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K.J. Jisha

Indian Institute of Technology Madras

Sunita Rajamani

Indian Institute of Technology Madras

Dharmendra Singh

Indian Institute of Technology Madras

Gyanendra Sharma

Indian Institute of Technology Madras

Ramesh L. Gardas (✉ gardas@iitm.ac.in)

Indian Institute of Technology Madras <https://orcid.org/0000-0002-6185-5825>

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1 **A comparative study of ionothermal treatment of rice straw using triflate**
2 **and acetate-based ionic liquids**

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4 K.J. Jisha.,^{1,†} Sunita Rajamani,^{1,2,†} Dharmendra Singh^{1,3}, Gyanendra Sharma^{1,4}, Ramesh L.
5 Gardas^{1,*}

6 ¹*Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India*

7 ²*Department of Chemistry, St. Joseph's College (Autonomous), Langford Road, Bengaluru*
8 *560027, Karnataka, India*

9 ³*Department of Applied Science & Humanities, Institute of Engineering & Technology, Dr.*
10 *Ram Manohar Lohia Avadh University, Ayodhya, U. P. - 224001, India*

11 ⁴*Faculty of Biological Science and Technology, Institute of Science and Engineering,*
12 *Kanazawa University, Kakuma-machi, Kanazawa, 920-1192, Japan*

13 [†]*These two authors have contributed equally to this work.*

14
15 *Corresponding author: Tel.: +91 44 2257 4248 fax: +91 44 2257 4202 E-mail:
16 gardas@iitm.ac.in

17 URL: <http://www.iitm.ac.in/info/fac/gardas>

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19
20 **Abstract**

21 Ionic liquids (ILs) have found applications in the pretreatment of waste lignocellulosic biomass
22 by interacting with the carbohydrate molecules present in the biomass materials. Pretreatment
23 is essential before biomass conversion into valuable chemicals, fuels, and many other value-
24 added products. This comparative study mainly focused on the pretreatment ability of four ILs
25 having acetate or triflate as a common anion with different cations. Among various studied ILs,
26 diazabicyclo[5.4.0]undec-7-ene (DBU)-based acidic ionic liquid when used as a dual
27 solvocatlyst showed significant structural modifications of the rice straw (RS) sample,
28 through C₆-O bond breakage assisted by the tertiary nitrogen in DBU cation. Structural
29 modifications due to the pretreatment were confirmed through SEM, PXRD, and FTIR
30 analysis. The elemental analysis confirmed that carbon content in original RS is reduced to
31 29% and 20% upon ionothermal treatment of RS with IL at 90 °C and 120 °C, respectively.
32 Additionally, TGA indicated that further pyrolysis could be easier with the pretreated rice straw
33 yielding biochar up to 9% thereby reducing wastes. Conversion of RS was found to be 60 %
34 which reduced marginally to 50 % after three cycles of recycling IL. The findings of this work
35 provide the proof of concept that studied ILs with high thermal stability and recyclability

1 should act as a potential solvocatalyst in sustainable pretreatment and other biomass
2 applications.

3 -----

4 *Keywords*

5 *Lignocellulosic biomass; Pretreatment; Rice Straw; DBU based ionic liquid: Ionothermal*
6 *process; Morphological changes*

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9 **1. Introduction**

10 Bio-based chemicals and products, including biofuels, are the major targets by many
11 agricultural biotechnologists. It is expected that nearly 27% of transportation fuels can be
12 replaced with biofuels by 2050 [1]. Implementing the biorefinery concept wholly depends on
13 biomass as a valuable feedstock for producing bio-based fuels, cosmetics, chemicals, textiles,
14 etc. [2]. Pyrolysis of lignocellulose, in which the feed substance is cracked thermally in the
15 absence of oxygen, is used to crack lignocellulosic materials [3]. Pyrolysis produces a solid
16 (also called char or biochar), liquid (also called bio-oils), and gas products (both condensable
17 and non-condensable). Different factors, including the addition of catalysts, temperature, and
18 type of lignocellulose/biomass, water content, inherent minerals, heating rates, residence time,
19 pressure, environment, and reactor patterns, contribute to this conversion process. Henceforth,
20 one can select the products needed through pyrolysis by adjusting the parameters. Among these
21 methods, catalytic pyrolysis has gotten the maximum attention in the last few years [3,4] In
22 this regard, thermogravimetric analysis (TGA) is becoming an imperative tool for judging the
23 pyrolysis of the treated biomass apart from other morphological studies[5,6].

24 The estimated global production of these lignocelluloses amounts to 200 billion tons,
25 thereby proving suitable candidates for sustainable development [7]. Lignocellulosic biomass
26 can be food as well as non-food. The non-food crop residues include removable materials left
27 after harvesting primary crops like corn, wheat, or rice straw. These are widely available, and
28 this waste is either burnt or disposed of each year to avoid the chances of any diseases in the
29 coming year's crop. However, this leads to one of the major causes of pollution of the year's
30 air quality. Hence to avoid this step that affects the air quality, these waste straws can be used
31 for various purposes, and one among them could be to convert into new bio-based materials or
32 biofuels, or any other valuable chemicals. Treating the biomass with various chemicals,
33 considering the complicated plant cell wall, converting waste biomass materials into useful
34 value-added products, etc. has been worked out by many researchers [8,9]

1 Rice straw (RS) or lignocellulose is a polymer of cellulose, hemicellulose, and lignin in
2 which the most resistant part of rice straw is lignin that serves as the “glue” by binding the
3 cellulose and hemicellulose or rather skeleton of plants that gives both rigidity and support to
4 the lignocellulosic structure. There are several studies on rice straw and its waste management
5 like using them for fibreboards and organic fertilizers [10–12]. The aromatic chemical structure
6 imparts a high calorific value to the lignin molecule, valuable for other chemical conversions.
7 The presence of lignin hinders carbohydrate molecules from reacting to acids or bases, and
8 thus most of the carbon bonds are not broken to give out valuable chemicals [13]. The efficient
9 valorization of biopolymers depends mainly on the pretreatment, which is necessary for the
10 biomass sample's structural modifications.

11 Pretreatment, the high energy demanding process, becomes something inevitable because
12 it adjusts the structural characteristics of lignocellulose, and the structural alterations are highly
13 connected to the mode of the pre-treatment method chosen [14–17]. The recalcitrance of the
14 biomass material obstructs the polysaccharide accessibility; hence, various pretreatment
15 techniques including physical, chemical, and biological methods were evolved. Negative
16 aspects of a few pretreatment techniques were the high energy requirement and the production
17 of unwanted by-products. A handful of reviews are available depicting the pros and cons of
18 each category of techniques [18]. Moreover, the combination of multiple factors like substrate
19 composition, pretreatment type, dosage, and efficiency of enzymes being used for hydrolysis
20 impacts the digestibility of the lignocellulosic biomass used. Application of selective and
21 benign solvents for biomass pretreatment would be preferable, and thus ionic liquids (ILs) were
22 introduced in this field as effective pretreatment solvents [19,20]

23 ILs comprise a weakly linked asymmetric cation (organic/inorganic) and anion (organic)
24 in their structure with a melting point lesser than room temperature [21–23]. The scientific
25 community was constantly looking for this kind of solvent where the properties could be tuned
26 according to the desired task. They are widely known as designer solvents owing to the
27 possibility of designing the ionic liquid structure with suitable properties [24,25]. They are well
28 known and are widely used in various fields such as catalysis, electrochemistry, pharmacology,
29 separation, and purification of biomolecules, extraction, etc. [26]. The fascinating properties of
30 ILs are many in which higher thermal as well as chemical stabilities, non-flammability,
31 negligible vapor pressure are quite a few to be listed [27,28]. Studies have shown that ILs can
32 be used to dissolve bagasse, corn stalks, wheat, wood, etc., and this process is called
33 ionothermal treatment in which ILs have acted as a dual solvocatlyst [29,30]. ILs fall into the
34 category of polar solvents which attribute different grades of hydrogen-bond formation ability.

1 Hydrogen bond basicity of anions present in IL play a key role in cellulose dissolution and
2 acetate [31] chloride [32], [33] carboxylates [34,35] etc. come in the front line in this category.
3 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) is mainly used for rice husk dissolution
4 and conversion [36]. However, this study used an additional amount of inorganic acid to meet
5 the pretreatment requirement. Recently, Badbedast and coworkers from Iran have conducted a
6 detailed study on rice straw pretreatment using an acidic IL namely 1-(carboxymethyl)
7 pyridinium chloride with acetate and chloride groups present in the structure. Various analyses,
8 including FT-IT, XRD, and SEM, revealed the restructuring and increased free volume
9 between cellulose chains in the rice straw sample [37]. Cholinium ILs with amino acid-based
10 anions were reported for selective delignification of lignocelluloses and found that the
11 pretreated samples were exhibiting higher saccharification rate as well as higher polysaccharide
12 digestibility [38]. In another study, biomass pretreatment with IL was coupled with membrane
13 filtration. FT-IR, XRD, SEM and Zeta potential assessments were used to explain the role of
14 ILs in lignocellulose dissolution and the ability of different imidazolium ILs in regenerating
15 the cellulose [39]. New generation of ILs, called deep eutectic systems (DES) was also reported
16 for the biomass pretreatment and found to be promising pretreatment solvents for future
17 biorefineries [40,41].

18 In this study, we have discussed the comparative pretreatment efficiency of four different
19 ILs having triflate and acetate-based anion. The acetate-based ILs were used due to the reported
20 studies which showed effective pretreatments for rice straw and other lignocellulosic materials
21 [42] whereas the reason behind choosing a triflate-based ILs was its better thermal stability.
22 On the selection of cation, the triazole-based IL was found to be high polar than organic
23 solvents [21] whereas DBU was spectated better air, water, and thermal stability, also the Lewis
24 basic property of its tertiary nitrogen which was capable of breaking the H-bonds between the
25 cellulose molecules thereby forming new H-bonding between the IL and the cellulose [43]. In
26 addition to that, DBU-based ILs are considered as having higher β values (between 0.8 to 0.9)
27 and again high π^* values (0.9) [44] which are found to be similar to the value of DMSO [45].
28 The high values of β and π^* are probably suggestions of van der Waals attractions and weak
29 hydrogen bonds. According to molecular simulation studies, the cations of ILs are seen to be
30 above and below the planes of the glucose ring. This effect is being explained by an anisotropic
31 molecular surface of the straight cellulose strands having a smaller hydrogen bonding periphery
32 [46].

1 Harsh conditions including high temperature, acidic and alkaline conditions, etc. make
2 cellulose significantly soluble in particular solvents [47] whereas ILs don't demand such higher
3 conditions to an extent. The use of high temperature accelerates the dissolution and degradation
4 leading to lesser yields for regenerated cellulose [29]. This kind of IL treatment has further
5 advantages such as the pretreatment uses lower temperatures, less hazardous process and
6 corrosion is not always a concern when the right choice is made with the combination of cation
7 and anion of the IL and finally the regeneration of the IL makes the process feasible and
8 economical. Additionally, ILs can be recycled and reused by taking into consideration the
9 economic aspects [48]. The pretreatment is intended to reduce the energy required for the rice
10 straw's chemical modification, limiting hydrogen bonding and decreasing the degree of
11 polymerization, thereby decreasing the crystallinity. One of the approaches was an IL
12 pretreatment process followed by enzymatic hydrolysis, which has proven that some ILs do
13 not deactivate enzymes ever [49]. Fundamental studies regarding pretreatment are getting
14 attention over basic research aspects, however, the attempts to bring in industrial-level
15 applications are restricted owing to the cost issues related to some ILs.

16

17 **2. Experimental Section**

18 **Materials and Methods**

19 *(i) Synthesis of ILs*

20 The synthesis of studied ILs having triflate anion i.e. ([DBUH][OTf]); [BtTzm][OTf]
21 was reported in our previous report [50,51]. In brief, the synthetic scheme (Scheme S1 and S2)
22 and characterization through ¹H-NMR and ¹³C-NMR was presented in supporting information
23 (Fig. S1 and S2). Further for assessing the comparative studies, acetate-based ILs were
24 developed with dimethyl ethanol ammonium (DMEA) and diethyl ethanol ammonium (DEEA)
25 cations. The synthetic procedure and its structural characterization of [DMEA][OAc] and
26 [DEEA][OAc] were shown in Scheme S3 and Fig. S3, S4 respectively [22,52].

27 *(ii) Rice Straw Sample Preparation*

28 Rice straw was collected from the fields of Ayodhya, Uttar Pradesh, India. It was stored
29 at 20–30 °C in dark followed by washing with water and acetone, after which it was then dried
30 in the oven at 70 °C for overnight.

1 (iii) *Rice Straw Pretreatment*

2 The detailed procedures of pretreatment are presented in the supporting information file (Fig.
3 S5). Briefly, the original rice straw (fig. S5 a) was added to the DBU-based IL (fig. S5 b). The
4 original rice straw was characterized by using SEM and PXRD. A total of 20:1 ratio of IL: rice
5 straw was added and stirred for 6 h at 90 °C. The anti-solvent was added when the mixture of
6 IL and the rice straw was at room temperature and then it was filtered. The IL along with water
7 formed the filtrate (fig. S5 c) and the undissolved part formed the residue (fig. S5 d).

8 (iv) *SEM and PXRD Studies*

9 The obtained residue was characterized using powder X-ray diffraction (PXRD) and
10 scanning electron microscope (SEM) to study the changes that occurred post-dissolution. The
11 morphology of the untreated RS, as well as the treated RS, was determined using SEM (Quanta
12 450, FEI, USA). The solid samples were fixed on carbon tapes on sample stubs and were
13 imaged in low vacuum mode. Images were acquired with a 30 kV acceleration voltage. PXRD
14 patterns were recorded in the reflection mode using Bruker D8 Advance in the 2 θ range 5-
15 50° with a step size of 0.03° and a step time of 1 s at 40 kV and 30 mA at room temperature.

16 (v) *FTIR*

17 FTIR JASCO was used for determining the functional groups in the biomass molecules
18 and the scanning was carried out between the wavelength ranges of 4000-400 nm. KBr (ratio
19 1:100) powder pellets were prepared to measure on a Nicolet5700 Fourier transform infrared
20 (FT-IR) spectrophotometer Co., USA) in the spectral range of 400 to 4000 cm⁻¹. A resolution
21 of 4 cm⁻¹ with 124 scans was carried out.

22
23 (vi) *CHN Analysis*

24 The elemental analysis (CHN) was carried out using a CHNS/O Analyzer (Perkin Elmer
25 instruments, Series II, 2400) where the measurement time was 8-10 minutes. TGA was
26 recorded using TA Instruments model Q500 Hi-Res TGA. The temperature scan rate is 20
27 °C/min in a nitrogen atmosphere, and the flow rate was 60 mL/min and was studied between
28 60 and 900 °C.

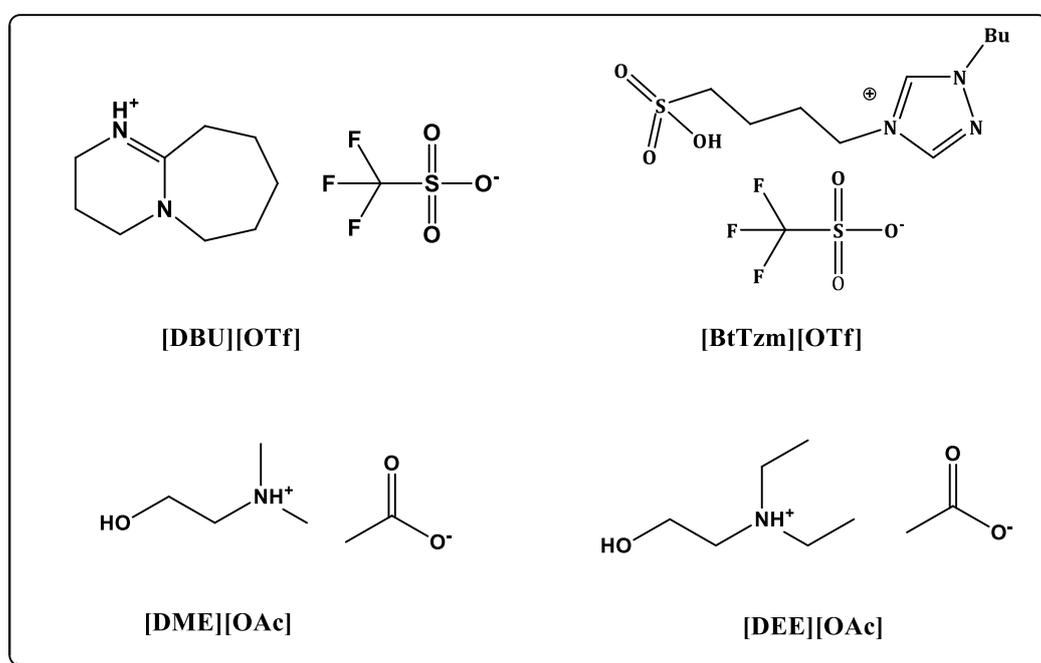
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3. Results and Discussion

2

3 Herein, the four ILs namely [DBU][OTf], [BtTzm][OTf], [DMEA][OAc] and
4 [DEEA][OAc] were used as a dual solvocatlyst in a 20:1 ratio of IL: RS. Structures of the
5 different ILs used here in this study are shown in **Fig. 1**. A similar type of pretreatment study
6 was already done where the biomass to solvent ratio was maintained to be 1:10 g/g. In such a
7 study the solvent was used as a binary mixture of [TEA][HSO₄]: water with 4:1 w/w ratio and
8 they have conducted the experiments in triplicate at 120 °C for 24 hrs [53]. The acidic character
9 of the ILs served to be useful for its dissolution and its larger amount helped for its behavior
10 as a solvent.

11



12

13 **Figure 1.** Diagram representing the structure of four ionic liquids used in this study. Where,
14 [DBU][OTf] = 1,8-Diazabicyclo[5.4.0]undec-7-en-ium triflate, [BtTzm][OTf] = Butyl
15 triazolium triflate, [DME][OAc] = Dimethyl ammonium acetate, and [DEE][OAc] =
16 Diethylethanolamine acetate.

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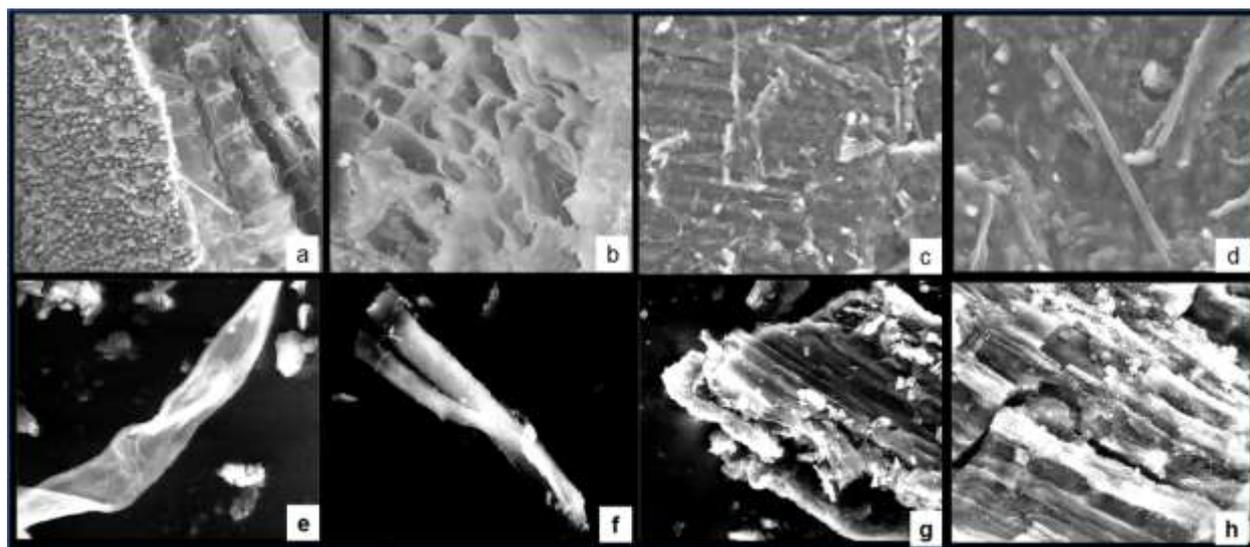
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19 Moreover, scanning electron microscopy (SEM) is an imperative tool for examining the
20 morphological aspects of biomass. The surface of the untreated RS was found to be well
21 organized due to the lignin; which acts as a skeleton where we can see a well-organized rib-
22 cage-like structure or binding agent to hemicellulose and cellulose (shown in **Fig. 2a and 2b**).

23 **Fig. 2c-g** represents the pretreatment of RS with [DBU][OTf]; where small and long fibers

1 started appearing in the 90 °C and 120 °C ionothermal treatment due to the thermo-mechanical
2 force applied besides the acidic media. The ionothermal treatment at 140 °C RS was observed
3 to the similar to untreated RS, which shows the worst effect on the structural change. This
4 could be mainly attributed due to the degradation of the IL as it turned black instantly. Further,
5 this degradation was confirmed through the NMR of the extracted IL via post-ionothermal
6 treatment, which is entirely different from the original NMR of [DBU][OTf].

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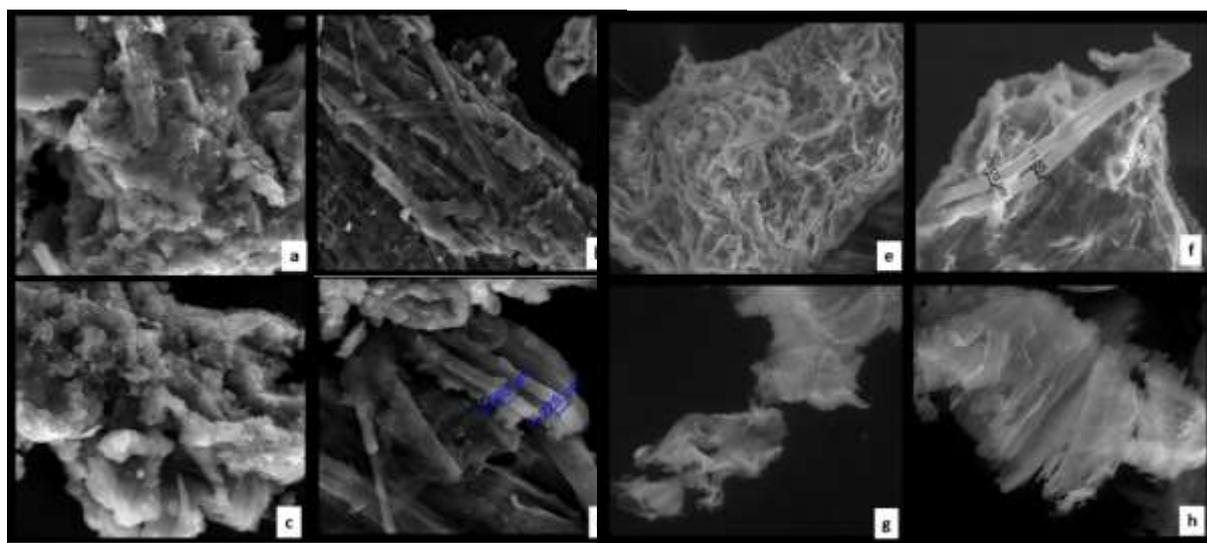
9 **Figure 2.** a) Outer and the cross-sectional organized surface of the original rice straw before
10 treatment at 100 μm ; b) cross-sectional view of original rice straw before treatment at 50 μm ;
11 Rice straw after pretreatment with [DBU][OTf] at different temperatures are viewed at
12 different sizes are shown in figures (c) – (h) where c) 90 °C at 100 μm ; d) 90 °C at 50 μm ; e)
13 120 °C at 100 μm ; f) 120 °C at 50 μm ; g) 140 °C at 100 μm and h) 140 °C at 50 μm .

14

15

16 Further, to examine the effect of ionic liquids having the same anion on pretreatment
17 of RS we have carried out similar studies using ([BtTzm][OTf]) IL. **Fig. 3a-d** represent the
18 morphology of RS after pretreated with [BtTzm][OTf] at a lower temperature 90°C. In the
19 presence of triazolium cation, only a few fibers were formed in the diameter range of 4.5 to 5.2
20 μm . Thus, the fibers were not completely released when triazolium cation was used for
21 pretreatment. Here, a lot of fibers were visible in case however those fibers were still bound to
22 each other. Moreover, two more ILs were compared having a common anion as acetate and
23 their cation was varied. However, [DMEA][OAc] and [DEEA][OAc] showed eroded surfaces,
24 and the formation of fewer fibers was observed only in the case of DEEA (**Fig. 3 e-h**). Overall,
25 observed SEM data suggest that complete disorganization of the lignocellulosic material when

1 [DBU][OTf] whereas in the case of the other three studied ILs we did not see any proper
2 reorganization. Since DBU-based IL has proved a better result among other studied ILs, we
3 went ahead to characterize other properties of the pretreated product obtained through
4 [DBU][OTf].
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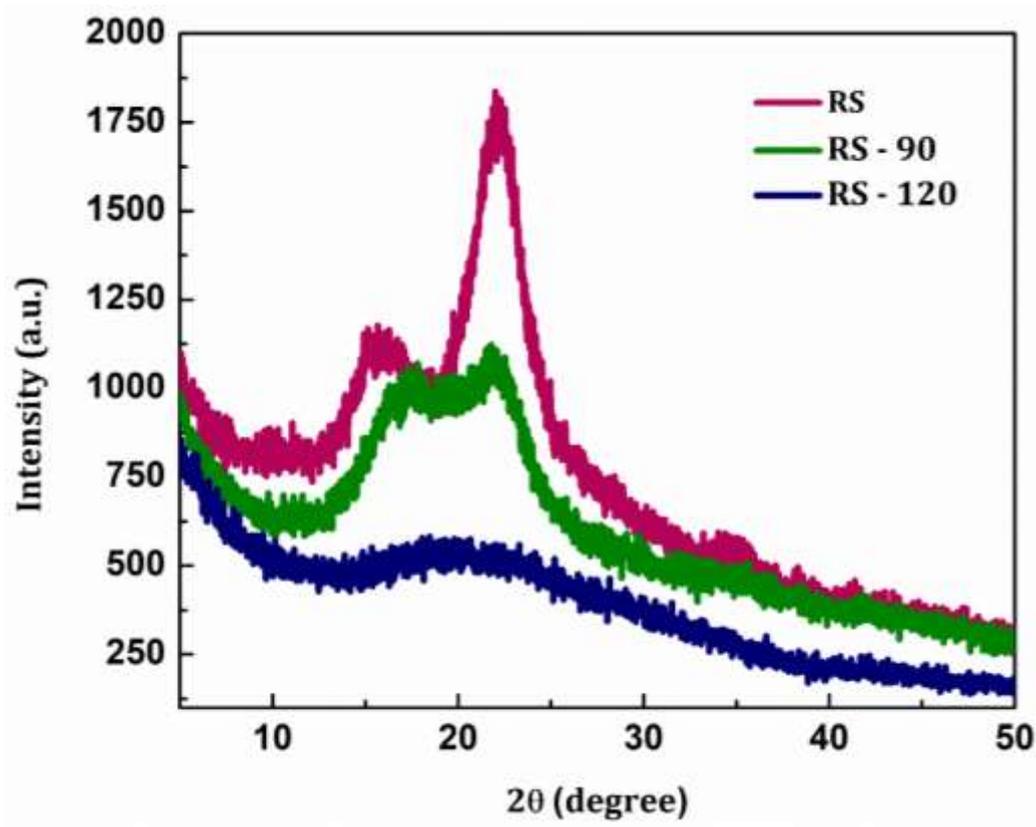


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8 **Figure 3:** SEM image for rice straw post-treatment with [BtTzm][OTf]-based IL **a,b)** at 100
9 μm and **c,d)** at 50 μm . **e,f)** at 100 and 50 for [DME][OAc] and **g,h)** at 100 and 50 for
10 [DEE][OAc]
11
12

13 PXR D patterns are useful in the study of the crystalline behavior of a material and to
14 relate the characteristics of the samples with the crystal structure. All of the lignocellulosic
15 biomass samples are complex molecules with partial crystalline and partial amorphous nature
16 but the crystallinity would differ from one sample to the other one. The crystalline portion
17 would be the indication of cellulose chains closely held together with the H-bonding whereas
18 the amorphous regions suggest the disordered region with no H-bonding is present. Ionic liquid
19 pretreatment strongly affected the crystallinity of the biomass samples and is compared with
20 the same for the untreated RS sample. Moreover, the pretreatment with IL at two different
21 temperatures indicated the possibility of a decrease in the peak intensities as the reaction
22 temperature increased [54]. The PXR D patterns for the rice straw samples with and without IL
23 pretreatment is shown in the fig.4 where the crystalline peaks are decreasing after the
24 pretreatment in comparison to the pure RS.

25 Several studies have reported the Segal method, however, there are many debates about
26 the same, and new methods have evolved [55], [56]. Our group carried out deconvolution using

1 Fityk software [57]. Commonly used functions for deconvolution of the diffraction patterns are
2 Gaussian, Lorentzian, and pseudoVoigt (mixtures of Gaussian & Lorentzian). But we used both
3 Gaussian and pseudoVoigt and compared the calculations of the CrI and the crystallite size.
4 French suggested that Gaussian peaks were not enough to satisfy the amorphous peaks alone.
5 Hence, pseudoVoigt was also taken into consideration.
6



7
8 **Figure 4.** PXRD patterns for original rice straw and the residue obtained post-treatment using
9 [DBUH] [OTf] (**RS**: Original Rice Straw, **RS - 90**: Rice Straw after heating at 90 °C, **RS -**
10 **120**: Rice Straw after heating at 120 °C)
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12

13 Yao et al 2020 reported background subtraction in the case of PXRD data where the
14 background must be removed before plotting the PXRD data for the experiments. The
15 background error might originate from the air scattering, thermal agitation of atoms, and
16 sample holder. The background was subtracted before peak deconvolution which ensured a
17 stable baseline fitting thereby helping in reducing error [58].

18 *Fityk's* Levenberg-Marquardt algorithm was used to run the fittings. The crystallite sizes
19 (L) for the main 200 peak, using full-width half maximum (FWHM) values were calculated
20 using the Scherrer equation, which is shown in equation 1.

1

$$L = \frac{K\lambda}{(\beta \cos\theta)} \quad (1)$$

2

3 $\lambda=1.54 \text{ \AA}$ (since Copper-K α was the target)

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The k value was taken as 0.94 as suggested by Rico et al [59] and the other parameters were calculated as shown in supplementary information (Table S1). The crystallinity index (CrI) of the rice straw samples before and after the pretreatment with the IL was calculated using the following equation.

$$CrI = 100 \times \left(\frac{A_{cryst}}{A_{Tot}} \right) \quad (2)$$

A_{cryst} = area of crystalline peak in this case the peak at 200 plane

A_{Tot} = area of total peaks

Table 1: Crystallite size and crystallinity index using Gaussian and pseudoVoigt fitting

Samples	Gaussian		pseudoVoigt	
	Crystallite size (nm)	CrI %	Crystallite size (nm)	CrI %
Pure RS	3.20	46.34%	2.41	36.00%
RS 90	2.16	46.22%	2.01	33.44%
RS 120	0.56	-	0.56	-

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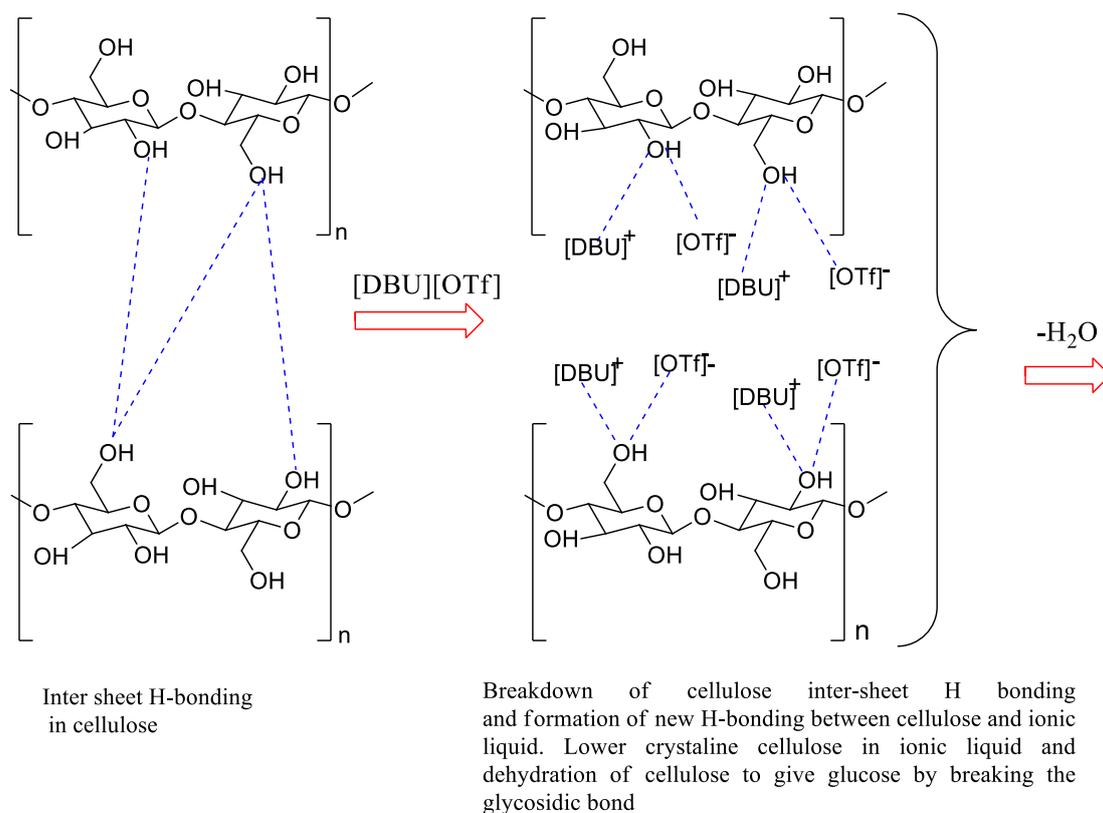
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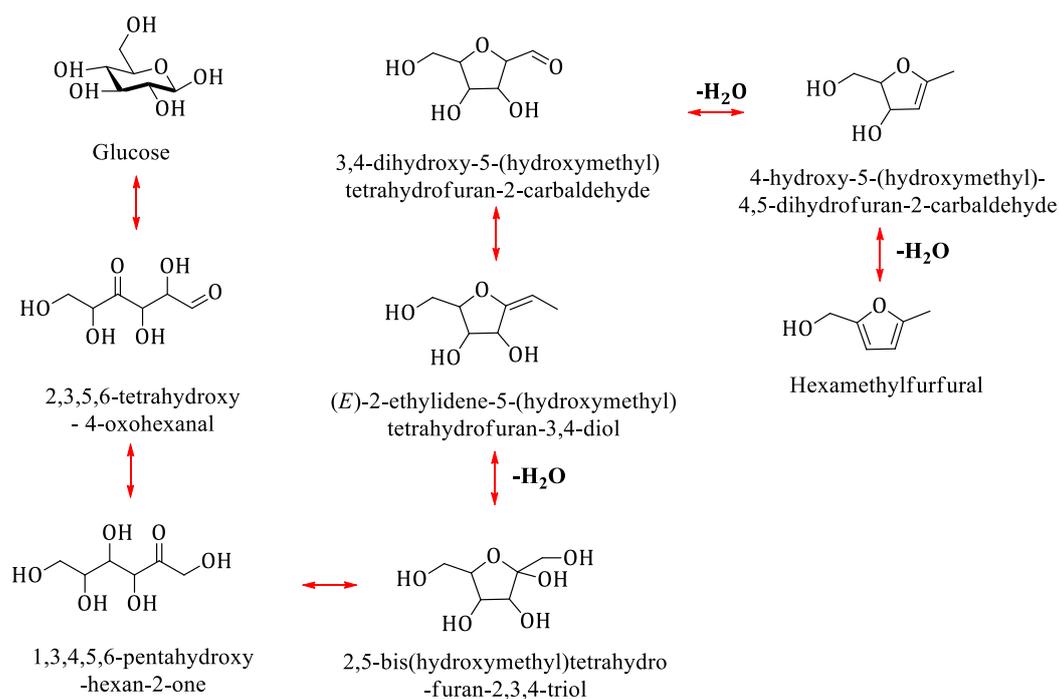
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1 possibility as the temperature was lower than 300 °C. The glycosidic bonds linking the glucose
 2 units in cellulose are not very strong. There are inter and intramolecular hydrogen bonds
 3 associated per glucosyl unit in raw cellulose. The packing of numerous cellulose flat sheets is
 4 mainly through van der Waals forces and H-bonding. (**Scheme 1**). However, the weak
 5 glycosidic bonds in cellulose cleave under acid or high-temperature conditions. The latter was
 6 proven due to the qualitative analysis of 5-hydroxymethylfurfural (HMF) using TLC sheets in
 7 the IL part post-filtration (**Scheme 1**).

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3 **Scheme 1:** Mechanism of cellulose interacting with IL (adapted and modified from [60], [61],
 4 and [62]. The blue dots indicate H-bonding.

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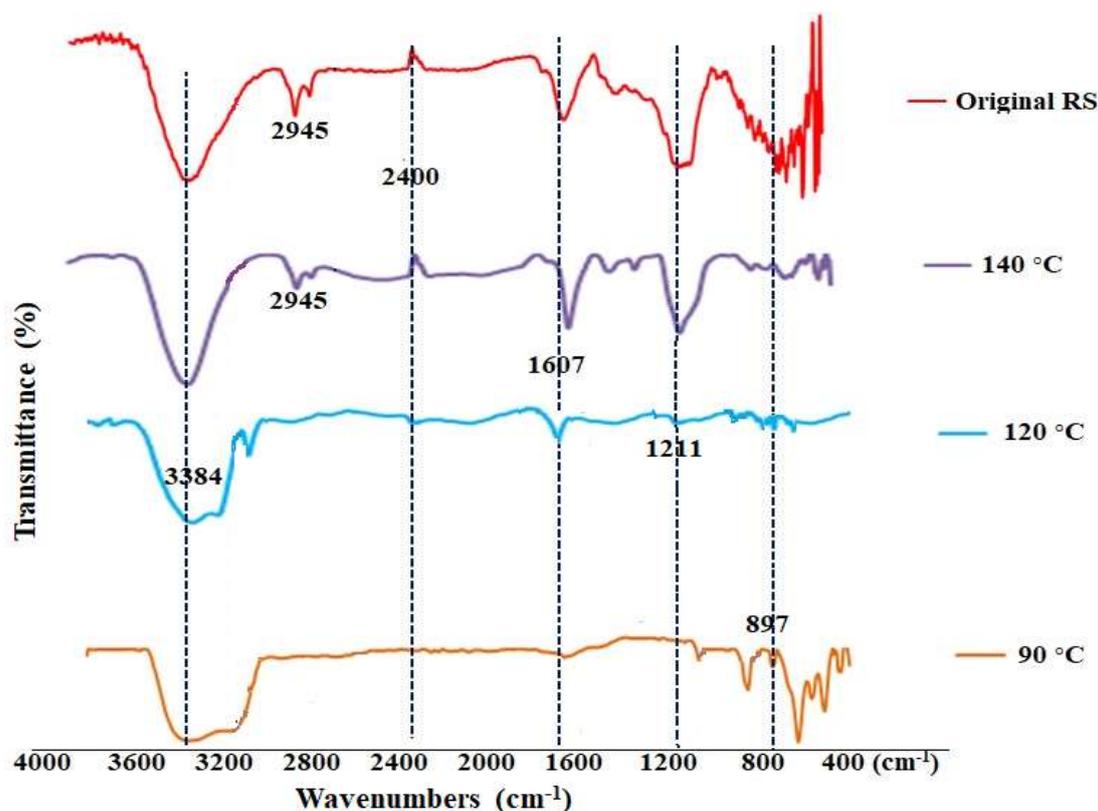
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7 This decrease in crystallinity made it more porous than before, and hence further
 8 treatments like enzymatic hydrolysis can be carried out more effectively. The effectiveness was
 9 tested by the pyrolysis method mentioned in the last section. The high temperature would have
 10 removed the volatile components, and due to these two factors, the morphological structures
 11 differed before and after treatment as also agreed with SEM images (**Fig. 2**).

12 Moreover, the Interaction of -OH groups present in cellulose with both cation and anion
 13 of ILs make it soluble in those solvents. Oxygen atoms that belong to the -OH groups of
 14 cellulose function as electron donors and hydrogen atoms serve as electron acceptors. IL anions
 15 also behave as electron donors. Cations having an electron-rich aromatic π system is not
 16 interacting much with hydroxyl oxygen atoms through either nonbonding electrons or π
 17 electrons whereas anions prefer to interact through hydrogen bonding to the hydroxyl proton
 18 of cellulose moiety [63].

19 Such interactions were mainly investigated through the FTIR analysis. Thus it was
 20 carried out for the RS as well as ionothermally treated RS at three different temperatures as
 21 shown in **Fig. 4**. The -OH stretching at 2945 from original RS disappeared in the 90 °C and
 22 120 °C indicating cleavage of some H-bonds (mainly $\text{O(6)H} \cdots \text{O(3)}$) during the process of

1 conversion of cellulose to HMF via glucose. At 140 °C, charring has occurred so the product
2 was not analyzed. In addition, FTIR was carried out for the original RS as well treated RS at
3 90, 120, and 140 °C. The FTIR at 140 °C also confirmed that IL degraded at this temperature
4 and so there was hardly any change in the RS's composition besides the charring and color of
5 IL turning to black. Treated RS at 140 °C was also used to measure the IR data and no
6 modification was observed in its peak because their chemical constituent looks quite similar to
7 the untreated one. The FTIR confirmed the removal of some lignin and cellulose H-bonding
8 when the RS was treated at 120 °C. Visible changes were observed in the texture and
9 composition of the RS after the dissolution in IL for 6 h. These conversions for the recycled
10 ILs were obtained by calculation of mass before and after the treatment.
11



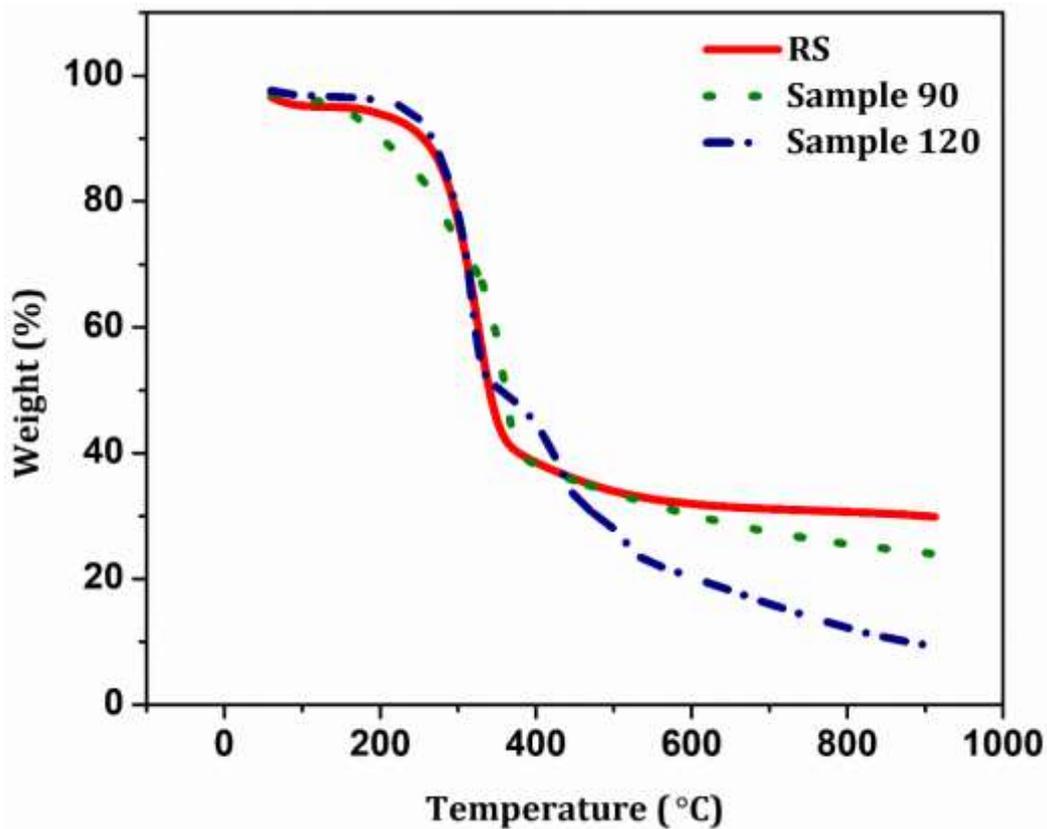
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13 **Figure. 4:** Comparative FT-IR studies on original rice straw (RS) and RS at three different
14 temperatures (90, 120, and 140 °C)
15

16 Next, the band at 3383 cm⁻¹ specifies the C-H and O-H stretching band of cellulose which
17 broadens on treatment at 90 °C and 120 °C. O-H stretching is obtained more in the case where
18 the treatment occurred at 120 °C. The peak at 2945 cm⁻¹ corresponded to the O-H and C-H
19 stretching band of the lignocellulosic matrix, and this was not present in the RS treated at 90
20 °C and 120 °C. The peak at 2400 cm⁻¹ corresponded to a methyl group of lignin (between 2915

1 and 2847 cm^{-1}) which disappeared at 90 °C and 120 °C treated RS. The peak around 1607 cm^{-1}
2 $^{-1}$ corresponded to lignin bonds which also disappeared in lower temperature treatments. The
3 peak at 1211 cm^{-1} corresponds to the syringyl ring and C-O stretching lignin character
4 vibration. The peaks between 1000 and 400 cm^{-1} corresponded to the presence of silica bonds
5 in the lignocellulose. The treatment at 120 °C showed deformation in the silica bonds as the
6 peaks did not appear. Barriers to the RS towards enzyme accessibility were removed after
7 ionothermal treatment, and the cellulose and some hemicellulose portion were exposed.

8 Additionally, the decrement of the extent of lignin has been monitored through TGA
9 analysis, where we can see that removal of cellulose and lignin and that was the reason lesser
10 biochar were obtained in these cases. TGA data supported that the pyrolysis temperature
11 decreased for the pretreated RS.

12



29

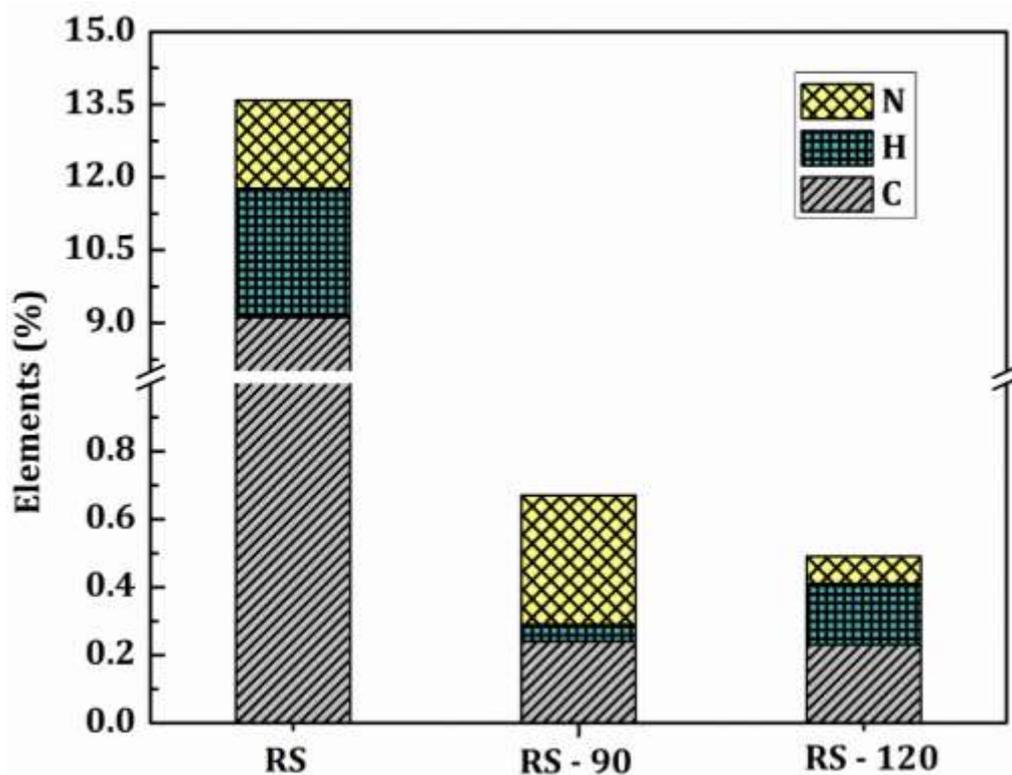
30 **Figure. 5.** TGA of the original RS compared with pretreated RS at 90 °C and 120 °C (RS:
31 Original Rice Straw, RS - 90: Rice Straw after heating at 90 °C, RS - 120: Rice Straw after
32 heating at 120 °C)

33

1 **Fig. 5** suggested the pyrolysis of biomass through TGA analysis, which was significantly
2 affected by the CrI. As displayed in Fig. 5, the decomposition temperature of hemicellulose,
3 cellulose, and lignin is observed in the range of 220–315 °C, 314–400 °C and 160 to 900 °C
4 respectively, which is the indication of generating a solid residue. The main gases could be
5 CO₂, CO, CH₄, and some organics, which are mainly responsible for the slow residence times
6 [64]. Thus, as suggested from Fig. 5, 29%, 21%, and 9% biochar was the solid carbon-rich
7 residue left after pyrolysis of pretreated RS biomass for original RS, pretreated at 90 and 120
8 °C, respectively (**Fig. 5**). Biochar is a low-grade fuel and can be collected in parts from all
9 pyrolysis reactions, which can be further used as a fuel for new pyrolysis reactions. The
10 European Bioenergy Research Institute (EBRI), Aston University runs a pyrolysis unit using
11 biochar. Biochar has also been used as an additive to increase soil fertility and improve the
12 water holding capacity. All these specify that the RS's waste after pretreatment can be utilized
13 for various applications. At higher temperatures, rapid cleavage of glycosidic bonds occur
14 leading to the formation of gaseous products both condensable and non-condensable and
15 further pyrolysis of the pretreated RS allows the cellulose structure to degrade sharply during
16 the initial stages of fast pyrolysis with the cleavage of more glycosidic bonds thereby leading
17 to lesser char yields.

18 The TGA profile can be roughly divided into three regions. (i) < 220 °C showed weight
19 loss (less than 10%) which may be due to dehydration and removal of volatile components; (ii)
20 between 220 and 360 °C showed weight loss up to 40%. Between 200 and 300, the cleavage
21 of intra- and intermolecular hydrogen bonds occurs and (iii) at 360 °C and higher temperatures.
22 The treated RS at 120 °C had only 9% remains of the feedstock which suggests that some
23 chemicals were formed and waste is reduced compared to the untreated RS (29% remains) and
24 also RS treated at 90 °C where 21% remains. These agree with the FTIR results i.e. removal of
25 some components.

26 Like petroleum cracking, many reactions occur during pyrolysis of biomass, like
27 condensation, depolymerization, dehydration, isomerization, and charring reactions and plenty
28 of pyrolyzed products are released [65]. Due to all the situations mentioned above, the bio-oil
29 or gases, when trapped are not pure and have to go through another process of distillation.
30 However, these products were not analyzed in this part of our study. Lignin pyrolysis gives
31 mainly aromatic compounds, and pyrolysis of cellulose and hemicellulose gives aliphatic
32 components. Due to various reactions going on simultaneously, it is a difficult task to identify
33 the exact mechanism.



1

2 **Figure. 6:** Comparative study on the elements before and after pretreatment of rice straw (**RS:**
 3 Original Rice Straw, **RS - 90:** Rice Straw after heating at 90 °C, **RS - 120:** Rice Straw after
 4 heating at 120 °C)

5

6

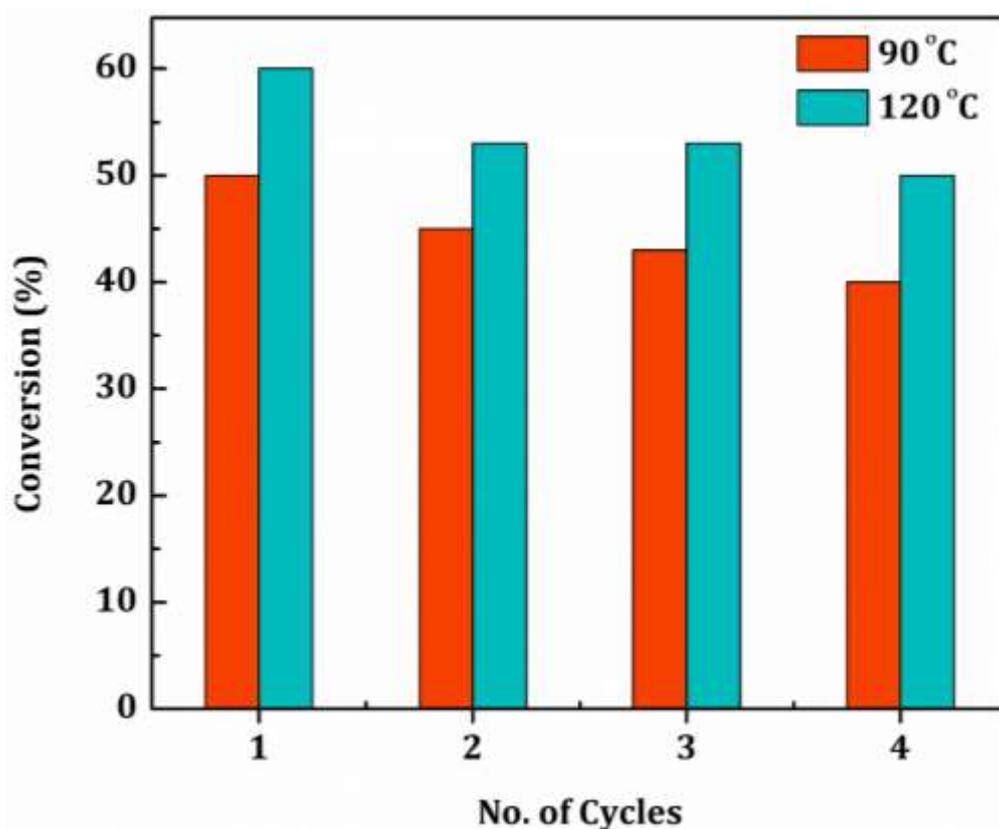
7 Further, the changes in the CHN composition were also carried out to understand the
 8 extent of pretreatment. The original RS possessed the elements C, H, and N as 9.12%, 0.24%,
 9 and 0.23%, respectively. On ionothermal treatment at 90 °C and 120 °C the C, H and N
 10 percentages changed to 2.65%, 0.05%, 0.38% and 1.81%, 0.38%, 0.08%, respectively (**Fig. 6**).
 11 As the Lewis basic nature of the DBU cation enhances the C₆-O bond breakage, which is
 12 mainly due to the tertiary nitrogen in the cation and helps in the dehydration of carbohydrate-
 13 kind polymers (Song et al. 2013). Also, the old report suggested that anion of ILs were mainly
 14 influenced the abstraction of the H-atom. Due to this, the glycosidic bond weakens and thus
 15 the crystallinity reduces. The cellulose finally breaks into glucose, which undergoes the
 16 ionothermal condition to give HMF. This was detected using a TLC in the liquid substrate but
 17 was not analyzed quantitatively.

18

19 Next, the recyclability of IL makes it more sustainable towards biomass applications.
 20 In this regard, the recycling was carried out and the percentage of conversion as the recycling

1 process continues is shown in **Fig. 7**. IL could be recycled at least 3 times for reutilization. In
2 all the cases we can see that the pretreatment at 120 °C was more efficient. ILs were washed
3 with dichloromethane (DCM) as IL is soluble in it also. RS samples were fresh and the IL was
4 used for several cycles after washing. Up to 89% of IL was recycled three times and
5 conversions reduced by 5%, 7%, 10% at 90 °C and 7%, 7%, 10%, at 120 °C. Additionally,
6 water was used as an antisolvent to make the unwanted particles settle down easily in the vial
7 used for experiments.

8
9



10

11 **Fig. 7:** Plot showing the effect of conversion to the reusability of [DBUH] [OTf] at different
12 temperatures (90 and 120 °C)

13

14 So far, owing to multiple issues like the high expense behind the production of IL,
15 large-scale uptake of ILs is impeded to some extent. Similarly, there are other factors like the
16 detailed explanation on micro-macro as well as the molecular level of the deconstruction
17 mechanisms which prevents the optimization and modeling, and the requirement of a techno-
18 economic stable assessment on large scale experiments [66]. Considering the high thermal and
19 chemical stabilities of the studied IL, possibilities of reuse exist, which opens up an economic
20 way of lignocellulose pretreatment in an energy-efficient method.

1 **4. Conclusions**

2 Ionothermal treatment alone could tear up RS into tiny fibers and cause a decrease in the
3 crystallinity. The acetate-based ILs used in this study had less thermal stability, thereby not
4 being better solvents at higher temperatures. DBU-based IL was obtained from relatively
5 inexpensive starting material, and due to its air, water, and thermal stability and Lewis basic
6 property of the tertiary nitrogen in the cation helped in the dehydration of carbohydrate-kind
7 polymers.

8 The Lewis basic property of the tertiary nitrogen of DBU cation helped in the dehydration
9 of carbohydrate kind polymers in 6 h. Thus this work opens up opportunities to convert waste
10 lignocellulosic biomass. Biochar/char yields decreased when the pretreatment was carried out
11 at higher temperatures, and thus 120 °C had only 9% of biochar/char remains. Limited
12 information can be obtained from TGA studies regarding the reaction intermediates, reaction
13 pathways, etc. but useful to understand the waste management when RS was pretreated.
14 However, the mechanism in air and nitrogen will vary. IL could be recycled at least three times
15 pointing towards the possibility of reuse to reduce the cost issues associated with the ionic
16 liquids.

17 Being an attractive field of research, the journey of searching for better ILs in the
18 pretreatment technique will continue until the research minds are satisfied with optimized
19 reactants and reaction conditions. The idea of using ILs has to be commercialized from the
20 narrow level of laboratory scales with suitable combinations of cheap solvents and ILs, in an
21 economic way without harming the environmental perspectives. There are still lots of hurdles
22 before ILs reach the biorefineries. Reusing possibilities have to be explored to achieve these
23 goals, and pure ILs have to be substituted with their mixtures with proper solvents. Further
24 studies in this regard as a continuation of this work will be exploring much more about the
25 quantitative approach and IL-solvent binary mixtures for dissolution.

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33
34

1 **Conflict of interest**

2
3 The authors declare that there are no known conflicts of interest related to the content of this
4 article. We certify that we have no financial or proprietary interests in any material discussed
5 in this article.
6

7 **Supplementary Information**

8
9 Detailed descriptions on the synthesis of ILs, characterization of the ILs, the experimental
10 procedure for the pretreatment of rice straw and crystallinity calculations are provided in the
11 Supplementary Information (SI).
12
13

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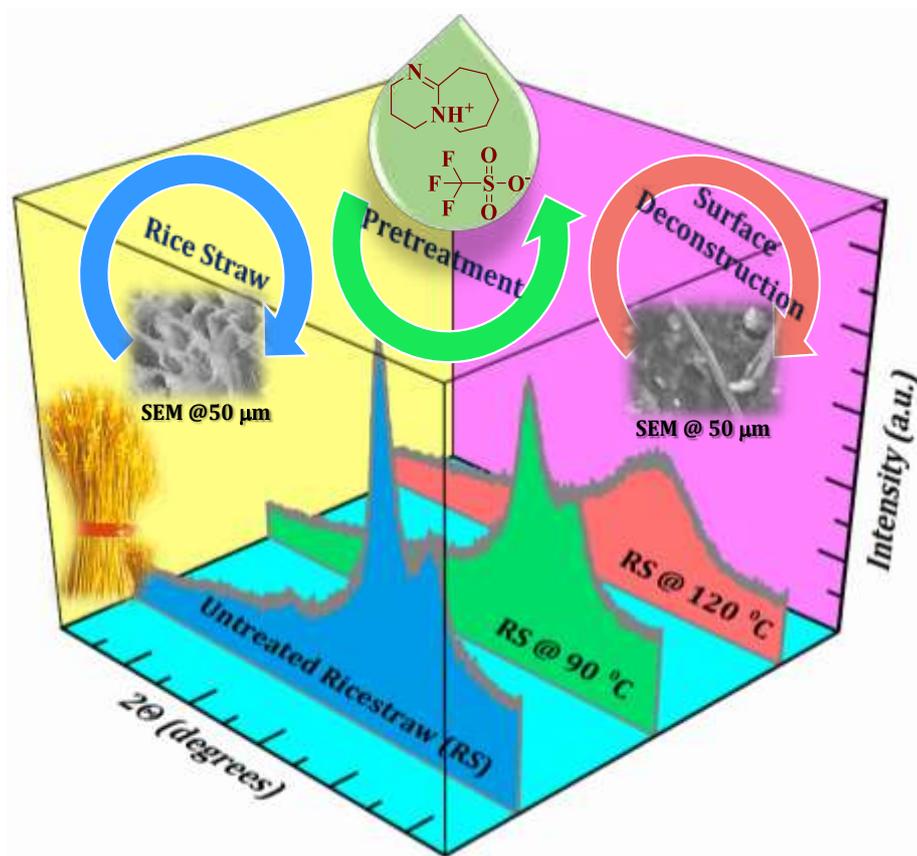
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2 Graphical Abstract

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