

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

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Research Article

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Abstract

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

1. Introduction

Bio-based chemicals and products including biofuels are the major targets by many agricultural biotechnologists. It is expected that nearly 27% of transportation fuels can be replaced with biofuels by 2050 (Popp et al. 2014). Implementation of the biorefinery concept wholly depends on biomass as a valuable feedstock for producing bio-based fuels, cosmetics, chemicals, textiles etc. (Dias et al. 2020). Pyrolysis of lignocellulose, in which the feed substance is cracked thermally in the absence of oxygen, is used to crack lignocellulosic materials (Dhyani and Bhaskar 2018). Pyrolysis produces a solid (also called as char or biochar), liquid (also called bio-oils), and gas products (both condensable and non-condensable). Different factors, including the addition of catalysts, temperature, and type of lignocellulose/biomass, water content, inherent minerals, heating rates, residence time, pressure, environment, and reactor patterns, contribute to this conversion process. Henceforth, one can select the products needed through pyrolysis by adjusting the parameters. Among these methods, catalytic pyrolysis has got the maximum attention in the last few years (Dhyani and Bhaskar 2018), (Kan et al. 2016). In this regard, thermogravimetric analysis (TGA) is becoming an imperative tool for judging the pyrolysis of the treated biomass apart from other morphological studies(Hameed et al. 2020), (Anca-Couce et al. 2020).

The estimated global production of these lignocelluloses amounts to 200 billion tons, thereby proving suitable candidates for sustainable development (Dahmen et al. 2019). Lignocellulosic biomass can be food as well as non-food. The non-food crop residues include removable materials left after harvesting primary crops like corn, wheat or rice straw. These are widely available, and this waste is either burnt or disposed off each year to avoid the chances of any diseases in the coming year's crop. However, this

leads to one of the major causes of pollution of the year's air quality. Hence to avoid this step that effects the air quality, these waste straws can be used for various purposes, and one among them could be to convert into new bio-based materials or biofuels or any other valuable chemicals. Treating the biomass with various chemicals, considering the complicated plant cell wall, converting waste biomass materials into useful value-added products, etc. has been worked out by many researchers (Baig 2020),(Machineni 2020).

Rice straw (RS) or lignocellulose is a polymer of cellulose, hemicellulose and lignin in which the most resistant part of rice straw is lignin that serves as the "glue" by binding the cellulose and hemicellulose or rather skeleton of plants that gives both rigidity and support to the lignocellulosic structure. There are several studies on rice straw and its waste management like using them for fibreboards and organic fertilizers (Gummert et al. 2020), (El-Kassas and Elsheikh 2021), (Goodman 2020). The aromatic chemical structure imparts a high calorific value to the lignin molecule which is valuable for other chemical conversions. The presence of lignin hinders carbohydrate molecules from reacting to acids or bases, and thus most of the carbon bonds are not broken to give out useful chemicals (Zhang et al. 2016). Efficient valorization of biopolymers depends mainly on the pre-treatment which is a necessary for the structural modifications of the biomass sample.

Pretreatment, the high energy demanding process, becomes something inevitable because it adjusts the structural characteristics of lignocellulose, and the structural alterations are highly connected to the mode of the pre-treatment method chosen (Ashoor and Sukumaran 2020), (Kumar and Sharma 2017), (Loow et al. 2016), (Shah et al. 2019). The recalcitrance of the biomass material obstructs the polysaccharide accessibility and hence various pretreatment techniques including physical, chemical, biological methods were evolved. Negative aspects of a few pretreatment techniques were the high energy requirement and the production of unwanted by-products. There are a handful of reviews available depicting the pros and cons associated with each category of techniques (Bhatia et al. 2020). Moreover, the combination of multiple factors like substrate composition, pretreatment type, dosage and efficiency of enzymes being used for hydrolysis plays a major impact over the digestibility of the lignocellulosic biomass used. Application of selective and benign solvents for biomass pretreatment would be preferable and thus ionic liquids (ILs) were introduced in this field as effective pretreatment solvents (Sathitsuksanoh et al. 2012), (Yang et al. 2018).

ILs comprises of a weakly linked asymmetric cation (organic/inorganic) and anion (organic) in their structure with a melting point lesser than room temperature (Singh et al. 2017), (Sharma et al. 2016), (Sarkar et al. 2017). The scientific community was constantly looking for this kind of solvent where the properties could be tuned according to the desired task. They are widely known as designer solvents owing to the possibility of designing the ionic liquid structure with suitable properties (Diallo et al. 2012), (Liu et al. 2012). They are well known and are widely used in various fields such as catalysis, electrochemistry, pharmacological, separation and purification of biomolecules, extraction, etc. (Mukhopadhyay et al. 2020). The fascinating properties of ILs are many in which higher thermal as well as chemical stabilities, non-flammability, negligible vapour pressure, are quite a few to be listed

(Rodriguez Castillo et al. 2018), (Nelson 2002). Studies have shown that ILs can be used to dissolve bagasse, corn stalks, wheat, wood, etc. and this process is called ionothermal treatment in which ILs have acted as a dual solvolytic catalyst (Usmani et al. 2020), (Rajan et al. 2021). ILs fall into the category of polar solvents which attribute different grades of hydrogen-bond formation ability. Hydrogen bond basicity of anions present in IL play a key role in cellulose dissolution and acetate (Liang et al. 2019) chloride (Mesa et al. 2020), (Naz et al. 2020) carboxylates (Moyer et al. 2018), (Zhao et al. 2012) etc. come in the front line in this category. 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) is mainly used for rice husk dissolution and conversion (Zhang et al. 2021). However, this study used additional amount of inorganic acid to meet the pretreatment requirement. Recently, M. Badbedast and coworkers from Iran have conducted a detailed study on rice straw pretreatment using an acidic IL namely 1-(carboxymethyl)pyridinium chloride with an acetate and chloride groups present in the structure. Various analyses, including FT-IT, XRD, and SEM revealed the restructuring and increase free volume between cellulose chains present in the rice straw sample (Abdolmaleki et al. 2021). Cholinium ILs with amino acid based anions were reported for selective delignification of lignocelluloses and found that the pretreated samples were exhibiting higher saccharification rate as well as higher polysaccharide digestibility (Hou et al. 2012). In another study, biomass pretreatment with IL was coupled with membrane filtration. FT-IR, XRD, SEM and Zeta potential assessments were used to explain the role of ILs in lignocellulose dissolution and the ability of different imidazolium ILs in regenerating the cellulose (Gogoi and Hazarika 2017). New generation of ILs, called deep eutectic systems (DES) was also reported for the biomass pretreatment and found to be promising pretreatment solvents for future biorefineries (Kim et al. 2018), (Sai and Lee 2019).

In this study we have discussed the comparative pretreatment efficiency of four different ILs having triflate and acetate based anion. The acetate-based ILs were used due to the reported studies which showed effective pretreatments for rice straw and other lignocellulosic materials (Magalhães Da Silva et al. 2013) whereas the reason behind to choosing a triflate-based ILs was its better thermal stability. On the selection of cation, the triazole-based IL was found to be high polar than organic solvents (Singh et al. 2017) whereas DBU was spectate better air, water and thermal stability, also the Lewis basic property of its tertiary nitrogen which was capable of breaking the H-bonds between the cellulose molecules thereby forming new H-bonding between the IL and the cellulose (Dong et al. 2016). In addition to that, DBU-based ILs are considered as having higher β values (between 0.8 to 0.9) and again high π^* values (0.9) (Bioni et al. 2020) which are found to be similar to the value of DMSO (Persson 1986). The high values of β and π^* are probably suggestions of van der Waals attractions and weak hydrogen bonds. According to molecular simulation studies, the cations of ILs are seen to be above and below the planes of glucose ring. This effect is being explained by an anisotropic molecular surface of the straight cellulose strands having a smaller hydrogen bonding periphery (Brandt et al. 2013).

Harsh conditions including high temperature, acidic and alkaline conditions, etc. make cellulose significantly soluble in particular solvents (Sharma et al. 2021) whereas ILs don't demand such higher conditions to an extent. The use of high temperature accelerates the dissolution and degradation leading to lesser yields for regenerated cellulose (Usmani et al. 2020) This kind of IL treatment has further advantages such as the pretreatment uses lower temperatures, less hazardous process and corrosion is

not always a concern when the right choice is made with the combination of cation and anion of the IL and finally the regeneration of the IL makes the process feasible and economical. Additionally, ILs can be recycled and reused by taking into consideration the economic aspects (Weerachanchai and Lee 2014). The pretreatment is intended to reduce the energy required for chemical modification of the rice straw, which limits hydrogen bonding and decreases the degree of polymerization, thereby decreasing the crystallinity. One of the approaches was where the process composed of an IL pretreatment followed by enzymatic hydrolysis has proven that some ILs does not deactivate enzymes ever (Pedersen et al. 2019). Fundamental studies regarding pretreatment are getting attention over basic research aspects, but the attempts to bring in industrial-level applications are restricted owing to the cost issues related to some ILs.

2. Experimental Section

Materials and Methods

(i) Synthesis of ILs

The synthesis of studied ILs having triflate anion i.e. ([DBUH][OTf]); [BtTzm][OTf] was reported in our previous report (Jisha et al. 2017), (Singh and Gardas 2016). In brief, the synthetic scheme (Scheme S1 and S2) and characterization through $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ was presented in supporting information (Fig. S1 and S2). Further for assessing the comparative studies, acetate-based ILs were developed with dimethyl ethanol ammonium (DMEA) and diethyl ethanol ammonium (DEEA) cations. The synthetic procedure and its structural characterization of [DMEA][OAc] and [DEEA][OAc] were shown in Scheme S3 and Fig. S3, S4 respectively (Sharma et al. 2016), (Sharma et al. 2017).

(ii) Rice Straw Sample Preparation

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

(iii) Rice Straw Pretreatment

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

(iv) SEM and PXRD Studies

The obtained residue was characterized using powder X-ray diffraction (PXRD) and scanning electron microscope (SEM) to study the changes that occurred post-dissolution. The morphology of the untreated

RS as well as the treated RS was determined using SEM (Quanta 450, FEI, USA). The solid samples were fixed on carbon tapes on sample stubs and were imaged in low vacuum mode. Images were acquired with a 30 kV acceleration voltage. PXRD patterns were recorded using Bruker D8 Advance in the 2θ range 10-35° with a step size of 0.03° and a step time of 1 s at 40 kV and 30 mA at room temperature.

(v) FTIR

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

(vi) CHN Analysis

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

3. Results And Discussion

Herein, the four ILs namely [DBU][OTf], [BtTzm][OTf], [DMEA][OAc] and [DEEA][OAc] were used as a dual solvocatlyst in a 20:1 ratio of IL: RS. Structures of the different ILs used here in this study are shown in Fig. 1. Similar type of pretreatment study was already done where the biomass to solvent ratio was maintained to be 1:10 g/g. In such study the solvent was used as a binary mixture of [TEA][HSO₄]: water with 4:1 w/w ratio and they have conducted the experiments in triplicate at 120 °C for 24 hrs (Chambon et al. 2018). The acidic character of the ILs served to be useful for its dissolution and its larger amount helped for its behavior as a solvent.

Moreover, scanning electron microscopy (SEM) is an imperative tool for examine the morphological aspects of biomass. The surface of the untreated RS was found to be well organized due to the lignin; which acts as skeleton where we can see a well-organized rib-cage like structure or binding agent to hemicellulose and cellulose (shown in Fig. 2a and 2b). Fig. 2c-g represents the pretreatment of RS with [DBU][OTf]; where, small and long fibers started appearing in the 90 °C and 120 °C ionothermal treatment due to the thermo-mechanical force applied besides the acidic media. The ionothermal treatment at 140 °C RS was observed to be similar to untreated RS, which shows the worst effect on the structural change. This could be mainly attributed due to the degradation of the IL as it turned black instantly. Further, this degradation was confirmed through the NMR of the extracted IL via post-ionothermal treatment, which is entirely different from the original NMR of [DBU][OTf].

Rice straw after pretreatment with [DBU][OTf] at different temperatures are viewed at different sizes are shown in figures (c) – (h) where (c) 90 °C at 100 μm ; (d) 90 °C at 50 μm ; (e) 120 °C at 100 μm ; (f) 120 °C at

50 μm ; **g**) 140 °C at 100 μm and **h**) 140 °C at 50 μm .

Further, for examine the effect of cation having same anion ([BtTzm][OTf]) on pretreatment of RS we have started to solubilize in similar extent. Fig. 3a-d represent the morphology of RS after pretreated with [BtTzm][OTf] at a lower temperature 90°C. In the presence of triazolium cation only a few fibers were formed in the diameter range of 4.5 to 5.2 μm . Thus, the fibers were not completely released when triazolium cation was used for pretreatment. Here, a lot of fibers were visible in case however those fibers were still bound to each other. Moreover, two more ILs were compared having a common anion as acetate and their cation were varied. However [DMEA][OAc] and [DEEA][OAc] showed eroded surfaces and formation of fewer fibers were observed only in the case of DEEA (Fig. 3e-h). Overall, observed SEM data suggest that complete deorganization of the lignocellulosic material when [DBU][OTf] whereas in case of the other three studied ILs we did not see any proper reorganization. Since DBU-based IL has proved a better result among others studied ILs, we went ahead to characterize other properties of the pretreated product obtained through [DBU][OTf].

Further for validating the above result, we have done the PXRD to determine the crystallinity index (Crl) which is a vital parameter to understand the intensity of crystallinity of any substance. The XRD intensity profile for the original RS (shown in orange, Fig. 3) showed the characteristic crystalline peak (I_{200}) and amorphous peak (I_{110}) or (I_{am}) at 2θ value of 22° and 18°, respectively. Hence, the crystallinity index (Crl) was calculated using the below formula (**equation 1**) (Segal et al. 1959).

$$\text{Crl} = ((I_{200} - I_{am}) / I_{200}) \times 100 \quad (1)$$

Where I_{200} is the peak intensity at plane (2 0 0) ($2\theta = 22^\circ$) and I_{am} / I_{110} is the minimum intensity at the valley between plane (2 0 0) and (1 1 0) ($2\theta = 18^\circ$).

The Crl for original RS (shown in orange, Fig. 3) and treated RS with IL at 90 °C (shown in green, Fig. 3) and RS treated with 120 °C (shown in violet, Fig. 3) were 50.77%, 35.27% and 18.16%, respectively. This indicates that ionothermal treatment at 90 °C and 120 °C is capable of decreasing the crystallinity of the polymer and temperature plays a significant role in decreasing the crystallinity. The decrease in crystallinity can be attributed to the fact that dissolution of some components from the polymer occurs in the IL. The SEM results completely agree with the PXRD results which mentions the change in the crystallinity and tearing up of the lignocellulose to fibers occurred when ionothermal treatment at 90 and 120 °C was provided.

The decrease in the crystallinity can be because of two reasons: first removal or conversion of lignin and second removal or conversion of cellulose to some furans such as HMF (via glucose) and gases/volatile components. Complete removal of lignin may not be a possibility as the temperature was lower than 300 °C. The glycosidic bonds linking the glucose units in cellulose are not very strong. There are inter and intramolecular hydrogen bonds associated per glucosyl unit in raw cellulose. The packing of numerous cellulose flatsheets is mainly through van der Waals forces and H-bonding. (Scheme 1). However, the weak glycosidic bonds in cellulose cleave under acid or high-temperature conditions. The latter was

proven due to the qualitative analysis of 5-hydroxymethylfurfural (HMF) using TLC sheets in the IL part post-filtration (Scheme 1).

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

Moreover, Interaction of $-OH$ groups present in cellulose with both cation and anion of ILs make it soluble in those solvents. Oxygen atoms that belong to the $-OH$ groups of cellulose function as electron donors and hydrogen atoms serve as electron acceptors. IL anions also behave as electron donors. Cations having an electron-rich aromatic π system is not interacting much with hydroxyl oxygen atom through either nonbonding electrons or π electrons whereas anions prefer to interact through hydrogen bonding to the hydroxyl proton of cellulose moiety (Feng and Chen 2008).

Such interactions were mainly investigated through the FTIR analysis. Thus it was carried out for the RS as well as ionothermally treated RS at three different temperatures as shown in Fig. 4. The $-OH$ stretching at 2945 from original RS disappeared in the 90°C and 120°C indicating cleavage of some H-bonds (mainly $O(6)H-O(3)$) during the process of conversion of cellulose to HMF via glucose. At 140°C , charring has been occurred so that product was not analyzed. In addition, FTIR was carried out for the original RS as well treated RS at 90 , 120 and 140°C . The FTIR at 140°C also confirmed that IL degraded at this temperature and so there was hardly any change in the RS's composition besides the charring and color of IL turning to black. Treated RS at 140°C was also used to measure the IR data and no modification was observed in its peak because their chemical constituent looks quite similar to the one that was untreated. The FTIR confirmed the removal of some lignin and cellulose H-bonding when the RS was treated at 120°C . Visible changes were observed in the texture and composition of the RS after the dissolution in IL for 6 h. These conversions for the recycled ILs were obtained by calculation of mass before and after the treatment.

Next, the band at 3383 cm^{-1} specifies C-H and O-H stretching band of cellulose which clearly broadens on treatment at 90°C and 120°C . O-H stretching is obtained more in case where the treatment occurred at 120°C . The peak at 2945 cm^{-1} corresponded to O-H and C-H stretching band of the lignocellulosic matrix and this was not present in the RS treated at 90°C and 120°C . The peak at 2400 cm^{-1} corresponded to a methyl group of lignin (between 2915 and 2847 cm^{-1}) which disappeared at 90°C and 120°C treated RS. The peak around 1607 cm^{-1} corresponded to lignin bonds which also disappeared in lower temperature treatments. The peak at 1211 cm^{-1} corresponds to the syringyl ring and C-O stretching lignin character vibration. The peaks between 1000 and 400 cm^{-1} corresponded to the presence of silica bonds in the lignocellulose. The treatment at 120°C showed deformation in the silica bonds as the peaks did not appear. Barriers on the RS towards enzyme accessibility were removed after ionothermal treatment and the cellulose as well as some hemicellulose portion was exposed.

Additionally, the decrement of extent of lignin has been monitored through TGA analysis, where we can see that removal of cellulose and lignin and that was the reason lesser biochar were obtained in these cases. The removal of some lignin components also agreed with the TGA data which clearly showed that the pyrolysis temperature decreased for the pretreated RS.

Figure 5 suggested the pyrolysis of biomass through TGA analysis, which was significantly affected by the CrI. As displayed in Fig. 5, the decomposition temperature of hemicellulose, cellulose and lignin is observed in the range of 220–315 °C, 314–400 °C and 160 to 900°C respectively, which is the indication of generating a solid residue. The main gases could be CO₂, CO, CH₄ and some organics, which is mainly responsible for the slow residence times (Yang 2007). Thus, as suggested from Fig. 5, 29%, 21% and 9% biochar was the solid carbon-rich residue left after pyrolysis of pretreated RS biomass for original RS, pretreated at 90 and 120 °C, respectively (Figure 5). Biochar is a low-grade fuel and can be collected in parts from all pyrolysis reactions, which can be further used as a fuel for new pyrolysis reactions. The European Bioenergy Research Institute (EBRI), Aston University runs a pyrolysis unit using biochar. Biochar has also been used as an additive to increase the soil fertility and improves the water holding capacity. All these specify that the RS's waste after pretreatment can be utilized for various applications. At higher temperatures rapid cleavage of glycosidic bonds occur leading to the formation of gaseous products both condensable and non-condensable and further pyrolysis of the pretreated RS allows the cellulose structure to degrade sharply during the initial stages of fast pyrolysis with the cleavage of more glycosidic bonds thereby leading to lesser char yields.

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

Like petroleum cracking, a large number of reactions take place during pyrolysis of biomass, like condensation, depolymerization, dehydration, isomerization and charring reactions and plenty of pyrolyzed products are released (Wang et al. 2020). Due to all the above mentioned situations the bio-oil or gases when trapped are not pure and have to go through another process of distillation. However, these products were not analysed in this part of our study. Lignin pyrolysis gives mainly aromatic compounds and pyrolysis of cellulose and hemicellulose gives aliphatic components. Due to so many simultaneous reactions going on at the same time it is a difficult task to identify the exact mechanism.

Further, the changes in the CHN composition were also carried out in order to understand the extent of pretreatment. The original RS possessed the elements C, H and N as 9.12%, 0.24% and 0.23%, respectively. On ionothermal treatment at 90 °C and 120 °C the C, H and N percentages changed to 2.65%, 0.05%, 0.38% and 1.81%, 0.38%, 0.08%, respectively (Fig. 6). As the Lewis basic nature of the DBU cation

enhances the C₆-O bond breakage, which is mainly due to the tertiary nitrogen in the cation and helps in the dehydration of carbohydrate-kind polymers (Song et al. 2013). Also, old report suggested that anion of ILs were mainly influence the abstraction of the H-atom. Due to this the glycosidic bond weakens and thus the crystallinity reduces. The cellulose finally breaks into glucose which undergoes in presence of the ionothermal condition to give HMF and this was detected using a TLC in the liquid substrate however was not analyzed quantitatively.

Next, the recyclability of IL makes it more sustainable towards the biomass applications. In this regards, the recycling was carried out and the percentage of conversion as recycling process continues is shown in Fig. 7. IL could be recycled at least 3 times for reutilization. In all the cases we can see that the pretreatment at 120 °C was more efficient. ILs was washed with dichloromethane (DCM) as IL is soluble in it also. RS samples were fresh and the IL was used for several cycles after washing. Upto 89% of IL was recycled three times and conversions reduced by 5%, 7%, 10% at 90 °C and 7%, 7%, 10%, at 120 °C. Additionally, water was used as an antisolvent to make the unwanted particles to settle down easily in the vial used for experiments.

So far, owing to multiple issues like high expense behind the production of IL, large scale uptake of ILs is impeded to some extent. Similarly, there are another factors like detailed explanation on micro-macro as well as molecular level of the deconstruction mechanisms which prevents the optimization and modeling, and the requirement of a techno-economic stable assessment on large scale experiments (Halder et al. 2019). Considering the high thermal as well as chemical stabilities of the studied IL, possibilities of reuse do exist and this opens up an economic way of lignocellulose pretreatment in an energy efficient method.

4. Conclusions

Ionothermal treatment alone was capable of tearing up RS into small fibers and caused a decrease in the crystallinity. The acetate-based ILs used in this study had less thermal stability thereby not being better solvents at higher temperatures. However, DBU-based IL was its relatively inexpensive starting material and its better air, water, and thermal stability and its Lewis basic property of the tertiary nitrogen in the cation helped in the dehydration of carbohydrate-kind polymers.

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

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

Declarations

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Conflict of interest

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

Supplementary Information

Detailed description on the synthesis of ILs, characterization of the ILs and the experimental procedure for the pretreatment of rice straw are provided in the supplementary Information (SI).

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Schemes

Scheme 1 is in the supplementary files section.

Figures

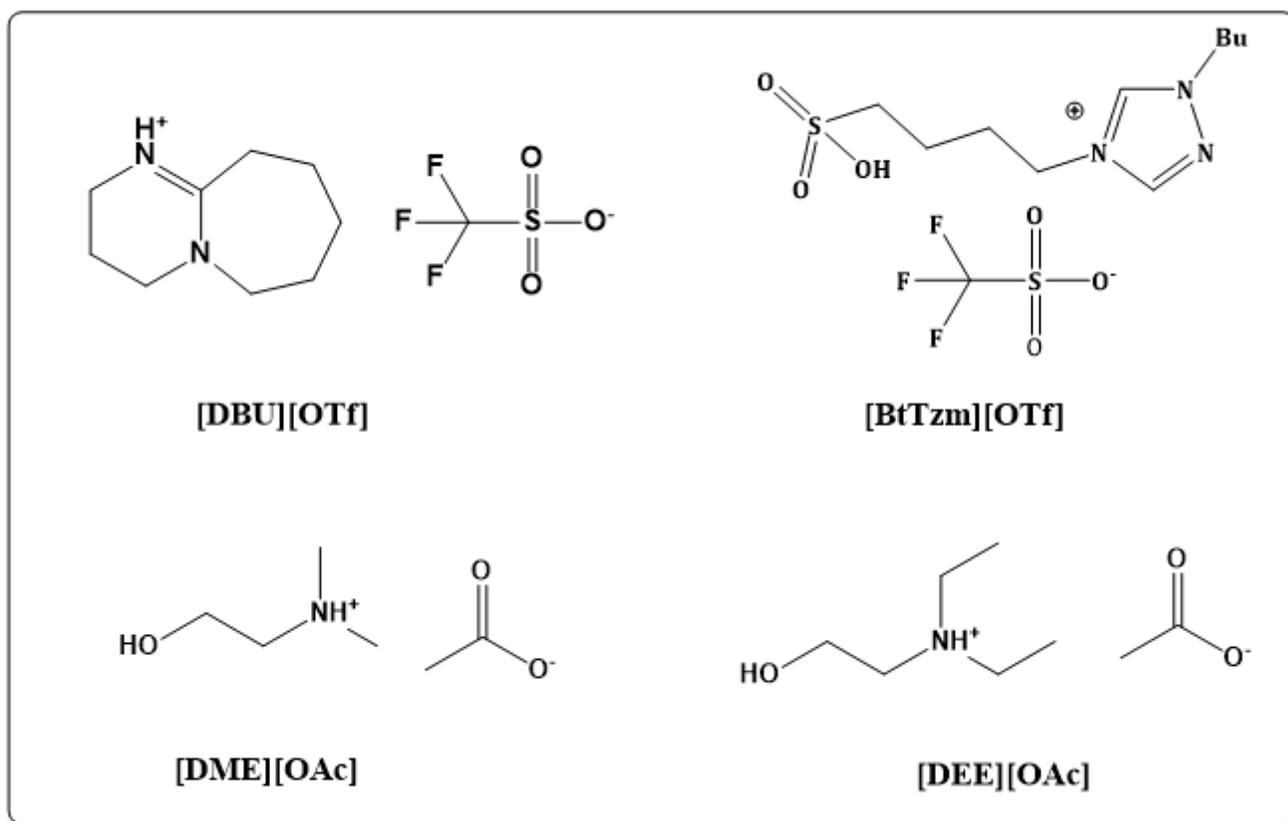


Figure 1

Diagram representing the structure of four ionic liquids used in this study

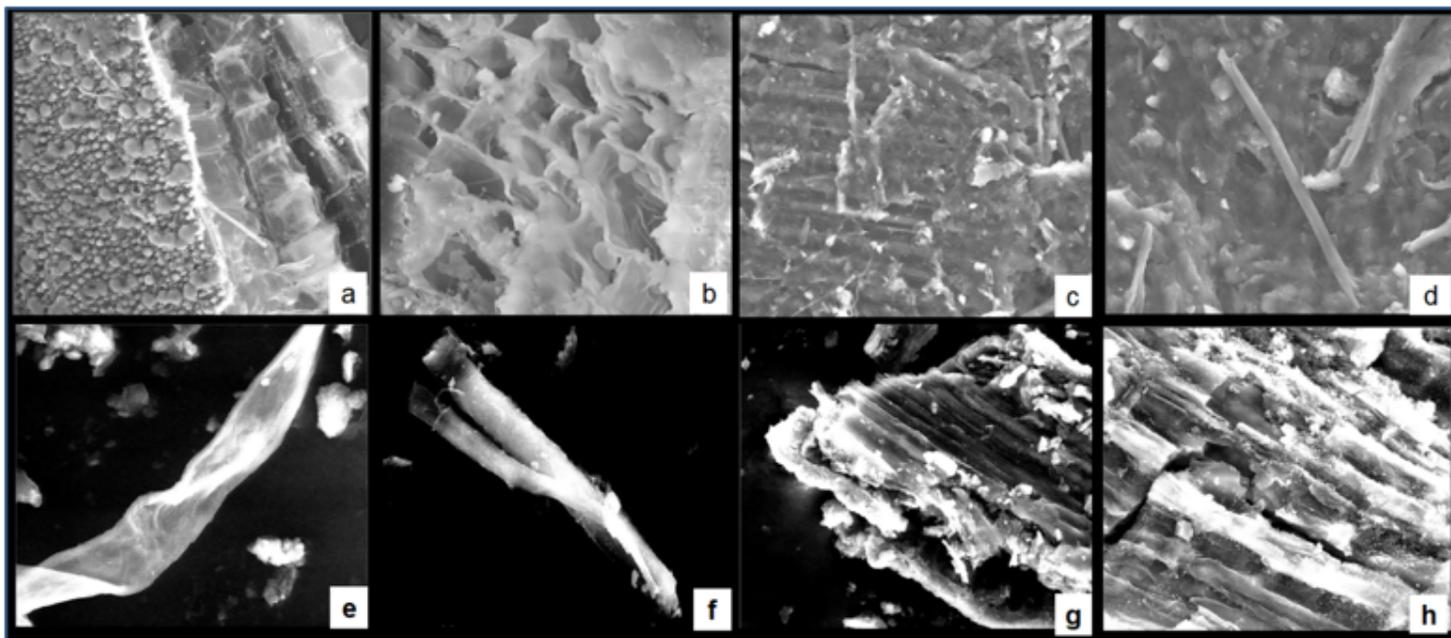


Figure 2

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

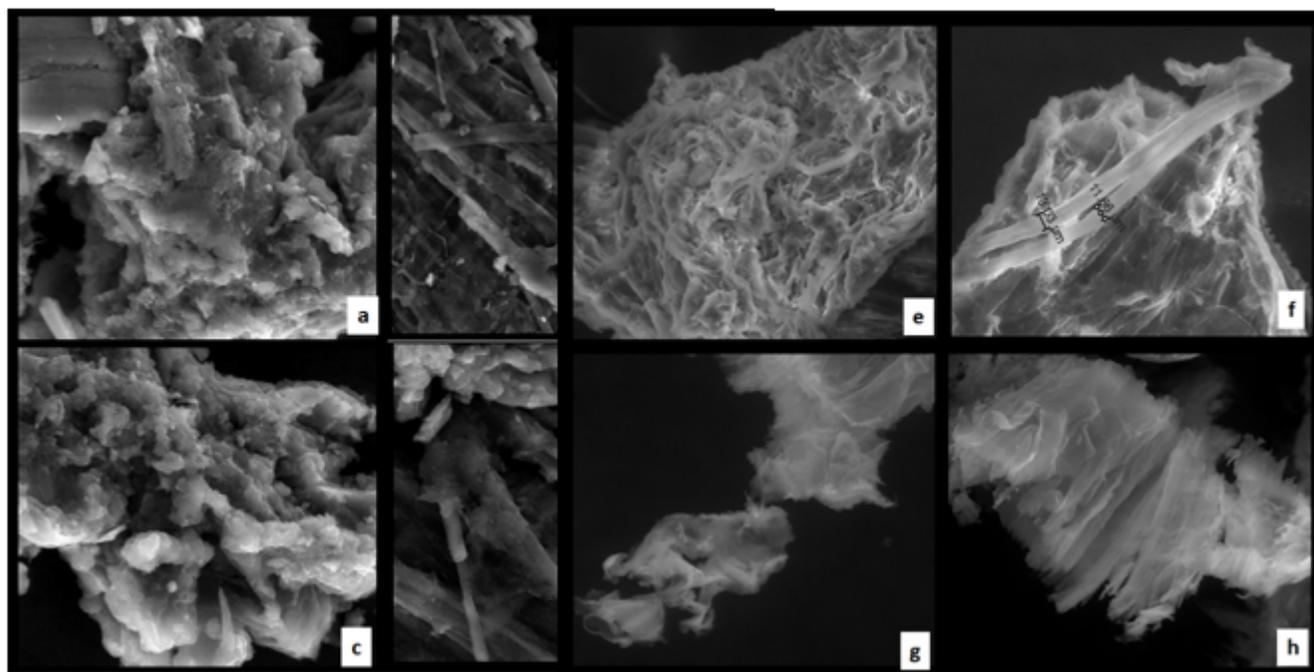


Figure 3

SEM image for rice straw post-treatment with [BtTzm][OTf]-based IL a,b) at 100 μm and c,d) at 50 μm . e,f) at 100 and 50 for [DME][OAc] and g,h) at 100 and 50 for [DEE][OAc]

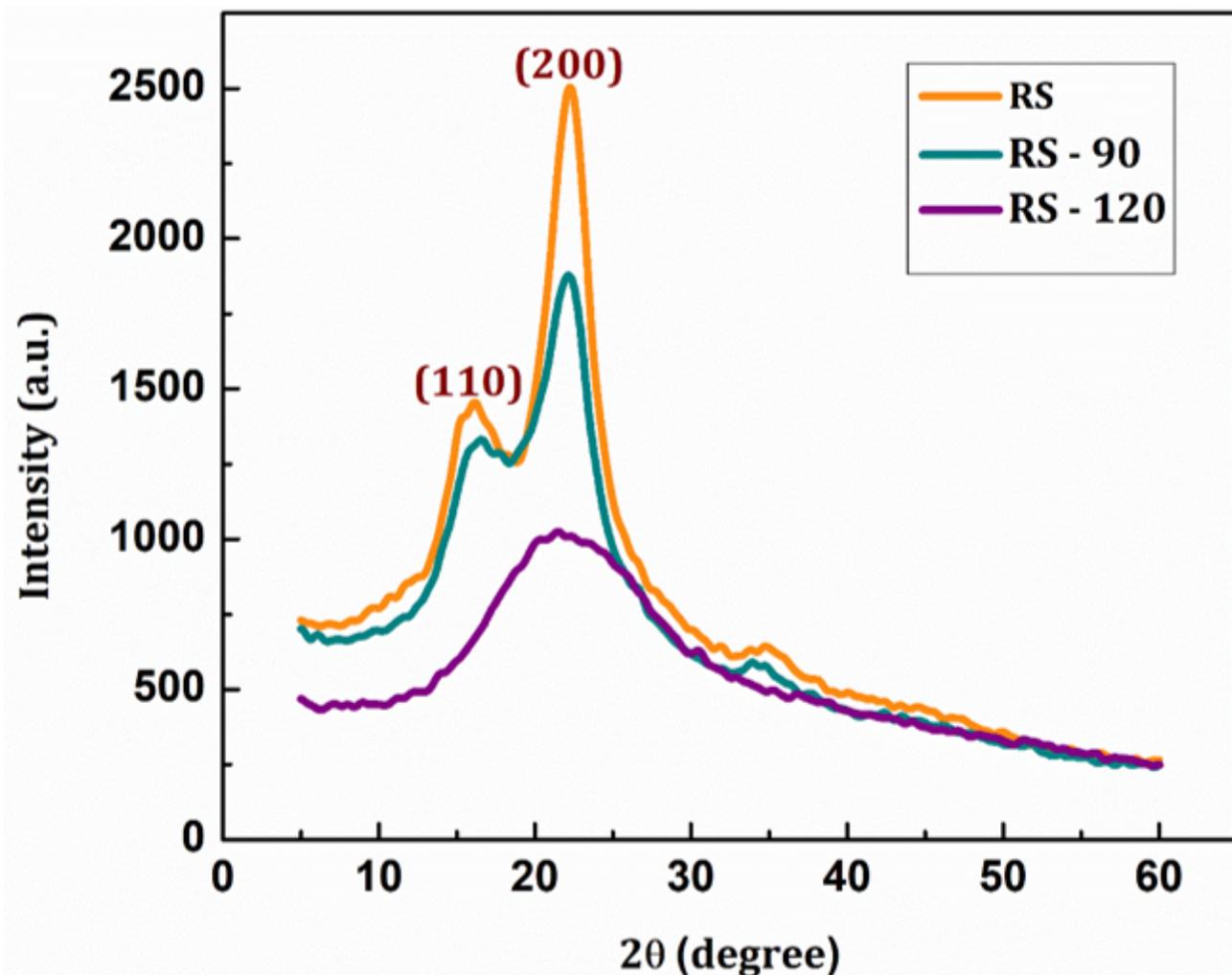


Figure 4

PXRD patterns for original rice straw and the residue obtained post-treatment using [DBUH] [OTf] (RS : Original Rice Straw, RS - 90 : Rice Straw after heating at 90 °C, RS - 120 : Rice Straw after heating at 120 °C)

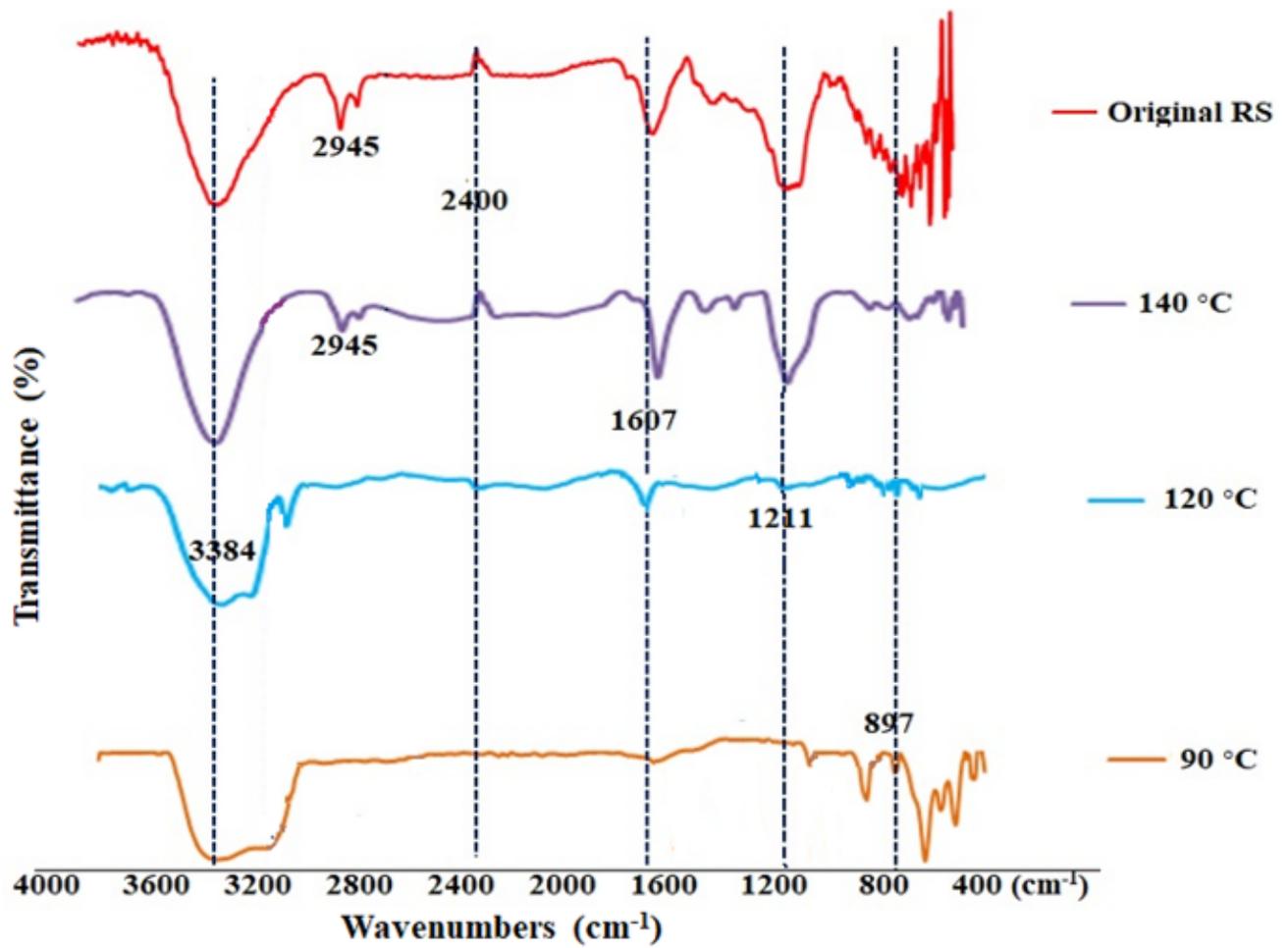


Figure 5

Comparative FT-IR studies on original rice straw (RS) and RS at three different temperatures (90, 120, and 140 °C)

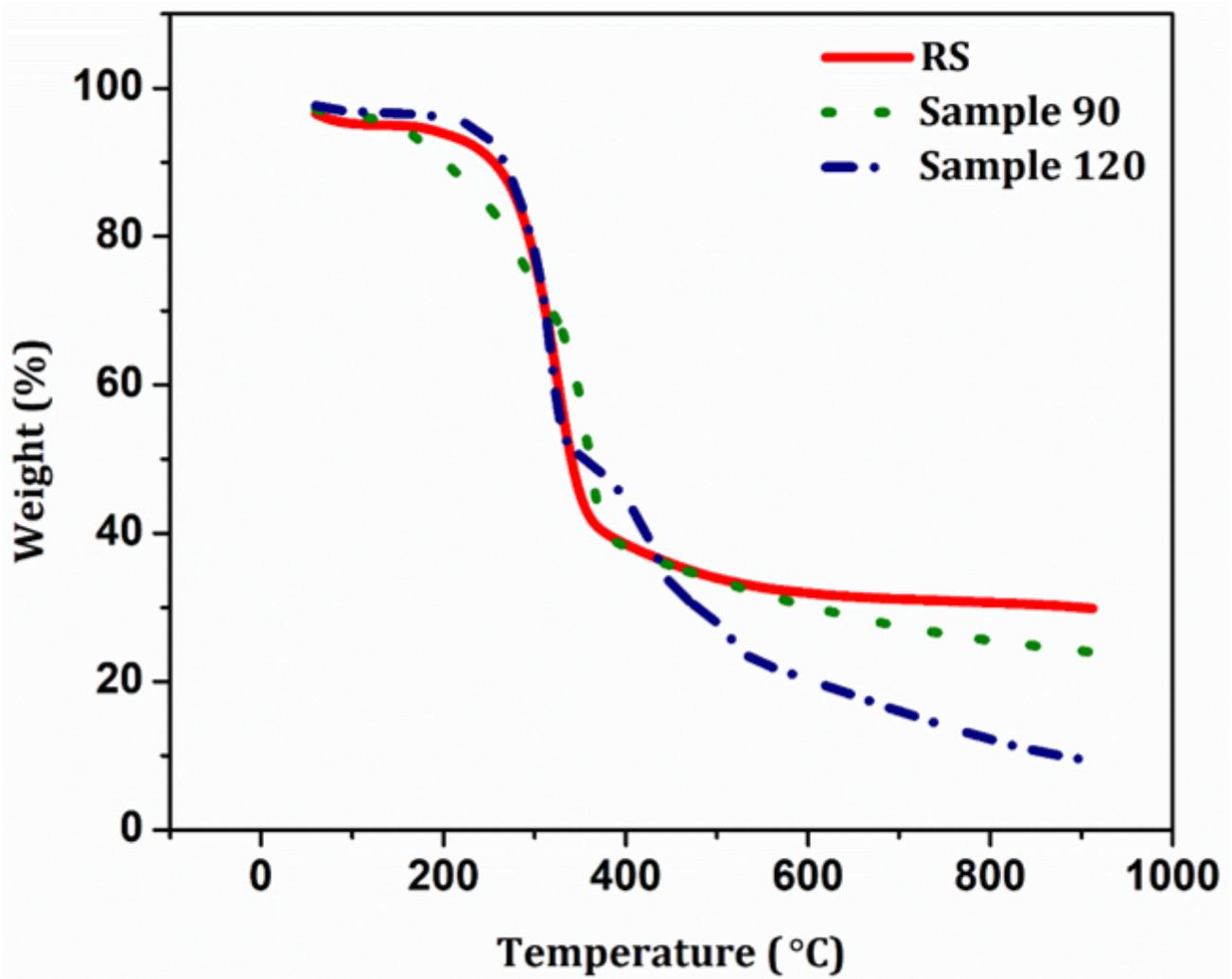


Figure 6

TGA of the original RS compared with pretreated RS at 90 °C and 120 °C (RS : Original Rice Straw, RS - 90 : Rice Straw after heating at 90 °C, RS - 120 : Rice Straw after heating at 120 °C)

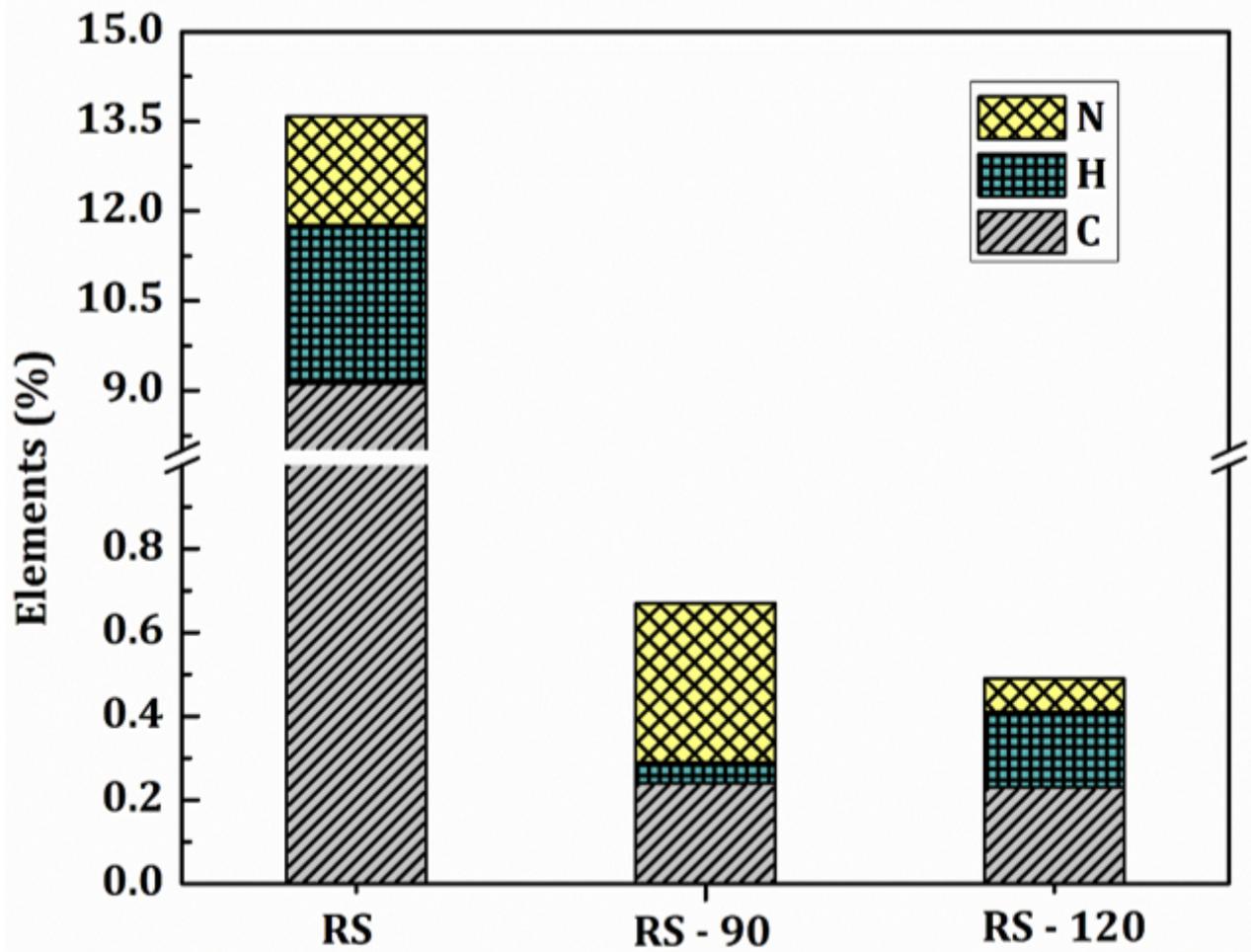


Figure 7

Comparative study on the elements before and after pretreatment of rice straw (RS : Original Rice Straw, RS - 90 : Rice Straw after heating at 90 °C, RS - 120 : Rice Straw after heating at 120 °C)

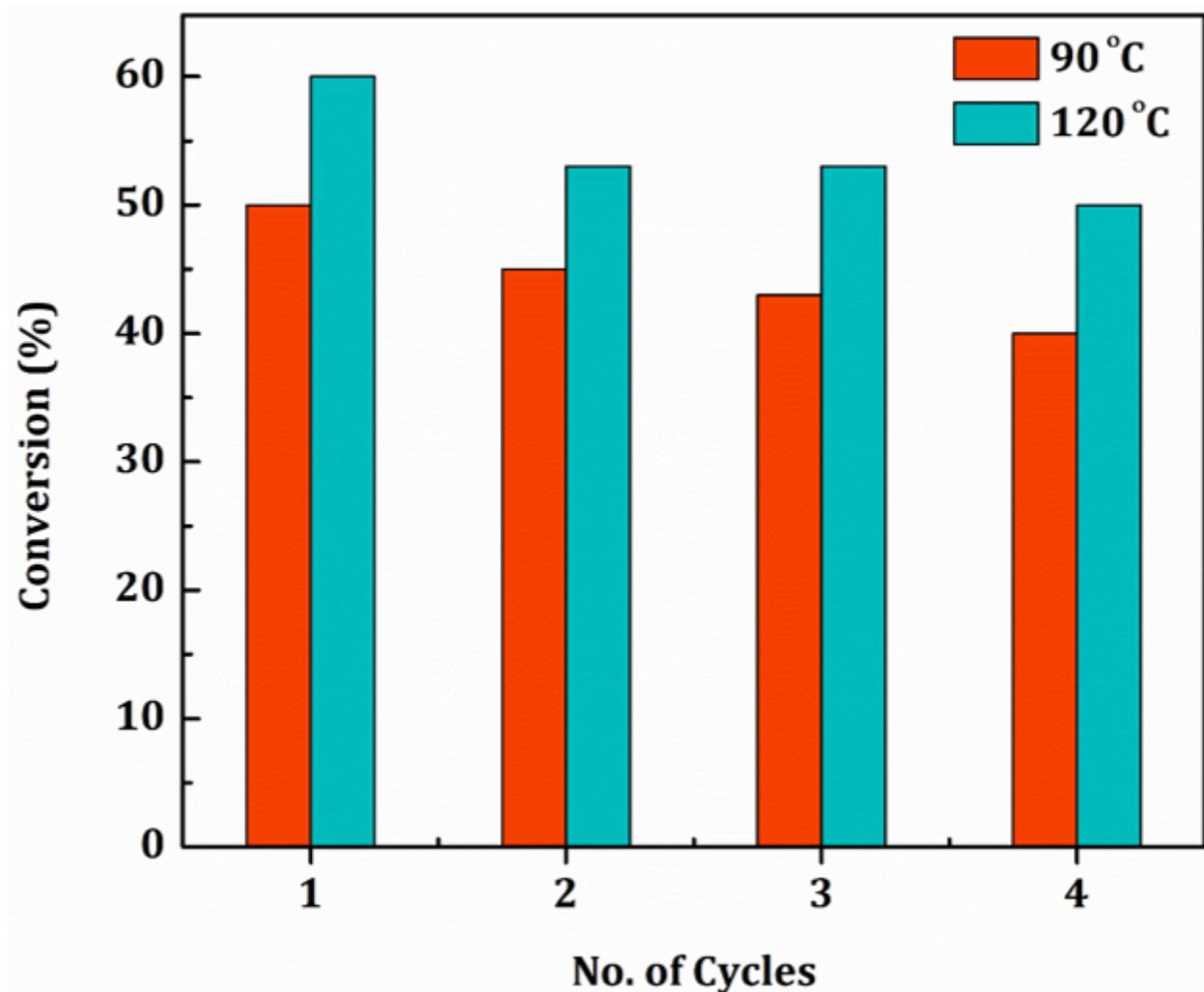


Figure 8

Plot showing effect of conversion with respect to the reusability of [DBUH] [OTf] at different temperatures (90 and 120 °C)

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Scheme1.docx](#)
- [GraphicalAbstractCELS30Sept2021.docx](#)
- [SICELS30Sept2021.docx](#)