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Production and recovery system for furan compounds from rice straw using an ionic liquid (1-methylimidazolium hydrogen sulfate) and vacuum steam distillation

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Abstract

Furan compounds, including 5-hydroxymethylfurfural and furfural, can be synthesized from biomass and have garnered attention for their potential applications in biofuels and resin precursors. In this study, the synthesis of the furan compounds from rice straw was explored using a combined approach of ionic liquid treatment, specifically 1-methylimidazolium hydrogen sulfate ([MIM]HSO_4), and vacuum steam distillation. Through the optimization of various processing parameters, we established that the best conditions for the furan compound production include: a cold trap cooling temperature of – 196 ℃, a system pressure of 10 hPa, a treatment temperature of 180 ℃, a reaction duration of 30 min, a sample loading of 1wt%, and a particle size range of 45–90 μm. Under these conditions, the resultant yield of the furan compounds was quantified at 27.9wt%. Additionally, the recyclability of the utilized ionic liquid was evaluated. Notably, even after four recycling cycles (encompassing a total of five reactions), the yield of the furan compounds remained consistent, underscoring the viability of ionic liquid reuse.

Keywords Ionic liquid, 1-Methylimidazolium hydrogen sulfate, Rice straw, 5-Hydroxymethylfurfural, Vacuum steam distillation

Introduction

In the quest to establish a sustainable society, there is a growing emphasis on biomass as a potential substitute for fossil resources. Bioethanol, derived from the starch and sugars obtained from crops such as corn and sugarcane, has been commercialized as a viable gasoline alternative [1]. Nonetheless, its production, relying on edible feedstocks, has raised concerns over competition with food supplies. Consequently, there is a burgeoning interest in research focused on exploiting non-edible biomass sources, including woody and herbaceous plants, which are both abundant and free from food competition implications. Significantly, agricultural residues like rice straw, wheat straw, and rice husks—inedible components of crops—are invariably generated alongside food production and are available in considerable volumes globally. In Japan, where rice cultivation is widespread, substantial amounts of rice straw are produced. Despite its current underutilization, rice straw is increasingly recognized as a promising non-edible biomass resource.

The primary constituents of rice straw are cellulose, hemicellulose, and lignin. Cellulose is a crystalline, linear polymer composed of cellobiose units in which glucose molecules are connected by β-1,4-glycosidic bonds. The predominant form of hemicellulose in rice straw is arabinoxylan, with its main chain composed of xylan formed by β-1,4-linked xylose units; arabinose and other sugars are present as side chains. The proportions of cellulose,

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hemicellulose, and lignin are 44%, 26%, and 18%, respectively [2]. Unlike woody plants, rice straw is distinguished by its higher content of polysaccharides, specifically cellulose and hemicellulose, and a reduced presence of the aromatic polymer, lignin. Upon hydrolysis, cellulose yields glucose, while hemicellulose primarily produces xylose [3, 4]. Dehydration of hexoses such as glucose and pentoses like xylose has been shown to generate furan compounds, including 5-hydroxymethylfurfural (5-HMF) and furfural (FF) [5]. From the standpoint of biorefinery, these furan derivatives are of significant importance. 5-HMF can be converted to 2,5-dimethylfuran (DMF), a promising biofuel candidate. DMF boasts an energy density of 31.5 MJ/L, surpassing bioethanol's 23 MJ/L by 40% and nearing gasoline's 35 MJ/L [6]. Furthermore, oxidizing 5-HMF produces 2,5-furandicarboxylic acid (FDCA), a compound gaining traction as a monomeric precursor for polyethylene furanoate [7]. Conversely, reducing FF can yield compounds such as furfuryl alcohol (FFA) and 2-methylfuran (MF). While FFA finds applications in casting resins, MF, akin to DMF, holds promise as a potential biofuel substrate [8–10].

The production of the furan compounds from cellulose and hemicellulose traditionally relies on the use of various acid catalysts, notably sulfuric acid [11–19]. While these catalysts have been effective, they introduce significant concerns. The potential harm they pose to both human health and the environment, coupled with their corrosive nature that threatens equipment, underscores the urgent need for alternative methods. To address these challenges, research has pivoted towards identifying safer and more efficient reaction systems. A particularly promising avenue that has garnered significant attention is the utilization of ionic liquids in the production of the furan compounds. This method offers a potentially safer and more environmentally benign alternative to conventional acid-catalyzed processes.

Ionic liquids are a class of organic salts that remain liquid near ambient temperatures, consisting of paired anions and cations. These compounds are notable for their remarkable solvation properties, elevated thermal stability, flame retardancy, and non-volatility [20]. The ability of certain ionic liquids to dissolve cellulose has been documented [21], leading to increased interest in their application for the chemical conversion of biomass. Lima et al. described a process wherein fructose was reacted in 1-ethyl-3-methylimidazolium hydrogen sulfate at 120 °C for 30 min, followed by extraction with methyl isobutyl ketone, achieving an 88% yield of 5-HMF [22]. Zhang and Zhao utilized $CrCl_3 \cdot 6H_2O$ as a catalyst and subjected cellulose and xylan to treatment in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) with microwave irradiation (400 W) for durations between 2 and 2.5 min [23]. Their results showed a 62% yield of 5-HMF from cellulose and a 63% yield of FF from xylan. Moreover, upon treating rice straw for 3 min, they reported 45% and 25% yields of 5-HMF and FF, respectively, when based on the hexose and pentose content of the rice straw. When these yields are expressed relative to the weight of the processed rice straw, they correspond to approximately 13% for 5-HMF and around 4% for FF. Yan et al. demonstrated a 44.1% yield of 5-HMF by treating corn stalk with a carbonaceous solid acid catalyst, sourced from corn stalk, in [BMIM]Cl at 150 °C for 30 min [24]. Collectively, these studies underscore the potential of ionic liquids as not only solvents but also catalysts, enhancing their efficacy for furan compound production from sources like rice straw.

In reaction systems where sugars are transformed into the furan compounds, these furans are known to be unstable and susceptible to degradation. From the generated 5-HMF, byproducts such as levulinic acid and formic acid can emerge [25], while from FF, byproducts including formic acid, lactic acid, and glyceraldehyde can be produced [26]. Moreover, the resultant furan compounds can react with the original sugar substrates to yield humins [27]. These side reactions reduce the yield of the furan compounds, underscoring the importance of continuously extracting them from the reaction medium. Solvent extraction is one methodology explored for this purpose. This technique employs immiscible solvents and leverages the differential solubilities of the desired compounds in the solvent for efficient extraction. Roman et al. described a process where, using a reaction medium comprising water, dimethyl sulfoxide (DMSO), and a polyvinylpyrrolidone mixture, and an extraction phase consisting of methyl isobutyl ketone and 2-butanol mixture, with hydrochloric acid as a catalyst, they treated fructose at 180 °C for 2.5 to 3 min, achieving a 73% yield of 5-HMF [28]. Chheda et al. utilized a reaction medium of water and DMSO mixture and an extraction phase of dichloromethane (DCM) [29]. By treating at 140 °C for 570 min, they obtained a 68% yield of 5-HMF from cellobiose. Additionally, a treatment for 3 h yielded an 87% of FF from xylan. Other solvents, such as 2-*s*-butylphenol and tetrahydrofuran, have also been investigated for extraction purposes [30]. Nevertheless, the use of solvents like DCM, which are toxic to humans, combined with challenges in reusing organic solvents, raises significant concerns.

Distillation serves as an alternative extraction method for 5-HMF (boiling point: 120 ℃ at 1.33 hPa) and FF (boiling point: 18.5 ℃ at 1.33 hPa). Various distillation techniques exist, with steam distillation and vacuum steam distillation notably allowing the extraction of substances prone to decomposition at high temperatures

or those possessing high boiling points, at reduced temperatures. Wei et al. reported an 86.1% recovery rate of 5-HMF in 1-methyl-3-octylimidazolium chloride at 180 °C via a 30-min vacuum distillation [31]. Kawamoto et al. treated cellulose in sulfolane at 200 °C for 6 min [32]. Combining this with steam distillation and vacuum steam distillation, they obtained 5-HMF and FF with yields of 35.7% and 4.4%, respectively. Additionally, Enomoto et al. investigated a method integrating vacuum steam distillation with ionic liquid treatment [33]. In their experiment, treating cellulose in an ionic liquid at 180 °C for 30 min resulted in a 68.3% yield of 5-HMF. This yield was significantly higher compared to the yield of 5-HMF when vacuum steam distillation was not employed, suggesting that the rapid removal of 5-HMF produced in the ionic liquid from the heating system prevented the undesired decomposition of 5-HMF. These methodologies, leveraging vacuum and water while eschewing harmful organic solvents, facilitate the extraction of target compounds. As such, they potentially offer a reduced environmental footprint compared to traditional solvent extraction. Additionally, the combined treatment with vacuum steam distillation becomes feasible by employing ionic liquids as the reaction medium, which possess virtually no vapor pressure. This approach can be regarded as a processing method that takes advantage of the unique properties of ionic liquids.

From prior research, it has been established that the furan compounds can be synthesized from rice straw utilizing ionic liquids. Specifically, 1-methylimidazolium hydrogen sulfate ([MIM]HSO_4) has been identified as an effective agent [34]. It has been found that the furan compounds can be efficiently produced from polysaccharides in this ionic liquid without the need for adding catalysts, including heavy metals. This efficiency is attributed to the high solubility of reactants, intermediates, and final products in [MIM]HSO_4, as well as the anionic component of the ionic liquid acting as a strong acid catalyst. However, it was also observed that extended processing with ionic liquids causes excessive degradation of the generated furan compounds, leading to their diminished yields [34]. Hence, for yield optimization, continuous extraction of the synthesized furan compounds is crucial. In this study, we explored a procedure for the continuous extraction of the furan compounds from rice straw treated with [MIM]HSO_4, employing vacuum steam distillation with the objective of achieving enhanced furan compound yields.

Experimental

Materials

Oven-dried and ground rice straw was utilized as the sample. The compositional analysis of the rice straw, as presented in a previous report [34], indicates the following content: cellulose, 26.3%; hemicellulose, 16.5%; Klason lignin, 14.7%; acid-soluble lignin, 1.9%; extractives with ethanol/benzene, 2.9%; extractives with hot water, 18.4%; and ash, 15.6%. For the ionic liquid, we used 1-methylimidazolium hydrogen sulfate ([MIM]HSO_4) from Sigma-Aldrich.

Ionic liquid treatment combined with vacuum steam distillation

Figure 1 presents a schematic representation of the reaction setup. Initially, 1.0 g of [MIM]HSO_4 was placed in a 50 mL two-necked flask and heated to a set temperature. Subsequently, rice straw was added and underwent a combined treatment involving ionic liquid processing and vacuum steam distillation for a specified

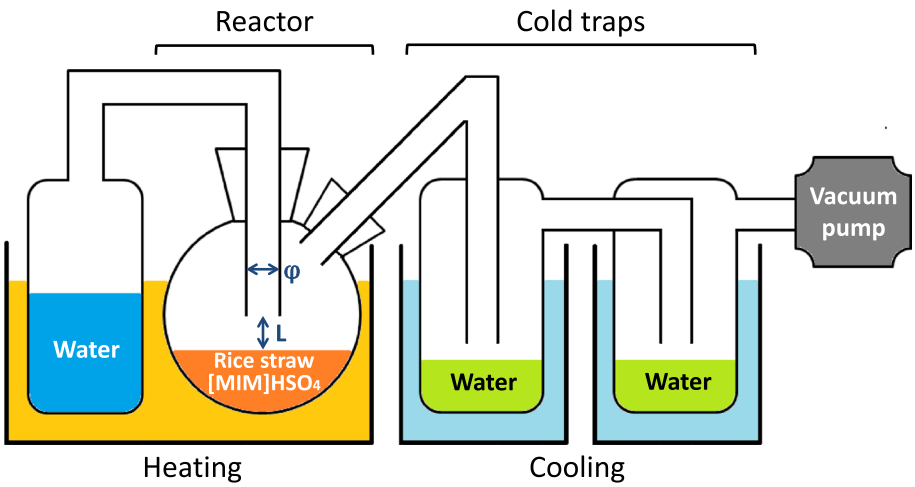

Fig. 1 Schematic diagram of the experimental apparatus. φ: Internal diameter of connector. L: Length from tip of connector to surface of reaction medium

duration. During the treatment, the system was maintained under reduced pressure using a vacuum pump, ensuring a consistent steam presence within the reaction vessel. The pressure within the reaction system was controlled to a predetermined value by a pressure control device introduced between the cold trap and the vacuum pump. To ensure a continuous supply of steam to the reaction system during the experiment, sufficient water was pre-introduced into the steam generation part. Steam was collected via two cold traps. To determine optimal conditions, several parameters were adjusted: the cooling temperature of the cold traps, the internal diameter of the connector through which steam entered the reactor (represented as ϕ in Fig. 1), the length from the tube tip of the connector to the surface of the reaction medium (represented as L in Fig. 1), system pressure, processing temperature, processing time, the weight ratio of the added sample to [MIM]HSO_4 (sample loading), and the particle size of the sample. For the position of the connector tip, the reaction medium surface was defined as zero, positions above were considered positive, and those below as negative. The procedure was halted by ceasing ionic liquid heating, turning off the vacuum pump, and stopping the steam input.

Analytical methods

The collected water from the two cold traps, along with the ionic liquid remaining in the flask after reaction, were each diluted tenfold using ultrapure water. These solutions were subsequently filtered through a 0.45-μm pore-sized filter. The produced 5-HMF and FF were analyzed using high-performance liquid chromatography (HPLC) utilizing the Prominence system by Shimadzu Corporation, with specific conditions outlined below. Moreover, the yields of 5-HMF and FF were calculated according to Eq. (1), and a cumulative value was derived from the substances captured in both cold traps.

Column: Sugar KS-801 (Shodex), column temperature: 80 °C, detector: ultraviolet detector set at 280 nm (UV_{280nm}), eluent: ultrapure water, flow rate: 1.0 mL/min, injection volume: 10 μL.

$$\text{Yield(wt\%)} = \frac{\text{Weight of produced 5-HMF or FF(g)}}{\text{Weight of rice straw loaded(g)}} \times 100. \quad (1)$$

Recyclability of [MIM]HSO_4

1.0 g of [MIM]HSO_4 and 10 mg of rice straw were added to a 50-mL two-necked flask. The vacuum steam distillation setup, as illustrated in Fig. 1, was assembled, with the cold trap being cooled to − 196 °C using liquid nitrogen. Once the reaction system was depressurized to 10 hPa with the aid of a vacuum pump, the reaction commenced by heating the flask in an oil bath maintained at 180 °C. After a duration of 30 min, the aqueous solution gathered in the cold traps underwent filtration using a 0.45 μm filter, followed by HPLC analysis as previously described. To assess the recyclability of [MIM]HSO_4, after the initial reaction, an additional 10 mg of rice straw was introduced to the flask, and both the reaction and HPLC analysis were conducted following the established procedure. The yield of the resultant furan compounds was determined based on Eq. (1).

Results and discussion

The influence of cooling temperature in the cold traps

Experiments were carried out with varying cooling temperatures of the cold traps under the subsequent parameters: a 5-mm inner diameter of the connector, a 30 mm tip position, a system pressure of 3 hPa, a processing temperature of 160 °C, a processing duration of 30 min, a sample loading of 1wt%, and a sample particle size ranging between 90 and 180 μm. For these experiments, the cold traps were cooled to 0 °C via ice cooling and to − 196 °C using liquid nitrogen.

Table 1 shows the yields of the furan compounds recovered and those that remained in [MIM]HSO_4 at different cold trap cooling temperatures. At 0 °C, the recovered 5-HMF yield was 12.4wt%, whereas at − 196 °C, it registered at 9.7wt%, showing a higher yield at 0 °C. Conversely, the yield of recovered FF stood at 0.7wt% at 0 °C and 5.0wt% at − 196 °C. The total yield of the recovered furan compounds at − 196 °C was 14.7wt%, surpassing that at 0 °C. These results suggest that decreasing the cooling temperature enhances FF recovery, thus

Table 1 Effect of cooling temperature for cold traps on the yields of 5-HMF and FF trapped or remained in [MIM]HSO_4

Cooling temperature (℃)	Trapped			Remained in [MIM]HSO_4		
	5-HMF (wt%)	FF (wt%)	Total (wt%)	5-HMF (wt%)	FF (wt%)	Total (wt%)
0	12.4	0.7	13.1	0.8	0.0	0.8
− 196	9.7	5.0	14.7	0.9	0.1	1.0

In both cases: inner diameter of the connector; 5 mm, tip position; 30 mm, system pressure; 3 hPa, processing temperature; 160 °C, processing duration; 30 min, sample loading; 1wt%, sample particle size; between 90 and 180 μm

increasing the overall furan compound yield. Moreover, the furan compounds that went unrecovered amounted to less than 1wt% at both 0 °C and − 196 °C. This signifies negligible residual furan compounds, with negligible variance due to cooling temperatures. In the HPLC analysis of the recovery solution from the cold trap, few peaks were observed other than those corresponding to 5-HMF, FF, and minor contaminations from ionic liquids, suggesting that the recovery solution contains furan compounds at a high purity (see Additional file 1 for a typical HPLC chromatogram). In the conducted experiments, cellulose and xylan in hemicelluloses are identified as the primary sources of 5-HMF and FF production, respectively. As noted in Sect. "Materials", the rice straw used in this study also contains a substantial amount of hot water extractives. While a detailed identification of the components within these extractives has not been performed, it is speculated that starch and water-soluble sugars, potentially present, could also contribute to the production of the furan compounds.

Given these findings, subsequent experiments adopted − 196 °C as the cooling temperature for the cold trap, owing to its superior furan compound yield.

The influence of the internal diameter and tip position of the connector

Experiments were carried out under the following conditions: a system pressure of 3 hPa, a processing temperature of 160 °C, a processing duration of 30 min, a sample loading of 1wt%, and a sample particle size between 90 and 180 μm. The cooling temperature of the cold trap was established at − 196 °C, a value identified in prior research to achieve the maximum recovery rate of the furan compounds. The study varied the position (L) of the connector's tip, with the its diameter denoted as ϕ. For reference, the surface of the reaction liquid was designated as 0, with positions above considered as positive and those below as negative.

Figure 2 presents the yield of the recovered furan compounds, whereas Fig. 3 depicts the yield of the unrecovered furan compounds. From Fig. 2, it can be discerned that with a decreasing tip position value, the 5-HMF yield demonstrates an increasing trend when the internal diameter of the connector measures 5 mm and 8 mm. Furthermore, when the tip position is set at 30 mm, the 5-HMF yield shows an increase with a widening internal diameter of the connector. When the tube's internal diameter is 5 mm and the tip position is adjusted to − 5 mm, submerging it in the reaction medium, the 5-HMF yield attains 16.6wt%. Although variations in the internal diameter and tip position had a minimal impact on the FF yield, the peak yield for FF was recorded at 9.1 wt% when the internal diameter measured 10 mm and

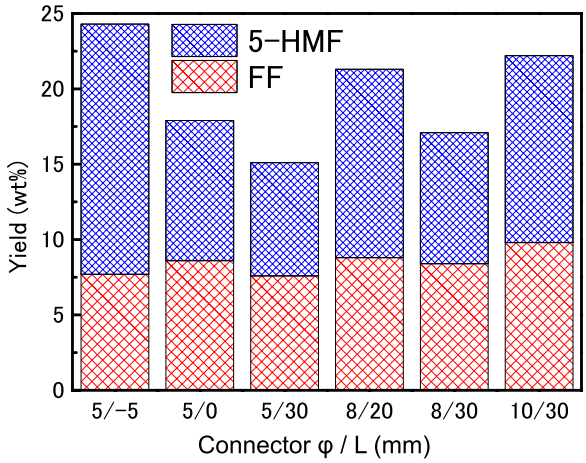

Fig. 2 Effect of connector φ and L on the yields for 5-HMF and FF trapped. In all cases: system pressure; 3 hPa, processing temperature; 160 °C, processing duration; 30 min, sample loading; 1wt%, sample particle size; between 90 and 180 μm, cooling temperature of the cold trap; − 196 °C

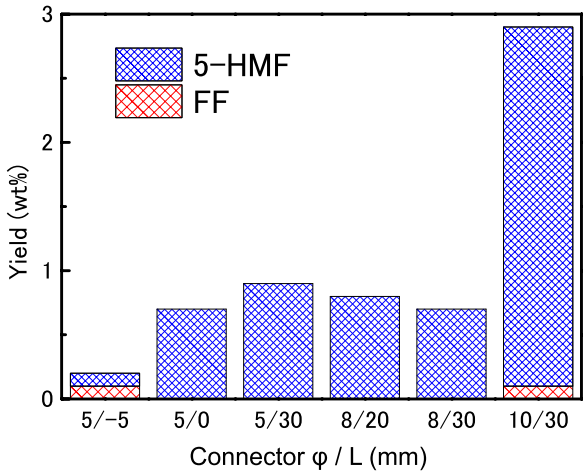

Fig. 3 Effect of connector φ and L on the yields for 5-HMF and FF remained. In all cases: system pressure; 3 hPa, processing temperature; 160 °C, processing duration; 30 min, sample loading; 1wt%, sample particle size; between 90 and 180 μm, cooling temperature of the cold trap; − 196 °C

the tip position was 30 mm. As inferred from Fig. 3, the amount of unrecovered 5-HMF declined with a reducing tip position value at an inner diameter of 5 mm, with no marked difference noted at 8 mm. In contrast, when the diameter was 10 mm, a considerable quantity of unrecovered 5-HMF was detected. Minimal unrecovered FF was found across all connector diameters. It is postulated that a decrease in the connector's internal diameter elevates steam velocity, agitating the reaction medium and facilitating advanced reactions. Based on these observations,

it is evident that with an internal diameter of 5 mm and a tip position at − 5 mm, when submerged in the reaction liquid, the maximum yield of the recovered furan compounds is achieved at 24.3wt%.

The influence of system pressure

Experiments were conducted by altering the system pressure under specified conditions: a processing temperature of 160 °C, a processing duration of 30 min, a sample loading of 1wt%, and a sample particle size between 90 and 180 μm. The cold trap was cooled to -196 °C, and the connector's internal diameter (φ) and tip position (L) were set to 5 mm and − 5 mm, respectively, based on their previously identified optimal performance in maximizing the recovery of the furan compounds.

Figure 4 shows the yield of the recovered furan compounds in response to varying system pressures, whereas Fig. 5 presents the yield of the unrecovered compounds. From Fig. 4, it is evident that as the system pressure decreased from atmospheric levels (1013 hPa), the 5-HMF recovery rate increased, attaining its maximum yield of 16.6wt% at 3 hPa. In contrast, FF's yield ascended as system pressure elevated from 3 hPa, peaking at 200 hPa with a yield of 11.5wt%. Nonetheless, when steam distillation took place at atmospheric pressure, vapors containing the products were seldom captured in the cold traps, subsequently leading to decreased yields of both 5-HMF and FF. At a system pressure of 10 hPa, the total yield of the recovered furan compounds was notably high at 24.5wt%. Figure 5 reveals an amplified unrecovered 5-HMF yield with increasing system pressure. This data implies that distillation of 5-HMF is impeded at elevated pressures but is facilitated as the pressure diminishes. Alternatively, FF undergoes distillation at high pressures, and at extremely low pressures, it likely is not captured in the cold traps and is possibly progressively drawn into the vacuum pump. This phenomenon is presumably rooted in the distinct boiling points of 5-HMF and FF, registered at 292 °C and 162 °C, respectively.

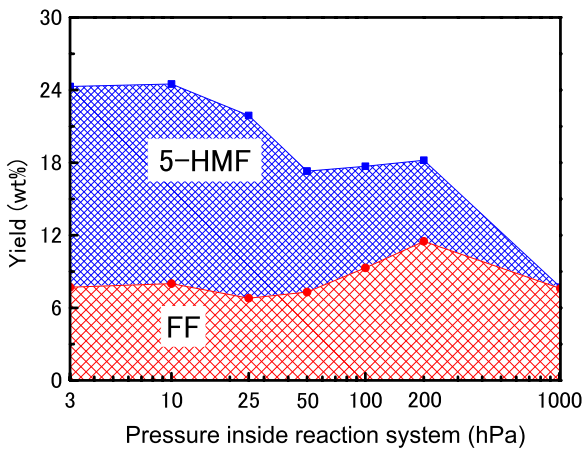

Fig. 4 Effect of degree of vacuum on the yields for 5-HMF and FF trapped. In all cases: processing temperature; 160 °C, processing duration; 30 min, sample loading; 1wt%, sample particle size; between 90 and 180 μm, cooling temperature of the cold trap; − 196 °C, internal diameter of the connector; 5 mm, tip position; − 5 mm

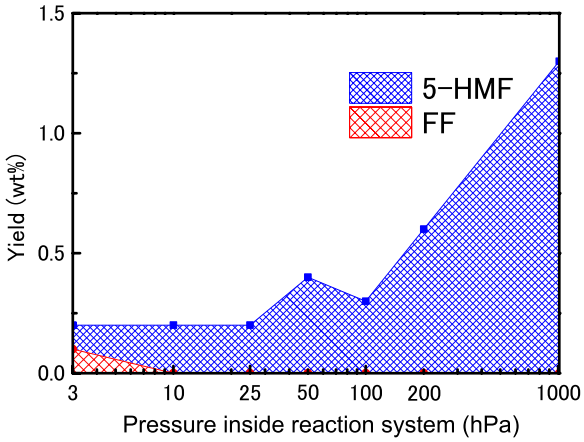

Fig. 5 Effect of degree of vacuum on the yields for 5-HMF and FF remained. In all cases: processing temperature; 160 °C, processing duration; 30 min, sample loading; 1wt%, sample particle size; between 90 and 180 μm, cooling temperature of the cold trap; − 196 °C, internal diameter of the connector; 5 mm, tip position; − 5 mm

The influence of reaction temperature

Experiments were carried out by adjusting the reaction temperature under the subsequent parameters: a processing duration of 30 min, a sample loading of 1wt%, a sample particle size between 90 and 180 μm, a cold trap cooling temperature of − 196 °C, a 5 mm internal diameter of the connector, a tip position of − 5 mm, and a system pressure of 10 hPa, which had been identified above as providing the optimal recovery rate for the furan compounds.

Figure 6 shows the recovery yield of the furan compounds as a function of processing temperature, while Fig. 7 represents the yield of the unrecovered furan compounds. According to Fig. 6, at a reaction temperature of 120 °C, the 5-HMF yield stood at 0.8wt%. This yield increased progressively, peaking at 18.1wt% at 180 °C. Nonetheless, at 200 °C, there was a decline in the 5-HMF yield to 15.6wt%, which was less than its yield at 180 °C. The FF yield rose between 120 and 140 °C, showing minimal fluctuation beyond 140 °C, and reached its apex at 9.1wt% at 200 °C. From Fig. 7, it is discernible that while unrecovered furan compounds were evident

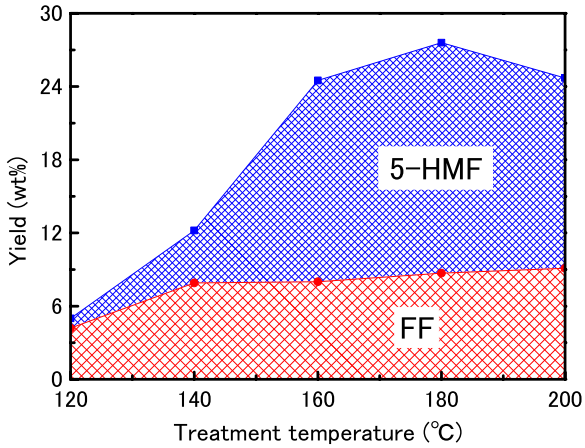

Fig. 6 Effect of treatment temperature on the yields for 5-HMF and FF trapped. In all cases: processing duration; 30 min, sample loading; 1wt%, sample particle size; between 90 and 180 μm, cooling temperature of the cold trap; − 196 °C, internal diameter of the connector; 5 mm, tip position; − 5 mm, system pressure; 10 hPa

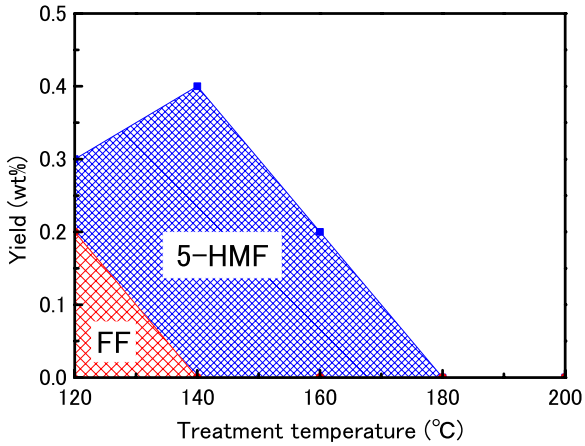

Fig. 7 Effect of treatment temperature on the yields for 5-HMF and FF remained. In all cases: processing duration; 30 min, sample loading; 1wt%, sample particle size; between 90 and 180 μm, cooling temperature of the cold trap; − 196 °C, internal diameter of the connector; 5 mm, tip position; − 5 mm, system pressure; 10 hPa

at temperatures below 160 °C, they were absent at 180 °C and higher. The diminished yield at 200 °C can likely be ascribed to the decomposition of the furan compounds in [MIM]HSO_4 before their potential recovery. Notably, at the processing temperature of 180 °C, the total yield of the recovered furan compounds was at its maximum, registering 27.6wt%. The responsiveness of furan compound yield to reaction temperature, as observed, is generally in agreement with our previous study, which conducted furan compound production in the same reaction medium without the introduction of vacuum steam distillation [34]. Within the temperature confines delineated in Figs. 6 and 7, a rise in temperature not only expedited the formation of the furan compounds but also augmented the efficiency of distillation, resulting in a reduced residue of the furan compounds in the system. Consequently, the processing temperature emerges as a pivotal parameter, influencing both reaction kinetics and distillation efficiency, and its meticulous regulation is posited to markedly influence furan compound yields.

The influence of reaction time

Experiments were conducted under varied processing duration and the following conditions: a sample loading of 1wt%, a sample particle size between 90 and 180 μm, a cold trap cooling temperature of − 196 °C, a 5 mm internal diameter of the connector, a tip position of − 5 mm, a system pressure of 10 hPa, and a processing temperature established at 180 °C. This temperature was selected based on the above investigation that identified it as the optimum for maximizing the total furan compound recovery rate.

Figure 8 presents the yield of the recovered furan compounds relative to the processing time. The yield of 5-HMF consistently increased with the processing time until 60 min, where it peaked at 19.1wt%. However, when the processing time was lengthened to 90 min, the yield of 5-HMF began to decrease. The yield of FF was at its maximum at 15 min, registering at 9.5wt%, after which it followed a downward trajectory. The 60-min mark witnessed the peak total furan compound yield, recorded at 28.0wt%. The observed decrease in 5-HMF yield at 90 min and the post-15-min drop in FF yield indicate

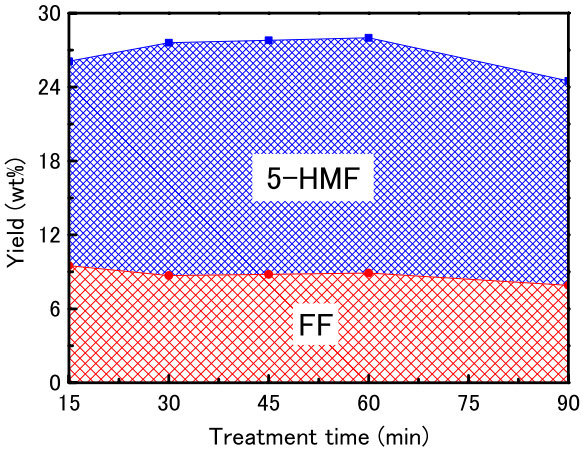

Fig. 8 Effect of treatment time on the yields for 5-HMF and FF trapped. In all cases: sample loading; 1wt%, sample particle size; between 90 and 180 μm, cooling temperature of the cold trap; − 196 °C, internal diameter of the connector; 5 mm, tip position; − 5 mm, system pressure; 10 hPa, processing temperature; 180 °C

that extended vacuum steam distillation could result in the furan compounds being inadvertently pulled into the vacuum pump. This is not ideal from a recovery efficiency perspective. Remarkably, at 30 min, the total furan compound yield was 27.6wt%, which is approximately 99% of the yield noted at 60 min. When accounting for production efficiency and environmental considerations, a processing span of 30 min emerges as the most suitable. It is also noteworthy that the uncollected furan compounds were consistently minimal, registering at less than 0.1wt% across all evaluated processing durations.

The influence of sample loading

Experiments were carried out by altering the sample loading, with the following conditions: a sample particle size between 90 and 180 μm, a cold trap cooling temperature of − 196 °C, a 5 mm internal diameter of the connector, a tip position of − 5 mm, a system pressure of 10 hPa, a processing temperature of 180 °C, and a predetermined processing duration of 30 min, as informed by the above investigations.

Table 2 shows the yield of the recovered furan compounds at varying sample loadings. Notably, the yield of 5-HMF demonstrated an increase as the sample concentration declined, culminating at 18.9wt% for a 1wt% concentration. The FF yield remained relatively consistent across concentrations ranging from 1 to 10wt%, recording its maximal at 8.7wt% for the 1wt% concentration. These observations highlight that the optimal total yield for the recovered furan compounds, 27.6wt%, was achieved at a sample loading of 1wt%. The residues of the uncollected furan compounds remained inconsequential, with values under 0.1wt%, across the 1 to 10wt% loading range. In contrast, at a loading of 30wt%, the yield of the recovered furan compounds was comparatively diminished. Additionally, due to the infiltration of the ionic liquid into the rice straw, the analysis of the uncollected furan compounds was rendered unfeasible.

Table 2 Effect of sample loading on the yields for 5-HMF and FF trapped

Sample loading (wt%)	Yield (wt%)		
	5-HMF	FF	Total
1	18.9	8.7	27.6
3	15.7	8.4	24.1
5	15.4	8.4	23.8
10	14.1	8.2	22.3
30	3.2	5.1	8.3

In all cases: sample particle size; between 90 and 180 μm, cooling temperature of the cold trap; − 196 °C, internal diameter of the connector; 5 mm, tip position; − 5 mm, system pressure; 10 hPa, processing temperature; 180 °C, processing duration; 30 min

The influence of sample particle size

Experiments were conducted with samples of varying sample particle sizes, using the following parameters: a cold trap cooling temperature of − 196 ℃, a 5 mm internal diameter for the connector, a tip position of − 5 mm, a system pressure of 10 hPa, a processing temperature of 180 ℃, and a set processing duration of 30 min. Based on previous studies, the sample loading was established at 1wt%, a loading that previously yielded the highest recovery rate for the furan compounds.

Figure 9 illustrates the yield of recovered furan compounds for several particle sizes. The 5-HMF yield peaked at 18.7wt% for sample particle sizes ranging from 90 to 180 μm. For sizes either exceeding 180 μm or below 45 μm, the 5-HMF yield was notably lower than that observed for the 90–180 μm range. The FF yield was maximized at 9.3wt% for particle sizes between 45 and 90 μm. Particle sizes greater than 180 μm or less than 45 μm yielded FF the amounts of which were comparatively lower than those obtained for the 45–90 μm range. The total yield for the furan compounds was highest, 27.9wt% (comprising 5-HMF at 18.6wt% and FF at 9.3%), for particle sizes between 45 and 90 μm. These findings suggest that decreasing particle size leads to an increase in surface area, subsequently augmenting the reaction efficiency with the ionic liquid, which in turn facilitates a higher furan compound yield. For particles smaller than 45 μm, there were observations of samples dispersing within the flask without undergoing reaction,

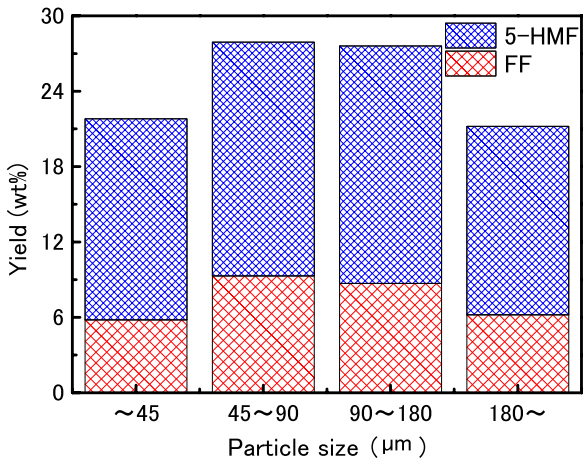

Fig. 9 Effect of particle size on the yields for 5-HMF and FF trapped. In all cases: cooling temperature of the cold trap; − 196 °C, internal diameter of the connector; 5 mm, tip position; − 5 mm, system pressure; 10 hPa, processing temperature; 180 °C, processing duration; 30 min, sample loading; 1wt%

potentially due to the influence of steam. This behavior is postulated to contribute to the reduced yield of the furan compounds. Across all particle sizes, the amount of unrecovered furan compounds remained minimal, registering below 0.1wt%.

In a prior study, when rice straw was processed in a batch processing using [MIM]HSO_4, the maximum yields for 5-HMF and FF were reported to be 7.9wt% and 4.3wt%, respectively, with the total yield for the furan compounds being 12.2wt% [34]. In the current study, utilizing a combination of the [MIM]HSO_4 treatment and vacuum steam distillation, the maximum yield for the furan compounds reached 27.9wt%, a significant increase compared to the batch processing. Moreover, as the furan compounds are extracted and recovered from [MIM]HSO_4, this method is believed to be more advantageous for downstream processing than the batch processing.

Chi van Nguyen et al. obtained 5-HMF at a yield of 19.4wt%, based on the weight of the input rice straw, by treating rice straw preprocessed with a 3% NaOH solution in a reaction system with 1-butyl-3-methylimidazolium chloride added with $CrCl_3$ at 120 ℃ for 2 h [35]. Kumar et al. achieved a yield of 5-HMF at 3.1% and FF at 9.3% from the rice straw's weight by treating it at 130 ℃ for 6 h in a reaction system containing methyl isobutyl ketone, butanol, and dimethyl sulfoxide mixed solvents with oxalic acid, HCl, and $AlCl_3$ added [36]. Compared to these results, the yields for 5-HMF and FF in our study are either comparable or higher. In this research, no special preprocessing was performed; the rice straw was processed as is, and the procedure involved only ionic liquids without the use of catalysts. The furan compound generation and the extraction/recovery of these generated compounds could be executed simultaneously. Furthermore, only water was used in the reaction system for extraction and recovery, not organic solvents, indicating various advantages over previous research.

From the above results, the optimal conditions for the furan compound production from rice straw using the [MIM]HSO_4 treatment combined with vacuum steam distillation were identified as: cold trap cooling temperature at − 196 ℃, connector's internal diameter of 5 mm, tip position at − 5 mm, system pressure at 10 hPa, processing temperature at 180 ℃, processing time of 30 min, sample loading at 1wt%, and sample particle size between 45 and 90 μm. An examination of the recyclability of [MIM]HSO_4 under these conditions was conducted.

Recyclability of [MIM]HSO_4

We investigated the impact of repeated use of the reaction medium under the above optimal conditions (1wt% sample loading, 45–90 μm particle size, 180 ℃, 10 hPa, 30 min) on the yield of the furan compounds (for detailed experimental procedures, refer to Sect. "Recyclability of [MIM]HSO4"). This study defines experiments involving this repeated use as recycling experiments. During these recycling experiments, byproducts and reaction residues progressively accumulate in the reaction medium with each cycle. We examined the effects of these accumulated impurities in the reaction medium on the furan compound production.

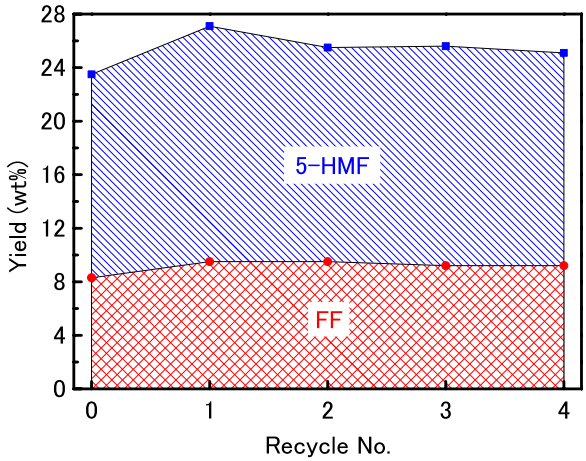

Fig. 10 Recyclability of [MIM]HSO_4 in the production of furan compounds. In all cases: cooling temperature of the cold trap; − 196 °C, internal diameter of the connector; 5 mm, tip position; − 5 mm, system pressure; 10 hPa, processing temperature; 180 °C, processing duration; 30 min, sample loading; 1wt%, sample particle size; between 45 and 90 μm

Table 3 The average of furan compounds yields in 4 times recycling experiment

	Yield (wt%)		
	5-HMF	FF	Total
Maximum[a]	18.6	9.3	27.9
Average in the recycling	16.2	9.1	25.3

In all cases: cooling temperature of the cold trap; − 196 °C, internal diameter of the connector; 5 mm, tip position; − 5 mm, system pressure; 10 hPa, processing temperature; 180 °C, processing duration; 30 min, sample loading; 1wt%, sample particle size; between 45 and 90 μm

[a] Data shown in Fig. 9

Figure 10 presents the furan compound yields obtained during the recycling experiments. Throughout the four recycling cycles, the yields of 5-HMF and FF showed no significant decline. The furan compound yield observed during the initial recycling cycle displayed an increase. This increment is likely due to the presence of some unreacted samples in the flask following the completion of the primary reaction. Table 3 shows the maximum furan compound yields, as documented in the previous sections (45–90 μm as shown in Fig. 9), with the average

yields from the recycling trials. Over the span of four recycling rounds, the average furan compound yield was 25.3wt%. This figure closely aligns with the peak yield of 27.9wt%. The sustained yield consistency over the recycling experiments indicates the potential for [MIM]HSO_4 to be efficiently recycled and repurposed. Additionally, this study adopted a streamlined recycling approach: after the reaction, rice straw was simply introduced to the reaction mixture, eliminating the need for the filtration of reaction residues or the purification of the reaction solution. This ability to employ such an uncomplicated method, and to maintain efficacy through at least four recycling endeavors (translating to five reaction iterations), underscores a notable strength of this method.

The reaction residues mentioned above primarily originate from lignin and inorganics present in the samples, as indicated by our previous study on furan compound production from a bamboo sample [37]. This previous report has indicated that the accumulation of residues in the reaction medium led to a decrease in the yield of furan compounds. In this study, we have not investigated the cause of the slight decrease in product yield with the increasing number of cycles, as shown in Fig. 10. However, it is conjectured that removing reaction residues after a certain number of cycles could be effective, especially when considering further increases in recycling numbers and/or conducting recycling experiments with larger sample loading concentrations.

Conclusions

We investigated the production of the furan compounds from rice straw using a combined approach of the [MIM]HSO_4 processing and vacuum steam distillation. Upon evaluating a range of reaction conditions, we determined the optimal parameters as follows: a cold trap cooling temperature set at − 196 ℃, a connector's internal diameter of 5 mm, a tip position at − 5 mm, a system pressure at 10 hPa, a processing temperature of 180 ℃, a processing time of 30 min, a sample loading of 1wt%, and a sample particle size between 45 and 90 µm. Under these conditions, the yields were 18.6wt% for 5-HMF and 9.3wt% for FF, culminating in a total furan compound yield of 27.9wt%. Furthermore, our examination of the recyclability of [MIM]HSO_4 revealed its potential for effective recycling and reuse. To realize practical applications, additional research is needed to improve the recyclability of [MIM]HSO_4 and to address the scalability of the reaction process.

Abbreviations

[MIM]HSO_4	1-methylimidazolium hydrogen sulfate
5-HMF	5-Hydroxymethylfurfural
FF	Furfural

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s10086-024-02129-1.

Additional file 1: Figure S1. HPLC chromatogram of the solution recovered in the cold trap after the treatment of rice straw in [MIM]HSO_4 at 180 ℃ combined with vacuum steam distillation.

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Not applicable.

Author contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by KE, TH and HM. The first draft of the manuscript was written by HM and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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