

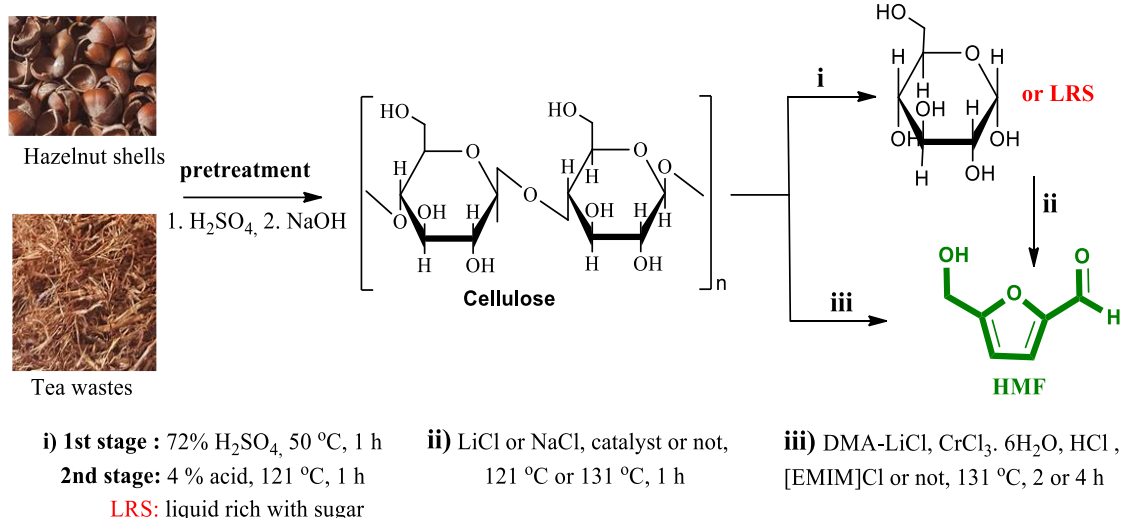
Production of 5-Hydroxymethylfurfural from Non-edible Lignocellulosic Food Wastes

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GRAPHICAL ABSTRACT



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The compound 5-(hydroxymethyl)furfural (HMF) has emerged as a versatile intermediate with the ability to undergo conversion into both fuel and a variety of platform chemicals. Lignocellulosic biomass, such as hazelnut shells and tea processing residues, was employed in this study for HMF production through two distinct methods. In the first method, cellulose from biomass was converted to sugars using a 4% acid solution, followed by catalytic conversion with NaCl/CrCl₃·6H₂O. After a 1-h reaction at 131 °C in a high-pressure system, HMF was obtained from tea processing waste and hazelnut shells with yields of 8.6% (82.3 mg/g) and 6.7% (66.7 mg/g), respectively. The second method involved LiCl/NaCl-doped N,N-dimethylacetamide (DMA) as an ionic solvent system for HMF production. After a 2-h reaction at 131 °C in the DMA-NaCl/[EMIM]Cl ionic solvent system, HMF was obtained from tea processing waste and hazelnut shell celluloses with yields of 5.7% (57.5 mg/g) and 3.1% (31.3 mg/g), respectively. This study contributes to the economic conversion of various food wastes into valuable chemicals, highlighting the potential of lignocellulosic biomass in sustainable chemical production.

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Keywords: Hydroxymethylfurfural; Lignocellulosic wastes; Food wastes; Hazelnut shell; Tea processing waste; Ionic solvent system

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INTRODUCTION

Waste materials such as bran, rice husks, corn stalks, and straw generated from food and feed industries contribute to the increase in atmospheric CO₂ emissions when left unutilized and burned (Dhanya 2022). Therefore, subjecting these waste materials to appropriate preprocessing opens up a significant opportunity for their transformation into important platform chemicals, especially for fuel and chemical production, thereby promoting renewable chemical production. Considering the rapid depletion of fossil fuel reserves, lignocellulosic wastes emerge as an appealing solution due to their abundance and diversity (Sanchez *et al.* 2019). Previously overlooked lignocellulosic wastes (such as corn cob, sugarcane bagasse, and wheat straw) (Batista *et al.* 2020) have gained attention in recent years through catalytic conversion studies (Li *et al.* 2019; Liu *et al.* 2022). The structural composition of lignocellulosic waste predominantly consists of cellulose, hemicellulose, and polyphenolic lignin. These components determine the biochemical properties of biomass (Okolie *et al.* 2021). Generally, cellulose and hemicellulose can be depolymerized into monosaccharides using acids, which can subsequently be transformed

into various chemicals. In light of their potential, the lignocellulosic wastes present a promising avenue for sustainable resource utilization and bio-based chemical production (Van-Putten *et al.* 2013).

HMF is a furanic compound formed during the thermal processing of foods by the direct dehydration of sugars under acidic conditions and as an intermediate in the Maillard reaction (Pasiadis *et al.* 2017). This compound, formed as a result of thermal processing in foods such as honey, is used as an indicator of freshness and quality (Scepankova *et al.* 2021). High HMF levels indicate that the product has been exposed to prolonged heat or poor storage conditions. Therefore, measuring HMF levels is an important parameter for assessing the quality and shelf life of food products (Korkmaz and Küplülü 2017). Its biochemical properties stem from the presence of furan ring, hydroxymethyl group, and aldehyde group, making it susceptible to oxidation and/or reduction reactions (Espro *et al.* 2021; Nguyen and Trinh 2022). Typically, HMF production takes place in aqueous systems of mineral acids (H_2SO_4 , HCl , H_3PO_4). Certain organic acids, enzymes, and metal salts can be employed to expedite the reaction and facilitate the HMF formation (Teong *et al.* 2014; Zunita *et al.* 2022).

In the production of HMF, natural or synthesized products containing C6 sugars such as hexoses, disaccharides, polysaccharides, food waste, lignocellulosic biomass, and their hydrolysates are used as feedstock. Industrially, HMF is obtained through a two-step process involving the isomerization of glucose to fructose, followed by the conversion of fructose to HMF (Zunita *et al.* 2021). However, since the market price of HMF is highly sensitive to raw material costs, using waste-derived alternatives instead of fructose is expected to improve the economic feasibility of the process (Menegazzo *et al.* 2018). Furthermore, it is crucial to consider the environmental and energy costs associated with the process, such as the cost of biomass feedstock and the potential for increased HMF production, when evaluating the overall feasibility of HMF production (Rosenfeld *et al.* 2020).

Due to the rapid depletion of fossil fuel reserves, plant biomass has the potential to be used as a future carbon source to reduce dependency on fossil fuels in the production of liquid fuels and chemicals. Lignocellulose is a functional composite that makes up over 90% of all plant biomass, consisting of cellulose, hemicellulose, and lignin (Delidovich *et al.* 2014). The hydrolysis of cellulose is a heterogeneous reaction due to its insolubility in water. In acid hydrolysis, the acid must first penetrate the amorphous regions of cellulose, where depolymerization occurs by breaking the glycosidic bonds. While the glycosidic bonds in amorphous cellulose are easily cleaved, acids cannot easily access the bonds in the crystalline regions. Lignin and hemicelluloses surrounding the cellulose create a physical barrier to penetration. The different hydrolysis rates in amorphous and crystalline cellulose regions, along with the protective lignin-hemicellulose matrix, result in a gradual release of sugars. The sugars undergo successive reactions. Before HMF synthesis, it is necessary to reduce the crystallinity and molecular weight of cellulose. These processes include mechanical milling, chemical pretreatment, hydrothermal treatment, dilute acid, and alkali pretreatments (Van Nguyen *et al.* 2016; Tayyab *et al.* 2018).

The synthesis of HMF from biomass involves a four-step reaction: pretreatment of lignocellulose, hydrolysis of cellulose to glucose, isomerization of glucose to fructose, and dehydration of fructose to HMF. Due to the breakdown of cellulose and hemicellulose into hexoses and pentoses, lignocellulose is promising for HMF conversion (Rosenfeld *et al.* 2020). However, the presence of non-convertible components such as lignin hinders the conversion reactions of glucose and fructose and increases by-product formation. This

negatively affects the yield and purity of HMF. If chemical pretreatments are used to produce fermentable sugars, attention should be paid to the formation of fermentation inhibitors. These include acetic acid, furfural, HMF, and phenolic compounds originating from lignin. Therefore, the limited release of all sugars from lignocellulosic structures restricts the efficiency. Additionally, HMF, under acidic conditions in an aqueous environment, rehydrates to form byproducts such as levulinic and formic acid. Additionally, self-condensation of HMF and its condensation with other compounds lead to the formation of humins. This results in a relatively low yield of HMF synthesized in an aqueous system (Steinbach *et al.* 2017). Selective removal of lignin significantly favors the conversion of lignocellulose into fermentable sugars and platform chemicals (Zhang *et al.* 2020; Tan *et al.* 2021). Therefore, the direct conversion of lignocellulosic biomass to HMF is more challenging than from pure carbohydrates (Menegazzo *et al.* 2018; Xu *et al.* 2022). However, the use of lignocellulosic waste is advantageous in terms of sustainability and economics. One reason for these studies is that such waste is low-cost and abundantly available. Moreover, the development of these methods has great potential for converting biomass waste into valuable chemicals and reducing dependence on fossil fuels. Therefore, despite the greater complexity of HMF production from lignocellulosic biomass, the environmental and economic benefits make overcoming these challenges worthwhile.

Although various studies have been conducted on the production of HMF from different lignocellulosic sources, there is currently no existing research on the use of hazelnut shells and tea processing residues, which are primarily used as animal feed and fuel, as starting materials for HMF production. In Türkiye, 30 to 50 thousand tons of plant tea waste containing lignocellulosic components are generated annually, and these wastes are generally burned, causing environmental damage (Germeç *and* Turhan 2014). The structural composition of tea processing residues includes approximately 29% cellulose, 19% hemicellulose, and 38% lignin (Demirbaş 1999). Hazelnut shells consist of three main polymers: 43% lignin, 30% cellulose, and 27% hemicellulose (Ceylan *et al.* 2022). Although hazelnut shells and tea processing residues may not have high cellulose content compared to other sources, they are chosen as potential starting materials for HMF production due to their abundance and the need to find sustainable alternatives to traditional feed and fuel usage, which often leads to environmental damage. This study aims to produce HMF from these lignocellulosic waste materials using two different methods described in the literature (acid hydrolysis method and catalyst/ionic solvent system) to generate an alternative HMF production from fructose and glucose.

EXPERIMENTAL

Materials

Chemicals

The analytical chemicals and high performance liquid chromatography (HPLC) solvents used in the study were obtained from Merck (Darmstadt, Germany). The HMF standard (99%), 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) (98%), and N,N-dimethylacetamide (DMA) (99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Chromium (III) chloride hexahydrate (CrCl₃·6H₂O) (98.4%) was sourced from Aromel Kimya (Konya, Türkiye).

Raw lignocellulosic biomass

The hazelnut (*Corylus colurna*) shells and tea (*Camellia sinensis*) waste used in the study were obtained as unprocessed from hazelnut and tea processing facilities in Trabzon, Türkiye. Hazelnut shells and tea residues were ground using a blender. The ground waste biomass was passed through a stainless steel sieve with a pore size of 0.63 mm to achieve a homogeneous particle size distribution. The material retained under the sieve was used in the study. The powdered hazelnut shells and tea processing waste were stored at +4 °C in tightly sealed plastic containers, away from moisture, until used in the experimental studies. To determine the dry matter content of the sample, 5 g of the sample was placed in a pre-weighed sample container, and the initial weight was recorded. The sample was dried in an oven at 103 °C for 6 h. At the end of the period, it was transferred to a desiccator, and the final weight was recorded. The dry matter content (w) of the samples was determined by finding the moisture content of the sample according to the ISO 1573 (Tea - Determination of Moisture Content) standard. The dry matter content was expressed as a percentage.

Methods

Cellulose from untreated biomass

The cellulose production was conducted in accordance with the TS ISO 15598 (2003) standard method (Çuhadar *et al.* 2023). The specified sample and chemical quantities in the method were adjusted according to the desired cellulose production. Initially, ground and sieved biomass (18 g) was boiled in a flask with 0.255 M H₂SO₄ solution (1200 mL) for 30 min. It was then filtered, and the sample was washed with hot water. Subsequently, the filtrate was boiled for an additional 30 min with 0.313 M NaOH solution (1200 mL). After another filtration, it was washed sequentially with 250 mL of hot water, HCl solution, and hot water again. After being held through two rounds of ethanol washes and three rounds of acetone washes, the residue was weighed with an approximate precision of 0.001 g and dried in an oven (105 °C) under vacuum conditions for 2 h in a glass crucible. The measured mass was recorded in grams. The raw fiber content was calculated using the following Eq. 1,

$$\text{Raw fiber (\%)} = \frac{m_1 - m_2}{m_0} \times 100 \times \frac{100}{w_D} \quad (1)$$

where m_0 is the mass of the sample (g), m_1 is the mass of the crucible and residue after drying in the furnace (g), m_2 is the mass of the crucible and residue after burning in the muffle furnace (g), and W_D is the dry matter content of the sample.

Three-step catalytic conversion of cellulosic biomass to HMF

The synthesis of HMF was conducted with modifications to the methodology established by Amezcua-Allieri *et al.* (2017). In the initial stage, the obtained cellulose (500 mg) was combined with 3 mL solution of 72% H₂SO₄ in an Erlenmeyer flask. Subsequently, the mixture was incubated at 50 °C in a water bath for 1 h. Following this, the solution in the Erlenmeyer flask was diluted with 54 mL distilled water to reach a weight percentage of 4% H₂SO₄, and the mixture was then incubated at 121 °C in a pressurized reactor for 1 h. Experiments at this stage were conducted for three different durations: 1, 2, and 4 h. After cooling, the mixture was filtered using coarse filter paper. A 10 mL portion of the obtained solution was transferred to an experimental tube, and the pH was adjusted to 0.6. Subsequently, the solution was saturated with LiCl and NaCl salts. In

this stage of the process, 0.02 g of chromium chloride catalyst was added to expedite the conversion of sugar to HMF in the tube. The transformation of sugar to HMF in the mixture was carried out at two different temperatures (121 °C, 131 °C) through experiments conducted in a pressurized reactor for 1 h. The resulting hot mixture was cooled, filtered, and subjected to HMF analysis using HPLC. The impact of different temperatures and catalyst usage on HMF yield was evaluated during the production process.

Conversion of cellulosic biomass to HMF in an ionic liquid-based solvent system

The conversion of cellulose to HMF in a complex ionic liquid-based solvent system was completed with some modifications to the method described by Binder and Raines (2009). In the initial stage, a mixture comprising 100 mg of cellulose, 130 mg of LiCl or NaCl, 795 mg of [EMIM]Cl, and 1260 mg of DMA was continuously stirred at 50 °C in a water bath for 24 h to obtain a homogeneous mixture. In the second stage, the mixture containing 250 mg of [EMIM]Cl, 25 mg of CrCl₃·6H₂O, and 25 µL of concentrated HCl was continuously stirred in a pressurized reactor at 131 °C for 2 h. To investigate the potential impact on HMF yield, the second stage of the experiment was conducted under two conditions: one where the ionic liquid ([EMIM]Cl) was added to the reaction mixture and the other where it was not added. After the completion of the reaction, the extracted mixture from the reactor was rapidly cooled, filtered, and then subjected to HPLC analysis to measure the HMF concentration. The reaction conditions and obtained yields are presented in Table 1, providing a comprehensive overview of the experimental studies.

HPLC analysis of hydroxymethylfurfural

The HMF analyses were conducted using an HPLC-UV system (Agilent 1100 series, Agilent Technologies, Santa Clara, CA, USA). Separation of HMF was performed on a reversed-phase C18 column (250 mm × 4.6 mm, 5 µm particle size, Nucleosil, Machereyull Nagel Inc., Allentown, PA, USA). A mobile phase of water-methanol (90:10 V/V) was utilized. The UV detector was set at a wavelength of 285 nm, and the flow rate was adjusted to 1.0 mL/min. Before starting the analysis, standards were prepared at concentrations of 1.0, 2.0, 4.0, 8.0, and 12.0 ppm using a commercial HMF standard solution. A 100 µL sample was injected into the instrument. A calibration curve was generated by plotting the peak areas of standards at five different concentrations. The calculations were performed utilizing the obtained calibration curve (Baltacı and Aksit 2016).

The calibration curve equation, defined as $y = a(x) + b$, represents the determination of y , which is the peak area obtained by the HPLC-UV detector for the sample. In this equation, x represents the concentration of HMF in mg/kg, b represents the y-intercept, a represents the calibration curve constant, and F represents the dilution factor.

The HMF yield (%) in the biomass solution was calculated using the following Eq. 2:

$$HMF (\%) = \left(\frac{y+b}{a} \times F\right) / 10000 \quad (2)$$

Statistical analysis

The experiments in this study were conducted with three replicates to enhance reliability. Each experiment was performed in triplicate, and the mean, along with the standard deviation, was calculated to ensure accuracy in data interpretation. Microsoft

Excel program with the assistance of XLSTAT(Addinsoft 2024), XLXTAT statistical and data analysis solution (New York, NY, USA).

RESULTS AND DISCUSSION

The moisture content of hazelnut shells and tea processing waste were $7.94 \pm 0.164\%$ and $3.78 \pm 0.122\%$, respectively. The amounts of cellulose obtained from hazelnut shells and tea processing waste biomass were determined as $48.56 \pm 0.42\%$ and $37.74 \pm 1.14\%$, respectively.

HMF Efficiency in Catalytic Conversion

In the first method, cellulose from hazelnut shells and tea processing waste was subjected to pretreatment with 72% (w/w) H_2SO_4 solution at 50 °C for 1.0 h. The hydrolysate concentration was diluted to 4% after the reaction, and under reactor conditions (131 °C, 1.0 h), it underwent a second hydrolysis. Following the pretreatment, sugars in the solution were converted to HMF as described in the section titled '*Three-stage catalytic conversion of cellulose biomass to HMF*'. As a result, the highest yields of HMF were obtained from tea processing waste and hazelnut shells, with values of 8.6% and 6.7%, respectively.

In light of recent studies, the performance of these methods was evaluated, particularly by comparing their results with those reported in the literature, analyzing the HMF yields from various biomass sources. For example, Shao *et al.* (2020) achieved an 8.1% HMF yield from sugarcane bagasse using a microwave hydrothermal liquefaction method under acidic seawater conditions, highlighting its potential as a sustainable approach for biomass conversion using seawater or saline wastewater. Similarly, Kumar *et al.* (2021) obtained a 15% HMF yield from sugarcane bagasse using a protocol involving mineral acid HCl. Binder and Raines (2009) reported HMF yields ranging from 15% to 40% from corn and pine wood chips with a LiCl catalyst. These studies clearly demonstrate that while these acids or other combinations individually exhibit poor performance, the correct combination shows high specificity and synergistic effects for this transformation. The use of acidic seawater promotes the conversion of fructose and glucose to HMF in conjunction with catalysts. Additionally, it has been reported that newly formed HMF can prevent dehydration to levulinic acid. During the reaction process, it was observed that the active sites of catalysts are in full contact with the substrate (Kumar *et al.* 2021).

Yemiş and Mazza (2012) conducted a comprehensive study on the optimization of furfural, 5-hydroxymethylfurfural (HMF), glucose, and xylose conditions for acid-catalyzed conversion of wheat straw using response surface methodology (RSM). Using a microwave-assisted process, the maximum HMF yield from wheat straw using dilute acid catalysis was determined to be 3.4%. The low yield is attributed to excessive acid in the reaction environment. This can lead to rapid heating of the solution in the microwave field (140 to 200 °C), causing thermal stress due to microwave absorption. Additionally, consecutive condensation reactions (cross and self-polymerization) have been reported to result in furfural loss during the acid-catalyzed conversion process. This could significantly decrease furfural yield at low initial pH and high temperatures (Zeitsch 2000). Kougioumtzis *et al.* (2018) conducted a brief hydrolysis of almond shells using dilute sulfuric acid (H_2SO_4) at 175 °C for 60 minutes. The hydrolysate was then mixed with a

DMSO (80%)/water (20%) solution containing $\text{Sn}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ catalyst. It was reported that approximately 3.6% HMF yield was obtained from the biomass after 1 hour at 150 °C.

In the study conducted by Hoşgün (2021), a 12.2% yield was documented for the production of HMF from poppy stalks using CuCl_2 as a catalyst in a 4% H_2SO_4 solution. Another investigation focusing on HMF production from cellulose through conventional acidic hydrolysis reported a maximum efficiency of 30% (Kono *et al.* 2005; Binder and Raines 2009). The results obtained are noteworthy in comparison to these reported efficiencies. While water, employed in the process, facilitates glucose hydrolysis, it does not effectively inhibit the formation of undesirable by-products (levulinic acid, formic acid), potentially leading to a reduction in HMF yield (Dashtban *et al.* 2014; Van-Nguyen *et al.* 2016). The presence of over 5% water by weight in the reaction system can significantly decrease the HMF yield (Qi *et al.* 2009).

Despite being a green option, the aqueous system has not yielded the desired final efficiencies of HMF. This can be ascribed to humin formation, the strong insoluble structure of cellulose, the degradation of HMF into by-products such as levulinic acid or formic acid, and the limited mass transfer between cellulose and heterogeneous catalysts. Additionally, the typical acidic hydrolysis methods applied in the studies have the capacity to withstand high temperatures and pressures (250 to 400 °C, 10 MPa) (Binder and Raines 2009). Although ionic liquids (IL) promote HMF production, these methods are costly and unsuitable for large-scale commercialization. The β -1,4-glycosidic bonds in cellulose are strong and resistant to degradation (Jassim 2013). Therefore, high yields can be obtained at moderate temperatures using concentrated acid instead of dilute acid. However, under acidic conditions ($\text{pH} < 2$), the rehydration of HMF into levulinic and formic acids increases. While both HCl and H_2SO_4 are strong acids, the yield of HMF with H_2SO_4 is approximately twice that obtained with HCl (Steinbach *et al.* 2017). Nonetheless, the formation of by-products such as levulinic acid is unavoidable. Adding catalytic concentrations of inorganic salts, especially chlorides, to the solvent system can further enhance the efficiency of fructose to HMF conversion with lower activation energy (Hou *et al.* 2021). Additionally, transition metals are suitable catalysts for the production of 5-HMF and levulinic acid (LA). Since they can obtain high yields of 5-HMF and LA within a short reaction time, many studies have combined metal salts with ionic liquids (Ramli and Amin 2020).

Therefore, the impact of reaction parameters, such as temperature and pressure, on efficiency should not be overlooked. The yields obtained in the first method are based on the conditions where pre-hydrolysis was carried out for 2 h. The reaction parameters and HMF yields used in the studies are given in Table 1.

HMF Yield in an Ionic Liquid-based Solvent System

The second method was conducted in a solvent system comprising DMA+[EMIM]Cl with either LiCl or NaCl. The process is detailed in the section titled '*Conversion of cellulosic biomass to HMF in an ionic liquid-based solvent system*'. At the conclusion of the process, using CrCl_3 hexahydrate catalyst and the catalytic activity of [EMIM]Cl ionic liquid, HMF yields of (5.74%) 57.48 ± 0.87 mg/g and (3.13%) 31.27 ± 0.65 mg/g were obtained from tea processing waste and hazelnut shells, respectively.

In the study conducted by Binder and Raines (2009), a purified cellulose yielded a 54% HMF efficiency in a solvent containing [EMIM]Cl. However, when the reaction was repeated without the addition of [EMIM]Cl, a reduced efficiency of 33% was reported. In the same study, it was noted that in the absence of CrCl_2 and HCl, the efficiency dropped

to 4%. Therefore, it can be inferred that Lewis acids (*i.e.*, CrCl₂, CrCl₃) and Bronsted acids (*i.e.*, HCl, H₂SO₄) have a positive impact on HMF synthesis (Binder and Raines 2009).

The obtained results exhibited clear differences when compared to those reported in the literature. The underlying cause for this disparity may be attributed to the insufficient temperature employed in the method for cellulose conversion to HMF. Additionally, there is speculation that the DMA-salt system used as a solvent may not exhibit sufficient solubility with cellulose, potentially leading to inadequate HMF production efficiency.

Indeed, the HMF yield is subject to variation and can be adversely affected by process parameters such as catalyst, type of solvent, temperature, duration, pH, and raw material source.

Table 1. Reaction Parameters in HMF Production

	Biomass	Solvent	Additives	Temperature (°C)	Catalyst	Time (h)	HMF Yield (mg/g) ^a	HMF Yield (%)
Method 1	Tea Processing Waste	4% H ₂ SO ₄	NaCl	121	-	1	8.39 ± 0.41	< 1
		4% H ₂ SO ₄	LiCl	121	-	1	10.64 ± 0.55	1.06
		4% H ₂ SO ₄	NaCl	131	-	1	10.15 ± 0.63	1.0
		4% H ₂ SO ₄	LiCl	131	-	1	15.30 ± 0.67	1.54
		4% H ₂ SO ₄	NaCl	131	CrCl ₃	1	82.34 ± 1.42	8.57
		4% H ₂ SO ₄	LiCl	131	CrCl ₃	1	40.72 ± 0.72	4.07
	Hazelnut Shell	4% H ₂ SO ₄	NaCl	121	-	1	6.01 ± 0.33	0.61
		4% H ₂ SO ₄	LiCl	121	-	1	8.72 ± 0.48	0.87
		4% H ₂ SO ₄	NaCl	131	-	1	7.87 ± 0.45	0.80
		4% H ₂ SO ₄	LiCl	131	-	1	14.59 ± 0.61	1.47
		4% H ₂ SO ₄	NaCl	131	CrCl ₃	1	66.70 ± 0.98	6.67
		4% H ₂ SO ₄	LiCl	131	CrCl ₃	1	61.55 ± 0.94	6.16
Method 2	Tea Processing waste	DMA-LiCl	[EMIM]Cl	131	CrCl ₃ ,HCl	2	15.57 ± 0.65	1.56
		DMA-NaCl	[EMIM]Cl	131	CrCl ₃ ,HCl	2	57.48 ± 0.87	5.74
		DMA-LiCl	-	131	CrCl ₃ ,HCl	2	0.35 ± 0.01	< 1
		DMA-LiCl	[EMIM]Cl	131	CrCl ₃ ,HCl	4	5.09 ± 0.21	< 1
	Hazelnut Shell	DMA-LiCl	[EMIM]Cl	131	CrCl ₃ ,HCl	2	6.04 ± 0.12	< 1
		DMA-NaCl	[EMIM]Cl	131	CrCl ₃ ,HCl	2	31.27 ± 065	3.13
		DMA-LiCl	-	131	CrCl ₃ ,HCl	2	0.15 ± 0.02	< 1
		DMA-LiCl	[EMIM]Cl	131	CrCl ₃ ,HCl	4	3.59 ± 0.32	< 1

^aValues are average of triplicate analysis

The purity analysis of the obtained HMF was conducted by comparing it with a ≥ 99% pure HMF standard using an HPLC device. The purity calculation was performed by detecting signals obtained at a wavelength of 285 nm using a UV detector. The calculation, based on the formula provided in the section titled 'HPLC Analysis of HMF' revealed that the obtained HMF demonstrated a purity of ≥ 98.0%.

CONCLUSIONS

1. The conversion of lignocellulosic biomass to 5-(hydroxymethyl)furfural (HMF) was examined by two different methods. In the first method, cellulose derived from hazelnut shells and tea processing waste was converted to HMF with yields of 8.6% and 6.7%, respectively. In the second method, cellulose biomass was converted to

HMF in an ionic liquid-based solvent system, resulting in HMF yields of 5.74% and 3.13% from hazelnut shells and tea processing waste, respectively. These results are quite competitive and promising when compared with some methods reported in the literature.

2. Although the organic solvents and systems used in these studies are effective in certain solvent systems, they have disadvantages such as high flammability, toxicity, and operational costs. Moreover, when organic solvents are used as the medium, the HMF yield tends to be relatively low. Since the selected acidic systems are effective only under specific solvent systems, the reaction rate can be significantly altered by slight modifications in the solvents. Therefore, it is crucial to adjust the solvent system to achieve high HMF yield through isomerization and dehydration. While the obtained results may not meet desired levels, similar outcomes have been reported in the literature, emphasizing the critical need for process improvement.
3. The HMF obtained from both methods was purified using column chromatography to ensure high purity, and its structure was confirmed by Fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR) techniques. The purity assessment indicated that the obtained HMF is of high purity.
4. Research evaluating the economic aspect of the process is still insufficient. Comprehensive process optimization is needed to increase the yield of HMF, considering factors such as temperature, pressure, solvent type, catalyst variety, and raw material.
5. Our study proposes a new application for low-economic-value food wastes such as hazelnut shells and tea residues. Future studies can explore the conversion of these wastes into various platform-value chemicals using different methods and techniques.

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