

## **DISSOLUTION OF RICE STRAW IN 1-BUTYL-3-METHYLIMIDAZOLIUM ACETATE [BMIM][OAc]**

Tun Tun Win<sup>1</sup>, Win Aung<sup>2</sup>, Ni Ni Sein<sup>3</sup>

### **Abstract**

Dissolution of rice straw (RS) in an ionic liquid (IL), 1-butyl-3-methylimidazolium acetate [BMIM][OAc] was studied with regard to effects of size, amount of rice straw powder, dissolution time and dissolution temperature. Highest yield percent (76.65 %) of regenerated cellulose was achieved using 0.149 mm size and 0.2 g of rice straw powder. Effect of dissolution time (10, 30, 90 min) on the yield percent of regenerated cellulose showed that higher yield percentages of 78.08 % and 76.65 % were achieved for dissolution times of 90 min and 30 min respectively. Three dissolution temperatures were set for dissolution study and it was found that the shortest dissolution time (10 min) was observed at 160 °C. Surface morphology of the regenerated cellulose samples showed amorphous and porous structure compared to highly organized fibril structure of raw rice straw powder. Amorphous structure of regenerated cellulose samples were also confirmed by FT IR spectral data. The appearance of amorphous band around 900cm<sup>-1</sup> of cellulose was observed in regenerated cellulose indicating the reduction of crystallinity. Crystalline peak of cellulose at (101) plane at 2θ value of 22° was clearly observed in raw rice straw powder whereas the peak intensity decreased or absent in regenerated sample. By the optimization of the dissolution condition, 0.2 g of rice straw powder with 0.149 mm size was chosen for dissolution of rice straw at 120 °C for 30 min.

**Keywords :** 1-butyl-3-methylimidazolium acetate,[BMIM][OAc], rice straw, ionic liquid, regenerated cellulose

### **Introduction**

The search for renewable feed stocks to produce useful chemicals, materials and fuels has become an important goal, with the ever-growing energy demands and environmental concerns, together with the diminishing fossil fuel reserves (Tuck *et al.*, 2012; Chatterjee *et al.*, 2015). Lignocellulosic biomass is a promising alternative to fossil resources because of its

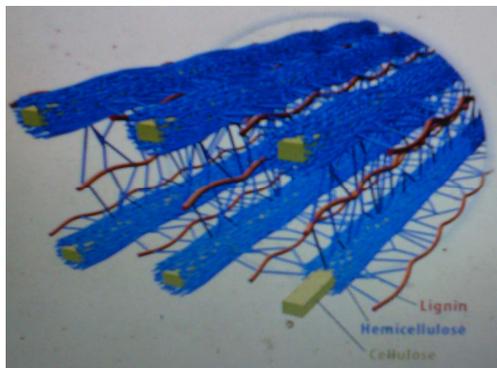
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abundance, renewability and versatility. Recently, lignocellulosic biomasses attract great attention of scientists as a potential feedstock for bioethanol production (Poornejad *et al.*, 2014). Lignocellulosic biomass is generated in large quantities, especially in countries that are predominantly agricultural. One of the examples of biomass is rice straw.

Lignocellulose is a composite material synthesized by plant cells, consisting mainly of polymeric carbohydrates (cellulose and hemicelluloses) and the aromatic polymer lignin (Figure 1).



**Figure 1:** Spatial arrangement of cellulose, hemicellulose and lignin in the cell walls of lignocellulosic biomass.

Cellulose may exist in crystalline or amorphous forms. Amorphous structures are less ordered than crystalline regions. The crystalline structures are highly ordered and poorly depolymerized by cellulose (Yong, 2005). The cellulose fibers are usually embedded in an amorphous matrix of hemicellulose and lignin. Lignocellulosic biomass is suitable source for conversion to bioethanol because of the abundance and cheapness. However, conversion of lignocelluloses to bioethanol is faced with physical and chemical barriers. More specifically, crystalline structure of cellulose, presence of lignin, and covalent cross-linkages between lignin and hemicelluloses in cell wall obstruct the decomposition process of lignocellulosic materials (Mood *et al.*, 2013). Therefore, the goal of pretreatment is defined to overcome these obstacles including breaking down lignin structure, disrupting the crystalline structure of cellulose and cross-linked matrix of lignin and hemicelluloses, and increasing the porosity and

surface area of cellulose (Alvira *et al.*, 2010; Li *et al.*, 2010). The most commonly applied methods involved, for example include steam or carbon dioxide explosions and hot water treatment. Chemical processes involve acid or alkali treatments and organosolv process for example, however, all these pretreatment methods have several disadvantages. Some of the solvents cause the degradation of lignocelluloses upon dissolving. These unwanted by-products can inhibit a subsequent hydrolysis or fermentation step (Larsson *et al.*, 1999). Some pretreatment methods are too slow (even weeks), and these methods cannot be considered as “green” since hazardous or toxic compounds are released. Therefore, more efficient pretreatment procedures are required. One potential alternative is the use of ionic liquids (ILs).

Ionic liquids (ILs) are a group of new organic salts that are liquids at relative low temperatures (below 100 °C). As the name suggest they are completely ionic with most ionic liquids consisting of an organic cation and an inorganic or organic anion. Many ionic liquids are also liquids at room temperature making it an ideal solvent to work with. Compared with traditional molecular solvents, ionic liquids express very interesting properties like broad liquid regions, high thermal stabilities and negligible vapour pressures (Brennecke and Maginn, 2001). Ionic liquids are also called green solvents because no toxic or explosive gases are formed when used (Anderson *et al.*, 2002). The ability of ionic liquids to dissolve cellulose depends on the nature of the native cellulose (its degree of polymerization and crystallinity) on the operating conditions (temperature, reaction time, initial concentration of cellulose in the IL) and the presence of impurities (water). Dissolved cellulose can be precipitated and separated from lignin and hemicelluloses by the addition of anti-solvents, such as water (Fort *et al.*, 2006).

This research is aimed to study the dissolution of rice straw powder in 1-butyl-3-methylimidazolium acetate [BMIM][OAc].

## Materials and Methods

### Sample

1-Butyl-3-methylimidazolium acetate [BMIM][OAc] was procured from Sigma-Aldrich and used without further purification. Rice straw sample was collected from Pynmagyi village in Kyaukpadaung Township, Mandalay Region.

### Sample Preparation

The collected sample was cut into small pieces and pulverized into powder with machine. The powdered samples were sieved with 30, 60 and 100 mesh size to obtain 0.595 mm, 0.250 mm and 0.149 mm sizes of rice straw respectively. The powdered samples were stored at room temperature.

### Dissolution Experiments

Dissolution of rice straw powder in [BMIM][OAc] was carried out according to the procedure of Poornejad *et al.* (2014) with some modifications.

### Investigation of the Effect of Size of Rice Straw on Dissolution in Ionic Liquid

A suspension of rice straw (0.595 mm) in [BMIM][OAc] with 2% solid loading was prepared in a 100 mL beaker. It was then put in an oil bath at 120 °C. The suspension was stirred every 15 min by a glass rod to ensure complete distribution of solid in the solvent. At the end of the pretreatment, the dissolved solid was regenerated by sudden addition of 30 mL boiling water. The precipitated solid was recovered by vacuum filtration and washed by ethanol and boiling water till clear filtrate was achieved. The regenerated cellulose was dried at 105 °C in oven for 3 h, and then stored in sealed bags for further use and analysis. The above procedure was also carried out with 0.250 mm and 0.149 mm rice straw samples in place of 0.595 mm rice straw while other parameters were kept constant.

### **Investigation of the Effect of Mass of Rice Straw on Dissolution in IL**

A suspension of rice straw (0.1 g, 0.2 g and 0.3 g each) of 0.149 mm size in [BMIM][OAc] was prepared in three separate 100 mL beakers. Then the beakers were put in an oil bath at 120 °C and heated for 30 min. The remaining procedure was the same as that described above.

### **Investigation of the Effect of Time on Dissolution of RS in IL**

A suspension of rice straw (0.149 mm) in [BMIM][OAc] with 2 % solid loading was prepared in a 100 mL beaker. It was then put in an oil bath at 120 °C and heated for 10 min. The suspension was occasionally stirred by a glass rod to ensure complete distribution of solid in the solvent. The remaining procedure was the same as that described above. Heating times of 30 min and 90 min were also studied using 0.2 g of rice straw (0.149 mm).

### **Investigation of the Effect of Temperatures on Dissolution of Rice Straw**

A suspension of rice straw (0.149 mm) in the ionic liquid with 2 % solid loading was prepared in a beaker. It was heated in an oil bath at 120 °C and the suspension was stirred every 15 min by a glass rod to ensure complete distribution of solid in the solvent. The remaining procedure was the same as that described above. The same procedure was carried out using two different temperatures of 140°C and 160°C while other parameters were kept constant.

### **Characterization Techniques**

Surface morphologies of raw rice straw and regenerated cellulose were investigated by scanning electron microscope (model Jeol-JSM-5610 LV, Japan) operating at an accelerating voltage of 15 kV and 550 X magnification at Universities' Research Center, Yangon.

Fourier Transform Infrared (FT IR) spectra of raw rice straw and regenerated cellulose were recorded in a range of wavenumber from 4000 to 550  $\text{cm}^{-1}$  on a FT IR spectrometer (FT IR-8400 SHIMADZU, Japan) at Universities' Research Center, Yangon.

X-ray diffraction patterns of raw rice straw and regenerated cellulose were recorded on X-ray diffractometer (Rigaku, Tokyo, Japan), using  $\text{CuK}_\alpha$

radiation ( $\lambda = 1.54 \text{ \AA}$ ) at 40 kV and 40 mA at Universities' Research Center, Yangon. The intensity data were collected over a  $2\theta$  range of  $10^\circ$  to  $70^\circ$ .

## Results and Discussion

### Effect of Size of Rice Straw on Dissolution in Ionic Liquid

The dissolution process was studied by three different sizes of rice straw (RS) *viz.*, 0.595 mm, 0.250 mm and 0.149 mm. From the investigation, RS with 0.149 mm size completely dissolved in [BMIM][OAc] within 30 min at  $120^\circ\text{C}$  ( Table 1 ). The dissolution time of RS with 0.250 mm mesh size was 90 min and that for 0.595 mm size was 110 min. The larger the size of rice straw powder the longer the dissolution time. Thus, for shorter time for dissolution, 0.149 mm size of rice straw was chosen for further experiments.

**Table 1.** Relationship between Size and Dissolution Time of Rice Straw in Ionic Liquid

No	Size (mm)	Dissolution time (min)
1	0.595	110
2	0.250	90
3	0.149	30

Mass of RS = 0.2 g, Temperature =  $120^\circ\text{C}$

After dissolution in [BMIM][OAc], the regenerated cellulose yield percentages were found to be  $69.4 \pm 0.15\%$ ,  $70.00 \pm 0.13\%$  and  $76.65 \pm 0.15\%$  for rice straw with 0.595 mm, 0.250 mm and 0.149 mm respectively (Table 2). As the size decreased, the rice straw particles dissolved more easily and higher yield of cellulose was achieved.

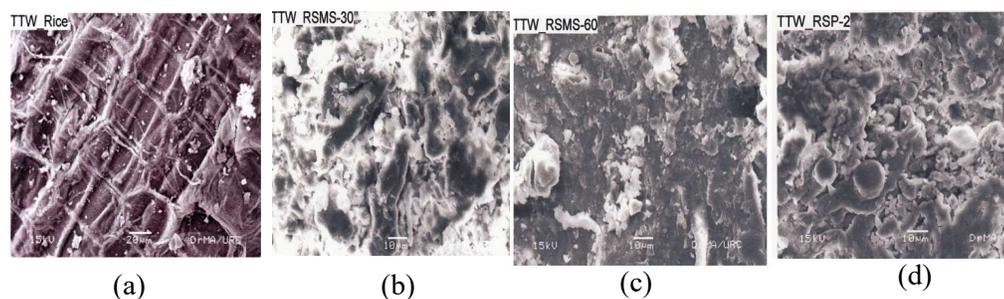
**Table 2:** Yield Percent of Regenerated Cellulose of Rice Straw Particles

No.	Size (mm)	Mass of regenerated cellulose (g)	Yield (%)
1	0.595	0.1388	69.40±0.15
2	0.250	0.1401	70.00±0.13
3	0.149	0.1533	76.65±0.15

Mass of RS= 0.2 g, Time = 30 min, Temperature = 120 °C

**SEM analysis of regenerated cellulose obtained using different sizes of rice straw**

SEM micrograph of rice straw sample in Figure 2 shows rigid and highly ordered fibrils. This compact and unavailable form could not assist and accelerate the penetration of the enzyme to the carbohydrates. Also there are spots on the rice straw. These spots are silica which is one of the problematic component of rice straw in conversion to ethanol ( Poornejad *et al.*, 2014). SEM images showed that the surface morphologies of regenerated cellulose were quite different from that of raw RS. On the other hand amorphous form of cellulose were seen in the SEM images of regenerated cellulose.

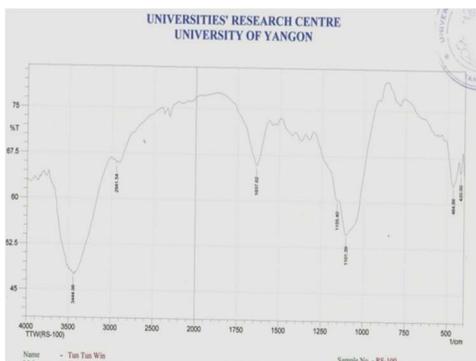


**Figure 2:** SEM images of (a) raw RS and regenerated cellulose from different sizes of RS (b) 0.595 mm (c) 0.250 mm and (d) 0.149 mm

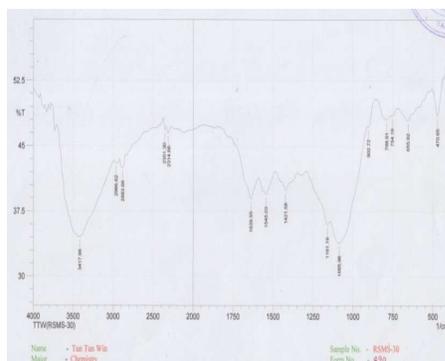
### FTIR analysis of raw RS and regenerated cellulose obtained using different sizes of RS

Figure 3 shows the FT IR spectra of raw particles and regenerated cellulose from RS particle of different sizes dissolved in [BMIM][OAc]. The corresponding spectral data are shown in Table 3. A broad band around  $3400\text{ cm}^{-1}$  was assigned to  $-\text{OH}$  stretching vibration and the bands at about  $2900$  and  $2800\text{ cm}^{-1}$  attributed to asymmetric and symmetric vibration of C-H in  $\text{CH}_2$  group. The appearance of absorption band around  $1640\text{ cm}^{-1}$  corresponds to the C-O stretching vibration of C-OH. The peak became stronger after cellulose was regenerated. The peak around  $1090\text{ cm}^{-1}$  attributes to the C-O bond stretching vibration of C-O-C group in the anhydroglucose ring. The peaks around  $900\text{ cm}^{-1}$  corresponds to the glycosidic C-H deformation with ring vibration and O-H bending which is the characteristic of glycosidic linkages between glucose in cellulose. This peak is designed as an amorphous band which is observed only in the regenerated cellulose (Ciolacu *et al.*, 2011). This may be indicated that the crystal structure of RS transformed from crystalline to amorphous.

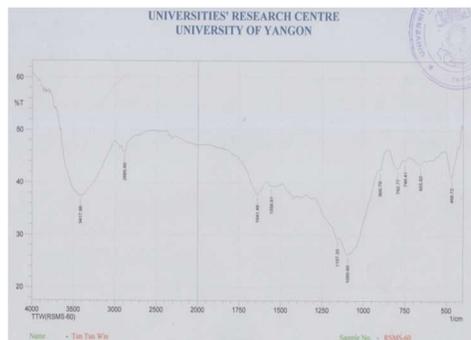
In addition, the FT IR absorption band around  $1430\text{ cm}^{-1}$ , assigned to symmetric  $\text{CH}_2$  bending vibration decreased in regenerated cellulose. This band is also known as “crystallinity band”, indicating that a decrease in its intensity reflects reduction in the crystallinity of sample.



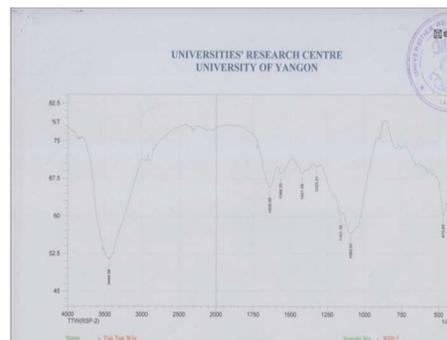
(a)



(b)



(c)



(d)

(d)

**Figure 3:** FT IR spectra of (a) raw RS and regenerated cellulose from different sizes of RS (b) 0.595 mm (c) 0.250 mm and (d) 0.149 mm

**Table 3:** FT IR Spectral Data of Raw RS Particles and Regenerated Cellulose Obtained from Different Sizes of RS

No	Observed wave number (cm <sup>-1</sup> )				Reported value* (cm <sup>-1</sup> )	Remark
	Raw RS	Regenerated cellulose 0.595 mm	Regenerated cellulose 0.250 mm	Regenerated cellulose 0.149 mm		
1	3444	3417	3417	3444	3362	-OH stretching vibration
2	2941	2966	2960	2966	2918	Asymmetric stretching band of C-H
3	2830	2833	2885	2880	2860	symmetric stretching band of C-H
4	1637	1639	1641	1634	1637	C-O stretching vibration of C-O-H of lignin
5	1540	1545	1556	1566	1598	C=C stretching vibration of aromatic ring (lignin)
6	1430	1421	1421	1421	1456	-CH <sub>2</sub> symmetric bending
7	1155	1161	1157	1161	1152	C-O asymmetric vibration of C-O-C in ring
8	1101	1085	1095	1093	1079	C-O bond stretching vibration of C-O-C group in anhydroglucose ring
9	-	902	900	900	896	Glycosidic C-H deformation with ring vibration.

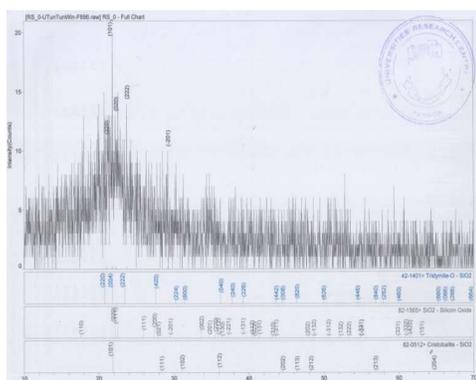
\*Ciolacu *et al.*, (2011) ; Zheng *et al.*, (2013)

### XRD analysis of raw RS and regenerated cellulose obtained using different sizes of RS

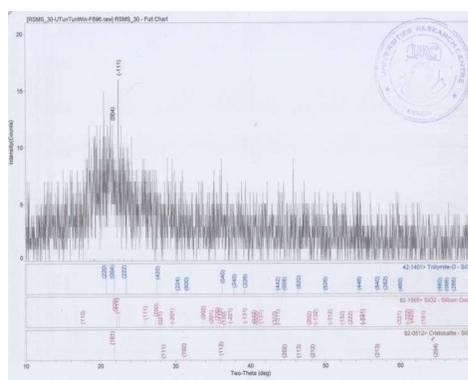
X-ray diffractograms of raw RS and regenerated cellulose obtained from different sizes of RS are shown in Figure 4. In the X-ray diffractograms of raw rice straw and regenerated cellulose samples, a peak of (101) plane at  $2\theta$  value of  $22^\circ$  shows the crystalline peak of cellulose structure. After the dissolution and regeneration process, the diffractograms of regenerated cellulose showed the decrease in the peak intensity. This finding indicates that IL [BMIM][OAc] breaks intermolecular and intramolecular hydrogen bonds of cellulose during dissolution process. The crystallinity percents for regenerated cellulose are shown in Table 4. The dissolution of the rice straw in [BMIM][OAc] was confirmed by decrease in crystallinity of the regenerated cellulose. The crystallinity percent was determined from the XRD analysis by the equation,

$$\text{Percent crystallinity} = (\text{crystalline area} / \text{total area}) \times 100$$

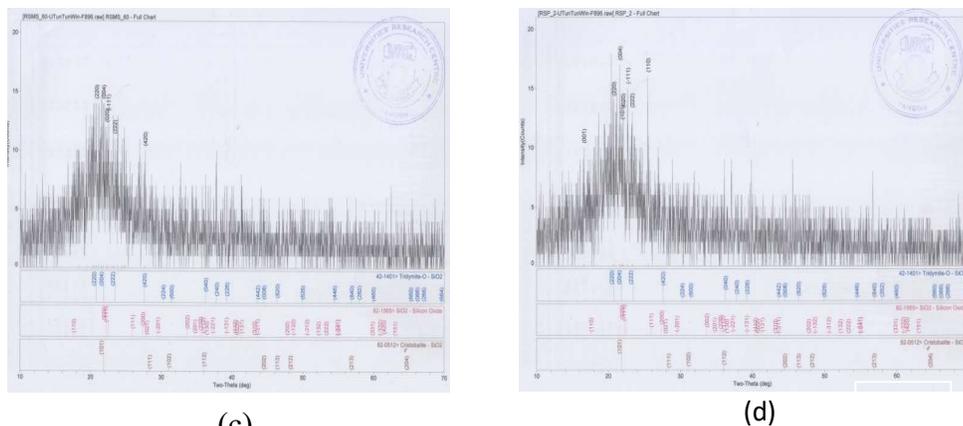
Crystallinity percent of raw rice straw was 37.27%. This result is in accordance with reported value of 37.72% (Sakdaronnarong and Jongiertjunya, 2012). Crystallinity percents of regenerated cellulose were found to be 12.63%, 12.25% and 12.77% for different sizes of RS dissolved in [BMIM][OAc] for 30 min. Crystallinity percents were not much different but noticeably decreased from that of raw RS particle. From this study, 0.149 mm size rice straw was chosen for further experiments because of higher yield of regenerated cellulose.



(a)



(b)



**Figure 4:** X-ray diffractograms of (a) raw RS and regenerated cellulose from different sizes of RS (b) 0.595 mm (c) 0.250 mm and (d) 0.149 mm

**Table 4:** Crystallinity Percent of Regenerated Cellulose Obtained by Dissolution of Different Sizes of RS

No	Size of rice straw (mm)	Crystalline peaks area ( nm <sup>2</sup> )	Total area of all peaks ( nm <sup>2</sup> )	Crystallinity (%)
1	Raw	53.6	143.6	37.27
2	0.595	22.8	180.5	12.63
3	0.250	22.3	182.1	12.25
4	0.149	23.2	181.7	12.77

Mass of RS= 0.2 g, Temperature = 120°C , Time = 30 min

**Effects of Mass of Rice Straw on Dissolution in IL**

In this study different amounts of RS powder were used to investigate the dissolution process. Yield percentages were in the range of 74.85% to 76.65% ( Table 5). Highest yield percentage was obtained from 0.2 g of RS. Thus, 2 % solid loading of suspension of RS was appropriate amount for dissolution in [BMIM][OAc].

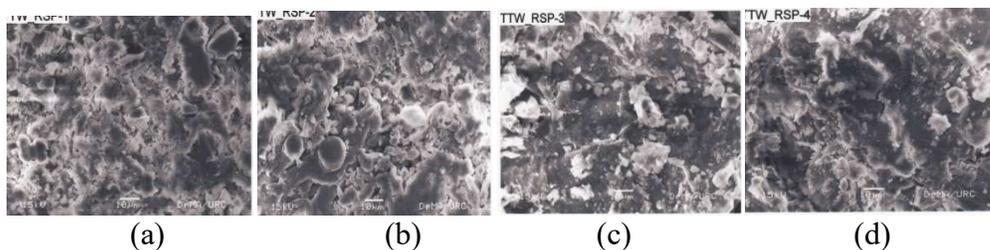
**Table 5:** Yield Percent of Regenerated Cellulose Obtained by Dissolution of Different Amounts of Rice Straw

No.	Amount of RS (g)	Mass of regenerated cellulose (g)	Yield (%)
1	0.1	0.0758	75.80±0.20
2	0.2	0.1533	76.65±0.15
3	0.3	0.2275	75.83±0.23
4	0.4	0.2994	74.85±0.20

Temperature = 120°C, Time = 30 min, Size = 0.149 mm

### SEM analysis of regenerated cellulose obtained using different amount of RS

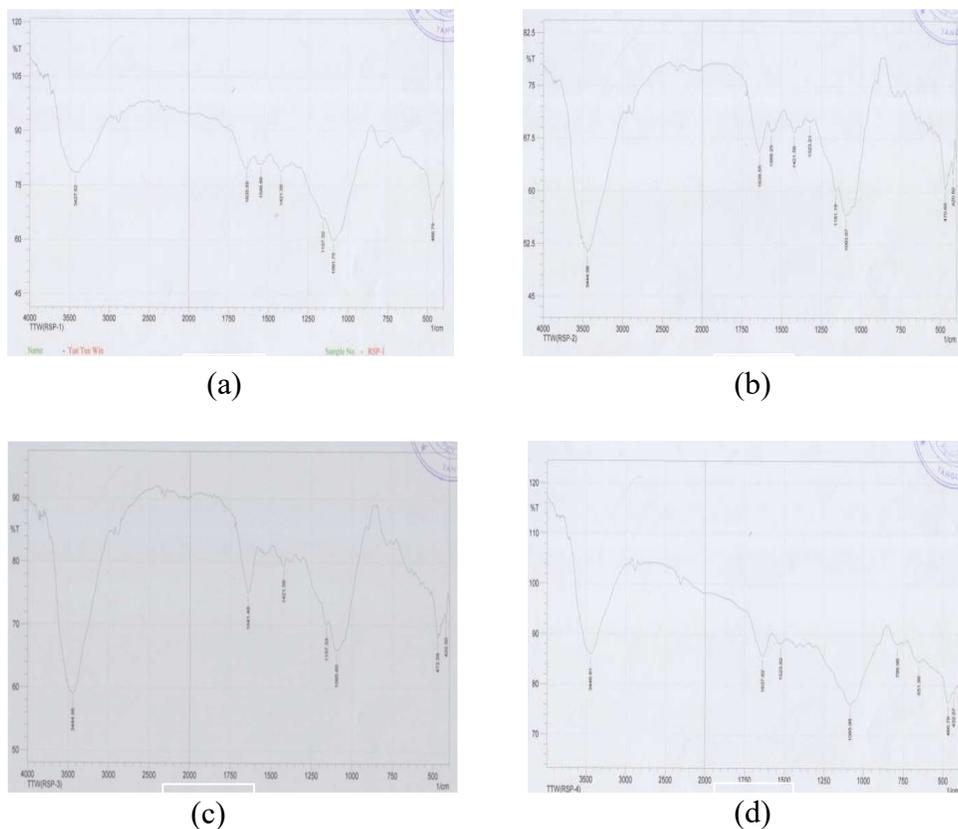
SEM images of regenerated cellulose are shown in Figure 5. Regenerated cellulose showed amorphous form indicating breakage of intermolecular hydrogen bond and intramolecular hydrogen bond by the ionic liquid. Therefore, the structure of the straw was changed from a compact and unavailable form to an open up and widely accessible form. This could assist and accelerate the penetration of the enzymes to the carbohydrates.



**Figure 5:** SEM images of regenerated cellulose obtained from different amounts of RS (a) 0.1 g (b) 0.2 g (c) 0.3 g and (d) 0.4 g

### FT IR analysis of regenerated cellulose obtained using different amount of RS

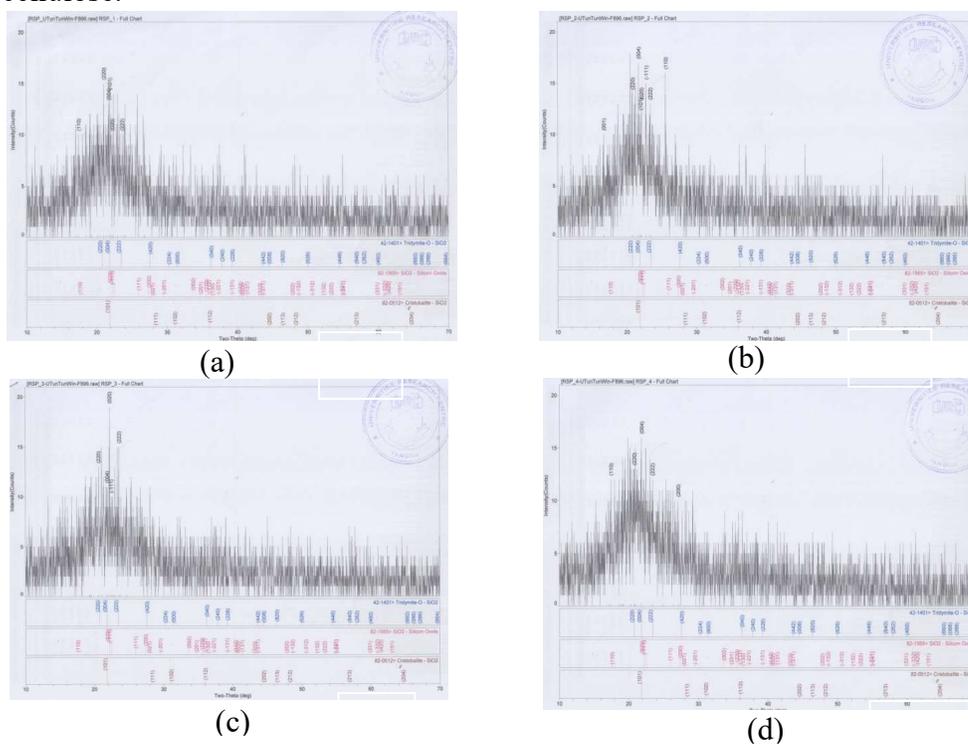
Figure 6 shows the FT IR spectra of regenerated cellulose from different amounts of RS particles dissolved in [BMIM][OAc]. The peaks around  $900\text{ cm}^{-1}$  corresponds to the glycosidic C-H deformation with ring vibration was observed in the regenerated cellulose. This may be indicated that the crystal structure of RS transformed from crystalline to amorphous.



**Figure 6:** FT IR spectra of regenerated cellulose obtained from different amounts of RS (a) 0.1 g (b) 0.2 g (c) 0.3 g and (d) 0.4 g

## XRD analysis of regenerated cellulose obtained using different amount of RS

X-ray diffractograms of regenerated cellulose obtained from different amounts of RS are shown in Figure 7. After the dissolution and regeneration process, the diffractograms of regenerated cellulose showed the decrease in the peak intensity of the crystalline peak at  $2\theta$  value of  $22^\circ$ . Breakage of intermolecular and intramolecular hydrogen bonds of cellulose by [BMIM] [OAc] was observed during dissolution process. The crystallinity percents for regenerated cellulose are shown in Table 6. Crystallinity percent of regenerated cellulose were found to be 12.37 %, 12.76 % , 9.12 % and 9.61 % for different amount of RS dissolved in [BMIM] [OAc] for 30 min. All the regenerated cellulose showed lower crystallinity percents than raw rice straw of 37.27 % indicating the transformation of crystalline to amorphous forms. It was noticed that crystallinity percents were decreased by using 0.3 g and 0.4 g of RS particles compared to 0.1 g and 0.2 g. In this study, mass of 0.2 g was chosen for further experiments because of higher yield of regenerated cellulose.



**Figure 7:** X-ray diffractograms of regenerated cellulose obtained from different amounts of RS (a) 0.1 g (b) 0.2 g (c) 0.3 g and (d) 0.4 g

**Table 6:** Crystallinity Percent of Regenerated Cellulose Obtained by Dissolution of Different Sizes of RS

No	Mass of rice straw (g)	Crystal area (nm <sup>2</sup> )	Total area (nm <sup>2</sup> )	% Crystallinity
1	0.1	22.2	179.4	12.37
2	0.2	23.2	181.7	12.76
3	0.3	16.1	176.4	9.12
4	0.4	18.8	195.5	9.61

Temperature = 120 °C, Time = 30 min, Size= 0.149 mm

### Effect of Time on Dissolution of RS in IL

In this study, effect of time on the dissolution of RS powder in IL was investigated at 120 °C for 10 min, 30 min and 90 min. Yield percentage of regenerated cellulose was shown in Table 7. Yield percentage increased as the dissolution time increased. Higher yield percents were obtained for 30 min and 90 min dissolution times. It was noted that 10 min dissolution time was not sufficient for complete dissolution. Since yield percent of regenerated cellulose was not much different for 30 min and 90 min shorter dissolution time of 30 min was chosen for pretreatment of the rice straw.

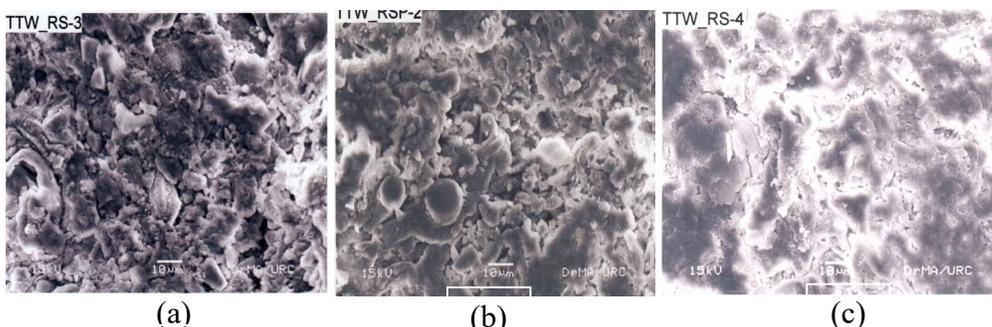
**Table 7:** Yield Percentage of Regenerated Cellulose of RS Powder during Different Dissolution Time

No.	Time (min)	Regenerated Cellulose (g)	Yield (%)
1	10	0.0490	24.50±0.22
2	30	0.1533	76.65±0.15
3	90	0.1561	78.05±0.22

Mass of RS=0.2 g, Temperature=120°C, Size = 0.149 mm

### SEM analysis

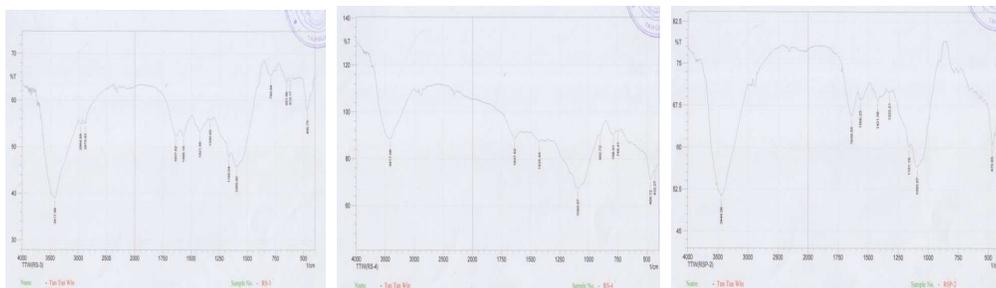
Figure 8 shows SEM images of regenerated cellulose. It was observed that the organized structure of RS is not completely destroyed in regenerated cellulose observed from 10 min dissolution time. The Change in the structure of RS was observed in widely accessibly amorphous form in regenerated cellulose by using dissolution times of 30 min and 90 min. This could assist and accelerate the penetration of the enzyme to carbohydrate.



**Figure 8:** SEM images of regenerated cellulose obtained using different dissolution times (a) 10 min, (b) 30 min and (c) 90 min of RS at 120 °C

### FT IR analysis of regenerated cellulose obtained using different dissolution times

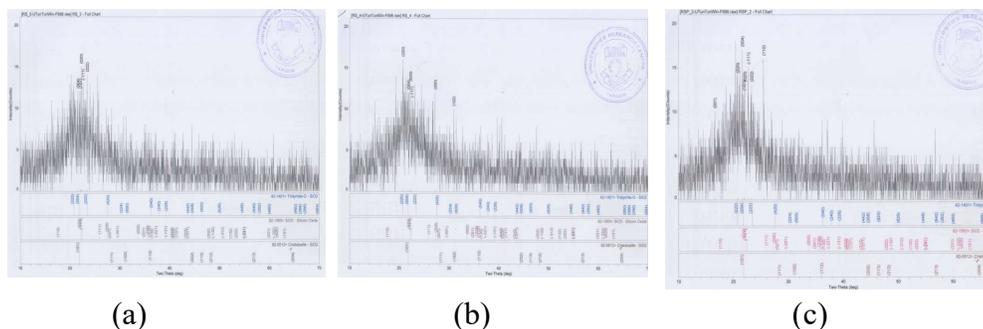
FT IR spectra of regenerated cellulose obtained by different dissolution times are shown Figure 9. As noted as earlier, C=C stretching of aromatic ring of lignin peak around  $1630\text{ cm}^{-1}$  became shorter as compared to that of raw RS. Crystallinity peak around  $1430\text{ cm}^{-1}$  due to bending of C-H in  $-\text{CH}_2$  decreased and amorphous peak around  $900\text{ cm}^{-1}$  appeared in regenerated cellulose. This indicates the breakage of inter- and intra-hydrogen bonds of cellulose. It was also noted that the peak around  $1630\text{ cm}^{-1}$  in regenerated cellulose obtained for 30 min and 90 min dissolution times are shorter than that obtained for 10 min. The crystal peak around  $1430\text{ cm}^{-1}$  obtained for 10 min dissolution time is more intense than those for 30 min and 90 min. It indicates that dissolution time for 10 min is not sufficient for complete dissolution.



**Figure 9:** FT IR spectra of regenerated cellulose obtained from (a) 10 (b) 30 and (c) 90 min dissolution times

**XRD analysis of regenerated cellulose obtained using different dissolution times**

XRD patterns of regenerated cellulose obtained by different dissolution times are shown in Figure 10. Amorphous form of cellulose were seen by the diffuse lines in the XRD patterns. As shown as before crystalline peak of (101) plane at  $2\theta$  of  $22^\circ$  became less intense indicating the change of crystalline to amorphous form. X-ray diffractogram of regenerated cellulose obtained for 10 min show crystalline peak at  $2\theta = 22^\circ$  indicating dissolution time for 10 min is not sufficient for complete dissolution.



**Figure 10:** X-ray diffractograms of regenerated cellulose obtained from (a) 30 (b) 60 and (c) 90 min dissolution times

The crystallinity percent of regenerated cellulose obtained by dissolution time of 10 min was found to be higher than those obtained by 30 min and 90 min (Table 8). This is because within 10 min RS did not completely dissolve in IL. RS powder were found to completely dissolved within 30 min. The crystallinity percent of regenerated cellulose obtained by dissolution time of 30 min was slightly higher than that of 90 min.

**Table 8: Crystallinity Percent of Regenerated Cellulose Obtained by Dissolution of Different Times**

No	Time (min)	Crystalline peak area (nm <sup>2</sup> )	Total peak area (nm <sup>2</sup> )	Crystallinity (%)
1	10	36.2	176.4	20.52
2	30	23.2	179.8	12.96
3	90	23.2	181.7	12.78

Mass of RS=0.2 g, Temperature = 120 °C, Size= 0.149 mm

#### Effect of Temperature on Dissolution of RS in IL

Three different temperatures *viz.*, 120 °C, 140 °C and 160 °C were chosen to study the effect of temperature on dissolution of RS powder. It was observed that at 120 °C RS powder completely dissolved within 30 min (Table 9). When the temperature was increased to 140 °C the dissolution time decreased to 25 min whereas at 160 °C the dissolution time was found to be 10 min. It was reported that 1-ethyl-3-methylimidazolium acetate, [Emim][OAc], is very effective at 160 °C for dissolution of rice straw within 10 min (Myint *et al.*, 2015; Myint *et al.*, 2016).

**Table 9: Dissolution Time of RS powder in [BMIM][OAc] with Different Temperatures**

No	Temperature (°C)	Dissolution time (min)
1	120	30
2	140	25
3	160	10

Mass of RS =0.2 g, Size =0.149 mm

Yield % of regenerated cellulose at 120 °C, 140 °C and 160 °C are shown in Table 10. It was found that yield percentage of regenerated cellulose at 120 °C was 76.65%. As the temperature increased the yield percentage of regenerated cellulose were found to decrease, *i.e.*, at 140 °C was 63.58 % and at 160 °C was 60.85 % .

**Table 10:** Yield Percentages of Regenerated Cellulose Obtained from Dissolution Different Temperatures and Times

No	Temperature (°C)	Dissolution time (min)	Mass of regenerated cellulose(g)	Yield (%)
1	120	30	0.1533	76.65±0.15
2	140	25	0.1271	63.58±1.5
3	160	10	0.1217	60.85±0.30

Mass of RS =0.2 g, Size= 0.149 mm

### Conclusion

Dissolution of rice straw powder in ionic liquid (IL) of [BMIM][OAc] was investigated in this study. Among three different sizes of rice straw (0.595 mm, 0.250 mm and 0.149 mm), the highest yield percent (76.65 %) was obtained using smallest size of 0.149 mm. Effect of mass of RS on dissolution in [BMIM][OAc] revealed that higher yield percent was achieved using 0.2 g of RS. Effect of dissolution time on regeneration of cellulose was studied for 10 min, 30 min and 90 min and the lowest yield percent (24.50 %) was obtained for the shortest dissolution time. The yield percentages of regenerated cellulose were comparable, *i.e.*, 76.65 % and 78.08 % for dissolution time of 30 min and 90 min respectively. Shorter dissolution time of 30 min was chosen for treatment of RS. For ease of carrying out the experiment, 120 °C was chosen for dissolution of RS. SEM images of regenerated cellulose samples showed the destruction of the highly ordered fibrils of raw rice straw. FT IR spectral data showed that the peak intensities of 1630 cm<sup>-1</sup> and 1430 cm<sup>-1</sup> (crystalline peak) decreased in all regenerated cellulose sample compared to those of raw RS. Amorphous peak of cellulose (900 cm<sup>-1</sup>) appeared after dissolution and regeneration of cellulose. After dissolution in [BMIM][OAc] and regeneration, the intensity of the crystalline

peak of (101) plane at  $2\theta$  value of  $22^\circ$  in raw RS sample decreased in all regenerated cellulose samples. Crystallinity percents of regenerated cellulose were lower than that of raw RS indicating the breakage of inter- and intra-hydrogen bonding in cellulose. Based on the results, the suitable conditions for dissolution of RS powder in [BMIM][OAc] were chosen as 0.2 g of 0.149 mm size RS with dissolution temperature for 30 min at  $120^\circ\text{C}$  for pretreatment of rice straw powder for bioethanol preparation.

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