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# Evolution process and controlled synthesis of humins with 5-hydroxymethylfurfural (HMF) as model molecule

Haiyan Shen,[a] Haozhe Shan,[a] and Li Liu*[ab]

**Abstract:** Elucidation of the chemical structure and formation mechanism of humins are requisite to further improve the efficiency of acid-catalyzed biomass conversion. By the low-temperature approach, the key intermediates resulting in the formation of HMF-derived humins were captured, revealing multiple elementary reactions such as etherification, esterification, aldol condensation, and acetalization. Through humins characterizations, it was found out that the aldol condensation moiety between aldehyde group and LA is critical to justify the characteristic IR peaks (1620 and 1710 cm$^{-1}$) and aromatic fragments from pyrolysis GC-MS. Based on the investigations by means of HPLC-MS/MS, IR, pyrolysis GC-MS and SEM, the structural models of humins at different temperatures were proposed, which are comprised of the elementary reaction types confirmed by the key intermediates. Our findings highlight the humins structures with varying content of aldol condensation could be controllably synthesized from different temperatures and times, demonstrating the evolution process of HMF-derived humins.

## Introduction

In view of diminishing fossil resources and increasing concern about environmental protection, great attention has been turned to produce fuels and chemicals from renewable biomass resources.[1] One of the promising routes is acid-catalyzed hydrolysis of cellulose to glucose, followed by dehydration of glucose to 5-hydromethylfurfural (HMF, **1**), and then rehydration of HMF to levulinic acid (LA).[2] Both HMF and LA are valuable platform chemicals.[3] During the process of acid-catalyzed conversion, dark-brown insoluble by-products (known as humins) were unavoidably formed. Most of the researches have been focused on the synthesis and formation pathway of water-soluble products (such as HMF, LA, furfural, formic acid). Only little attention has been paid to the formation and structure of humins, which however compete with desired products, restrain the activity of catalyst and hinder the recycling of catalyst and separation of products.[2c, 4] To further improve the efficiency of acid-catalyzed biomass conversion, unambiguous elucidation of the chemical structure and formation mechanism of humins are requisite.

In the past few decades, several groups have made efforts to speculate the structure and mechanism of humins from various feedstocks including cellulose, carbohydrates and HMF. A big part of the literature report supports the notion that humins formation could be ascribed to HMF. Moreover, compared with cellulose or carbohydrate-derived humins, HMF-derived humins are structurally less complicated. Herein, HMF was chosen as the model molecule to simplify the humins investigation. By singling out HMF model, the reaction complexity caused by the additional constituents in the system could be greatly reduced, thus enhancing the chances to identify the key intermediates during the formation of humins.

Humins from hydrothermal treatment of biomass in the absence of catalyst are usually called hydrothermal carbon (HTC) or hydrochar, which have been more thoroughly characterized than those from acid-catalyzed conversion.[5] Though close attentions have been paid to the formation and structure of HTC, a unified conclusion has not been drawn either. Matsumura and co-worker[6] investigated hydrothermal treatment of HMF under both subcritical and supercritical conditions, whereas HTC was only observed under the subcritical conditions. Under the supercritical conditions, HMF decomposed rapidly and produced no HTC. While under the subcritical conditions, HMF proceeded through two reaction pathways concurrently: decomposition and polymerization. By means of FT-IR spectroscopy and Raman spectrometry, they proposed that HMF and aromatic liquid products from decomposition (e.g., 1,2,4-benzenetriol, 1,4-benzenediol) polymerized to form water-insoluble HTC, characteristic of cyclic and aromatic structures of both furan and benzene ring but lacking aliphatic fragments. Titirici and co-workers[7] believed that the morphologies and chemical structures of HTC synthesized from hexoses at 180 °C for 24 h could be directly related to that from HMF. Based on the similarities with that of HMF-derived humins, they proposed hydrothermal carbonization of glucose proceeds only through two main reaction pathways: from hexoses to HMF and from HMF to carbon. Further, with the help of SEM, elemental analysis and solid-state MAS $^{13}$C NMR investigations, Titirici et al.[8] developed the mechanistic model for HTC. During hydrothermal treatment, glucose first dehydrates to form HMF, LA and formic acid.[8b] Then the acidic compounds act as in situ catalysts to promote further dehydration of glucose into HMF, which subsequently undergoes various polymerization-polycondensation reactions to give polyfuranic compounds. If the process temperature is higher than 180 °C， these polyfuranic substances react further through intramolecular condensation, dehydration and decarboxylation reaction to form more aromatic materials with less oxygenous functional groups.

The structural insights obtained for HTC are nonetheless valuable because similar characteristics are involved in humins under acidic catalysis. In parallel with the investigations of HTC, humins formed during acid-catalyzed HMF conversion have

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been studied in detail. Horvat et al.[9] was one of the first to investigate the acid-catalysed humins, whereas they proposed 2,5-dioxo-6-hydroxyhexanal (DHH) intermediate that could polymerize to form humins subsequently. However, DHH has not been detected experimentally. Sumerskii et al.[10] suggested that the humins consist of 60% of furan rings and 20% of aliphatic fragments. For hexoses, humins formation occurs via HMF which enters into polycondensation processes by the mechanism of electrophilic substitution, with the formation of ether or acetal bonds. Lund and co-workers[11] adopted IR analyses to demonstrate that furan ring and hydroxymethyl group of HMF are present in HMF-derived humins, but the carbonyl group is not. On the basis of HMF conversion pathway incorporating DHH intermediate suggested earlier by Horvat,[9] they proposed a model where humins growth occurs via aldol addition/condensation of HMF with DHH. van Zandvoort et al.[12] proposed a polyfuranic molecular structure wherein HMF, LA and DHH undergo nucleophilic addition to the α and β carbons on HMF. Their structure model of humins took into account both DHH mechanism and aldol condensation mechanism suggested by Horvat[9a,9b] and Lund,[11a,11b] respectively. The discrepancy lies in that Lund suggested LA and formic acid may not participate in the formation of humins, while van Zandvoort et al. inferred aldol condensation of HMF with the ketone group of LA is a plausible way to include LA in the humins structure. Recently, Vlachos and co-workers[13] applied ATR-FTIR spectroscopy, SEM and Dynamic Light Scattering (DLS) experiments to postulate that initially soluble oligomeric humins form via aldol condensation and/or etherification reactions in which HMF reacts with DHH-like intermediates or other HMF molecules, followed by nucleophilic attack as proposed by van Zandvoort et al.[12]

Though a lot of excellent researches have been conducted in this field, the formation mechanism of humins is still not clearly understood yet. On account that the current researches are mainly targeted at the static structure of humins, the dynamic process of how humins are formed from solution to solid has not been described exactly and remains challenging up to date. The previous investigations were mostly undertaken at high temperature ranging from 120 ℃ to 450 ℃, while it could be difficult to identify the key intermediates for they are prone to oligomerize rapidly into humins at high temperatures. Herein, the humins formed from HMF were investigated thoroughly by low-temperature approach, whereby the structural evolution process of humins has been demonstrated for the first time.

## Results and Discussion

### The process from HMF to humins solid

In our study, the color of HMF mixture in the presence of $H_2SO_4$ changed from dark brown to black during storage, until the emergence of humins solid. As shown in Figure 1, the reaction mixture lost its fluidity after 14 days and 4 days at 4 ℃ and 20 ℃, respectively, indicating humins were formed much faster at 20 ℃ than 4 ℃. When the temperature was increased to 170 ℃, the yield of humins ascended more quickly than 20 ℃, and reached 70% after 10 min. Apparently, chemical reactions take place for HMF in the presence of acidic catalyst, even at low temperatures of 20 ℃ or 4 ℃, which could account for the formation of humins.

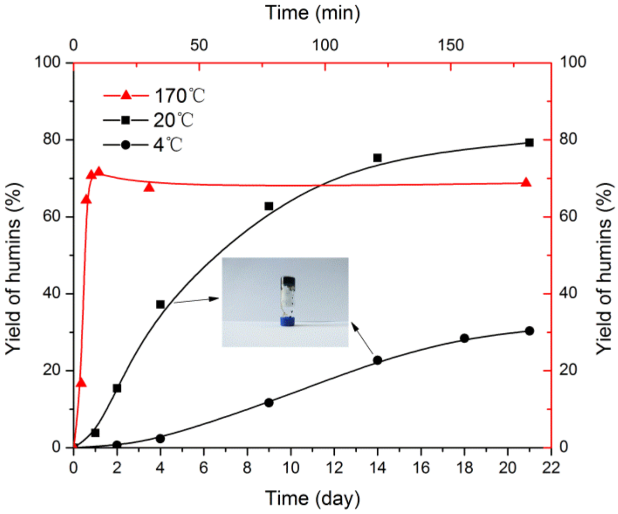

**Figure 1.** The yields of humins from HMF at different temperatures under acidic catalysis.

### Identification of the intermediates

In order to elucidate the chemical reactions to form humins, capture of the key intermediates could definitely provide direct evidence. For higher temperature such as 170 ℃, over 70% of HMF turned into humins solid after 10 min, so that the intermediates are transformed into humins too fast and the remaining intermediates in solution are too minimal to characterize. On the other hand, for lower temperature such as 4 ℃, the conversion of HMF is too slow to accumulate enough intermediates, resulting in that it took over 14 days to obtain the samples rich of intermediates. To keep a balance between the concentration of intermediates and reaction period, the chemical reactions of HMF was monitored at 20 ℃, in the presence of acidic catalyst. The $^1$H NMR spectrum shows a new set of peaks at 9.64, 7.22, 6.58 and 4.64 ppm in coexistence with HMF (Figure S1), which is distinctively different from those of HMF. Through column chromatography, the new set of peaks were ascribed to 5,5'-oxy(bis-methylene)-2-furaldehyde (OBMF, **2**), the dimer of HMF through self-etherification reaction. In fact, the etherification of HMF into OBMF was very easy to occur under acidic condition. Galkin et al.[14] discovered the presence of OBMF during the storage of HMF ascribed to acidic impurities. Besides OBMF, $^1$H NMR spectrum shows the presence of LA and formic acid, which are usually obtained at higher temperature (Figure S1). Similar to OBMF, the content of LA and formic acid in samples stored at 20 ℃ were higher than 4 ℃.

In addition to $^1$H NMR, the reaction mixture after certain intervals was dissolved in $CH_3CN$ and analysed by HPLC-MS/MS, revealing new intermediates of **3** and **4**, besides **1** (HMF) and **2** (OBMF). Through column chromatography, **3** and **4** were characterized to be HMF formate and HMF levulinate, respectively, which were further confirmed by comparison with the standard compounds. The intermediates of HMF formate and HMF levulinate indicated that HMF can undergo esterification under acidic catalysis.

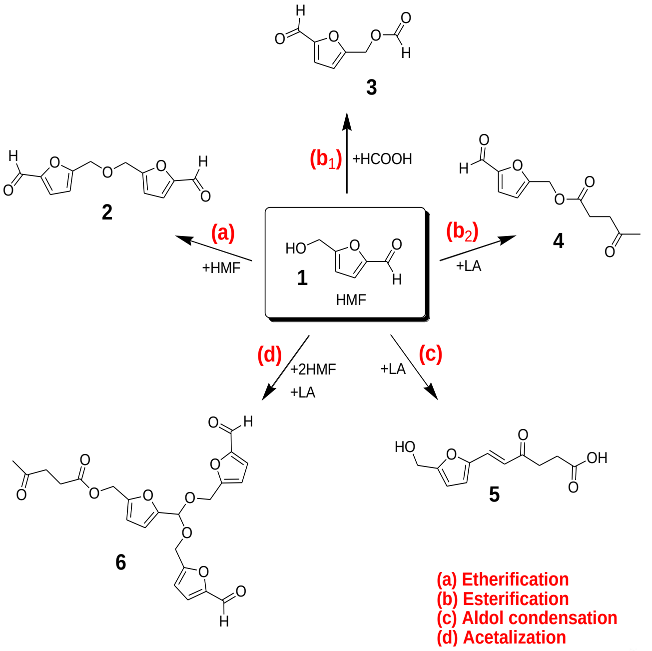

**Figure 2.** The elementary reaction types detected through HPLC-MS/MS analysis.

Furthermore, the intermediate **5** was characterized to be (E)-6-[5-(hydroxymethyl)furan-2-yl]-hex-4-oxo-5-enoic acid, the aldol condensation product of HMF and LA, which was also confirmed by comparing with the standard compound. Herein, LA provides the α-H for the aldol condensation with HMF to occur. Patil et al. also proposed aldol condensation reactions as important reactions for HMF-humins, except that they believed that DHH provides the α-H required for the aldol condensation reaction.[11a]

Ananikov et al. proposed higher molecular weight compounds of acetalization with three to ten furan cores during HMF aging in the presence of acidic imputities based on the MS/MS data.[14] In our system, simple acetalization intermediates of HMF were not detected by MS/MS. However, the intermediate **6** was proposed to be acetalization product of HMF levulinate, verifying that acetalization can proceed under acidic catalysis.

Therefore, as Figure 2 shows, the HPLC-MS/MS results indicated that multiple elementary reactions were involved in the acidic catalysis of HMF, such as etherification, esterification, aldol condensation, and acetalization. These findings confirm the possibility that the rehydration product of HMF, i.e. LA and formic acid, are involved in the formation of humins, which differs from Lund et al.'s assumption about the non-involvement of LA and formic acid in the humins structure.**[11]**

With increasing the temperature to 170 ℃, these active intermediates could also be detected in the reaction mixture, albeit at a far low concentration, which indicated the formation mechanisms of humins are similar under low temperature and hydrothermal condition (170 ℃). It was assumed that through these elementary reactions, humins oligomers started to grow in the solution until precipitation as humins solid, which could be further supported by means of IR and pyrolysis GC-MS in the subsequent sections. The previous literature mainly focus on the humins growing process ever since its appearance in solid, whereas the key step from the feedstock to the active intermediates in solution growing towards humins in solid is regretably missing all this time. Luckily, the formation process was slowed down by the low-temperature approach. Thereby the key intermediates resulting in the formation of humins was captured, offering opportunity to reveal the structure of humins, so as to the successive growth mechanism of humins.

### FT-IR study on the structural evolution of humins

As reported in the literature, the IR spectra of humins derived from HMF exhibit two characteristic absorption peaks positioned at around 1710 and 1620 $cm^{-1}$, which are the most evident feature of IR spectra. There have been many arguments on the functional groups corresponding to these two peaks until now.[11,15,16] And how these functional groups are formed through chemical reactions has not been explained unambiguously so far.

Interestingly, in our system, it was found that the IR spectra of the humins change regularly with varying temperatures. For the humins formed at 4 ℃, the IR spectrum shows only a strong absorption peak appeared at 1674 $cm^{-1}$, which could be ascribed to the HC=O group of HMF moiety (Figure 3a). Among the elementary reactions, this indicated that the furanics were mainly connected through etherification and acetalization into poly-furanics. Therefore, the aldehyde groups were consumed much less than –OH groups, resulting in solely strong stretching vibrations of HC=O on the IR spectra, whereas the peak at 1716 $cm^{-1}$ is very weak and the peak at 1624 $cm^{-1}$ is negligible.

For the humins formed at 20 ℃, the IR spectrum at the early stage was quite similar to that at 4 ℃ (Figure 3b), whereas the HC=O stretching vibrations at 1674 $cm^{-1}$ was solely strong. Then the peak at 1674 $cm^{-1}$ was weakened gradually, concomitant with a relative increase of two peaks at 1716 and 1624 $cm^{-1}$. Through comparison of the IR spectra with HMF and intermediates (Figure 3c), it was deferred that 1624 $cm^{-1}$ could be attributed to the C=C group from aldol condensation moieties between aldehyde group and LA. In addition, 1716 $cm^{-1}$ could be ascribed to the carbonyl group conjugated with C=C from the aforementioned aldol condensation moieties, together with the ester groups from the moieties of HMF formate and HMF levulinate. When increasing the temperature from 4 ℃ to 20 ℃, the aldol condensation between aldehyde group and LA was promoted, due to higher LA content. Thereby, the intensities of two peaks at 1716 and 1624 $cm^{-1}$ ascend and get closer to that at 1674 $cm^{-1}$.

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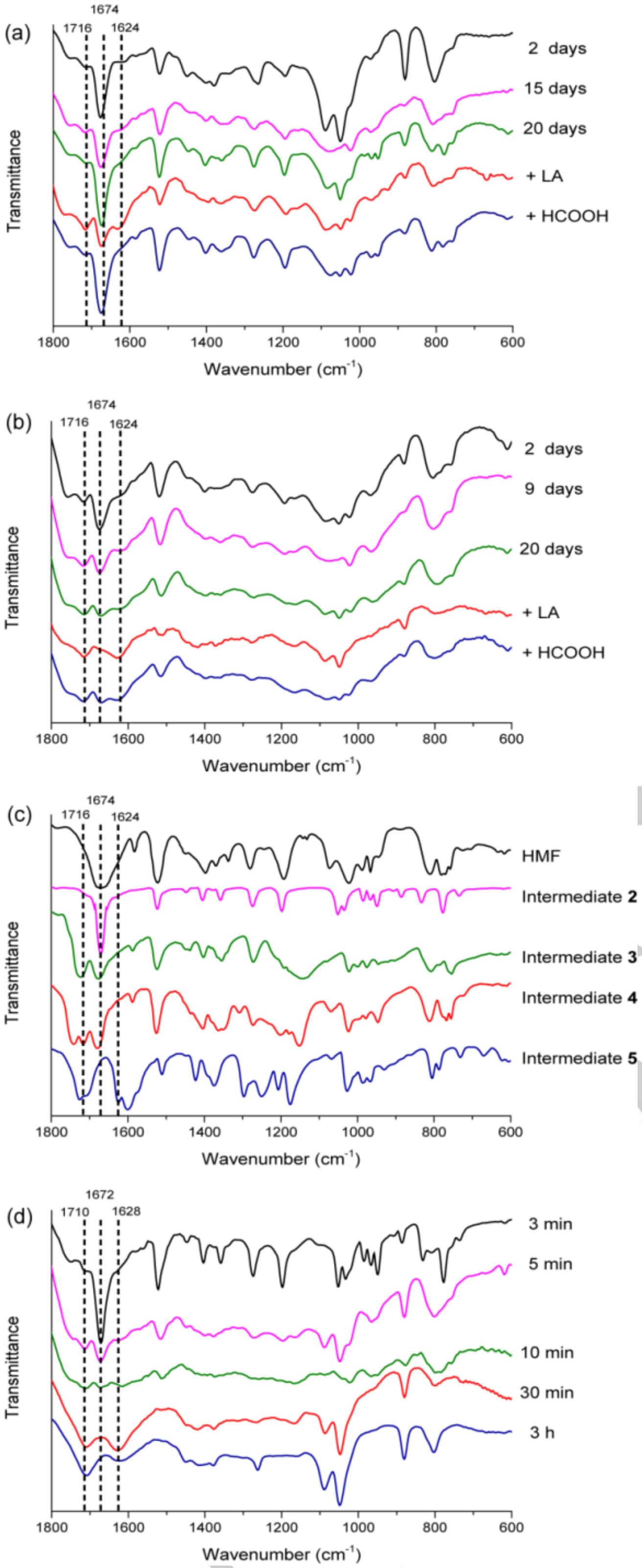

**Figure 3.** FT-IR analyses of humins from HMF at (a) 4 ℃, (b) 20 ℃ and (d) 170 ℃, with (c) blank controls of HMF and intermediates.

In order to verify the IR characterizations, additional LA was added into the reaction mixture. Consequently, the peak at 1674 $cm^{-1}$ decreased at 4 ℃ (Figure 3a) and disappeared at 20 ℃ (Figure 3b), while the two peaks at 1716 and 1624 $cm^{-1}$ increased. Apparently, the aldehyde groups can be indeed consumed by the additional LA into aldol condensation moieties incorporated in the humins structure. In contrast, aldol condensation between aldehyde group and formic acid could not occur for formic acid does not contain an α-H. Therefore, with additional formic acid, the peak at 1674 $cm^{-1}$ didn't change significantly.

When the temperature was further increased to 170 ℃, the IR spectra after 3 min and 10 min were similar to those at 4 ℃ for 20 days and at 20 ℃ for 20 days, respectively, showing the peak at 1672 $cm^{-1}$ decreased gradually. After 30 min, the IR spectra exhibit only two peaks at 1710 and 1628 $cm^{-1}$, with the peak at 1672 $cm^{-1}$ disappeared completely (Figure 3d), indicating the aldehyde groups were totally consumed by the aldol condensation with LA. This was due to the enhanced amount of LA produced from HMF at higher temperature. Thus, on the basis of the IR characterizations, the humins structures with varying content of aldol condensation could be obtained from different temperatures and times, which were in good correlation with the amount of LA in the system, demonstrating the continuous evolution process of HMF-humins.

## Pyrolysis GC-MS study of humins

To gain further insights of humins structure, analytical pyrolysis GC-MS was performed on humin samples. It can be seen from Figure 4, pyrolysis of humins produces various furanics fragments dominantly (e.g. 2-methylfuran, 2,5-dimethylfuran, 5-methyl-2-furancarboxaldehyde, 2,5-furandicarboxaldehyde, HMF), confirming the poly-furanic nature of humins.

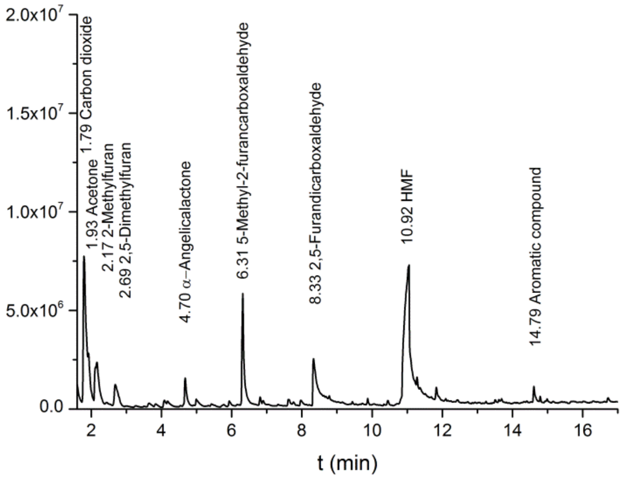

**Figure 4.** A typical pyrogram of humins from HMF (at 20℃ for 2 days).

Besides furanics fragments, it is worthy to note that aromatic compounds such as arenes and phenolics were produced in the pyrolysis process.[10, 15] As discussed before, hydrothermal treatment of HMF in sub/supercritical water would generate 1,2,4-benzenetriol (BTO), whereas it is difficult for BTO production at relatively low temperature. As a matter of fact, we didn't detect any intermediates of aromatics such as BTO by HPLC-MS/MS in the temperature range of 4-170 ℃, suggesting that the aromatics might be formed by the secondary reactions of the fragments under the pyrolysis condition.

To verify this hypothesis, analytical pyrolysis GC/MS was performed on four intermediates (**2**-**5**) as blank controls under the same conditions. According to the pyrolysis results on intermediates, the aromatics selectivities pyrolyzed for OBMF, HMF formate, HMF levulinate and (E)-6-[5-(hydroxymethyl)furan-2-yl]-hex-4-oxo-5-enoic acid are 1.68, 0, 0 and 19.88%, respectively. Thereby, our hypothesis of aromatics was testified, while the aromatics could be actually generated by the secondary reactions of the fragments under the pyrolysis condition. It further indicated the remarkable effect of C=C from aldol condensation moieties on the aromatics selectivity after pyrolysis. As illustrated by IR analyses, the amount of C=C bond produced by aldol condensation between aldehyde group and LA increased with increasing temperature and time. Consequently, as Figure 5 shows, the selectivity of aromatics for the pyrolyzed products increased with the rise of temperature and time, which was in good agreement with the IR results.

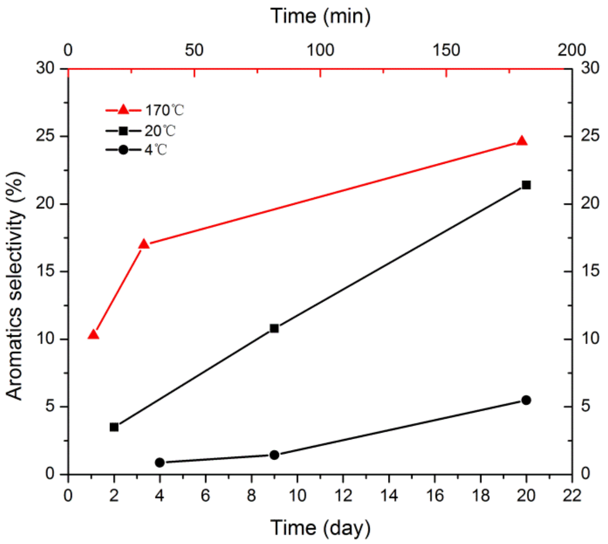

**Figure 5.** Aromatics selectivities for humins pyrolyzed products at different temperatures and reaction times.

More specifically, it was assumed that Diels-Alder cycloaddition reactions occur between furanics and C=C of aldol condensation moieties under pyrolysis conditions, leading to aromatic fragments. This was consistent with the literature reports. Huber et al. synthesized aromatics by Diels-Alder reactions with furans and olefins pyrolyzed over ZSM-5 catalyst.[17] Heeres et al. used HZSM-5 ($SIO_2/Al_2O_3$=50) catalyst in humins pyrolysis to obtain humins oil such as benzene, toluene and xylene, assumably through Diels-Alder reactions as well.[18]

## SEM study on the morphology evolution of humins

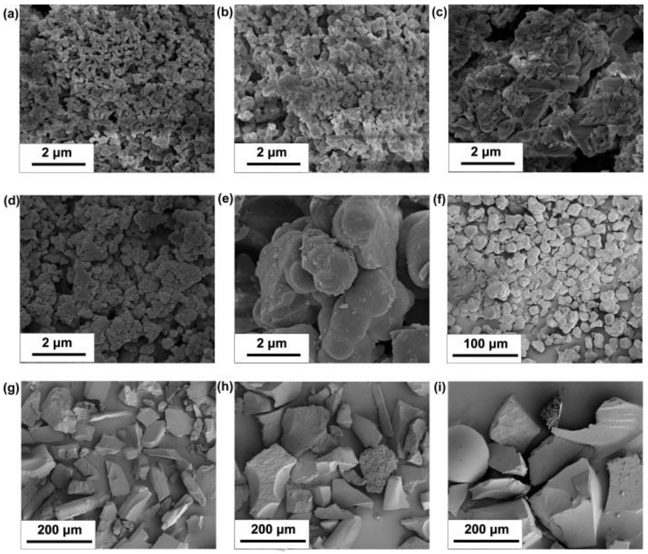

**Figure 6.** SEM images of humins for HMF stored at 4℃ for (a) 2 days, (b) 9 days, (c) 20 days, 20℃ for (d) 2 days, (e) 9 days, (f) 20 days, and 170℃ for (g) 10 min, (h) 30 min, (i) 3 h.

Figure 6 presents SEM images of humins that were formed at 4 °C, 20 °C and 170 ℃. Surprisingly, the humins obtained at 4°C exhibit a layered structure after 20 days (Figure 6a-c). It was speculated that the linkage of HMF mainly through etherification and acetalization at 4 ℃ produces poly-furanics structure which intends to stack closely into layered structure. For the humins obtained at 20°C, the initial stage also shows a layered structure but loosely packed (Figure 6d-e), and then agglomerated particles at micrometer scale prevail after 20 days (Figure 6f). Presumably, with more aldol condensation between aldehyde group and LA occurred together with esterification, the higher involvement of LA into the poly-furanics hinders the highly ordered stacking orientation, leading to more agglomerated particles coexistent with less layered structure. When the reaction temperature was further increased to 170 ℃, as the reaction rate was too fast, bigger clusters were formed (Figure 6g-i).

Under the traditional hydrothermal conditions, the humins solid obtained were mostly dispersed or agglomerated spherical particles.[11b, 12, 15] Herein, when increasing temperature and prolonging reaction time, a series of morphologies vary from layered structure, coexistent layered structure and agglomerated particles, agglomerated particles to big clusters, thus verifying the molecular-scale evolution process of humins from perspectives at micrometer scale.

## Proposed structure models of humins

On the basis of the aforementioned investigations by means of HPLC-MS/MS, IR, pyrolysis GC-MS and SEM, the structure models of humins containing the typical linkages were proposed (Figure 7), which are comprised of the elementary reaction types

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confirmed by the key intermediates. Etherification and acetalization were the major reaction types to form humins at 4 ℃ (Figure 7a), while the humins structures at 20 ℃ (Figure 7b) and 170 ℃ (Figure 7c) contain more LA's involvement through aldol condensation and esterification, mainly due to the higher LA content at higher temperatures.

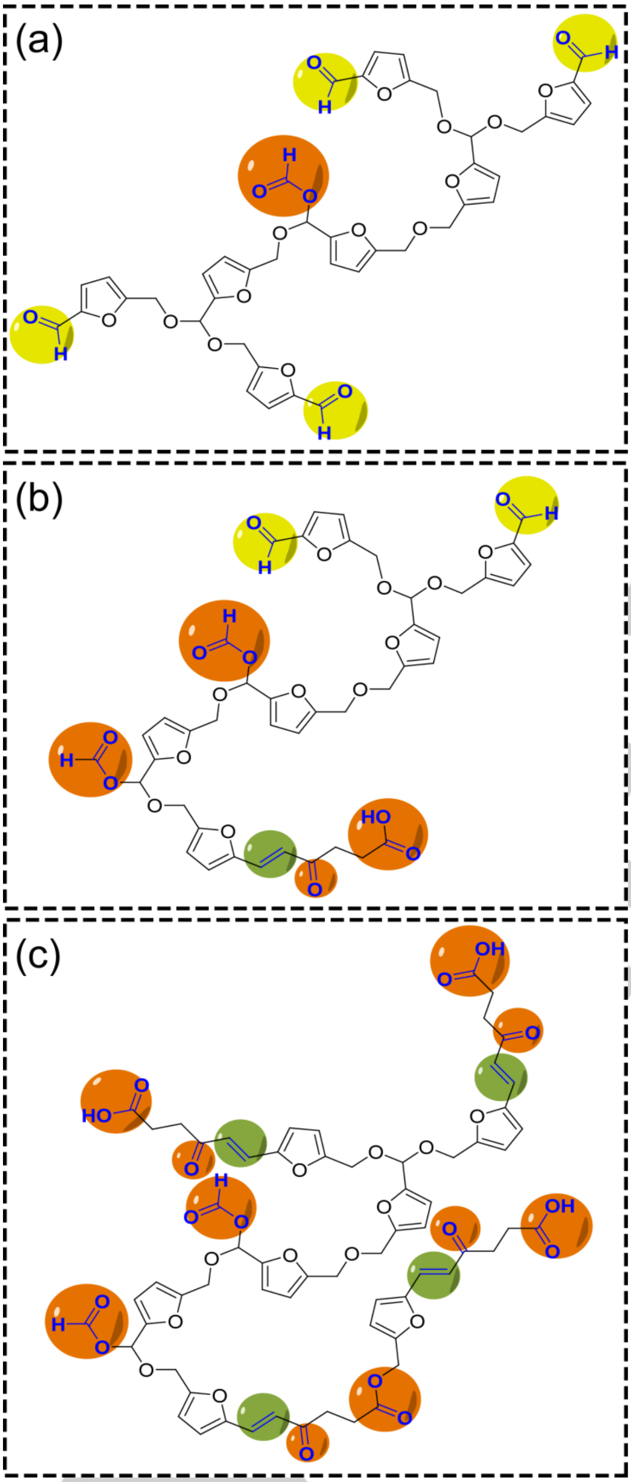

**Figure 7.** Proposed humin models for HMF at (a) 4 ℃, (b) 20 ℃ and (c) 170 ℃, which contain the typical linkages.

## Conclusion

For the first time, low-temperature approach was adopted to demonstrate the growth mechanism of HMF-derived humins. The key intermediates were identified in our study, which were ascribed to etherification, esterification, acetalization and aldol condensation. Through humins characterizations, it was found out that the aldol condensation moiety between aldehyde group and LA is critical to justify the characteristic IR peaks (at 1620 and 1710 cm-1) and aromatic fragments from pyrolysis GC-MS. Furthermore, the humins structures with varying content of aldol condensation could be controllably synthesized from different temperatures and time, which were in good correlation with the amount of LA in the system, demonstrating the continuous evolution process of HMF-humins. Thereby, the missing step from the feedstock in solution to humins in solid has finally been completed, with the active intermediates revealed and the structure discrepancies between low temperature and hydrothermal conditions compared unambiguously. We believe elucidation of the chemical structure and formation mechanism of HMF-derived humins is deemed to provide new insights in the field of biomass conversion.

## Experimental Section

HMF was used as the model compound in this study. HMF and 50% $H_2SO_4$ were mixed up in a glass vial, wherein the molar ratio of HMF/$H_2SO_4$ was 1/0.36. The mixture was stored at different temperatures for a certain time. Then the reaction mixture can be subjected to HPLC-MS/MS analysis or silica gel column chromatography with MeOH/$CH_2Cl_2$ (1/100 to 1/10, v/v) for separation of the intermediates. On the other hand, the humins solid can be obtained by washing thoroughly with deionized water until the liquid phase was neutral. Then the humin samples were centrifuged and dried in desiccator for 2 days, followed by characterisations.

The NMR spectra were recorded using Bruker Avance II 400 MHz spectrometer. The scanning electron microscopy (SEM) images were obtained on NOVA NanoSEM 450 field emission scanning electron microscopy. The infrared spectra were recorded on Thermo Fisher 6700 infrared spectrometer.

The HPLC-MS/MS analyses of the reaction mixture were conducted on Thermo Scientific LTQ Orbitrap XL mass with electrospray ionization (ESI) in positive ion polarity mode. The applied spray voltage was 3500 V. The capillary temperature and voltage was 350 °C and 35 V, respectively. The separation by the HPLC method was carried out using Thermo Fisher Accela 1250 LC equipped with a diode array detector and a chromatographic column ZORBAX SB-C18 (150 × 4.6 mm, 5 μm). The reaction mixture was analysed using gradient elution, with mobile phase of acetonitrile/water and flow rate 0.8 mL/min.

Analytical pyrolysis GC-MS of humins was performed on a CDS 1500 equipped with Agilent 5975-6890N GC-MS. The pyrolysis program was set to ramp from 60 °C to 550 °C at a rate of 20 °C/ms and maintained at 550 °C for 10 s. After pyrolysis, the pyrolyzed products were transferred into a capillary column (Angilent 19091J-433, 30 m × 250 μm × 0.25 μm) with helium as the carrier gas (1.0 mL/min). The GC temperature program was applied: initial temperature of 60 °C for 3 min, followed by heating to 280 °C at a rate of 10 °C /min, and finally at 280 °C for 35 min. The electron multiplier voltage was set at 1964.7 V.

The interface temperature was kept at 260 °C. The quadrupole and ionization temperature was 150 °C and 230 °C respectively. A scan range of m/z 20.0-600.0 was applied.

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**Keywords:** biomass • humins • 5-hydroxymethylfurfural • reactive intermediates • aldol reaction

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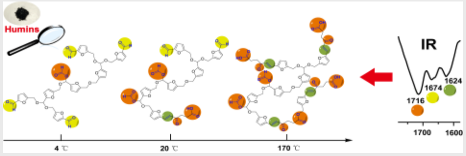
## Entry for the Table of Contents

### RESEARCH ARTICLE



By the low-temperature approach, the key intermediates towards HMF-derived humins were captured, revealing multiple elementary reactions such as etherification, esterification, aldol condensation, and acetalization. Furthermore, the humins structures with varying content of aldol condensation could be controllably synthesized from different temperatures and times, demonstrating the evolution process of HMF-derived humins.

*Haiyan Shen, Haozhe Shan, Li Liu**

***Page No. – Page No.***

**Evolution process and controlled synthesis of humins with 5-hydroxymethylfurfural (HMF) as model molecule**