



Rice straw (*Oryza sativa* L.) biomass conversion to furfural, 5-hydroxymethylfurfural, lignin and bio-char: A comprehensive solution



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ABSTRACT

A sustainable, easy to operate, scalable, and chemically pre-treatments free method has been explored for rice straw (RS) biomass conversion to furfural, 5-hydroxymethylfurfural (5-HMF), lignin and bio-char production. Initially, the RS was dipped into liquid nitrogen in a thermos flask and grinded easily to fine powder for better handling of biomass under reaction conditions in a reactor. The process also reduces the volume of biomass and enhances the surface area of RS biomass which was further analysed by SEM, TEM, IR, TGA and DSC, and further validated by its fruitful conversion to furfural, 5-HMF, lignin and bio-char synthesis in satisfied yields. The developed acidic process was performed at 130 °C for 6 hrs under a closed reaction system in reflux conditions. The ultra-performance liquid chromatography (UPLC) purity of furfural and 5-HMF was measured to >90% without additional purification technique. Moreover, the method was also examined in 250-gram scale and found to perform well.

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Introduction

Rice (*Oryza sativa* L.) is the third most cultivated grain crop in the earth after wheat and corn. Every year, the global production of this crop is estimated to be around 760 million tons [1]. This mammoth production is usually considered to generate 1140 million tons of straw as per food and agriculture organization of united nation (FAO) [1]. India itself contributed a major share (122 million tons/year) in this bulk product among other Asian and European countries [2].

Generally, in common life, rice straw (RS) is either used as cattle feed or majorly remained as waste. Its slow degradation tendency and short time duration (harvesting rice and cultivating wheat) oftenly enforce farmers for stubble burning in open fields as best disposal management. Every year, this stubble burning issue becomes more profound in India especially in Punjab region. According to Indian Agricultural Research Institute (IARI), the stubble burning enhances the annual release of CO₂ by more than 64 times in NCT Delhi [3]. In addition, the emission of black carbon, carbon monoxide, particulate matter, and other harmful sulphur oxides also gets increased by a significant value [3]. Therefore, surplus abundance, limited utility, and the environmental and societal

impact of this crop residue highly demands a proper mechanistic channel for its disposal.

Considering the adverse effects, and most importantly the availability of sufficient biopolymer contents mainly cellulose (30–50%) [4], hemicellulose (15–35%) [4], and lignin (10–20%) [4], the crop residue could be assumed as a potential candidate for bio-fuels and value added chemicals [5]. The basic structural skeleton of this biomass mainly involves an interconnecting bridge between cellulose and hemicellulose through covalent and ether/ester linkages, which is further encapsulated by the covalent bonded layers of lignin matrix [6a–h]. In addition, the protective layers of silica (around the straw) also make this crop residue more resistant towards its hydrolysis to hexose/pentose sugar monomer, and then further conversion to valuable platform products [6i]. The existence of such complicated bonding patterns is further consolidated by the excessive polymerization degree in cellulose and hemicellulose. Hence, as a whole, this makes RS biomass very rigid and heterogeneous [7]. This recalcitrant behaviour of the straw does not allow it to undergo saccharification more easily. Over the years, the literature has continuously been witnessing number of biological/chemical pathways for RS utilization to bioethanol production prominently. However, almost each developed approach yet now initially requires fractionation of the biomass into respective constituent polymeric materials before performing further transformation to ethanol production [8]. The process of fractionation is

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normally governed by number of established pre-treatment techniques utilizing acids [9], alkalis [10], steam explosion [11], electron beam irradiation [12], microwave assisted irradiation [13], organosolv assisted treatment [14] etc. Each pre-treatment technique alters distinctly the structural motif of the biomass and thereof the productivity of the enzymatic/chemical hydrolysis to bioethanol production [15,16]. Therefore, yet now, the development of effective pre-treatment techniques is considered as the main operational mode for biomass refinery [4,17]. However, in general, bioethanol production exploits only two carbon atoms per each hexose/pentose sugar unit involved in cellulosic biomass leaving behind four/three carbon atoms per unit as waste. Therefore, the bioethanol production is not assumed to be a sustainable and atom economic process. Hence, the complete exploitation of cellulosic biomass is a growing challenge for the present scientific community. Considering the importance of this idea, nowadays research has been shifting from bioethanol production to furan compounds synthesis i.e. furfural and 5-hydroxymethylfurfural (5-HMF). From a long time, the industrial production of furfural is being targeting from various cellulosic biomass like sugarcane bagasse, corncob, wood, straw etc. However, the development of efficient and economical process is still a challenging task till date. The literature survey concluded that the reports including direct valorisation of biomass (avoiding chemical pre-treatment) to furfural and 5-HMF are very scarce. Very recently, Cabrera *et al.* reported an industrial method for furfural production utilizing rice husk as initial feedstock [18]. The method resulted furfural in 6 wt % yield (55% theoretical yield) using 0.10 wt% H_2SO_4 at 200 °C temperature. The method provided highest yield of furfural in currently available processes at industrial level. The economic and sustainable development of bio-refinery also witnessed the most abundant rice straw as initial feed for furanic compounds synthesis, although, very few reported protocols have been explored till date. Zhao *et al.* reported a lab scale applicable and microwave assisted direct conversion of RS to furfural and 5-HMF under specifically designed ionic liquids as solvent media and catalyst (Fig. 1) [19]. They reported 25 and 47% yields of furfural and 5-HMF respectively under experimental conditions of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $[\text{C}_4\text{mim}]\text{Cl}$ at 400 W microwave irradiations. Though the direct conversion of this biomass is very difficult task to perform therefore, nowadays people are also getting more focused about the

development/designing of pre-treatment techniques like for bioethanol production. An exhaustive investigation of the literature survey suggested the development of solid acid based catalysts accompanied by pre-treatments to execute the said conversion. Recently, in 2020, Tung *et al.* has firstly converted RS to glucose unit through enzymatic process, and then treated with zeolite based catalyst ($\text{HSO}_3\text{-ZSM-5}$) under sonication at 120–140 °C to 5-HMF synthesis (Fig. 1) [20]. Similarly, the production of furfural was also achieved utilizing solid acid catalyst, HZSM-5 at 160 °C and steam explosion as pre-treatment [21]. Since very limited literature had been found for RS valorisation therefore, the exploration of this crop residue under bio-refinery framework is still underway and need scientific interventions for its effective and economical utilization.

The concept of mechanochemistry in organic synthesis has been gaining much attentions from the beginning of 20th century, and afterward being continuously prevailing [22]. There are numerous examples reported in the literature wherein mechanochemistry played significant contribution, and affected the kinetics and thermodynamics of the reactions very predominately [23]. The application of this chemistry is also exploring for biomass/biomass derived carbohydrates exploitation to fine chemicals and fuels synthesis from last decade [24]. A close look of the literature exhibited that milling of acid impregnated cellulose powder resulted 91 and 96% conversion into glucose and xylose respectively at 130 °C temperature for 1 hr [25]. The process also yielded most sustainable 5-HMF and furfural as minor products in 1 and 4% conversion respectively. However, there still remains a gap for direct conversion of raw biomass to furfural and 5-HMF as major products under mechanochemical approach.

Our research group is dedicatedly working on biomass utilization to furan analogues synthesis and its scale-up, from last few years [26]. Through our exhaustive study, we found that the recalcitrant behaviour of RS does not allow the crop residue to undergo acidic hydrolysis to yield furfural and 5-HMF as final products. Hence, by keeping this issue as challenge, herein, our group first time utilized liquid nitrogen (LN) as grinding media through mechanical grinder to valorise RS for furfural and 5-HMF production. The used LN treatment does not involve any chemical for RS biomass preparation and is easy to operate, sustainable and economical. Under this study, the crucial role of liquid nitrogen grind-

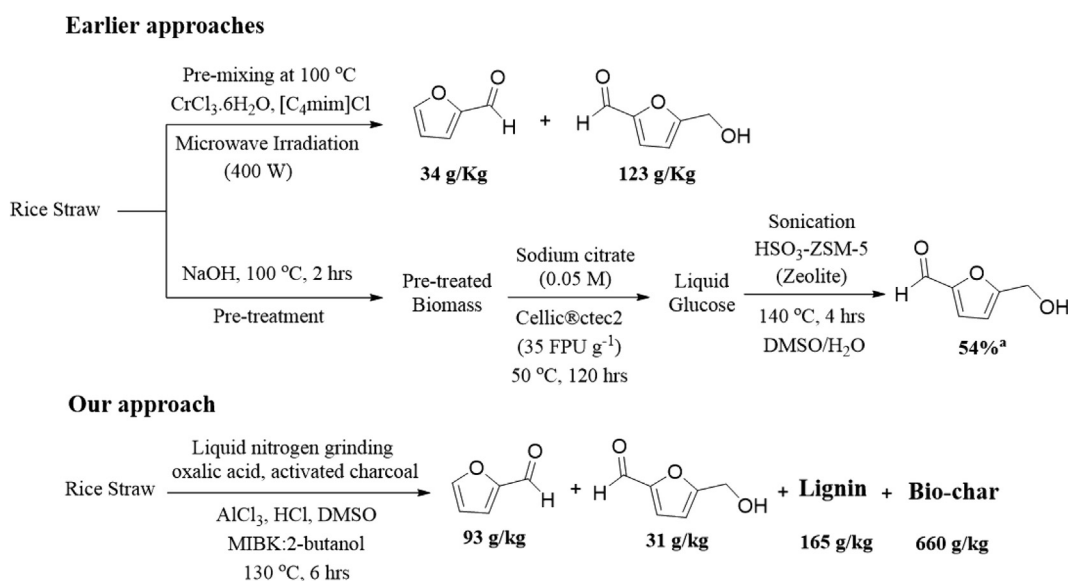


Fig. 1. Comparative study of recent established industrial approaches for furan compounds synthesis with our developed method; *yield calculated in regards to liquid glucose content.

ing (LNG) for RS on furfural and 5-HMF production was critically examined and validated through IR, SEM, TEM, TGA, and DSC analytical techniques. The process was tested up to 250-gram scale to check the industrial viability, and additionally also provided lignin and bio-char for other possible applications.

Materials and methods

Chemicals and materials

All used reagents and solvents under present study were of AR/LR analytical grade and utilized without additional purification. Under this investigation, the utilized activated charcoal (LR), oxalic acid dihydrate (99.80%), formic acid (85.00%), methylisobutylketone (MIBK) (99.00%), dimethylsulphoxide (DMSO) (99.50%) and sodium sulphate anhydrous (99.50%) were purchased from SD fine-chem. Ltd. In addition, the used 2-butanol (98.00%), aluminium chloride anhydrous (98.00%), hydrochloric acid (35.00–38.00%) and sodium chloride (99.90%) were purchased from Central Drug Health (P) Ltd. The standard 5-HMF ($\geq 99.00\%$) and furfural (99.00%) used for preparing the calibration curves for the same were purchased from Sigma Aldrich and Across Organics respectively. The used celite 545 was purchased from Merck. The Millipore milli-Q water which was filtered through 0.22 μm PTFE filter was used during the analytical analysis. The acetonitrile (99.90%) and methanol (99.80%) of HPLC grades were also purchased from SD fine-chem. Ltd. The used liquid nitrogen was brought from our institutional facility. The raw RS biomass was collected from local rice straw cultivated fields nearby our institute.

Biomass preparation

The collected RS biomass was allowed to dry in an open air environment. The air-dried biomass was then further chopped into small pieces by using a chopping tool. One portion of this biomass was directly grinded by electric mortar and considered as grinded rice straw (G-RS) in the experiment. Another portion (10 g) was treated with LN (350 mL) in a thermos for 18 minutes (twice) and then grinded in an electric mortar to fine powder and considered as a liquid nitrogen grinded rice straw (LNG-RS) in the experiment. The process was repeated multi times to get the sufficient amount of LNG-RS for performing the experiments. The liquid nitrogen grinded crop residues were finally utilized as initial feed under established reaction conditions.

Analytical methods

The morphological characterization and particle size distribution of normally and liquid nitrogen grinded rice straw powder were performed by using Scanning Electron Microscope (SEM; Hitachi S-3400N, Japan). The internal structure and size of nano scaled particles were analysed through Transmission Electron Microscope (TEM; FEI Technai G2sTwin, USA). The structural changes and disruptions in bonding patterns within the straws before and after LNG were analysed by Fourier Transform Infrared Spectroscopy (FTIR, Shimadzu) in range between 4000–400 cm^{-1} . The alteration in bonding interactions lying between and within the biopolymers were analysed by Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC; NETZSCH Geratebau GmbH STA 449 F1 jupiter). The mass spectra of both furanic compounds (furfural and 5-HMF) were obtained by Waters micro mass Q-TOF Ultima spectrometer using electron spray ionization (ESI) technique. ^1H and ^{13}C NMR spectra were recorded through a Bruker Advance 600/300 MHz (^1H) and 150/75 MHz (^{13}C) NMR.

All spectra were obtained at 25 $^\circ\text{C}$ in CDCl_3 [residual CHCl_3 (δ_{H} 7.26 ppm) or CDCl_3 (δ_{C} 77.00 ppm)]. All chemical shifts were recorded in δ (ppm) relative to tetramethylsilane (TMS) and NMR solvent signal. The coupling constants (J) were provided in Hz, and multiplicities were reported as s, singlet; d, doublet; m, multiplet. The UPLC method was developed on Water Acquity UPLC[®] H Class machine with PDA detector. “Acquity UPLC[®]-BEH C18, 1.7 μm , 2.1*50 mm” was the UPLC column that used for analytical analysis. The standard curves for 5-HMF and furfural were obtained with $R^2 = 0.9999$ for each. The analysis of bio-char was performed using CHN Elemental Analyser (Vario Micro Cube, Elementar GmbH, Germany) and Scanning Electron Microscope.

Yield calculation

The furfural and 5-HMF yields were calculated based on the quantity of hemicellulose and cellulose present in the raw RS biomass.

Theoretical yield

In our all calculations, the yields were calculated with respect to the xylose/arabinose and glucose monomer units present in hemicellulose and cellulose respectively. Since 150 g of xylose/arabinose would lead to procure 96 g of furfural if the conversion and selectivity is considered to be 100%. Therefore, as per our case 255 mg of hemicellulose (xylose/arabinose) will provide 163.20 mg of furfural (for 100% conversion and selectivity). Hence, under our study the furfural yield (%) is calculated according to Eq. (1):

$$\text{Yield}(\%) = [(W_{o(f)} + W_{a(f)})/W_{t(f)}] \times 100 \quad (1)$$

where $W_{o(f)}$ stands for weight of furfural in organic phase and $W_{a(f)}$ represents the weight of furfural in aqueous phase. Also, $W_{t(f)}$ stands for weight of furfural (theoretical).

In the same manner, for 5-HMF synthesis, 180 g of glucose will give 126 g of 5-HMF (for 100% conversion and selectivity). Therefore, under our system 310 mg of cellulose (glucose) will provide maximum 217 mg of 5-HMF. Hence, under our study the 5-HMF yield (%) is calculated according to Eq. (2):

$$\text{Yield}(\%) = [(W_{o(h)} + W_{a(h)})/W_{t(h)}] \times 100 \quad (2)$$

where $W_{o(h)}$ stands for weight of 5-HMF in organic phase and $W_{a(h)}$ represents the weight of 5-HMF in aqueous phase. Also, $W_{t(h)}$ stands for weight of 5-HMF (theoretical).

Weight percent yield

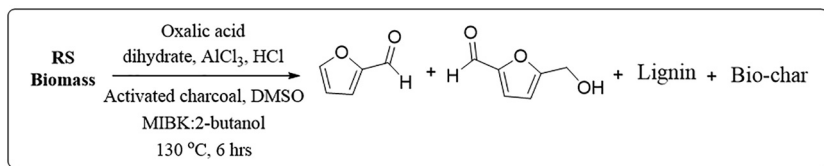
Under these studies, the weight percent yields (wt%) of furfural, 5-HMF, lignin, bio-char, cellulose and hemicellulose were calculated according to equation (3).

$$\text{Yield}(\text{wt}\%) = [W_{(f/h/l/b/c/hc)}/W_{i(r)}] \times 100 \quad (3)$$

where W_f , W_h , W_l , W_b , W_c , W_{hc} stand for weight of furfural, 5-HMF, lignin, bio-char, cellulose and hemicellulose respectively and $W_{i(r)}$ represents the initial weight of raw RS biomass.

Experimental methods

General procedure for furfural and 5-HMF synthesis from RS



The fine powder of prepared RS biomass was charged in a cleaned and dried reaction vessel. The charged biomass was further subjected to mix with oxalic acid dihydrate (1 wt equiv.), AlCl_3 (30 wt%), activated charcoal (20 wt%) and 4 N HCl (30 wt%). The whole mixture was solvated by MIBK:2-butanol and DMSO, and further allowed to stir at 130 °C temperature in a closed system under reflux conditions for 6 hrs. The reaction progress was monitored by thin layer chromatography (TLC). Once the reaction got completed as per TLC then the entire reaction mass was allowed to filter through a celite pad (Celite 545). The celite pad was washed three to four times by ethyl acetate. The collected filtrate was then diluted by milli-Q water and ethyl acetate. The samples of both organic and aqueous phase were collected for UPLC identification and quantification of furfural and 5-HMF. Furthermore, both furanic compounds were then extracted from organic phase (ethyl acetate) in repeated iterations, washed by saturated brine solution and then dried over Na_2SO_4 . The extract was concentrated by reduced pressure system, and finally freeze-dried. Next, furfural was separated from extract using hexane as extracting solvent and dried under reduced pressure system. The UPLC purity of furfural was found to be >90%. The remaining extract was then collected and completely dried in rotary evaporator to give 5-HMF in >90% purity. Both compounds were further analysed by UPLC chromatogram based on UV wavelength and retention time (compared with standard), and further reconfirmed by ESI-MS and NMR (see ESI for more information). Finally, the solid residue remained after filtration was further subjected to 5% NaOH treatment at 90 °C for 3 hrs. After basic treatment, the reaction mass was filtered, and the filtrate was allowed to keep pH = 2 by H_2SO_4 ; resulting in the precipitation of lignin. The lignin was then centrifuged, dried and further characterized by IR spectroscopy (see ESI for more information). Lastly, the filtered solid biomass was dried in an oven (40 °C) for overnight and gave bio-char.

Result and discussion

After preparing biomass, both G-RS and LNG-RS were further analysed thoroughly by SEM, TEM, IR, TGA and DSC to identify their characteristic changes and suitability for chemical conversion.

Morphological and structural characteristics

Scanning and transmission electron microscopic analysis of G-RS and LNG-RS

To understand the morphology of the RS residue, both the G-RS and LNG-RS samples were first analysed by Scanning Electron Microscopy (SEM). As shown in Fig. 2a, the G-RS sample showed needle like shape with higher particle size and lower surface area whereas the LNG-RS sample in Fig. 2b–c resulted as smaller particle size (spherical and fibrous) with higher surface area. Moreover, the length and width of most of the G-RS needles (Fig. 2a) were found to lie in 200–400 and 50–100 μm (Fig. 2e and f) respectively. However, through LNG-RS micrograph analysis, we observed that the length and width parameters of the sample reduced remarkably to 20–40 and 5–10 μm respectively (Fig. 2g and h). Hence, it is clear from this study that LNG strongly influenced the morphology

and particle size distribution of the RS biomass. Also, through Transmission Electron Microscopy (TEM), we observed the oval like shape of RS (Fig. 2d) and reduction in its particle size to 0–50 nm scale (Fig. 2i). Hence, such morphological and drastic particle size alterations explicitly showed the significant reduction in the stiffness of the RS structure.

Infra-red spectroscopic analysis of G-RS and LNG-RS samples

Further, we performed the FT-IR spectroscopy of both the samples (G-RS and LNG-RS) in order to know more about the structural changes and disruptions in bonding linkages occurred within the biopolymers. As shown in Fig. 3, the FT-IR spectrum of both the samples were looked like to be same, although the position, intensity and sharpness of some of the characteristics peaks got altered. A close examination of Fig. 3 clearly revealed the presence of fingerprint absorption bands lying in 500–4000 cm^{-1} region for cellulose, hemicellulose and lignin biopolymers [27]. On comparing the FT-IR spectrum of G-RS and LNG-RS samples, we found a small peak at 795 cm^{-1} for G-RS, which was assigned to the stretching vibration of Si-O-Si linkage [27c]. However, this peak was found to be almost absent in case of LNG-RS. The disappearance of the peak might be subjected to the breaking of this particular type of linkage in silica, which in turns clearly suggested the fractionation/loosening of the silica components in LNG-RS. In addition, the critical investigation of both the spectrums also showed a sharper and more intense peak at 1041 cm^{-1} if compared to 1028 cm^{-1} (Fig. 3). This characteristic peak was ascribed to C-O bond vibrations existed for cellulose and hemicellulose [28]. It has been observed that this particular peak got shifted by 13 cm^{-1} towards higher wavenumber after LNG. This significant shift in peak position explicitly suggested the enhancement in C-O bond strength, which might be responsible for weakening/breaking of the ether bond linkage existing between cellulose, lignin and hemicellulose or within each of them (Fig. 3). Also, the peak at 1041 cm^{-1} was seen to be comparatively more intense and slightly sharper than 1028 cm^{-1} . This slight increase in sharpness clearly reflected that C-O bond linkage under LNG not getting engaged with other molecules i.e. there might be rupturing of this particular ether linkage under LN environment. Moreover, the increase in intensity directly indicated the enhancement in number of C-O bonds, which might be possible if the ether linkage existing between biopolymers or with in each of them underwent disruption under established environment. In the same manner, a deep inspection of both the spectrums around 1735–1750 cm^{-1} range showed a shoulder peak at 1749 cm^{-1} for G-RS, however, this shoulder peak was almost absent in IR spectrum of LNG-RS as shown in Fig. 4. This peak was attributed to the presence of aliphatic ester linkage existed between lignin-hemicellulose, cellulose-lignin and cellulose-hemicellulose complexes [29]. The disappearance of this peak clearly reflected the weakening/breaking of the ester linkages. Through this study, we also observed a more intense and broader band at 3157–3485 cm^{-1} (LNG-RS), although the band shifted to 3206–3491 cm^{-1} for G-RS. The Fig. 3 distinctly exhibited that the absorption band centred at 3338 cm^{-1} was more intense if compared to the band centred at 3332 cm^{-1} . This upsurge in the intensity after LNG comprehensively suggested the increment in the number of -OH bonds, and this is only possible if the ether linkages existing among the biopolymers/monomer units got ruptured.

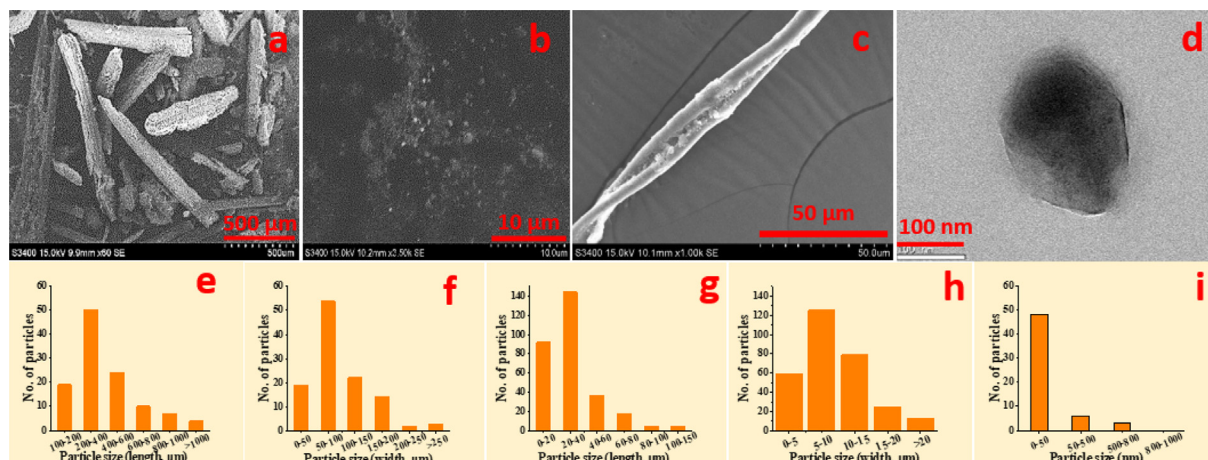


Fig. 2. Morphological characterisation of RS: a) SEM image of G-RS; b) SEM image of LNG-RS; c) SEM image of LNG-RS fibre; d) TEM image of LNG-RS; e) particle size distribution of (a) (length); f) particle size distribution of (a) (width); g) particle size distribution of (b) (length); h) particle size distribution of (b) (width); i) particle size distribution of (d).

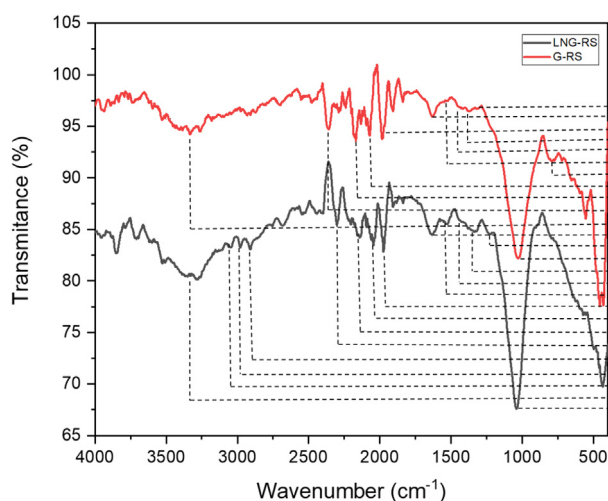


Fig. 3. Comparison of FT-IR spectra of LNG-RS and G-RS.

Hence, as a consequence, the IR study clearly disclosed that the LNG comprehensively disrupted the internal structure of the RS and made its components (cellulose, hemicellulose, lignin, silica) more fractionated comparatively from G-RS.

Thermogravimetric and differential scanning calorimetry analysis of G-RS and LNG-RS

Further to investigate the bonding interactions and modifications being happened among the main constituents (cellulose, hemicellulose and lignin) of RS biomass before and after LN treatment, herein, we performed Thermogravimetric Analysis (TGA) and then Differential Scanning Calorimetry (DSC) studies for G-RS and LNG-RS samples. As it can be seen from TGA thermogram (Fig. 5) that the curve corresponding to LNG-RS was seemed to be uplifted more if compared to G-RS. This uplifting of LNG-RS curve clearly reflected that the thermal stability of the straw has been enhanced significantly under LN treatment. Through the close examination of TGA thermogram, it was noticed that initial 5% weight loss in biomass due to dewatering was found to be at 39.79 °C (onset temperature) for G-RS, which after LNG got incremented significantly to 82.62 °C (Table 1). In the same manner, the onset temperatures for 20, 50 and 85% weight loss were recorded for both experimental samples as thoroughly described in Table 1. Under this investigation, the same increasing trend in onset temperatures was observed for LNG-RS as previously noticed for 5% mass loss. Therefore, this regular trend in enhancement of onset temperatures might be attributed to the particle size reduction of RS to nano-scale as the nanoparticles are well known for enhancing the thermal stability of polymers [30]. After the exciting results of TGA analysis, further we keenly focused on DSC thermogram to see the energy consumption property of each constituent present in

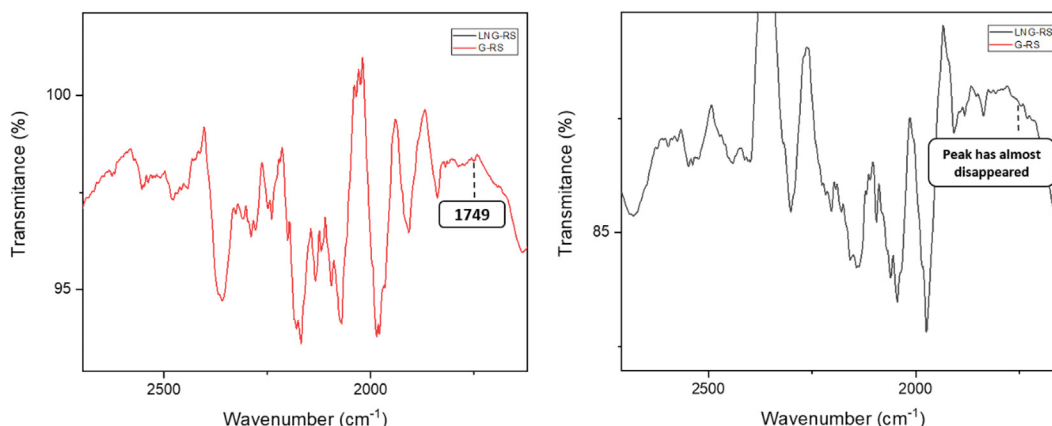


Fig. 4. The characteristic peak for aliphatic ester linkage existed among biopolymers in RS.

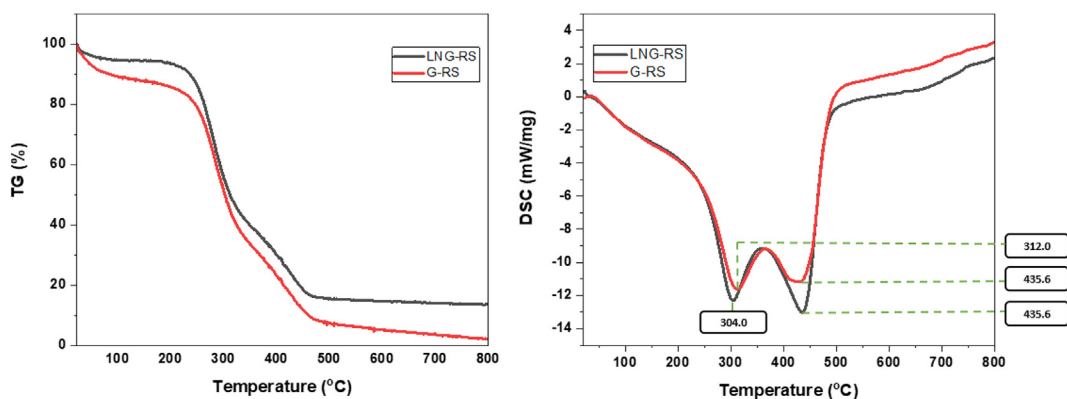


Fig. 5. TGA and DSC thermograms of LNG-RS and G-RS.

straw before and after LN treatment. The DSC thermogram (Fig. 5) clearly exhibited the existence of two endotherms, one around 300–315 °C and other at particular 435.6 °C for each experimental sample. These two endotherms for each experimental sample were corresponded to hemicellulose and cellulose respectively as per literature [28b]. It was clear from DSC thermogram that the maximum decomposition rate for hemicellulose biopolymer shifted by 8 °C from 312 to 304 °C after LNG. Although, for cellulose biopolymer it remained unaltered i.e. 435.6 °C. The alteration in the position of maximum decomposition rate to lower temperature range suggested the significant weakening in the intermolecular interactions existing between hemicellulose molecules and with other neighbouring molecules i.e. cellulose and lignin [31]. Moreover, we also observed that the endotherms corresponding to LNG-RS looked to be sharper and intense than G-RS (Fig. 5). The sharp and intense peak of such endotherms clearly revealed that the rate of decomposition for hemicellulose and cellulose is faster in case of LNG-RS than G-RS. This argument distinctly indicated that all sort of bonding (inter- and intra-molecular) and non-bonding (hydrogen bonding) interactions lying among cellulose, hemicellulose, lignin, silica, water and biopolymers are getting weaker under LN treatment. Since the decomposition isotherm corresponding to lignin usually covers a long temperature range, and hence that was almost found to be missed in the thermogram [31]. Therefore, as a whole, it concluded that TGA and DSC studies were found to be in agreement with IR, SEM and TEM analysis.

Quantification of cellulose, hemicellulose, lignin, ash and moisture contents in RS

Under this investigation, initially we prepared the biomass as thoroughly explained earlier and then further subjected under reported protocols to quantify the contents of cellulose, hemicellulose and lignin [32]. The amount of each biopolymer i.e. cellulose, hemicellulose and lignin present in RS biomass were found to be 31.00, 25.50 and 18.20 wt% respectively. The amount of ash and moisture present in biomass were also quantified as per the method (2010) described by standard association of analytical communities (AOAC), and measured to be 14.20 and 8.90 wt% respectively [33].

Synthesis of furfural and 5-HMF from RS biomass in one gram-scale reaction

Through the exhaustive frame of period and continuously working for the development of biomass conversion, we explored some of the efficient methods/processes for 5-HMF and furfural synthesis from carbohydrates and ligno-cellulosic biomass, and its further applications [26]. Our earlier developed process was found to be ineffective for G-RS conversion to furan compounds synthesis [26a]. Whereas, by slight modification in biomass preparation process (Section “Biomass preparation”) through LNG, the same process under further optimization study was found to be effective for its fruitful conversion to furfural and 5-HMF compounds with lignin and bio-char as additional products. Therefore, motivated by analytical results, the prepared LNG-RS biomass (1 g) was then allowed to react with a combination of oxalic acid dihydrate, AlCl_3 , 4 N HCl and activated charcoal at particular solvent, temperature and time (Table 2, entry 1). On monitoring the progress of reaction in thin layer chromatography (TLC), surprisingly this time we noticed the formation of furfural and 5-HMF as only final products. Moreover, the applied experimental conditions resulted furfural and 5-HMF in 38 and 8% yields (theoretical) respectively (Table 2, entry 1). This experimental result boosted us to further optimize the acid loading, solvent media, and reaction conditions in order to maximize the yields of final products. Through this optimization study, we observed that enhancing or lowering the loading of organic (oxalic acid) and inorganic (AlCl_3 and HCl) acids significantly altered the yields of furfural and 5-HMF as described in Table 2 (entry 1–9). Under this investigation, the best optimized acid loading for oxalic acid dihydrate was found to be 1 equiv. while that for AlCl_3 and HCl was 30 wt%. Now, since the bio-refinery conversion of cellulosic biomass to furfural and 5-HMF generally required higher temperature; hence, once the acid loading got optimized then we further focused on finding the suitable reaction temperature for this conversion (Table 2, entry 4, 10–12). It was noticed that, enhancing the reaction temperature to 150 °C did not alter the yield of furfural and 5-HMF significantly (Table 2, entry 10), besides increasing temperature to 200 °C resulted final products in very trace amount (Table 2,

Table 1
Thermal degradation data of LNG-RS and GRS.

Sample	T _{5%} (°C)	T _{20%} (°C)	T _{50%} (°C)	T _{85%} (°C)	Final residue left at 798 °C (%)
LNG-RS	82.62	263.62	312.62	548.62	13.50
G-RS	39.79	246.79	302.79	434.79	2.0

T_{n%} represents the thermal degradation temperature of LNG-RS and G-RS at 5, 20, 50 and 85% weight loss respectively.

Table 2Process optimization for rice straw biomass conversion to furfural and 5-HMF synthesis.^a

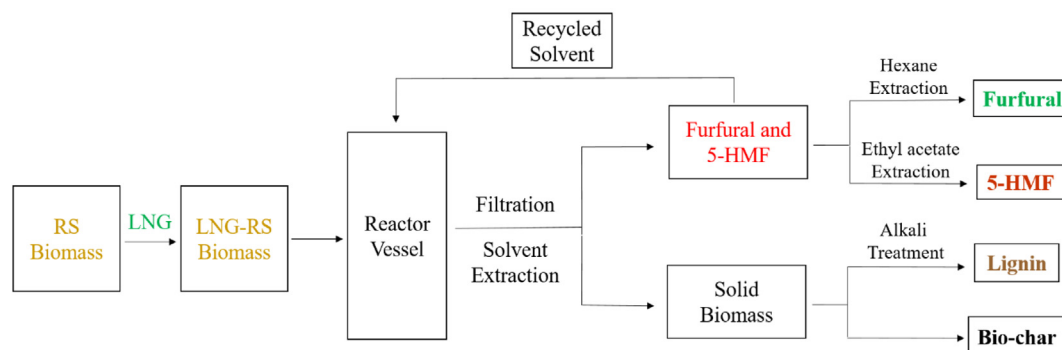
Entry	Acid loading (wt%)			Temperature (°C)	Time (hrs)	Furfural yield		5-HMF yield	
	Oxalic acid dihydrate (equiv.)	AlCl ₃ (wt%)	4N HCl (wt%)			UPLC (mol%) ^b	(g/kg) ^c	UPLC (mol%) ^b	(g/kg) ^c
1.	1	15	15	130	6	38	62	8	18
2.	1	30	15	130	6	32	52	11	24
3.	1	15	30	130	6	28	45	8	16
4.	1	30	30	130	6	57	93	14	31
5.	1	40	30	130	6	57	93	10	21
6.	1	30	45	130	6	41	68	10	22
7.	0.5	30	30	130	6	43	70	11	24
8.	0.1	30	30	130	6	44	73	11	25
9.	1.5	30	30	130	6	28	45	6	12
10.	1	30	30	150	6	55	90	13	28
11.	1	30	30	170	6	32	52	8	18
12.	1	30	30	200	6	nd	-	nd	-
13.	1	30	30	130	3	40	66	8	18
14.	1	30	30	130	9	45	73	10	22
15 ^d .	1	30	30	130	6	38	63	12	25
16 ^e .	1	30	30	130	6	49	81	8	16
17 ^f .	1	30	30	130	6	56	92	14	30
18 ^g .	1	30	30	130	6	nd	-	nd	-

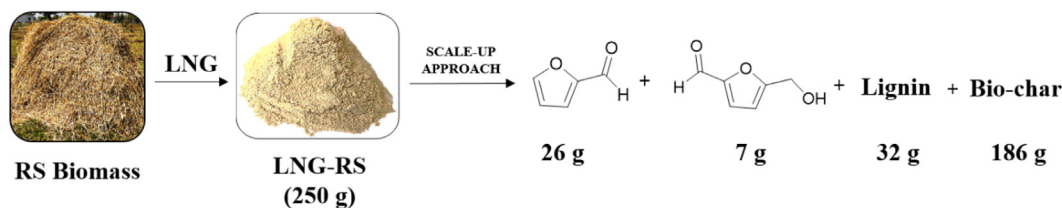
^aAll reactions were performed using LNG-RS powder in 1 gram-scale, activated charcoal (200 mg, 20 wt%) and 4 N HCl (0.8 mL, 30 wt%) in DMSO (6 mL) and MIBK:2-butanol (4.5:1.5) mL biphasic solvent system; ^bTheoretical yields were calculated through UPLC with respect to cellulose and hemicellulose contents present in RS; ^cyields were calculated with respect to raw RS weight; ^dThe reactive phase solvent volume (DMSO) enhanced to 10 mL; ^eReactive phase solvent used in proportion DMSO = 5 mL, H₂O = 1 mL; ^fActivated charcoal increased to 300 mg; ^gGRS was used as initial feed; nd = not detected.

The bold values signify the best optimized reaction conditions and yields for furfural and 5-HMF production.

entry 12). Similarly, when the reaction time shortened to 3 hrs, then furfural and 5-HMF yields decreased by 17 and 6% respectively, although enhancing it to 9 hrs still decreased the yields of both the respective products (Table 2, entry 13–14). Hence, the optimized temperature and reaction time for this transformation was set to 130 °C and 6 hrs respectively. In addition, under this study we also enhanced the volume of reactive phase solvent (DMSO) to 10 mL just to increase the solubility of RS biomass, however, unfortunately the yield of furfural drastically got reduced to 38% while that of 5-HMF slightly altered to 12% (Table 2, entry 15). Furthermore, the standard conditions were also checked by adding small amount of H₂O (1 mL) to see whether its enhancing the yields or not as most of the industrial processes involved the use of this in improving the yields. Although, the addition of H₂O in our conditions was not found to be suitable as it decreased the yields of furfural and 5-HMF by 8 and 6% respectively (Table 2, entry 16). Also, enhancing the loading of activated charcoal to 30 wt% slightly altered the yields of respective products (Table 2, entry 17). In addition, the optimized reaction parameters when further implemented

on G-RS biomass then it did not result furfural and 5-HMF as observed by TLC (Table 2, entry 18). Moreover, the time based studies of biomass preparation and its impact on furfural and 5-HMF synthesis were also examined (see ESI for more details). Therefore, throughout this study, the best optimized reaction conditions for RS biomass conversion to furfural and 5-HMF were found to be 1 equiv. oxalic acid dihydrate, 30 wt% AlCl₃ and 4 N HCl, and 20 wt% activated charcoal at 130 °C temperature for 6 hrs reaction time under DMSO and MIBK:2-butanol solvent system. Under this study, the best optimized reaction parameters delivered the final products furfural and 5-HMF in maximum 57.00 ± 0.22 and 14.00 ± 0.19% yields (theoretical) respectively (Table 2, entry 4) when performed in 1 g scale. Both final products (furfural and 5-HMF) were easily isolated through solvent extraction in >90% UPLC purity, and then structural analysis was confirmed after performing the NMR spectroscopy. Moreover, the existence of other possible small molecules (glucose, fructose, xylose, arabinose, levulinic acid) was also examined through UPLC with ELS detector and GC-MS studies, although not found even in trace amount.

**Fig. 6.** Flow diagram for RS biomass conversion.



Scheme 1. Scale-up approach for RS biomass conversion to furfural, 5-HMF, lignin and bio-char.

Production of lignin and bio-char from leftover reaction mass

After performing the reaction under standard experimental conditions as mentioned in Section “Experimental methods”, the reaction crude was then passed through the celite pad (Celite 545). This process resulted in solid biomass production accompanied by the filtrate. The filtrate was further processed to isolate furfural and 5-HMF. However, the leftover solid biomass after treatment through an alkaline media (5% NaOH) followed by acidification (pH ~ 2) led to pure lignin in 165.00 ± 6.00 mg (16.50 ± 0.60 wt%) amount. The obtained lignin was well characterized by IR-spectroscopy (Refer to ESI). Further, the remaining solid residues (bio-char) after lignin separation were then dried and weighed to 660.00 ± 11.00 mg. The obtained bio-char exhibited 32.83 ± 0.73 , 3.49 ± 0.13 and $0.77 \pm 0.03\%$ carbon, hydrogen and nitrogen contents respectively using elemental analyser (CHN), and also showed porous morphology through SEM analysis (Refer to ESI).

Scale-up synthesis of furfural and 5-HMF from RS biomass

Under this development, initially LNG-RS biomass was prepared as mentioned earlier. Finally, the prepared 250 g LNG-RS biomass was allowed to undergo optimized acidic media in standard experimental conditions. After monitoring the reaction by TLC and filtering the filtrate through celite pad, the filtrate was then further diluted by ethyl acetate and ice chilled water. The furfural and 5-HMF were extracted from reaction crude through ethyl acetate in repetitive manner. The ethyl acetate extract was then dried over Na_2SO_4 , concentrated by a reduced pressure system, and finally freeze dried. Then the furfural was isolated from freeze dried reaction crude by using hexane as extracting media in repetitive iterations and resulted in $63.00 \pm 0.09\%$ yield. The remaining reaction mass after furfural extraction, was then completely dried and resulted 5-HMF in $12.50 \pm 0.08\%$ yield. Also, through following the extraction procedure of lignin and bio-char mentioned in section “Production of lignin and bio-char from leftover reaction mass”, amount of each was found to be 32.00 ± 2.00 and 186.00 ± 4.00 g respectively. The detailed process for RS biomass conversion is also represented graphically as shown in Fig. 6. Hence, our developed method was found to perform well in scale-up development (Scheme 1), and further in future it could be utilized in commercial valorisation of RS biomass. On comparing with the literature reports [19–21], we found that our process avoids costly and tedious enzymatic, microwave assisted and steam explosion treatments, and multi-steps requirement. Also, as per literature survey and to the best of our knowledge, this is the highest scale-up attempt for RS biomass.

Conclusion

First time an easy to operate, single step and sustainable approach has been explored for complete exploitation of abundant RS biomass to furfural, 5-HMF, lignin and bio-char in single pot. Through the entire study, the critical role of LNG in RS biomass conversion is thoroughly examined. Under this examination, the

SEM and TEM analysis clearly validated the morphological changes that have been attained by RS residues after grinding in LN environment. A significant particle size reduction (almost ten times) is also noticed through these studies. Moreover, the impact of LNG on the weakening of inter- and intramolecular interactions among each biopolymer, removal of silica, and delignification is also well studied and validated by IR, TGA and DSC analytical techniques. Further, the combination of optimized organic (oxalic acid) and inorganic acids (AlCl_3 and HCl) is also found suitable to result furfural and 5-HMF in >90% UPLC purity. The process avoids the extra purification steps and also provides lignin and bio-char as useful products in agriculture, polymer and other applications. The method is also applicable in 250 g scale for industrial process development.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability statement

The data that supports the findings of this study are available in the [supplementary material](#) of this article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jiec.2021.08.025>.

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