

Review

Progress in Catalytic Conversion of Renewable Chitin Biomass to Furan-Derived Platform Compounds

Benjing Xu ^{1,2}, Ziting Du ², Jinhang Dai ^{2,*} , Ronghe Yang ², Delong Yang ², Xingxing Gu ², Ning Li ^{2,*} and Fukun Li ^{1,2,*}

¹ Engineering Research Center for Waste Oil Recovery Technology and Equipment of Ministry of Education, Chongqing Technology and Business University, Chongqing 400067, China; huichengxu@163.com

² Key Laboratory of Catalysis Science and Technology of Chongqing Education Commission, School of Environment and Resources, Chongqing Technology and Business University, Chongqing 400067, China; 2021312051@email.ctbu.edu.cn (Z.D.); 2021312046@email.ctbu.edu.cn (R.Y.); 2019124115@email.ctbu.edu.cn (D.Y.); x.gu@ctbu.edu.cn (X.G.)

* Correspondence: jinhangdai@ctbu.edu.cn (J.D.); tdljohn@ctbu.edu.cn (N.L.); lfkok@ctbu.edu.cn (F.L.)

Abstract: Chitin is one of the most abundant biopolymers on Earth but under-utilized. The effective conversion of chitin biomass to useful chemicals is a promising strategy to make full use of chitin. Among chitin-derived compounds, some furan derivatives, typically 5-hydroxymethylfurfural and 3-acetamido-5-acetylfuran, have shown great potential as platform compounds in future industries. In this review, different catalytic systems for the synthesis of nitrogen-free 5-hydroxymethylfurfural and nitrogen-containing 3-acetamido-5-acetylfuran from chitin or its derivatives are summarized comparatively. Some efficient technologies for enhancing chitin biomass conversion have been introduced. Last but not least, future challenges are discussed to enable the production of valuable compounds from chitin biomass via greener processes.

Keywords: biorefinery; chitin; furan; 5-hydroxymethylfurfural; 3-acetamido-5-acetylfuran



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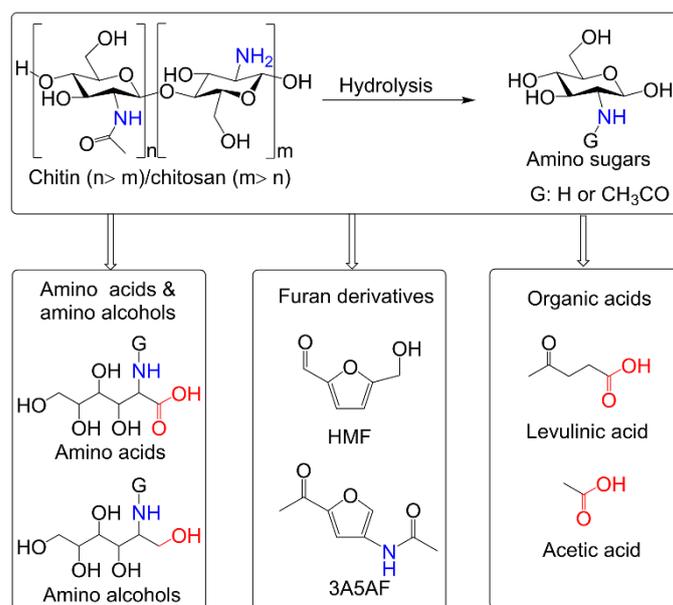
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1. Introduction

The fast consumption of unrenewable fossil resources for the production of bulk chemicals and fuels has led to serious resource and environmental problems, which has attracted more interest in the utilization of renewable resources [1–5]. Due to renewability, abundance, and structure diversity, biomass is regarded as the best candidate to replace fossil resources. Cellulose, chitin, hemicellulose, and lignin are typical biomass resources [6,7]. Among these, chitin is one of the most abundant biopolymers and can be extracted from cheap crustacean shells, exoskeletons of insects, and the cell walls of fungi [8,9]. Similar to cellulosic biomass-based biorefinery, the novel concept of “Shell Biorefinery” was proposed last decade [10,11]. This concept has driven the development in the extraction of major components (typically chitin) from crustacean shells and the transformation of them into useful products. Owing to ca. 7 wt% of bio-fixed nitrogen in chitin, the utilization of chitin or its derivatives provides an alternative method for the preparation of nitrogen-containing chemicals and materials, which is independent of ammonia synthesis by the Haber process.

Chitosan is the deacetylation product of chitin. Nitrogen-containing glucosamine (GlcNH₂) and N-acetylglucosamine (GlcNAc) can be prepared by the hydrolysis of chitin and chitosan, respectively. Some interesting works have been devoted to the catalytic conversion of chitin biomass (mainly referring to chitin-based polymers and monomers) to value-added chemicals, such as 5-hydroxymethylfurfural (HMF), 3-acetamido-5-acetylfuran (3A5AF), 5-(chloromethyl)furfural, levulinic acid, acetic acid, glucosaminic acid, and 2-acetamido-2-deoxysorbitol [12–15], as shown in Scheme 1. Among these, both as furan derivatives, HMF and 3A5AF are typical products of chitin biomass conversion. HMF,

usually obtained from fructose, glucose, and their polysaccharides, is a well-known versatile platform compound and can be converted into building blocks of polymers, liquid fuel additives, pharmaceuticals, and other fine chemicals [16–18]. Compared to HMF that has been extensively investigated, 3A5AF is an emerging platform chemical, which has exhibited the potential to be a substrate for the synthesis of nitrogen-containing fine chemicals [19]. In this review, we focus on the production of furan-derivatives (typically HMF and 3A5AF) from chitin biomass, where different feedstocks and catalytic systems are discussed briefly.



Scheme 1. Some useful chemicals from chitin biomass.

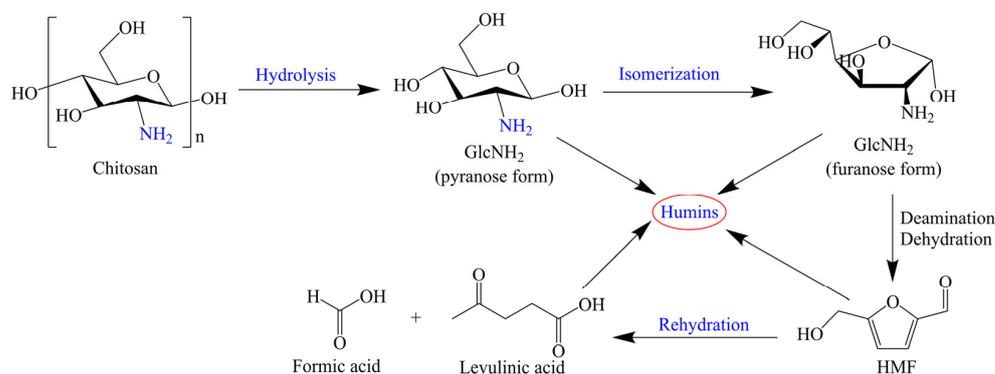
2. Conversion of Chitin Biomass to HMF

2.1. Bronsted Acid as Catalyst

Bronsted acids (i.e., H₂SO₄, HCl) have been widely used in the acid-catalyzed conversion of biomass. They have some advantages, such as low cost and easy production, on a large scale. Jeong [20] studied the hydrothermal transformation of GlcNH₂·HCl by dilute H₂SO₄. The highest HMF yield was about 3.0 mol% at 175 °C for 5 min employing 2 wt% H₂SO₄. Levulinic acid, a rehydration product of HMF, was another main product. With the increase in reaction time, the HMF yield decreased and the levulinic acid yield remarkably increased. After 65 min, a 44 mol% yield of levulinic acid was obtained while HMF was not detectable. Due to the instability of HMF especially in an acidic medium, the catalytic conversion of chitin biomass to HMF need be conducted under relatively mild conditions. Interestingly, Jeong et al. [21] subsequently reported a similar catalytic system to produce HMF from chitosan, the polymer of GlcNH₂, giving the highest HMF yield of 15 mol% at 174 °C for 36.9 min in a 2.2 wt% aqueous H₂SO₄ solution. Both long reaction time and high temperature could enhance the further decomposition of HMF to levulinic acid and formic acid.

In addition to H₂SO₄, Jeong's group has also studied the synthesis of HMF and levulinic acid over other Bronsted acids [22–24]. Sulfamic acid bearing both acidic and basic sites has nonvolatile, odorless, nonhygroscopic, and noncorrodible physical properties. Sulfamic acid could effectively catalyze the sequential hydrolysis of chitosan and the dehydration/deamination of GlcNH₂, giving an HMF yield of 27 mol% at 200 °C for 2 min, while the yield of levulinic acid was only 0.6 mol%. In comparison with the H₂SO₄-catalyzed chitosan conversion, the short reaction time employing sulfamic acid is an advantage. The synergetic effect of Bronsted–Lewis acid sites might contribute to good catalytic performance. A possible reaction pathway of sulfamic acid-catalyzed HMF

production from chitosan has been proposed, as shown in Scheme 2. First, the hydrolysis of chitosan over Bronsted acid sites produces GlcNH₂ bearing an amine group (–NH₂). Then, GlcNH₂ in pyranose form is isomerized to form furanose one. Under the acidic conditions, the amine group in GlcNH₂ is eliminated through a deamination reaction, and the further dehydration and keto-enol tautomerization afford HMF. Under harsh conditions (i.e., strong acidic medium), HMF is remarkably unstable, which reduces the yield of HMF and produces byproducts (i.e., levulinic acid, humins) [22]. Another example using Bronsted acid is methanesulfonic acid [23]. Methanesulfonic acid was effective for the conversion of GlcNH₂ and chitosan, and levulinic acid was the main product in most cases due to the strong acidity of the catalyst. Starting from chitosan (2 wt%), the low methanesulfonic acid concentration (0.1 M) and short reaction time (15 min) at 200 °C gave a 19 mol% yield of HMF (Table 1, entry 4), but the HMF yield significantly decreased to 8.2 mol% with a reaction time of 30 min (Table 1, entry 5).



Scheme 2. Possible reaction pathways of HMF formation from chitosan by sulfamic acid-catalyzed hydrothermal conversion. Adapted with permission from Ref. [22]. Copyright 2018, Wiley.

Table 1. Catalytic conversion of chitin biomass to HMF over Bronsted acid catalysts.

Entry	Substrates	Reaction Conditions	HMF Yield (mol%)	Ref
1	GlcNH ₂ ·HCl	90 g/L substrate, 2 wt% H ₂ SO ₄ , 175 °C, 5 min	3.0	[20]
2	Chitosan	2.2 wt% H ₂ SO ₄ , 174 °C, 36.9 min	15	[21]
3	Chitosan	3 wt% chitosan, 0.7 M sulfamic acid, 200 °C, 2 min	27	[22]
4	Chitosan	2 wt% substrate, 0.1 M methanesulfonic acid, 200 °C, 15 min	19	[23]
5	Chitosan	2 wt% substrate, 0.1 M methanesulfonic acid, 200 °C, 30 min	8.2	[23]
6	GlcNH ₂	100 g/L substrate, 0.1 M methanesulfonic acid, 160 °C, 40 min	2.3	[24]

Some typical results of the Bronsted acid-catalyzed production of HMF from chitin biomass are summarized in Table 1.

2.2. Lewis Acid as Catalyst

A number of Lewis acids have been used for chitin biomass conversion. Omari et al. [25] investigated the catalytic performance of several Lewis acids for the production of HMF and levulinic acid. Some interesting findings have been summarized as follows. Metal salts as Lewis acids consist of anions and cations. The experiment results reveal that both anions and cations have an effect on chitosan conversion and anions play more important roles. Under relatively dilute conditions (100 mg of chitosan, 0.12 mmol of catalyst, and 15 mL of water), the HMF yield was dependent significantly on the anion and followed the trend: CF₃SO₃[−] < ClO₄[−] < Cl[−]. Among these Lewis acids, SnCl₄·5H₂O gave the best results with an HMF yield up to 13 mol%, while no levulinic acid was detected.

Notably, with the increase in $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ concentration to 0.06 M (100 mg of chitosan, 0.24 mmol of catalyst, and 4 mL of water), a 33 mol% yield of levulinic acid with a small amount of HMF (less than 1 mol% yield) was obtained, indicating the significant effect of acid usage on product selectivity. In addition, the application of microwave irradiation as a heating technology enhanced the production of HMF and other compounds. This catalytic system was effective for the conversion of different chitosan materials, including commercial chitosan with different molecular weights, and extracted chitosan from shrimp or crab, giving an 11–13 mol% yield of HMF. Wang et al. [26] studied the conversion of chitin biomass to HMF over a concentrated ZnCl_2 aqueous solution. Owing to the strong interaction of Zn^{2+} with the hydroxyl/amino/acetamide group, the solubility of chitin biomass in concentrated ZnCl_2 aqueous solution was improved. In a 67 wt% ZnCl_2 solution, the HMF yields from GlcNH_2 and Chitosan-1K reached 22 mol% and 10 mol%, respectively. Though HMF could be produced in this medium, the high ZnCl_2 usage (mass ratio of ZnCl_2 /substrate as 20/1) might result in separation difficulty.

In the above-mentioned studies, green and cheap water is the sole solvent. However, the poor stability of HMF in water usually leads to the formation of many unwanted side-products. The addition of an appropriate organic solvent is a good approach to improve HMF selectivity. For example, dimethyl sulfoxide (DMSO) is a typical organic solvent that benefits the production of HMF from carbohydrates (i.e., fructose and glucose) because of its unique features [27]. DMSO is not only a good catalyst for the dehydration of fructose to HMF, but also a solvent that can inhibit some undesirable side-reactions effectively. Yu et al. [28] demonstrated the conversion of chitin biomass to HMF in a DMSO-water mixture over metal salts, affording 27 mol% and 38 mol% yields of HMF over $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ from chitosan-350K and GlcNAc at 180 °C for 5 h, respectively. In addition to DMSO, the combination of water and tetrahydrofuran as a reaction medium also gave an enhanced HMF yield from GlcNAc . This $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ -DMSO-water catalysis system was effective for the conversion of chitin-400K to HMF with a 19 mol% yield. Due to the poor solubility of biopolymers caused by abundant intra- and intermolecular hydrogen bonds, the yields of HMF from chitin and chitosan were lower than that from GlcNAc . In fact, the bad solubility is still a major challenge for the efficient utilization of polysaccharides, including cellulose, chitin, and chitosan [15,29].

Some typical results of the Lewis acid-catalyzed production of HMF from chitin biomass are summarized in Table 2.

Table 2. Catalytic conversion of chitin biomass to HMF over Lewis acid catalysts.

Entry	Substrates	Reaction Conditions	HMF Yield (mol%)	Ref
1	Chitosan with different molecular weight	100 mg chitosan, 42 mg $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 5 mL water, in sealed vessels, under microwave irradiation, 200 °C, 30 min	Ca. 13	[25]
2	GlcNH_2		22	[26]
3	GlcNAc	1 g substrate, 20 g ZnCl_2 , 10 g water, 200 °C, 90 min	2.8	[26]
4	Chitosan-1K		10	[26]
5	GlcNAc	100 mg substrate, 628 mg $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 20 g solvent (4 g DMSO and 16 g water), 180 °C, 5 h	38	[28]
6	$\text{GlcNH}_2 \cdot \text{HCl}$	100 mg substrate, 646 mg $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 20 g solvent (4 g DMSO and 16 g water), 180 °C, 5 h	24	[28]
7	Chitosan-350K		27	[28]
8	Chitosan-1050K	100 mg substrate, 1111 mg $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 20 g solvent (8 g DMSO and 12 g water), 190 °C, 6 h	21	[28]
9	Chitin-400K	100 mg substrate, 881 mg $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 20 g solvent (8 g DMSO and 12 g water), 190 °C, 6 h	19	[28]

2.3. Ionic Liquid as Catalyst

As mentioned earlier, the large number of hydrogen bonds in chitin-based biopolymers lead to difficulties in the dissolution and degradation of chitin and chitosan. Ionic liquids exhibit the ability to cleave hydrogen bonds in polysaccharides and form new hydrogen bonds between anions and the hydroxyl groups of biopolymers, improving the dissolution [30,31].

Several studies from Zang's group have proven the potential of ionic liquids as catalysts for chitin biomass conversion to HMF. Acidic ionic liquids exhibited a better catalytic performance [32]. Among these ionic liquids, N-methyl imidazolium hydrogen sulfate ([MIM]HSO₄) as a catalyst in aqueous medium gave the highest HMF yield of 30 mol% from low-molecular-weight chitosan at 180 °C for 5 h. The protons generated from acidic ionic liquids in water were believed to play a key role in destroying existing hydrogen bonds and forming new ones, which enhanced the hydrolysis of chitosan. Notably, the recovered [MIM]HSO₄ showed no obvious activity loss for chitosan-HMF conversion after five catalytic runs.

The ionic liquid type, solvent, and other reaction parameters have remarkable effects on HMF formation from chitin biomass. Zhang et al. [33] reported that benzimidazolium chloride ([Hbim]Cl) could effectively catalyze the synthesis of HMF from chitosan in water, and the addition of DMSO with a mass ratio of DMSO/water of 1/9 increased the HMF yield from 31 mol% to 35 mol%. The further increase in DMSO/water ratio gave a lower HMF yield, indicating the synergistic effect of DMSO and water in this conversion. In brief, water is beneficial for HMF formation and DMSO suppresses the undesirable conversion of HMF. Zang et al. [34] focused on the degradation of the monomer of chitin, GlcNAc, to HMF. N-methylimidazolium hydrogen sulfate ([Hmim][HSO₄]) exhibited good catalytic performance in a DMSO-water medium, giving a 65 mol% yield of HMF at 180 °C for 6 h. In addition, this catalytic system could catalyze the conversion of GlcNH₂·HCl, chitosan, and chitin to HMF in 55 mol%, 35 mol%, and 26 mol% yields, respectively, and the recycled [Hmim][HSO₄] also exhibited good activity. As ionic liquids have some drawbacks, including high cost, complicated manufactory process, and poor biodegradability, the use of ionic liquids as catalysts instead of solvents is a more practical method in biorefinery.

Some typical results of the ionic liquid-catalyzed production of HMF from chitin biomass are summarized in Table 3.

Table 3. Catalytic conversion of chitin biomass to HMF over ionic liquid catalysts.

Entry	Substrates	Reaction Conditions	HMF Yield (mol%)	Ref
1	Low-molecular-weight chitosan	100 mg substrate, 20 mL water, 4 wt% concentration of [MIM]HSO ₄ aqueous solution, 180 °C, 5 h	30	[32]
2	Chitin		19	[32]
3	Chitosan-350K	100 mg substrate, 2.5 wt% [Hbim]Cl, 20 g water, 180 °C, 3 h	31	[33]
4	Chitosan-350K	100 mg substrate, 2.5 wt% [Hbim]Cl, 18 g water, 2 g DMSO, 180 °C, 3 h	35	[33]
5	GlcNAc		65	[34]
6	GlcNH ₂ ·HCl	100 mg substrate, the molar ratio of [Hmim][HSO ₄] with substrate as 20:1, 12 g water, 8 g DMSO, 180 °C, 6 h	55	[34]
7	Chitosan		35	[34]
8	Chitin		26	[34]

2.4. Other Catalyst Types

In addition to traditional Bronsted acids, Lewis acids, and emerging ionic liquids, there are a few examples of HMF production from chitin biomass using other catalysts or combinations of them. Recently, Islam et al. [35] demonstrated that polyoxometalate as a catalyst could catalyze the conversion of pretreated chitin to HMF in DMSO-water medium. It is well-known that the high crystallinity and poor solubility are two main

challenges for the effective degradation of chitin. Therefore, compared to chitosan, GlcNH₂, and GlcNAc, the use of chitin usually gives a lower HMF yield. Consistent with previous reports [36], the ball milling treatment of the chitin-H₂SO₄ mixture obviously reduced the crystallinity and improved the solubility. The H₂SO₄-assisted ball milling produced a large amount water-soluble products with a total yield of nearly 80%. Overall, the combination of pretreatment and microwave heating technology afforded an enhanced HMF yield of 23 mol% over H₄SiW₁₂O₄₀ at 180 °C for 3 min.

Another interesting example has been reported by Dandekar's group [37]. This investigation employed a combination of homogenous and heterogeneous acid catalysts for the conversion of chitosan to HMF. Solid acids can be easily isolated from the reaction mixture, and it is easier for homogeneous acids to gain access to the glycosidic linkage because of less steric hindrance. Under optimized conditions, the combination of H-β zeolite and dilute acetic acid aqueous solution gave the highest HMF yield of 15 mol% to 28 mol% depending on the molecular weight of the parent chitosan. Acetic acid as a "green" organic acid can be produced from biomass-based feedstock [38,39]. Unfortunately, the obvious activity loss of recovered H-β zeolite was observed, and only half the HMF yield compared to fresh H-β zeolite was obtained. Thus, despite being a promising strategy, the development of stable heterogeneous solid acid catalysts for chitin biomass conversion still needs more effort.

3. Conversion of Chitin Biomass to 3A5AF

The deamination and dehydration of chitin biomass in a water-containing solvent produce HMF as a product employing different acid catalysts. Although some efforts have been devoted to this research topic, in comparison with cellulose-based feedstock (cellulose and its degradation derivatives), the use of chitin, chitosan, and their monomers to produce HMF is not such a good option. First, both the organic nitrogen-containing groups in chitin biomass and NH₃ generated by deamination reaction can interact with acid catalysts, resulting in a loss of catalytic activity. Moreover, organonitrogen compounds are mainly obtained starting from the energy-intensive Haber ammonia synthesis. Therefore, the direct production of organonitrogen compounds by the retention of bio-fixed nitrogen is an attractive strategy for chitin biomass valorization. Under some reaction conditions, the dehydration of GlcNAc with the retention of nitrogen element gives another furan-derivative 3A5AF. As an emerging biochemical with high reactivity, 3A5AF can be converted into a number of value-added compounds, as shown in Scheme 3. For example, Sadiq et al. [40] demonstrated the total synthesis of anticancer alkaloid proximicin A starting from 3A5AF. Compared to previous methods [41,42], safer reagents, reactants, and mediums were used, and biorenewable nitrogen in 3A5AF was transferred to a biologically active alkaloid. In fact, it is difficult to install a nitrogen substituent at the C3 position of the furan heterocycle, and 3A5AF with its special structure is a promising precursor for the synthesis of many useful 3-amidofurans [43,44]. Recently, the catalytic conversion of GlcNAc and chitin toward 3A5AF has attracted increasing attention.

3.1. GlcNAc as Reactant

The selective removal of three water molecules from GlcNAc produces 3A5AF, which is similar to the dehydration of glucose to HMF [45]. Franich et al. [46] investigated the direct pyrolysis of GlcNAc in vacuo, and a 2% isolated yield of 3A5AF with 5% 3-acetamidofuran was obtained. This is a simple method to produce 3A5AF, but the selectivity is unsatisfactory.

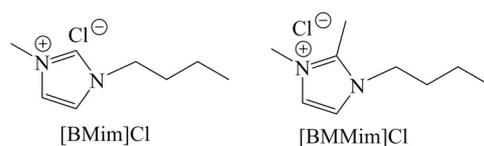
chloride could be recycled and exhibited stable catalytic performance, with the 3A5AF yield slightly decreasing from 43 mol% (1st run) to 37 mol% (8th run). This work used renewable and nontoxic amino acids as precursors to prepare recyclable catalysts, which is highly attractive. Subsequently, more ionic liquids have been reported for this reaction, and the 3A5AF yield reached 70 mol% in DMA using pyrazine hydrochloride ionic liquid and additives ($B(OH)_3$ and $CaCl_2$) [51].

Because of unique characteristics, ionic liquids can act as both solvent and catalyst. Drover et al. [54] demonstrated the direct conversion of GlcNAc to 3A5AF in ionic liquids, giving 34 mol% and 33 mol% yields of 3A5AF in 1-butyl-3-methylimidazolium chloride ([BMim]Cl) and 1,2-dimethyl-3-butylimidazolium chloride [BMMim]Cl, respectively, in the absence of any other catalysts or additives (Table 4, entry 7–8). The structures of [BMim]Cl and [BMMim]Cl are shown as Scheme 4. The anion of ionic liquid has a significant effect on 3A5AF selectivity, where a chloride counterion was found necessary to form 3A5AF compared to bromide and acetate. Due to the advantages of microwave heating, the reaction time was short as 3 min. The addition of 10 mol% $B(OH)_3$ in [BMim]Cl and the use of oil bath heating gave a 79 mol% yield of 3A5AF for 60 min. Considering the cost and high viscosity, the use of ionic liquid as a medium is uneconomic and difficult to operate.

Table 4. Catalytic conversion of GlcNAc to 3A5AF.

Entry	Catalyst and Additive	Solvent	Reaction Conditions	3A5AF Yield (mol%)	Ref
1	100 mol% $B(OH)_3$, 200 mol% NaCl	DMA	MW ¹ , 220 °C, 15 min	77	[47]
2	100 mol% $AlCl_3 \cdot 6H_2O$	DMF	CH ² , 120 °C, 30 min	30	[48]
3	200 mol% NH_4Cl , 400 mol% LiCl	DMF	CH ² , 160 °C, 5 min	43	[49]
4	glycine chloride (100 wt%)	DMA	CH ² , 200 °C, 10 min	43	[50]
5	glycine chloride (100 wt%), $CaCl_2$ (100 wt%)	DMA	CH ² , 200 °C, 10 min	53	[50]
6	200 mol% pyrazine hydrochloride, 100 mol% $B(OH)_3$, 100 mol% $CaCl_2$	DMA	CH ² , 190 °C, 60 min	70	[51]
7	None	[BMim]Cl	MW ¹ , 180 °C, 3 min	34	[54]
8	Non	[BMMim]Cl	MW ¹ , 180 °C, 3 min	33	[54]
9	200 mol% $B(OH)_3$	[Bmim]Cl	CH ² , 180 °C, 60 min	79	[54]

¹ Microwave heating; ² Conventional heating.



Scheme 4. Two typical ionic liquids for 3A5AF synthesis.

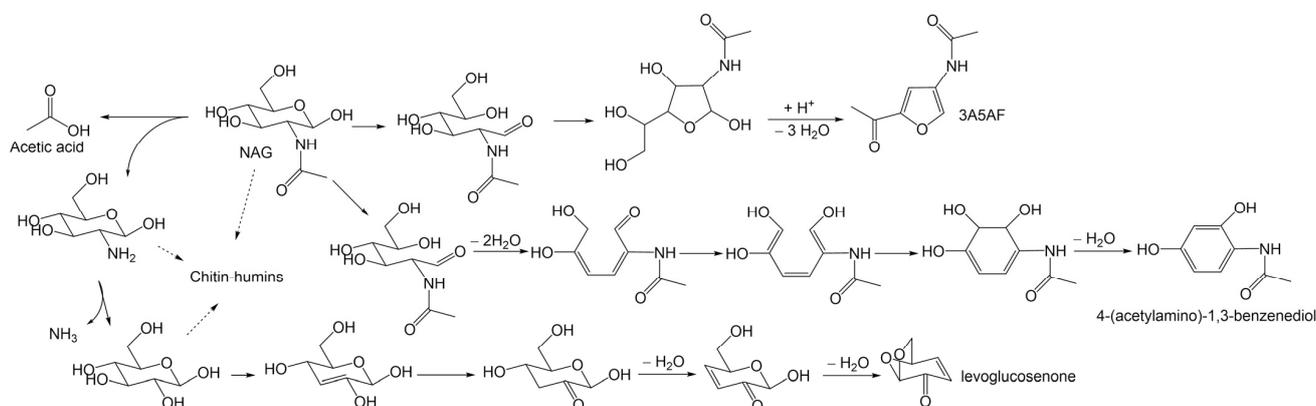
Some typical results of GlcNAc conversion to 3A5AF are summarized in Table 4.

3.2. Chitin as Reactant

As discussed in Section 3.1, a considerable 3A5AF yield has been obtained from GlcNAc. However, the selective production of GlcNAc from chitin is still challenging, which requires the cleavage of the glucosidic bond and retention of the acetamido group [55]. Therefore, the selective production of 3A5AF from chitin can avoid the purification of intermediate GlcNAc, which is desired but difficult. Limited efforts have been devoted to this topic.

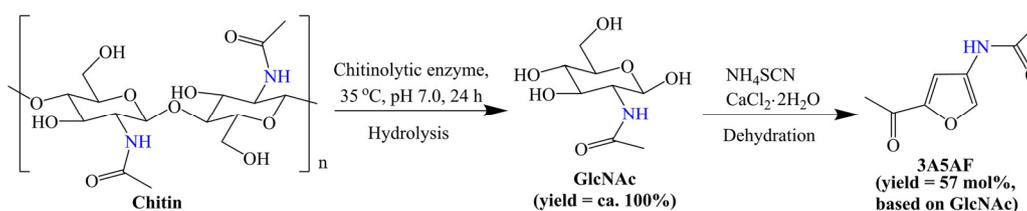
Chen et al. [56] explored the preparation of 3A5AF from chitin in a “one-pot, one-step” process, affording a ca. 8 mol% yield of 3A5AF with 50% conversion in NMP at 215 °C for 2 h. The use of chitin as a substrate required harsh conditions, such as a larger usage of $B(OH)_3$ and NaCl, higher reaction temperature, and longer reaction time, but produced

less 3A5AF and a large amount of side-products, such as levoglucosone, 4-(acetylamino)-1,3-benzenediol, acetic acid, and chitin-humins. A proposed reaction network is shown as Scheme 5. Notably, the degradation of the crystalline region in chitin was found to be the rate-determining step, which was supported by kinetic study results and provided a clue to promote chitin conversion.



Scheme 5. Proposed reaction pathways for the conversion of chitin to identified products. Adapted from Ref. [56], copyright Royal Society of Chemistry.

Some methods have been used to destroy the crystalline structure of chitin, which facilitates the further conversion of chitin to small-molecule products. As mentioned earlier, some ionic liquids can promote the dissolution of biopolymers. Chen et al. [57] investigated 3A5AF synthesis from chitin in a range of ionic liquids. Notably, the Cl^- in the ionic liquids not only promoted the dissolution of chitin, but also participated in the degradation of it. After optimization, a ca. 7 mol% yield of 3A5AF, which is comparable to that in NMP, was obtained in the presence of $\text{B}(\text{OH})_3$ and HCl under milder conditions [56,57]. In addition to the use of special solvents, the pretreatment of chitin is another useful method. The same group [58] found that ball mill treatment without additives was beneficial to the destruction of the hydrogen-bond network and crystalline region, which significantly enhanced the reactivity of chitin and gave a 29 mol% yield of 3A5AF in $[\text{BMIm}]\text{Cl}$. Very recently, Chen et al. [59] demonstrated a novel chemo-enzymatic protocol for the transformation of chitin to 3A5AF, as shown in Scheme 6. Unlike previous investigations [56–58], chitin was nearly 100% converted into GlcNAc over the recyclable chitinolytic enzyme. The produced GlcNAc was separated and used as a substrate for 3A5AF synthesis in organic solvents. A new finding is that both ammonium thiocyanate (NH_4SCN) and thiourea ($\text{CH}_2\text{N}_2\text{S}$) were effective for the dehydration of GlcNAc to 3A5AF, and a 57 mol% yield of 3A5AF was obtained in DMA over NH_4SCN with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ as an additive. Unfortunately, the recovered enzyme and NH_4SCN exhibited decreasing catalytic performance. This protocol provides a step-wise conversion of chitin over enzymes and inorganic catalysts, giving an enhanced overall yield of 3A5AF. In addition, the recyclability of catalysts was also considered, which pushes the effective and green production of 3A5AF from chitin.



Scheme 6. Step-wise conversion of chitin to 3A5AF. Adapted with permission from Ref. [59]. Copyright 2021, copyright Elsevier.

4. Conclusions and Perspectives

4.1. Conclusions

Chitin is an abundant nitrogen-containing polysaccharide. The effective transformation of chitin and its derivatives (i.e., chitosan, GlcNAc, and GlcNH₂) to valuable chemicals has become an emerging research topic. Among chitin-derived compounds, two typical furan-derivatives, including HMF and 3A5AF, have attracted the most attention.

HMF is a nitrogen-free platform compound that is widely obtained by the dehydration of C₆ carbohydrates and their oligosaccharides/polysaccharides. Chitin biomass has also been converted into HMF and its downstream products. Different acid catalysts, such as Bronsted acids, Lewis acids, acidic ionic liquids, heteropolyacids, and the combination of solid acid and homogeneous acids, have been used for HMF production. Moderate HMF yields (up to 66 mol% and 55 mol%) have been obtained from GlcNAc and GlcNH₂·HCl, respectively. In contrast, the use of biopolymers (chitin and chitosan) usually gives lower HMF yields (lower than 40 mol%), which can be explained by the difficulties in dissolution and hydrolysis of these biopolymers. The special structure characteristics, mainly including high crystallization and abundant hydrogen bonds, should be the reasons for worse selectivity. Limited examples using heterogeneous catalysts have been reported, but the catalytic performance and stability are still unsatisfactory.

Compared to the synthesis of HMF, the production of 3A5AF from chitin biomass is a more interesting option because of its organonitrogen group. A few efforts have been devoted to 3A5AF production from GlcNAc. The selectivity of 3A5AF is highly dependent on the reaction medium. Some polar aprotic organic solvents (i.e., DMA, DMF, and NMP) and ionic liquids bearing Cl[−] are favorable choices, while the addition of a small amount of water decreases the 3A5AF yield remarkably. Chlorine-containing metal salts/ionic liquids and B(OH)₃ as catalysts/additives are beneficial to the formation of 3A5AF. A ca. 80 mol% yield of 3A5AF has been obtained in DMA or [BMim]Cl. The conversion of chitin is a more promising strategy, which can avoid the isolation of GlcNAc. However, a larger amount of catalysts/additives and harsher conditions are usually required. The use of appropriate solvents (typically chlorine-containing ionic liquids) can enhance the dissolution and degradation, resulting in chitin conversion under milder conditions. In addition, the pretreatment of chitin by mechanical force can destroy the regular crystal region in chitin and increase the reactivity. A step-wise conversion of chitin to 3A5AF is an effective method to enhance the overall yield, and biocatalysis has shown its advantages such as high efficiency, mild conditions, and relative stability.

In comparison to cellulose, the investigations on the catalytic conversion of chitin biomass to value-added furan derivatives are still not sufficient. Particularly, the direct utilization of biopolymers encounters a number of challenges, and many catalytic systems do not meet the principles of green chemistry. Hence, many more efforts need be devoted to this area.

4.2. Perspectives

Based on our knowledge, we provide some research suggestions as follows. (1) The selective depolymerization of chitin/chitosan to monomers is a crucial step to produce valuable chemicals with low molecular weight. Some new technologies, such as biocatalysis, pretreatment (i.e., ball mill grinding), and microwave heating, might be potential methods for the effective dissolution/degradation of chitin and chitosan. (2) Novel, green, and efficient catalytic systems are still lacking. Both catalytic performance and environmental impact should be considered. The recyclability of catalysts/additives/solvents and the isolation of products need be further investigated. (3) There are few insightful studies on the reaction mechanism, which limits the deep understanding of the investigated reactions. (4) Compared to the synthesis of HMF-based products, the production of nitrogen-containing 3A5AF and its derivatives is of more significance, which makes full use of bio-fixed nitrogen in chitin biomass.

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