Journal of Molecular Liquids 330 (2021) 115667

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Short Communication

Valorization of chitin derived *N*-acetyl-D-glucosamine into high valuable N-containing 3-acetamido-5-acetylfuran using pyridinium-based ionic liquids

Hongjun Zang *, Jing Lou, Shuolei Jiao, Huanxin Li, Yannan Du, Jiao Wang

State Key Laboratory of Hollow Fiber Membrane Materials and Processes, School of Chemistry and Chemical Engineering, Tiangong University, Binshuixi Road, Tianjin 300387, China.

ARTICLE INFO

Article history:
Received 9 December 2020
Received in revised form 6 February 2021
Accepted 12 February 2021
Available online 16 February 2021

Keywords:
Chitin
NAG
3-acetamido-5-acetylfuran
Pyridinium-based ionic liquid

ABSTRACT

Chitin and its derivatives contain biologically fixed nitrogen elements, which can provide nitrogen sources for N-containing chemicals. Herein, a series of pyridinium-based ionic liquids were synthesized to directly catalyze the conversion of *N*-acetyl-D-glucosamine (NAG, the monomer of chitin) to 3-acetamido-5-acetylfuran (3A5AF). The yield of 3A5AF in 1-carboxymethyl pyridinium chloride ionic liquid reached 37.49%, without any additives. Using B_2O_3 and $CaCl_2$ as additives, the optimum yield increased to 67.37% at 180 °C in 20 min. In addition, HPLC-MS analysis has been utilized to elucidate the reaction mechanism. This research on turning “waste” into “wealth” opens up new ways for the utilization of biomass waste, which not only reduces environmental pollution but also has potential economic value.

1. Introduction

Since the shortage of non-renewable fossil fuels, many efforts are being made to find renewable alternative energy. Biomass, which is called as “the fourth largest energy source” in the industry other than coal, oil and natural gas, because it is abundant, renewable and widely distributed in nature. Conversion of biomass into value-added platform chemicals has become an important research area, as a way to alleviate the energy crisis [1]. Currently, the utilization of biomass is mainly concentrated on woody biomass, such as lignin and cellulose [2]. However, limited attention has been paid to ocean-based biomass [3].

Chitin, a classic example of ocean-based biomass, is the second-largest abundant biomass in the world after cellulose, with a global annual output of about 100 billion tons [4]. Research on the conversion of chitin biomass was still in its infancy until the concept of “shell biorefinery” was proposed [5]. One of the main reasons why chitin is worthy of attention is that its composition contains 7 wt% of biologically-fixed nitrogen [6]. It thus represents a potential raw material for the production of N-containing chemicals which cannot be obtained from lignocellulosic biomass. The industrial mass production of chitin is carried out by extracting shellfish wastes from the fishing industry [7], such as shrimp and crab shells. Therefore, the conversion of chitin biomass into valuable chemicals instead of pouring them into landfills and oceans, not only reduces environmental pollution but also brings economic benefits.

There have been some studies on the conversion of chitin and its derivatives to platform compounds, such as 3-acetamido-5-acetylfuran (3A5AF) [8–10], 5-hydroxymethylfurfural (HMF) [11–14], levulinic acid (LA) [14–16], pyrrole [17] and so on. 3A5AF is a potential N-containing platform compound, which can be used to prepare a series of high value-added downstream products. For instance, the alkaloids hyrtioseragamine A and B, pyrrolosine and the anticancer agent proximicin A all contain 3A5AF fragments [6,18]. However, 3A5AF is usually challenging to synthesize by conventional methods due to its special molecular structure. Therefore, obtaining 3A5AF by direct conversion from chitin and its derivatives is simpler and faster, which can further simplify the synthesis steps of a series of bioactive molecules.

In 1984, Franich et al. [19] obtained 3A5AF for the first time by degrading NAG under high temperature, though the yield was only 2%. The pyrolysis reaction at high temperature is complicated, with many by-products, poor selectivity and high energy consumption, which limits its research and application. Until 2012, Drover et al. [8] found that [BMim]Cl ionic liquid can effectively catalyze the conversion of NAG to 3A5AF, and the yield of 3A5AF can reach 25% under microwave heating. More surprisingly, the addition of $B(OH)_3$ increased the yield to more than 60%. At the same time, Omari et al. [9] reported that with dimethylacetamide (DMA) as the solvent, the presence of NaCl and $B(OH)_3$ can catalyze the conversion of NAG to 3A5AF with a yield of 58.0% under microwave irradiation. Chen et al. [3] found that in the presence of [BMim]Cl, $B(OH)_3$ and HCl, the yield of 3A5AF can

---

* Corresponding author.
E-mail address: chemhong@126.com (H. Zang).

https://doi.org/10.1016/j.molliq.2021.115667

reach 55.6% at a lower temperature (180 °C) under microwave condition. The above studies showed that boron and chlorine play a critical role in the formation of 3A5AF. However, the reaction conditions of the above experiments were relatively harsh. Although higher yields were obtained under the microwave, those reaction conditions cannot be widely used in industrial production. As a monomer of chitin, NAG is relatively easy to convert into 3A5AF. However, there is still much room for improvement in the yield of 3A5AF.

In our laboratory's previous work, Wang et al. [20] used amino acid ILs as catalysts to efficiently convert NAG into 3A5AF. The reaction was heated at 180 °C in an oil bath to replace the microwave reactor, and the yield of 3A5AF reached 52.61% in 10 min. Moreover, substituting microwave conditions may increase the possibility of industrial application.

There have been some reports using ionic liquids (ILs) as solvents or catalysts in biomass conversion [21–23]. The use of ILs conforms to the trend of environmentally friendly catalytic systems. However, most of them are currently only in the laboratory stage, and there is almost no industrialization report. Besides, the types of ILs used in this field are relatively single, and it is highly desired to explore new catalytic systems.

Pyridinium salts are important scaffolds for many natural and biologically active products, which have a wide range of applications. Pyridinium salts that are liquids at room temperature are called pyridinium-based ILs (PyILs) [24]. Chinnappan et al. [25] observed that compared with imidazolium-based ILs, PyILs had better catalytic performance in organic conversion reactions. Subsequently, they used pyridyl double cationic IL to catalyze the conversion of fructose to HMF, and the yield reached 95% [26]. Taheri et al. [27] used PyIL/water mixture to effectively dissolve cellulose, chitin and chitosan. Naz et al. [28] used PyIL-metal salt system to effectively deconstruct lignocellulose and convert it into reducing sugars. Based on the above researches, we applied PyILs to the conversion of chitin biomass.

In this paper, we used a series of PyILs as catalysts to convert NAG to 3A5AF. Besides, we screened the effects of solvents and additives, and optimized the amount of PyIL, reaction temperature and reaction time. Under the optimal conditions, the yield of 3A5AF reached 67.37%. The possible reaction process of converting NAG to 3A5AF was tested by HPLC-MS.

2. Materials and methods

2.1. Materials

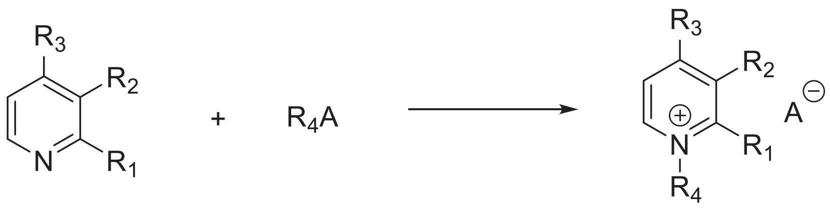
N-acetyl-D-glucosamine (NAG) and chitin were purchased from Shanghai Aladdin Reagent Co., Ltd. (Shanghai, China). Methyl-2-pyrrolidone (NMP) and Dimethyl sulfoxide (DMSO) were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). *N*, *N*-Dimethylacetamide (DMA) and *N*, *N*-Dimethylformamide (DMF) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Methanol (HPLC grade) was purchased from Tianjin Kangkede Technology Co., Ltd. (Tianjin, China). Ethanol absolute was purchased from Tianjin Huihang Chemical Technology Co., Ltd. (Tianjin, China). Boric acid and all Lewis acids were purchased from Tianjin Sailboat Chemical Reagent Technology Co., Ltd. (Tianjin, China). Acetonitrile (HPLC grade) was purchased from Tianjin Saifu Century Technology Development Co., Ltd. (Tianjin, China). Boron oxide and nicotinamide were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Pyridine was purchased from Tianjin Rgent Chemical Co., Ltd. (Tianjin, China). Monochloroacetic acid, 2-Hydroxypyridine, 4-Aminopyridine, 4-Dimethylaminopyridine, 2-Methypyridinel were purchased from Tianjin Heowns Biochemical Technology Co., Ltd. (Tianjin, China). All the chemicals were used as received.

2.2. Synthesis of pyridinium-based ionic liquids

Synthesis of pyridinium-based ILs according to the method reported in the literature [27] and developed in the experiment. For instance, the synthesis steps of 1-carboxymethyl pyridinium chloride ([CMPy]Cl) IL are as follows. Equimolar monochloro acetic acid and pyridine were mixed in ethanol, and the mixture was stirred for 1.5 h in an ice bath. After 1.5 h, the mixture was transferred to an oil bath at 80 °C, stirred and refluxed for 60 min. Then, the yellowish precipitate was formed, indicating that the structure of the ionic liquid has been synthesized. At last, the precipitate was recrystallized in ethanol. The product was dried under vacuum at 80 °C for 12 h to obtain the [CMPy]Cl.

The [CMPy]Cl was characterized by ^{1}H Nuclear Magnetic Resonance (^{1}H NMR) spectroscopy (400 M, Bruker, Germany) and Fourier transform infrared (FTIR) spectroscopy (vertex80, Bruker, Germany). The characterization results are consistent with those reported in the literature [29], proving that the [CMPy]Cl was successfully synthesized.

Other pyridinium-based ionic liquids were prepared in a similar manner, using pyridine ring with different substituents to react with monochloro acetic acid. As shown in Scheme 1, including 1-carboxymethyl-2-methyl pyridinium chloride ([CMMPy]Cl), 1-carboxymethyl-4-amino pyridinium chloride ([CMAPy]Cl), 1-carboxymethyl-4-dimethylamino pyridinium chloride ([CMDAPy]Cl), 1-carboxymethyl-3-formamido pyridinium chloride ([CMFPy]Cl), 1-carboxymethyl-2-oxhydryl pyridinium chloride ([CMOPy]Cl), pyridinium chloride ([Py]Cl), and pyridinium



$R_1 = CH_3$, OH

$R_2 = CONH_2$

$R_3 = NH_2 , N(CH_3)_2$

$R_4 = H , CH_2COOH$

$A = Cl, HSO_4$

Scheme 1. Synthesis of PyILs.

hydrogen sulfate ([Py]HSO_4). The characterization results are listed in the supplementary information.

2.3. Conversion of NAG to 3A5AF

In a typical reaction, NAG, PyIL, additives and solvent were mixed in a round bottom flask, and then the mixture was stirred in an oil bath at a certain temperature for a certain time. When the reaction was over, the mixture was immediately moved to an ice water bath to cool down, then diluted with 50% methanol aqueous solution. In order to remove solid residues, the solution was filtered through a 0.22 μm PTFE filter. The sample solution was determined by High Performance Liquid Chromatography (HPLC). Three parallel experiments were conducted to calculate the average yield of 3A5AF.

2.4. Determination of the products

HPLC was used for quantitative analysis of 3A5AF. HPLC instrument (LC3000, Beijing Chuangxin Tongheng Science and Technology Co., Ltd.) with a Kromasil C18 reversed phase column (5 μm, 250 mm × 4.6 mm) and the temperature of the column was maintained at 30 °C. The UV detector wavelength was set to 230 nm. The mobile phase consisted of methanol and water (40/60 *v*/v) with a flow rate of 0.5 mL/min, and the sample injection volume was 20 μL. The peak of 3A5AF as the main product in the HPLC spectrum appeared at 17 min. The concentration of 3A5AF was quantified by a standard curve obtained with a standard substance of known concentration. The standard curve was $Y = 405{,}943\times + 260{,}422$, ($R^2 = 0.9998$), where Y was the peak area data detected by HPLC analysis, and X was the concentration of 3A5AF in the sample.

High Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS, Xveo G2Q-Tof, Waters, America) can explore the reaction mechanism by analyzing the intermediate products produced in each reaction stage.

3. Results and discussion

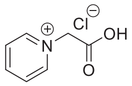
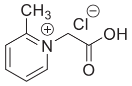
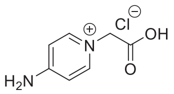
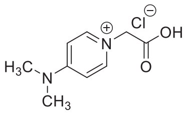
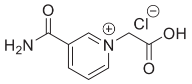
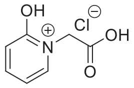
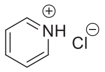
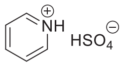
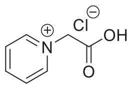
3.1. Catalyst and solvent screening

We screened the catalytic effects of eight different cations and anions PyILs. At the beginning of this study, NMP was used as the solvent. 100 mg NAG, 100 mg PyIL and 10 mL NMP were mixed, and the mixture was stirred in an oil bath at 180 °C under atmospheric reflux for one hour. Under the same experimental conditions as above, the results of 3A5AF yield that obtained from this reaction using different PyILs are listed in Table 1.

The best performance was obtained in the presence of [CMPy]Cl, and the yield of 3A5AF reached 37.49% (entry 1). The anions in ionic liquids are critical to the reaction, especially the chloride ions [6]. Compared with other ILs containing chloride ions, the IL containing HSO_4^- anion obtained lower yield, only 6.36% (entry 8). In addition, by comparing [CMPy]Cl and [Py]Cl, we can find that the carboxyl linked to the nitrogen atom in pyridine greatly improved the catalytic effect (entries 1 and 7). The use of pyridine as a cation has achieved a significant catalytic effect. Unfortunately, the different substituents on the pyridine ring did not significantly promote the reaction (entries 2–6). Besides, we measured the pH value of the PyILs. All of them have strong acidity and [CMPy]Cl has the strongest acidity, indicating that the acidic environment is conducive to NAG conversion. However, when using [CMPy]Cl to degrade chitin, the yield was only 1.21% (entry 9). Due to its high degree of polymerization, chitin is more difficult to degrade than NAG.

The four solvents selected include DMA, DMF, DMSO and NMP, which have been reported to be frequently used for sugar dehydration [30–34] and chitin dehydration [10]. NAG and PyIL were dispersed in

Table 1
Effect of different PyILs on the conversion of NAG into 3A5AF under normal atmospheric reflux conditions.

Entry	Catalyst	Substrate	pH value of PyILs	3A5AF yield (mol %)
1		NAG	1.17	37.49
2		NAG	1.38	27.66
3		NAG	2.86	34.07
4		NAG	1.82	34.45
5		NAG	1.62	13.23
6		NAG	2.01	14.18
7		NAG	2.50	17.45
8		NAG	1.31	6.36
9		chitin	1.17	1.21

Experimental conditions: Substrate, 100 mg; PyIL, 100 mg; NMP, 10 mL; temperature, 180 °C; reaction time, 60 min.

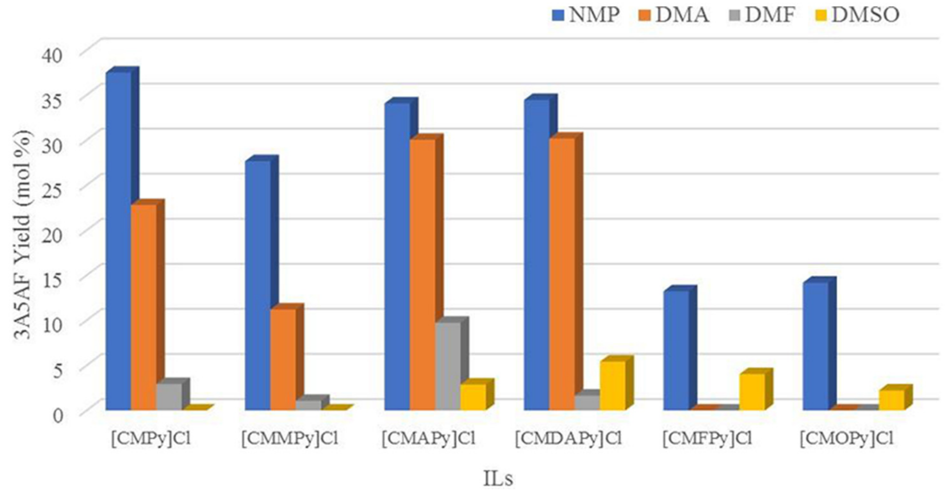
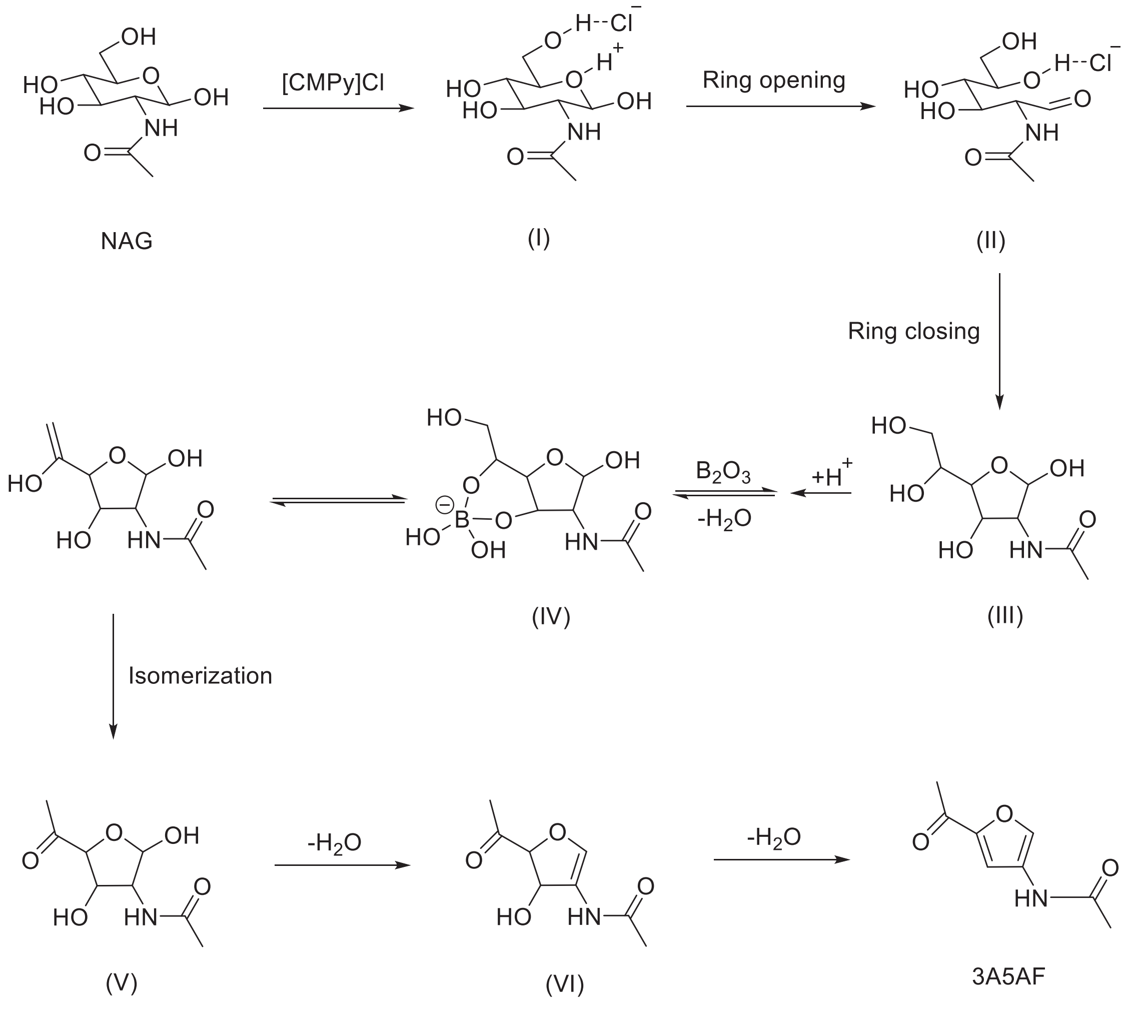


Fig. 1. Effect of PyILs in different solvents on 3A5AF production under normal atmospheric reflux conditions. Reaction conditions: NAG, 100 mg; PyIL, 100 mg; solvent, 10 mL; reaction temperature, 180 °C; reaction time, 60 min.

these four solvents at 180 °C for one hour, and the results are shown in Fig. 1. From above DMA and NMP are all suitable solvents for NAG conversion, but NMP appears to be most effective. Chen et al. [10] proposed that DMA and DMF were the best solvents for NAG dehydration, while NMP was the best solvent for chitin dehydration. It is speculated that the reason may be related to the structural difference between chitin



Scheme 2. Possible reaction pathways.

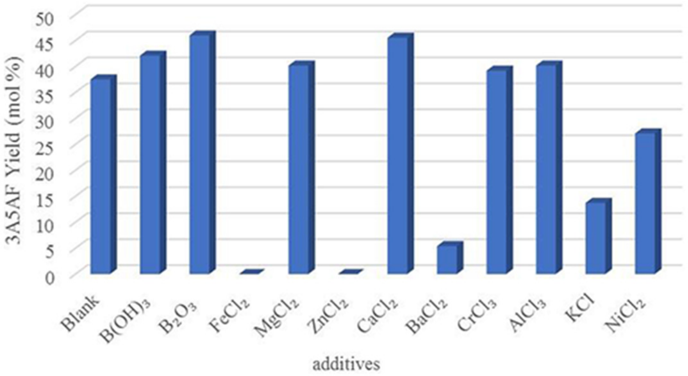


Fig. 2. Single additive screening for NAG conversion into 3A5AF under normal atmospheric reflux conditions. Reaction conditions: NAG, 100 mg; [CMPy]Cl, 100 mg; additive, 100 mg; NMP, 10 mL; reaction temperature, 180 °C; reaction time, 60 min.

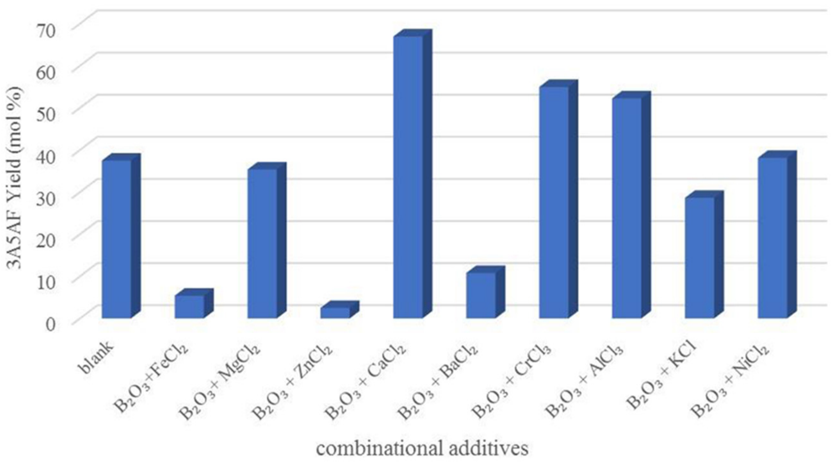


Fig. 3. Combinational additives screening for NAG conversion into 3A5AF under normal atmospheric reflux conditions. Reaction conditions: NAG, 100 mg; [CMPy]Cl, 100 mg; B_2O_3, 100 mg; Lewis acid, 100 mg; NMP, 10 mL; reaction temperature, 180 °C; reaction time, 60 min.

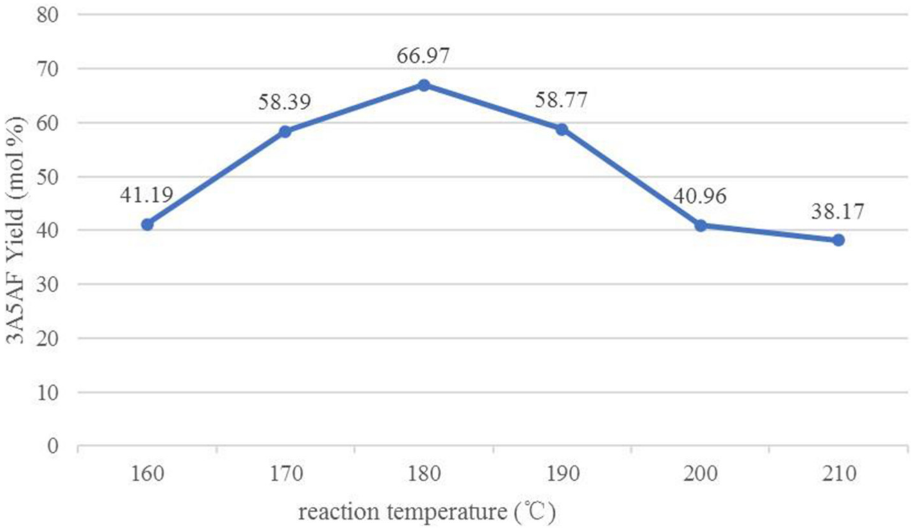


Fig. 4. Effect of reaction temperature on 3A5AF production under normal atmospheric reflux conditions. Reaction conditions: NAG, 100 mg; [CMPy]Cl, 100 mg; B_2O_3, 100 mg; $CaCl_2$, 100 mg; NMP, 10 mL; reaction time, 60 min; reaction temperature 160–210 °C.

and NAG. The molecular size of DMA and DMF is relatively small, which is more conducive to the solute-solvent interaction in NAG conversion. Obviously, this conclusion is inconsistent with the results of our solvent screening. However, the solvent effect is a complex problem affected by many factors, among which the interaction between solvent and catalyst is the most important factor, and the catalytic performance is

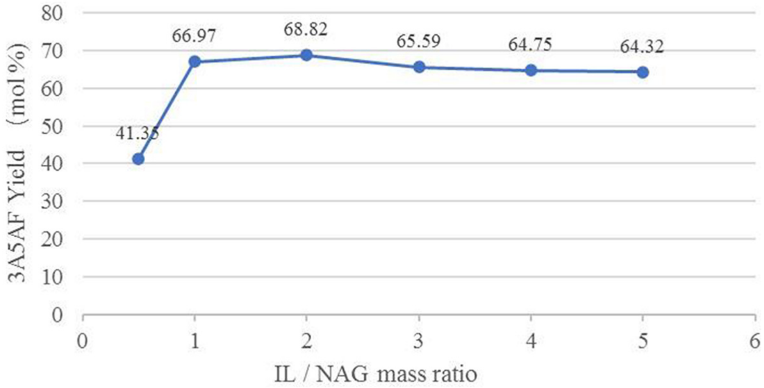


Fig. 5. Effect of the IL/NAG mass ratio on 3A5AF production under normal atmospheric reflux conditions. Reaction conditions: NAG, 100 mg; [CMPy]Cl, 50 mg ~ 500 mg; B_2O_3, 100 mg; $CaCl_2$, 100 mg; NMP, 10 mL; reaction temperature, 180 °C; reaction time, 60 min.

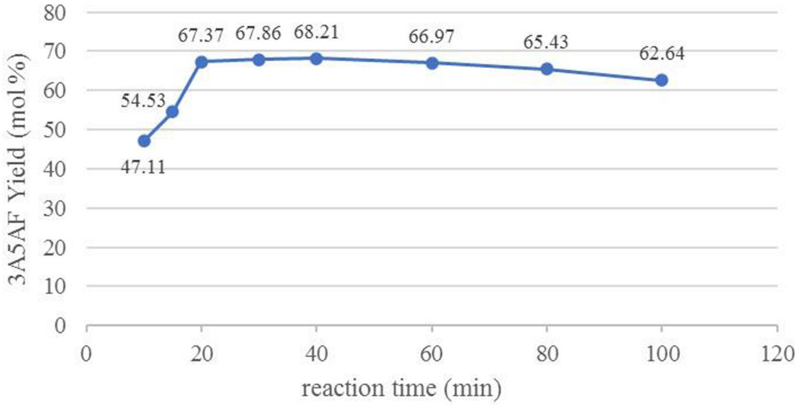


Fig. 6. Effect of reaction time on 3A5AF production under normal atmospheric reflux conditions. Reaction conditions: NAG, 100 mg; [CMPy]Cl, 100 mg; B_2O_3, 100 mg; $CaCl_2$, 100 mg; NMP, 10 mL; reaction temperature, 180 °C; reaction time, 10 min ~ 100 min.

strongly influenced by solvent effects [35]. Therefore, we consider that it is due to the stronger interaction between NMP and PyILs, not just judged by the interaction between the substrate and the solvent. On the other hand, Pumrod et al. [36] found that NMP can promote the isomerization of fructose to fructofuranose, thereby promoting the formation of HMF. The conversion process in this work also has an isomerization process (see Scheme 2), so NMP may have a good effect by promoting molecular isomerization. In addition, NMP can also be used as an aqueous phase to prevent humin formation and reduce the formation of other by-products [36]. From the standpoint of solvent effects, we hypothesize that the synergistic effect between solvent molecular and PyILs could result in a higher yield of 3A5AF.

3.2. Additives screening

[CMPy]Cl was selected as the catalyst in the following experiments because it had the highest yield in the above experiment. Herein, additives were screened to increase the target product yield. The following experiments explored single additives and additive combinations.

3.2.1. Single additive screening

Boron-based compounds have the advantages of non-corrosion, non-toxic, non-metal, good biocompatibility, cheap and easy to obtain, so they have a large space for utilization in biomass conversion. Chen et al. [10] found that $B(OH)_3$ can effectively promote the degradation of chitin to produce 3A5AF, chitin and $B(OH)_3$ can form a boron complex to promote the formation of 3A5AF. Lewis acids are often used to catalyze the preparation of 3A5AF from chitin biomass and show certain catalytic performance [3,10]. Therefore, we used boron-based compounds and Lewis acids as additives, and the results are shown in Fig. 2.

Among them, the catalytic effects of B_2O_3 and $B(OH)_3$ were equivalent, and both increase the yield of 3A5AF to a certain extent. We infer that B_2O_3 can react with trace water in the reaction system (from the solvent or water produced by the dehydration of NAG) to form $B(OH)_3$. Hence, the catalytic effects of B_2O_3 and $B(OH)_3$ were almost equivalent.

Among a series of Lewis acids, $CaCl_2$ gave the highest 3A5AF yield. Similarly, the presence of $MgCl_2$, $AlCl_3$ and $CrCl_3$ also slightly increased the yield. However, $BaCl_2$, $ZnCl_2$, $NiCl_2$, KCl and $FeCl_2$ had a negative effect on the reaction.

The reason, first of all, from the perspective of Lewis acid's promoting effect, it is mainly divided into two aspects. Above all, Lewis acid can promote some isomerization reactions [37,38], so it is likely to promote the enol isomerization process of this reaction. Secondly, Lewis acid can play a strong dehydration effect. However, while accelerating the dehydration reaction, it also accelerates the carbonization of the substance, resulting in the formation of undesired humin [37]. The deposition of humin will inevitably affect the catalyst's activity and the progress of the reaction, thereby negatively affecting the reaction. Therefore, we hold that the relative strength of promotion and negative effects can explain the catalytic performance of Lewis acids in this study, as each catalyst has its own optimum operating conditions.

3.2.2. Combination of additives

For the purpose of obtaining higher yields, combinations of additives were tried. B_2O_3 is the best single component additive, and it is more

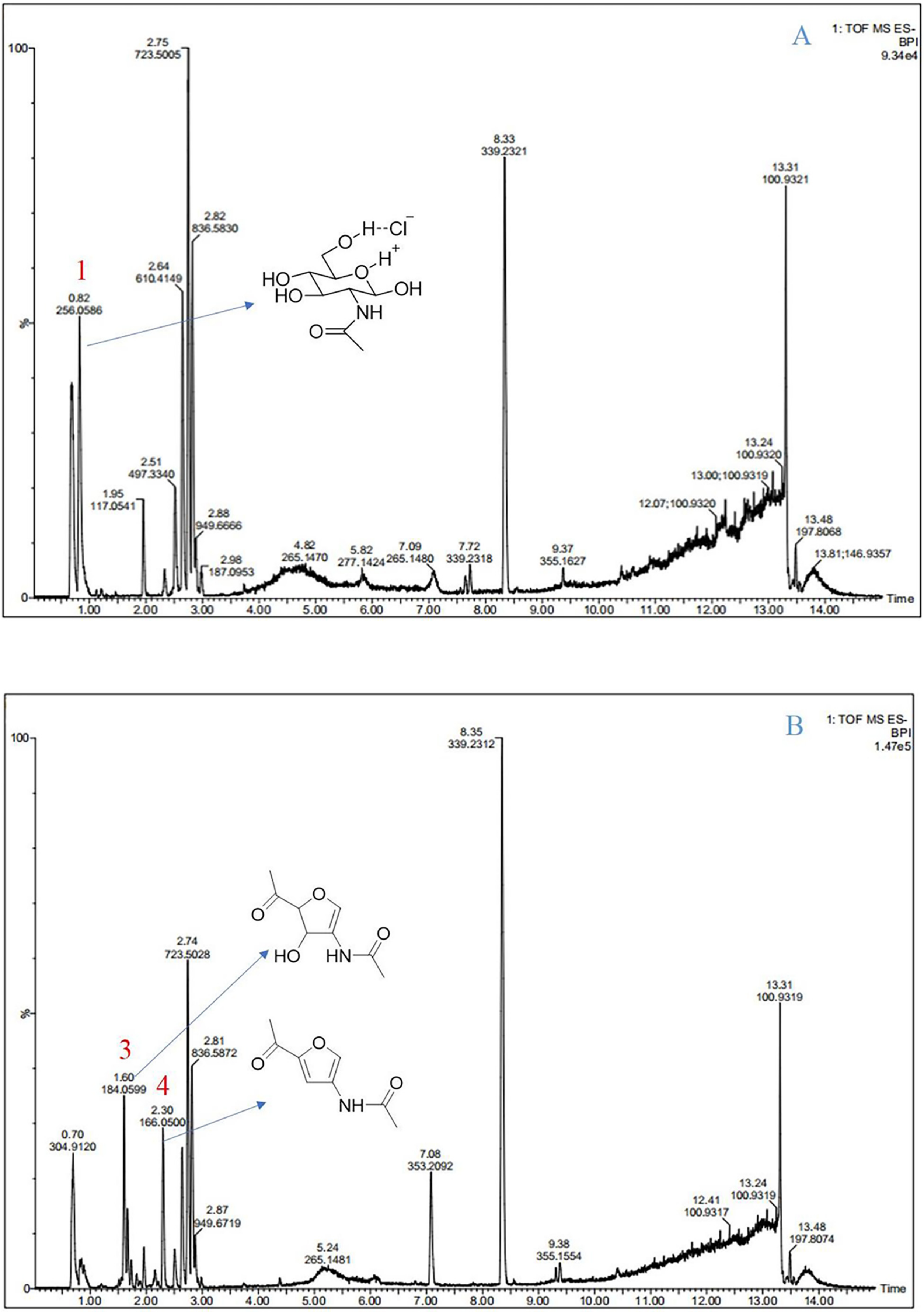


Fig. 7. HPLC-MS spectra of the reaction system. A, reaction for 0 min; B, reaction for 7 min; C, reaction for 10 min; D, reaction for 20 min.

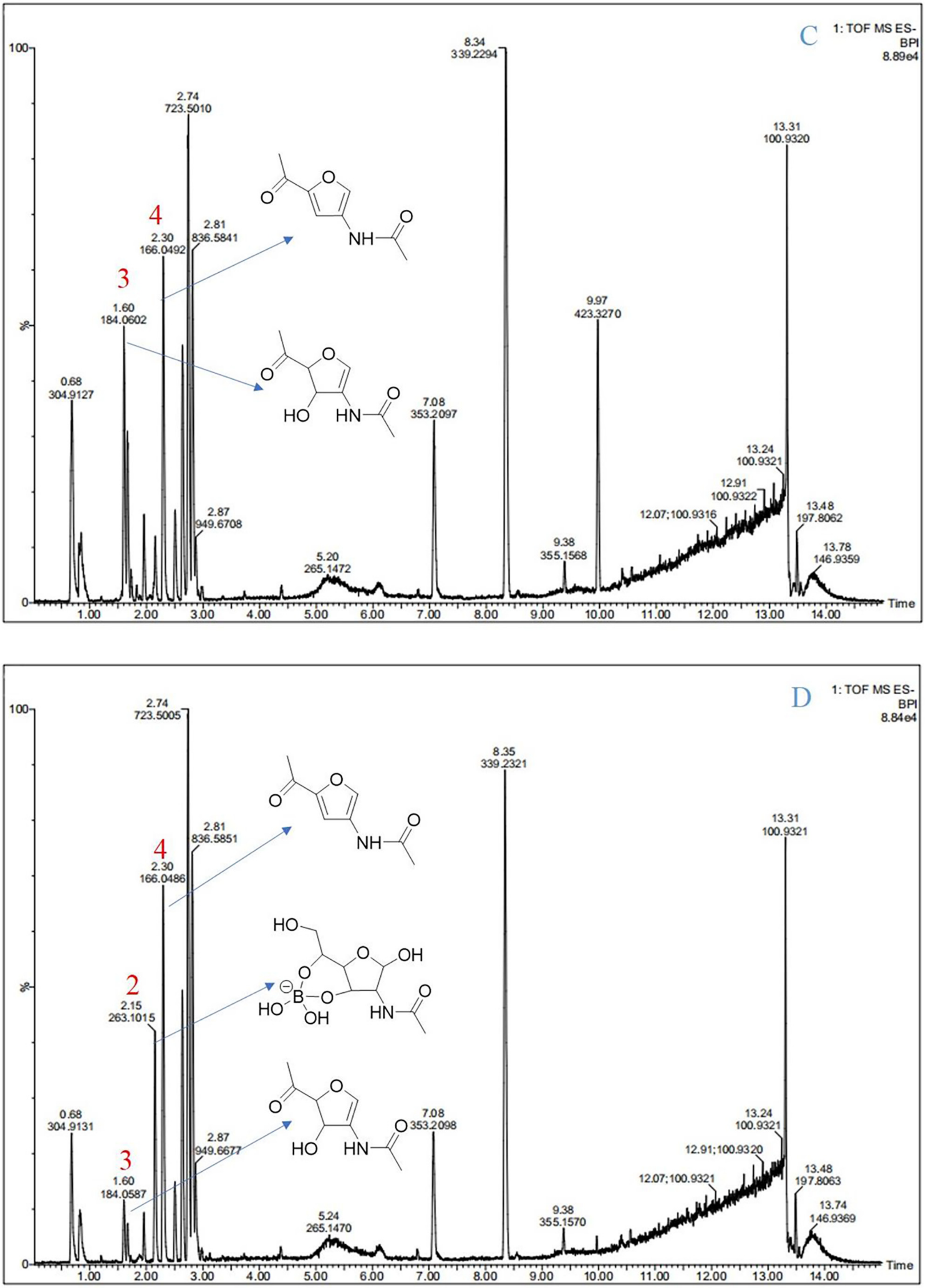


Fig. 7 (*continued*).

environmentally friendly and cheaper than $B(OH)_3$. Therefore, the combinations consist of B_2O_3 and another additive.

As shown in Fig. 3, the combinations of B_2O_3 and $AlCl_3$, $CrCl_3$ and $CaCl_2$ can increase the yield. The combination of B_2O_3 and $CaCl_2$ performed best, the yield of 3A5AF reached 66.97%. For other Lewis acids, the 3A5AF yield increased to a certain extent due to the addition of B_2O_3, but it was lower than that of using B_2O_3 alone. It is speculated that the combined additives produced synergistic effects. We found that $CaCl_2$ has good catalytic properties in many other studies. For instance, Nan et al. [39] found that $CaCl_2$ as a catalyst can play various roles such as dehydration, deamination, decarboxylation and dehydrogenation. In the work of Lin et al. [40], $CaCl_2$ can promote the ionization of its substrate and chelate with the substrate. In our work, $CaCl_2$ may play a role in strengthening dehydration and promoting enol isomerization.

In summary, we use B_2O_3 and $CaCl_2$ as a combination additive to co-catalyze the conversion of NAG to 3A5AF with [CMPy]Cl.

3.3. Optimization of reaction conditions

The influences of temperature, time and IL concentration on the reaction were examined.

The temperature factor was investigated first, and the reaction was carried out in the temperature range of 160 °C to 210 °C. As shown in Fig. 4, the yield increased with increasing temperature in the range of 160 °C to 180 °C, and reached the highest value at 180 °C. However, the yield began to drop at 190 °C, which may result from the thermal decomposition of 3A5AF. And there may be another reason that IL became unstable and decomposed at high temperature, affecting the catalytic effect. Therefore, the optimal temperature for this reaction was 180 °C.

And then, the concentration of the IL was optimized by conducting experiments at the mass ratio of [CMPy]Cl to NAG from 0.5 to 5 (Fig. 5). It can be seen that with the increase of [CMPy]Cl concentration, the yield of 3A5AF did not change much. When the mass ratio was 2, the highest yield of 3A5AF reached 68.82%, slightly higher than the yield when the mass ratio was 1. From the perspective of reducing the amount of IL, the mass ratio of 1 was selected as the best feeding ratio in the subsequent experiments.

Finally, to determine the best reaction time, the experiments carried out for 10 min, 15 min, 20 min, 30 min, 40 min, 60 min, 80 min and 100 min. As shown in Fig. 6, the results showed an upward trend in the range of 10–20 min and then stabilized. With the extension of reaction time, the yield dropped slightly, which may be due to the decomposition of 3A5AF. Therefore, the best reaction time was determined to be 20 min.

3.4. Possible reaction pathways

The reaction mechanism was determined by HPLC-MS, and the reaction pathway was inferred from the test results, as shown in Scheme 2.

Fig. 7 shows the HPLC-MS analysis results when the reaction time was 0 min, 7 min, 10 min and 20 min respectively. [CMPy]Cl dissolved in NMP and ionized Cl^-. Cl^- broke the intramolecular and intermolecular hydrogen bonds in the NAG molecular structure, and then formed a new hydrogen bond with -OH. Therefore, the characteristic peak 1 (t_R (retention time) = 0.82 min, Mr. (Relative molecular mass) = 256) in Fig. 7 (A) corresponds to “I”, which is the NAG-Cl^- complex.

NAG opened its ring under acidic conditions and changed from hemiacetal form to open chain aldehyde form “II”. Subsequently, the open chain aldehyde structure was isomerized to form an enol intermediate. And then, the lone pair of electrons on the O atom connected to the C_5 position of the enol intermediate attacked the double bond at the C_2 position to form a new C_2—O bond, forming a five-membered ring intermediate (III).

The boron-oxygen bond in B_2O_3 cooperated with the hydroxyl group of “III” to form a boron complex (IV). “IV” corresponds to the characteristic peak 2 (t_R = 2.15 min, Mr. = 263) in Fig. 7 (*D*), which proves the existence of “IV”.

“IV” formed an aldehyde structure (V) through enol isomerization, and then “V” removed one molecule of water to form “VI”. “VI” corresponds to the characteristic peak 3 (t_R = 1.60 min, Mr. = 184) in Fig. 7 (B, C, D), which proves the existence of “VI”.

Subsequently, “VI” removed one molecule of water to form 3A5AF.The characteristic peak 4 (t_R = 2.30 min, Mr. = 166) in Fig. 7 (B, C, D) corresponds to 3A5AF, which proves that the product 3A5AF was obtained.

4. Conclusions

We have synthesized a series of pyridinium-based ionic liquids and applied them to the conversion of NAG to 3A5AF. Under the synergistic catalysis of [CMPy]Cl and additives, the yield of 3A5AF under optimal conditions can reach 67.37%. We analyzed the reaction mechanism of NAG to 3A5AF through HPLC-MS test. This research made a breakthrough in the yield of 3A5AF and enriched the catalytic system of chitin biomass. However, the research on the conversion of chitin biomass into N-containing compounds is still in its infancy, and there are many aspects that require our efforts. This work still has problems that need improvement. For instance, our catalytic system is only suitable for the degradation of chitin monomer, and more in-depth researches are needed on the degradation of chitin. In future work, we should explore more low-cost, green and recyclable catalysts, such as solid acid catalysts, which are easy to separate and recycle to reduce costs. In addition, there are few reports on the preparation of other types of N-containing compounds by chitin biomass, so more other types of products should be explored to broaden the application range of chitin in the field of N-containing chemicals manufacturing.

Author statement

Hongjun Zang: Conceptualization, Methodology, Writing - Review & Editing, Project administration, Supervision, Revising manuscript.

Jing Lou, Methodology, Software, Validation; Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft , Revising manuscript.

Shuolei Jiao, Methodology, Software, Validation;

Huanxin Li, Resources, Software,

Yannan Du, Investigation.

Jiao Wang, Formal analysis.

Declaration of Competing Interest

The authors declared that we have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Acknowledgements

The following funding sources are correct. National Natural Science Foundation of China (No. 21406166) and Natural Science Foundation of Tianjin Science and Technology Correspondent Project (No. 18JCYBJC87200).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2021.115667.

References

[1] A.J. Ragauskas, The path forward for biofuels and biomaterials [J], Science 311 (5760) (2006) 484–489.

[2] Xi Chen, Yongjun Gao, Lan Wang, et al., Effect of treatment methods on chitin structure and its transformation into nitrogen-containing chemicals [J], ChemPlusChem 80 (10) (2015) 1565–1572.

[3] Xi Chen, Yi Liu, Francesca M. Kerton, et al., Conversion of chitin and N-acetyl-D-glucosamine into a N-containing furan derivative in ionic liquids [J], RSC Adv. 5 (26) (2015) 20073–20080.

[4] Xi Chen, Huiying Yang, ZiYi Zhong, et al., Base-catalysed, one-step mechanochemical conversion of chitin and shrimp shells into low molecular weight chitosan [J], Green Chem. 19 (12) (2017) 2783–2792.

[5] Ning Yan, Xi Chen, Don't waste seafood waste [J], Nature 524 (7564) (2015) 155–157.

[6] Alejandro D. Sadiq, Xi Chen, Ning Yan, et al., Towards the Shell biorefinery: sustainable synthesis of the anticancer alkaloid proximicin a from chitin [J], ChemSusChem 11 (2018) 532–535.

[7] Francesca M. Kerton, Yi Liu, Kelly Hawboldt, et al., Green chemistry and the ocean-based biorefinery [J], Green Chem. 15 (4) (2013) 860–871.

[8] Marcus W. Drover, Khaled W. Omari, Jennifer N. Murphy, et al., Formation of a renewable amide, 3-acetamido-5-acetylfuran, via direct conversion of N-acetyl-D-glucosamine [J], RSC Adv. 2 (11) (2012) 4642–4644.

[9] Khaled W. Omari, Linda Dodot, Francesca M. Kerton, A simple one-pot dehydration process to convert N-acetyl-D-glucosamine into a nitrogen-containing compound, 3-acetamido-5-acetylfuran [J], ChemSusChem 5 (9) (2012) 1767–1772.

[10] Xi Chen, Shu Ling Chew, Francesca M. Kerton, et al., Direct conversion of chitin into a N-containing furan derivative [J], Green Chem. 16 (4) (2014) 2204–2212.

[11] Jiaxuan Feng, Hongjun Zang, Qing Yan, et al., Conversion of chitosan into 5-Hydroxymethylfurfural via hydrothermal synthesis [J], Adv. Mater. Res. 1095 (5) (2015) 411–414.

[12] Emma Savitri, Sri Rachmania Juliastuti, Anitarakhmi Handaratri, et al., Degradation of chitosan by sonication in very-low-concentration acetic acid [J], Polym. Degrad. Stab. 110 (2014) 344–352.

[13] Sang-Bum Lee, Gwi-Taek Jeong, Catalytic conversion of chitosan to 5-Hydroxymethylfurfural under low temperature hydrothermal process [J], Appl. Biochem. Biotechnol. 176 (4) (2015) 1151–1161.

[14] Khaled W. Omari, Jessica E. Besaw, Francesca M. Kerton, Hydrolysis of chitosan to yield levulinic acid and 5-hydroxymethylfurfural in water under microwave irradiation [J], Green Chem. 14 (5) (2012) 1480–1487.

[15] Ármin Szabolcs, Márk Molnár, Gábor Dibó, et al., Microwave-assisted conversion of carbohydrates to levulinic acid: an essential step in biomass conversion [J], Green Chem. 15 (2) (2013) 439–445.

[16] Gwi-Taek Jeong, Production of levulinic acid from glucosamine by dilute-acid catalyzed hydrothermal process [J], Ind. Crop. Prod. 62 (2014) 77–83.

[17] Xiaoyun Gao, Xi Chen, Jiaguang Zhang, et al., Transformation of chitin and waste shrimp shells into acetic acid and pyrrole [J], ACS Sustain. Chem. Eng. 4 (2016) 3912–3920.

[18] Thuy Trang Pham, Gökalp Gözaydın, Tilo Söhnel, et al., Oxidative ring-expansion of a chitin-derived platform enables access to unexplored 2-amino sugar chemical space [J], Eur. J. Inorg. Chem. 2019 (2019) 1355–1360.

[19] R.A. Franich , S.J. Goodin , A.L. Wilkins. Acetamidofurans, acetamidopyrones, and acetamidoacetaldehyde from pyrolysis of chitin and n-acetylglucosamine [J]. J. Anal. Appl. Pyrolysis, 1984, 7(1–2): 91–100.

[20] Jiao Wang, Hongjun Zang, Shuolei Jiao, et al., Efficient conversion of N-acetyl-D-glucosamine into nitrogen-containing compound 3-acetamido-5-acetylfuran using amino acid ionic liquid as the recyclable catalyst [J], Sci. Total Environ. 710 (2019) 136293–136299.

[21] Chenlin Li, Bernhard Knierim, Chithra Manisseri, et al., Comparison of dilute acid and ionic liquid pretreatment of switchgrass: biomass recalcitrance, delignification and enzymatic saccharification [J], 101 (13) (2009) 4900–4906.

[22] Brandt Agnieszka, J. Ray Michael, To Trang Q, et al., Ionic liquid pretreatment of lignocellulosic biomass with ionic liquid–water mixtures [J], Green Chem. 13 (9) (2011) 2489–2499.

[23] Brandt Agnieszka, Grsvik John, Jason P. Hallett, et al., Deconstruction of lignocellulosic biomass with ionic liquids [J], Green Chem. 15 (3) (2013) 550–583.

[24] F.E.L. Hajjaji, E. Ech-Chihbi, N. Rezki, et al., Electrochemical and theoretical insights on the adsorption and corrosion inhibition of novel pyridinium-derived ionic liquids for mild steel in 1 M HCl [J], J. Mol. Liq. 314 (2020) 113737.

[25] Amutha Chinnappan, Hern Kim, Environmentally benign catalyst: synthesis, characterization, and properties of pyridinium dicationic molten salts (ionic liquids) and use of application in esterification [J], Chem. Eng. J. 187 (2012) 283–288.

[26] Amutha Chinnappan, Arvind H. Jadhav, Hern Kim, et al., Ionic liquid with metal complexes: an efficient catalyst for selective dehydration of fructose to 5-hydroxymethylfurfural [J], Chem. Eng. J. 237 (2014) 95–100.

[27] Taheri Nazanin, Abdolmaleki Amir, Fashandi Hossein, Pyridinium-based ionic liquid/water mixture intended for efficient dissolution of cellulose, chitosan and chitin: the pivotal contribution of water [J], Carbohydr. Polym. 195 (2018) 413–419.

[28] Naz Sadia, Uroos Maliha, Asim Azmat Mehmood, et al., One-pot deconstruction and conversion of lignocellulose into reducing sugars by pyridinium-based ionic liquid–metal salt system [J], Front. Chem. 8 (2020) 236.

[29] Taheri Nazanin, Abdolmaleki Amir, Fashandi Hossein, Impact of non-solvent on regeneration of cellulose dissolved in 1-(carboxymethyl)pyridinium chloride ionic liquid [J], Polym. Int. 68 (12) (2019) 1945–1951.

[30] Juben N. Chheda, Yuriy Román-Leshkov, James A. Dumesic, Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides [J], Green Chem. 9 (4) (2007) 342–350.

[31] Juben N. Chheda, James A. Dumesic, An overview of dehydration, aldol-condensation and hydrogenation processes for production of liquid alkanes from biomass-derived carbohydrates [J], Catal. Today 123 (1–4) (2007) 59–70.

[32] Ananda S. Amarasekara, LaToya D. Williams, Chidinma C. Ebede, Mechanism of the dehydration of D-fructose to 5-hydroxymethylfurfural in dimethyl sulfoxide at 150 degrees C: an NMR study [J], Carbohydr. Res. 343 (18) (2008) 3021–3024.

[33] Mika Ohara, Atsushi Takagaki, Shun Nishimura, et al., Syntheses of 5-hydroxymethylfurfural and levoglucosan by selective dehydration of glucose using solid acid and base catalysts [J], Appl. Catal. A Gen. 383 (1–2) (2010) 149–155.

[34] Jianjian Wang, Jiawen Ren, Xiaohui Liu, et al., High yield production and purification of 5-hydroxymethylfurfural [J], AICHE J. 59 (7) (2013) 2558–2566.

[35] Yueqing Wang, Guoqiang Ding, Xiaohai Yang, et al., Selectively convert fructose to furfural or hydroxymethylfurfural on Beta zeolite: the manipulation of solvent effects [J], Appl. Catal. B Environ. 235 (2018) 150–157.

[36] S. Pumrod, A. Kaewchada, S. Roddecha, et al., 5-HMF production from glucose using ion exchange resin and alumina as a dual catalyst in a biphasic system [J], RSC Adv. 10 (16) (2020) 9492–9498.

[37] Ahmad Ginés-Molina, Mérida-Morales, et al., Selective conversion of glucose to 5-hydroxymethylfurfural by using l-type zeolites with different morphologies [J], Catalysts 9 (12) (2019) 1073.

[38] Jinghua Wang, Hongyou Cui, Yong Wang, et al., Efficiently catalytic conversion of cellulose to levulinic acid in biphasic molten salt hydrate and methyl isobutyl ketone [J], Green Chem. 22 (13) (2020) 4240–4251.

[39] Hongyan Nan, Ziyue Xiao, Ling Zhao, et al., Nitrogen transformation during pyrolysis of various NContaining biowastes with participation of mineral calcium [J], ACS Sustain. Chem. Eng. 8 (32) (2020) 12197–12207.

[40] Changqu Lin, Hongli Wu, Junyi Wang, et al., Preparation of HMF from high fructose corn syrup using organic weak acid in situ as catalyst [J], Ind. Eng. Chem. Res. 59 (10) (2020) 4358–4366.