to the amorphous portion of the particle [1515]. Therefore, higher temperature promotes reactions and amorphization of the cellulose which reduce the cellulose crystalline regions [25]. This result was in agreement with previous reports, which attributed that rice straw particles were disrupted when heated between 160-190°C for 1-5 min in dilute acid [26]. Rice straw consists of heterogeneous regions such as hydrophilic amorphous cellulose and hemicellulose which can induce readily swell at higher temperatures [27]. Similar pretreatment on switchgrass showed enlarged cell walls at elevated temperature [28]. Another reason for more rapid dissolution is the [Emim][OAc] viscosity decreases with increasing temperature which promotes higher mass transfer to and away from the dissolving particle surface [29].

Rice Straw Particle Volume Particle Area Ratios

The area ratios of the RS particles in [Emim][OAc] as a function of heating times were plotted. The particle volume can be estimated using two different methods: manually by measuring the particle thickness and multiply it by its area since it has a rectangular shape as shown in Figure 7 and by computer image simulation based upon 2D images taken as a function of particle thickness (slices) using 3D imaging software.

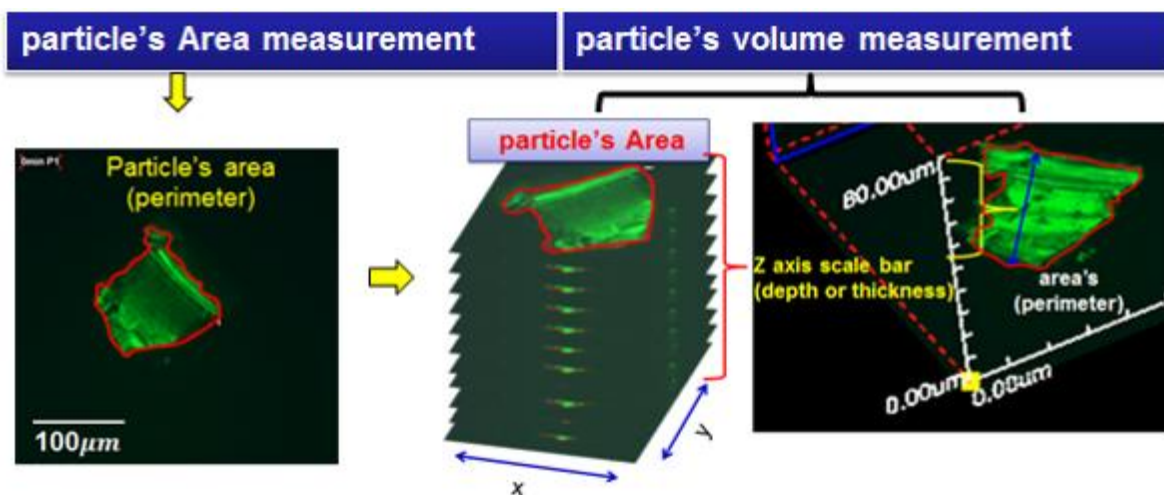


Figure 7. Diagram showing the volume rendering images taken sequentially by raising microscopy stage a known distance/step, refocusing and tracing the particle's perimeter, calculating the area and multiplying by the particle thickness to estimate the volume with a confocal microscope

Both methods were used initially for comparison. In the case of simulation of the 3D particle surface, Volocity® 3D Image Analysis Software of PerkinElmer was used to measure the volume (Figure 7) and was measured manually. It was observed that the volume measurements by both methods gave similar values for a particle volume of 516,261 μm^3 where the difference between the two methods was 1.3%.



Figure 8. Measurement of rice straw particle volume ($516,260.6 \mu\text{m}^3$) by the confocal microscope and the 3D projected image simulated by velocity 3D image analysis software

In this dissolution model, the volume ratio of RS particles decreased as a function of heating time at elevated temperature. The volume ratio vs time decreased to 0.4 within 10 min when heated at 160°C (Figure 9).

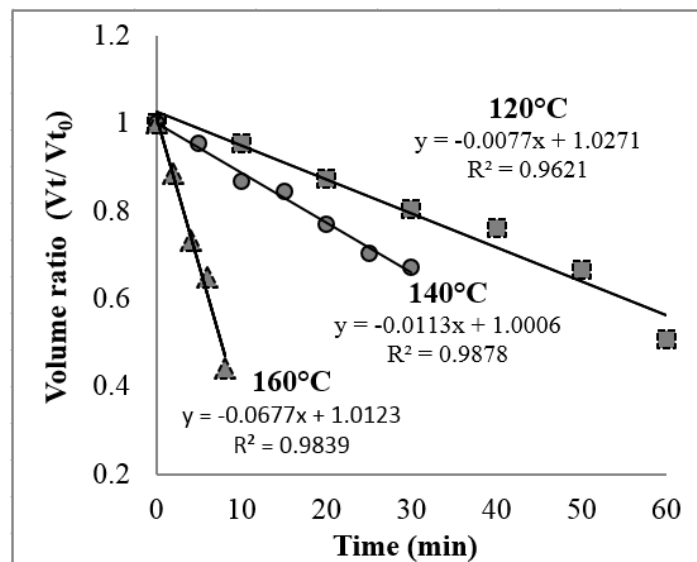


Figure 9. The volume ratio of rice straw particles during dissolution in [Emim][OAc] at three different temperatures 120° , 140° and 160°C as a function of time

However, at the same time instance when heated at 120° and 140°C , the volume ratios of RS particles were 0.95 and 0.87 respectively, based upon linear regression analysis. Hence, it is not only the particle area which is changing with time but also the volume (thickness). The observed trend of increased swelling with decreasing particle thickness is confirmed by negative linear correlations between area ratio and volume ratio at all three temperatures studied (Figure 10).

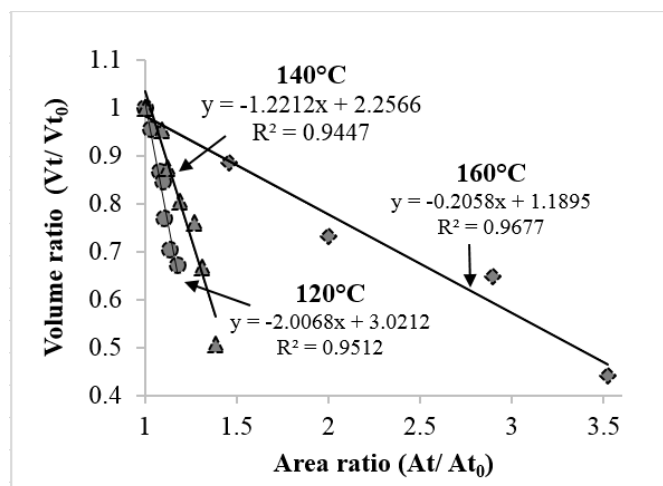


Figure 10. Swelling ratio vs. volume ratio of rice particles during dissolution in [Emim][OAc] at three different temperatures 120°, 140°, and 160°C

Correlation coefficients (R^2) values were calculated by linear regression and were 0.95, 0.94 and 0.97 at 120°, 140° and 160°C, respectively (Figure 11). Actually, similar results have been observed previously for a layered triblock terpolymer where swelling increased when placed in water while thickness decreased reported by Gensel et al. [30]. A similar trend of decreased swelling degree with increasing thickness was also observed for block copolymers [31]. An analogy would be pulling of a rubber band from its ends. Stretching a rubber band makes it thinner but overall volume of the stretched region is nearly the same. It is interesting that particles do not appear to dissolve from the particle edge, which we attribute to the physical layered structure. Previous work proposed swelling is the precursor of the dissolution step, which occurs by disrupting the cell wall cellulose structure. Navard et al. reported that swelling of cellulose is a process in which ionic liquid molecule penetrates the fiber structure by interacting with the cellulose polymer. After the fiber swells, the particle dissolution begins in the ionic liquid as intermolecular bonds are broken resulting from internal stress [17]. It is speculated that inner crystalline region dissolve and swell, which is contained by the outermost surface layer which expands [32].

Conceptual Relationship of Dissolution Process Model

From the above results [Emim][OAc] is very effective at 160°C to dissolve biomass dissolution analyzed by light intensity ratio of RS particles by optical microscope and confocal microscope were 0.96 and 0.95, respectively, in (Figure 5). These values are very similar indicating endpoint dissolution of RS particles within 10 min. For lower temperatures of 120° and 140°C, it took longer time (60 min and 30 min respectively) to approach the intensity ratio of 1.0. The correlation coefficients values are also nearly equal for both optical and confocal light intensity ratios showing different but positive slopes (Figure 5). The general trend is that dissolution at 120° and 140°C occurs without swelling whereas dissolution at 160°C is accelerated by swelling.

As can be seen from Figure 6, swelling area ratios at 160°C were 3.49 and 3.52 by optical and confocal microscopes respectively, within 10 min, showing excellent agreement. The area ratios were 1.2 and 1.4 after extended heating of 30 min at 140°C and 60 min at 120°C. Linear regression analysis for the particle volume ratios at 120°, 140° and 160° C with slopes of -0.008, -0.011 and -0.068 in Figure 9, show an order of magnitude difference. The data of Figure 10 indicated that the higher heating temperature has a faster volumetric dissolution rate, which is expected. Negative slope value means that the volume of the particle was reduced at heating temperature as the function of heating time. Since the area increased with heating time the volume reduction was due to the decreasing thickness.

Correlation coefficient value (R^2) of area and volume ratios was higher than 0.9 indicating a good fit.

The main process parameters impacting the dissolution are the heating temperature and time which influence RS particle dissolution rate. A summary of the dissolution process at the three different temperatures is shown in Figure 11.

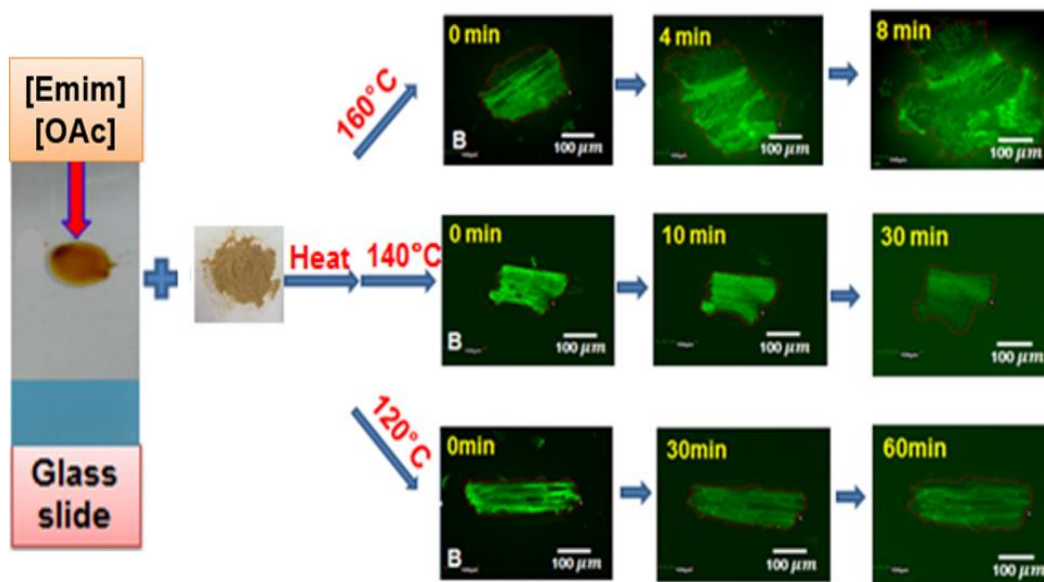


Figure 11. Dissolution process model of rice straw particles in [Emim][OAc] at 120-160°C versus time

From the overall dissolution particle model the particle dissolved from the surface which correlated well to changes in the light intensity ratio and volume ratio. Actually, light intensity ratio and volume ratio were more accurate indicators of the dissolution endpoint than area ratios since swelling was sensitive to heating temperature. Although research reported here focused on three temperatures, given the linear relationship of dissolution it is possible to consider dissolution at other intermediate temperatures would also follow a linear relationship. We believe that the model put forward because of its linearity has potential to be used for predicting the dissolution end point. For example, if dissolution data was taken over a shorter period of time at intermediate temperatures it appears that the particle dissolution time can be estimated. It is expected that, other types of biomass that consist of flat particles, this model would apply to them as well. Therefore, the dissolution model put forward here appears to have wider applications particular when screening ionic liquids dissolution ability of biomass in order to reduce the dissolution time.

Ionic liquids are not yet ready for large scale industrial applications when it comes to lignocellulosic biomass processing. However, in order for the dissolution process modeling concept to be successful, it needs to meet two criteria: the biomass dissolution process needs to be efficient, reproducible and understanding the process sufficiently is needed in order to predict particle end point dissolution. To address the above issues, in this study, various ratios were defined as shown in equations 1-3. All three ratios showed linear relationships versus heating time and temperature. Specifically, volume and light intensities ratios could be used to predict the particle dissolution endpoint. On the other hand, the area ratio was more dependent upon the heating temperature which impacted particle swelling probably due to its heterogeneous composition making it less useful as a figure of merit for end point prediction.

Conclusions

This study investigated the rice straw particle dissolution process analytically in [Emim][OAc] while at heating temperatures of 120°, 140° and 160°C using optical and confocal laser microscopy. The results showed that this dissolution process can be clearly divided into two stages, 1) penetration of IL inside the RS particle inducing its surface dissolution and swelling, 2) as the particle dissolved, it became thinner and the light intensity ratio increased with heating time. The key process parameters were temperature and heating time, with temperature having the largest impact. Observing the dissolution of RS particle by confocal and optical microscopy allowed for the development of key process ratios and a 3D dissolution particle model. Scientific research on light intensity change and using it to model the dissolution of biomass by confocal microscopy is still rather undeveloped. In this work we put forward several different ratios to quantify the dissolution rate and observed that the light intensity ratio is the best figure of merit to model dissolution. We speculate that the reason why particles dissolve from the surface is due to the preferential ionic liquid penetration along the cell walls and disruption of hydrogen bonds within the biomass. We anticipate that the proposed model has wider ranging applications to predict particulate dissolutions at intermediate temperatures, predict dissolution endpoints without waiting for complete dissolution and potential use for screening other ionic liquids for biomass dissolution and process optimization.

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