



Formation of humins during degradation of carbohydrates and furfural derivatives in various solvents

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Abstract

Humins are undesired solids formed during the hydrothermal degradation of carbohydrates. In order to reveal the mechanism of formation of humins, we studied the degradation behavior of 11 model compounds including carbohydrates and furfural derivatives, within water and various pure organic solvents as reaction media. All the studied carbohydrates could generate solid humins in both water and studied organic solvents except ethanol, while the furfural derivatives could generate solid humins in only water. The results could be explained by regarding the formed α -carbonyl aldehydes and α,β -unsaturated aldehydes as primary precursors for formation of humins. Furfural derivatives could generate chain α -carbonyl aldehydes (for example, 6-hydroxy-2,5-dioxohexanal from 5-hydroxymethylfurfural and 2-oxopentanedial from furfural) through hydrolytic ring opening reaction; thus, water is essential for these furfural derivatives to generate humins. As for carbohydrates, they could generate α -carbonyl aldehydes and α,β -unsaturated aldehydes through simple step of β -elimination in all solvents; thus, they could form humins in both water and studied organic solvents except ethanol. Ethanol could react with α -carbonyl aldehydes by acetalization; thus, the condensation between α -carbonyl aldehydes was suppressed in ethanol, leading to few humins formation from carbohydrates. Based on the above analysis, we proposed that the formed α -carbonyl aldehydes and α,β -unsaturated aldehydes should be the primary precursor of humins.

Keywords Carbohydrates · Furfural derivatives · Humins · Condensation · α -Carbonyl aldehyde

1 Introduction

The depletion of fossil fuels and the increasing demand for fuel, energy, and chemicals have generated interest in alternative, sustainable resources. The abundant and renewable

lignocellulosic biomass is one sustainable carbon resources; thus, increasing interest has been paid to transform the raw biomass into valuable chemicals and fuels. Carbohydrate polymers, such as cellulose and hemicellulose, account for about 70% of the lignocellulosic biomass, so conversion of these polysaccharides to bio-based platform chemicals play critical roles for the sustainable development of human society [1, 2]. Catalytic hydrothermal conversion is regarded as one effective method to convert the cellulose and hemicellulose into valuable platform chemicals such as 5-hydroxymethylfurfural (HMF), furfural, levulinic acid, and lactic acid [3–6]. Unfortunately, the formation of humins, one kind of low-value solid by-product, greatly diminishes the yield of valuable platform chemicals in the hydrothermal treatment of lignocellulosic biomass and reduces the economy of the hydrothermal conversion process [7–11]. Although great amount of work are reported to valorization the solid humins by regarding them as sustainable and harmless carbon resources [12] to produce hydrogen [13], synthesis gas [14], carbon materials [15–18], adhesive [19], and even thermoset-like resins [10, 20], it seems that suppressing formation of

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humins could be more favored to improve the economy of the biorefinery process.

Studying the formation of humins mechanism could be helpful to developing efficient method to suppress their formation; thus, great efforts have been devoted to reveal the formation of humins mechanism [21–25]. As has been shown in Fig. 1, different routes are proposed by the previously literatures for formation of humins from carbohydrates: (1) humins are formed by directly polycondensation between the furfural and related derivatives through electrophilic substitution [23] (Route 1 in Fig. 1); (2) humins are formed by aldol addition/condensation between furfural derivatives and chain aldehydes rich in carbonyl group (2,5-dioxo-6-hydroxyhexanal for example) formed by hydrolytic ring opening of these furfural derivatives [24, 25] (Route 2 in Fig. 1); (3) humins are formed by condensation of carbohydrates with the furfural-related derivatives through acetalization and etherification [21] (Route 3 in Fig. 1); (4) humins are formed by polymerization of carbohydrates with the furfural-related derivatives through aldol condensation [22] (Route 4 in Fig. 1). Although great efforts on the formation of humins mechanism have been devoted, the formation of humins mechanism remains unclear and still needs to be studied in depth.

Identification of the key primary precursors would be very helpful to understand the formation of humins mechanism.

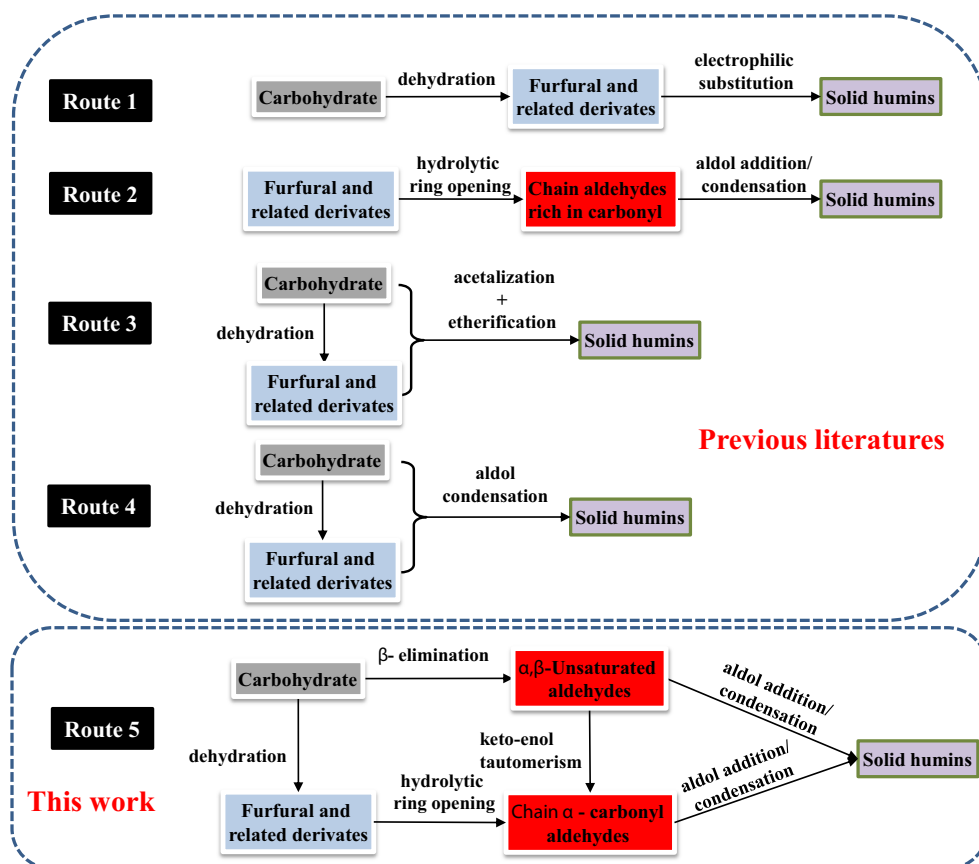
Herein, we studied the formation of humins during the degradation of four species of model compounds (furfural derivatives, aldoses, ketoses, and 2-deoxyaldoses) in various solvents and found that the formation of humins from these model compounds could be satisfactorily explained by regarding the formed α -carbonyl aldehydes and α,β -unsaturated aldehydes as the key primary precursor for formation of humins (Route 5 in Fig. 1); thus, we proposed that the humins are formed by aldol addition/condensation of the formed α -carbonyl aldehydes and α,β -unsaturated aldehydes during hydrothermal degradation of carbohydrates.

2 Experimental sections

2.1 Experimental materials

Glucose (AR, 99%), fructose (AR, 99%), sorbose (AR, 99%), xylose (AR, 99%), ribose (AR, 99%), 2-deoxyglucose (98%), 2-deoxyribose (98%), 5-hydroxymethylfurfural (98%), 5-methylfurfural (98%), furfural (99%), furfuryl alcohol (97%), ethyl acetate (AR, 99%), tetrahydrofuran (AR, 99%), and ethanol(AR, 99%) were all purchased from Aladdin reagent company (Shanghai, China). All these chemicals were used without further treatment.

Fig. 1 Possible formation of humins routes from carbohydrates proposed by previous literature and this work



2.2 The hydrothermal decomposition of the model compounds

Thirty-milliliter deionized water and model compounds containing 0.12 mol carbon atoms were placed in a Teflon-lined autoclave and kept at 493 K for 5 h to carry out the hydrothermal degradation process. After the hydrothermal degradation process, the solid products were separated by filtering, washed with distilled water and ethanol, and finally dried at 373 K and weighed, while the filtrates were evaporated and dried at 373 K to obtain the involatile products (403 K for conditions with water as reaction media). The carbon yields of the humins were calculated by dividing the total mass of carbon in solid residues (assuming that the carbon content in the solid residues be 65%) by the carbon in the feedstock, while the carbon yields of the involatile products were calculated by dividing the total mass of carbon in the involatile products (assuming that the carbon content in the involatile products to be 60%) by the total mass of carbon in the feedstock. The carbon yield of volatiles was calculated by 100% minus the carbon yield of humins and the carbon yield of non-volatiles [4].

The concentrations of carbohydrates and furfural derivatives were analyzed on an Agilent 1200 series HPLC (Bio-Rad HPX-87H) with a RI and UV detector (210 nm), using a 5 mM aqueous sulfuric acid solution as the eluent at a flow rate of 0.5 mL/min. The column and RI detector temperature were set at 55 °C and 45 °C, respectively [5, 6]. The conversion of the carbohydrates and furfural derivatives is calculated by dividing the model compounds in the filtrate by the feed model compounds.

The volatile products in filtrate were analyzed by gas chromatography with mass spectroscopy detection (GC/MS), which was performed using a Agilent 7890B GC System

equipped with Agilent 5977A MSD. The column used was a HP-5 ms Ultra Inert capillary column (30 m × 0.25 mm × 0.25 μm). The oven temperature was programmed to hold at 45 °C, ramp at 10 °C/min to 220 °C, and hold at 220 for 2 min. The flow rate of the He carrier gas was 1.2 mL/min. Experiments were performed in at least duplicate and the results presented an average of two or three measurements.

3 Results and discussion

3.1 Degradation behavior of furfural derivatives in water and ethyl acetate

In the beginning, we compared the degradation behavior of furfural derivatives in water and in pure ethyl acetate. As shown in Table 1, the conversions of all these furfural derivatives in ethyl acetate were always lower than those in water, suggesting that these furfural derivatives were more stable in ethyl acetate than in water. The yields of humins obtained from these furfural derivatives in water were also much different from those in ethyl acetate. The yields of humins from HMF, 5-methylfurfural, furfural, and furfural alcohol in water were 64.6%, 12.1%, 23.4%, and 29.2%, respectively (Table 1, entry 1–4), indicating that these furfural derivatives all could generate humins in water. However, no solid humins were formed when degradation of these furfural derivatives was carried out in ethyl acetate (Table 1, entry 5–8), suggestion that the formations of humins from these furfural derivatives were suppressed. The carbon yield of non-volatiles (1.3–10.5%) generated from these furfural derivatives in ethyl acetate was also much lower than those in water (12–30%), indicating

Table 1 Carbon yields of humins and other products from furfural derivatives in water and ethyl acetate

Entry	Feed stock ^a	Solvent	Conversion (%)	Carbon yield of products (%)		
				Humins	Non-volatiles	Volatiles
1	HMF	Water	100	64.6 ± 2.0%	14.5 ± 1.0%	20.9 ± 2.0%
2	5-Methylfurfural	Water	62.3 ± 2.0%	12.1 ± 2.0%	19.2 ± 1.0%	68.7 ± 2.0%
3	Furfural	Water	74.6 ± 2.0%	23.4 ± 2.0%	12.4 ± 1.0%	64.2 ± 2.0%
4	Furfuryl alcohol	Water	100	29.2 ± 2.0%	30.2 ± 1.0%	40.6 ± 2.0%
5	HMF	Ethyl acetate	84.6 ± 2.0%	N.D.	10.5 ± 1.0%	89.5 ± 2.0%
6	5-Methylfurfural	Ethyl acetate	5.9 ± 0.5%	N.D.	3.6 ± 0.5%	96.4 ± 2.0%
7	Furfural	Ethyl acetate	4.8 ± 0.5%	N.D.	1.2 ± 0.5%	98.8 ± 1.0%
8	Furfuryl alcohol	Ethyl acetate	38.3 ± 2.0%	N.D.	2.9 ± 0.5%	97.1 ± 2.0%

Reaction condition, 30 mL H₂O, 493 K, 5 h

N.D., not detected

^a 0.12 mol carbon atoms contained in raw material

that the condensation/polymerization of these furfural derivatives (or their degradation products) was suppressed. The results confirmed that water is essential for these furfural derivatives to form humins and non-volatiles. It should be noted that the conversions of HMF and furfuryl alcohol (both of which contain $\text{CH}_2\text{-OH}$ group linked on the furan ring) in both solvents are higher than 5-methylfurfural and furfural, suggesting that the $\text{CH}_2\text{-OH}$ group is more active than HC=O group under the condition.

The volatiles generated from degradation of all these furfural derivatives in ethyl acetate were much higher than those in water. We employed GC-MS to identify the volatile compounds formed in ethyl acetate. As has been shown in Figs. 2, 5-formylfuran-2-yl)methyl acetate and 5,5'-(oxybis(methylene))bis(furan-2-carbaldehyde) were the main products from HMF, while furfuryl acetate and 2,2'-(oxybis(methylene))difuran were the main products

from furfuryl alcohol in ethyl acetate (Fig. 2a and b), suggesting that etherification and transesterification (all of which involves the reaction of $\text{CH}_2\text{-OH}$ group) are the two main reactions for HMF and furfuryl alcohol when ethyl acetate was employed as reaction media [26–28]. On the contrary, 5-methylfurfural and furfural were quite stable, and only very little volatile degradation product was detected by GC-MS (Fig. 2c), indicating that the HC=O group is stable in ethyl acetate. Besides, negligible hydrolytic ring opening products (levulinic acid, ethyl levulate, etc.) were detected by GC-MS analysis from all these furfural derivatives, confirming that ring opening of these furfural derivatives was also suppressed in ethyl acetate [29]. The MS profiles of HMF, 5-formylfuran-2-yl)methyl acetate, 5,5'-(oxybis(methylene))bis(furan-2-carbaldehyde), furfuryl alcohol, furfuryl acetate, 2,2'-(oxybis(methylene))difuran, and furfural are shown in Fig. S1–S7.

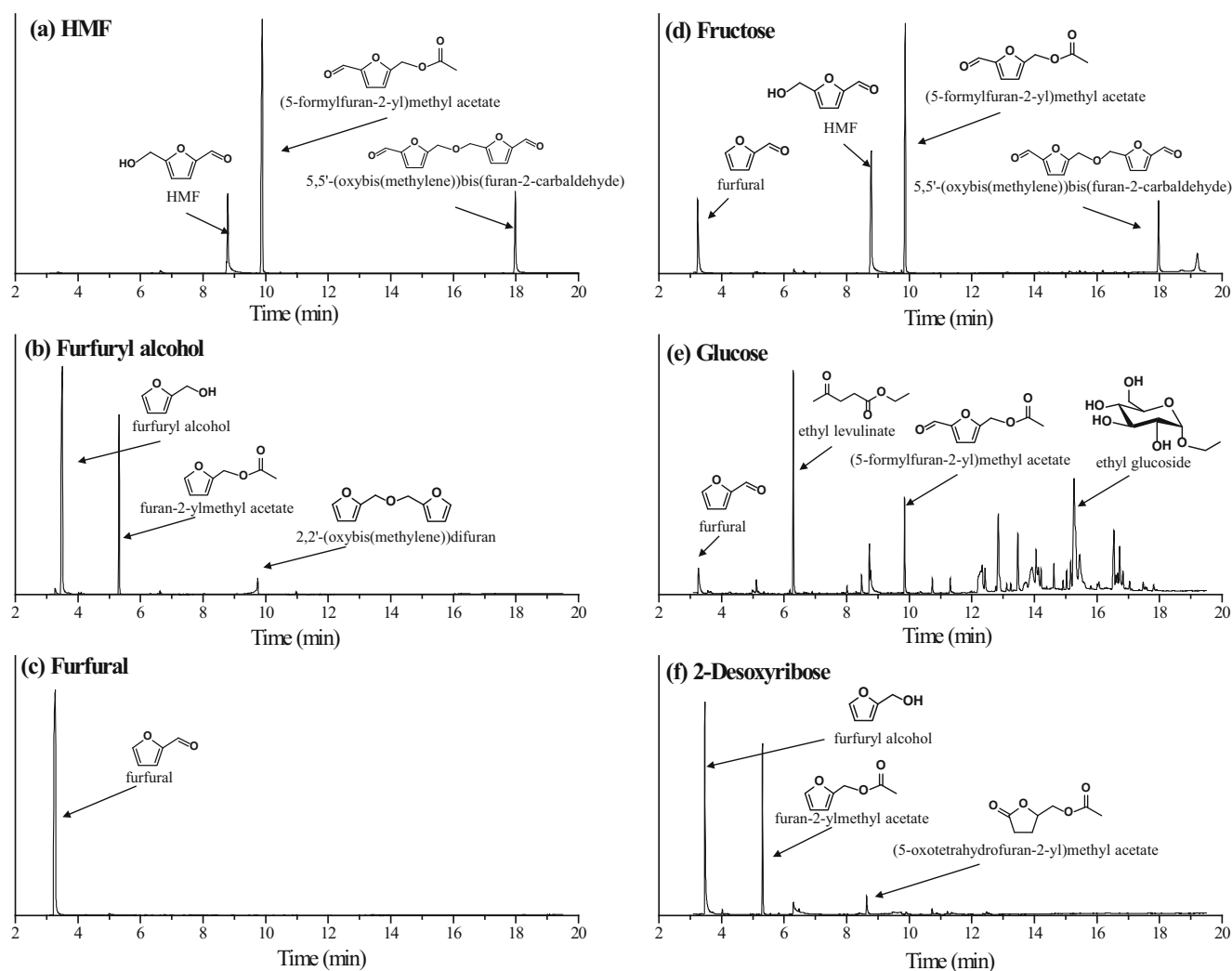


Fig. 2 Products identified by GC-MS during degradation in ethyl acetate from HMF (a), furfuryl alcohol (b), furfural (c), fructose (d), glucose (e), and 2-desoxyribose (f). Reaction condition, 30 mL H_2O , 493 K, 5 h, 0.12 mol carbon atoms contained in raw material

Because no humins and hydrolytic ring opening products were generated from furfural derivatives in ethyl acetate, we proposed that the intermediates formed by hydrolytic ring opening of these furfural derivatives, such as 2,5-dioxo-6-hydroxy-hexanal from 5-hydroxymethylfurfural and 2-oxopentanedial from furfural [29], are the key primary precursors for these furfural derivatives to generate the solid humins (Route 2 in Fig. 1), as has been proposed by Patil et al. [24, 25]

3.2 Degradation behavior of carbohydrates in water and ethyl acetate

Above results had confirmed that furfural derivatives could only generate humins in water instead of ethyl acetate. If the furfural derivatives are the only intermediate for these carbohydrates to generate humins, then the degradation behavior of carbohydrates should be consistent with these furfural derivatives. So we further studied the degradation behavior of carbohydrates in water and ethyl acetate.

As shown in Table 2, the degradation behaviors of carbohydrates were quite different with these furfural derivatives. The conversion of the studied carbohydrates all reached 100% in both water and ethyl acetate, suggesting that carbohydrates are instable in both solvents. Besides, all these studied carbohydrates could generate solid humins in both water and ethyl acetate, indicating that the formation of humins from these carbohydrates could not be suppressed in ethyl acetate. Degradation of fructose, sorbose, glucose, xylose, and ribose in water could generate humins at yields of 54.1%, 52.8%, 60.7%, 42.5%, and 41.0%, respectively (Table 2, entry 1–5).

However, when ethyl acetate was employed as the solvent, the yield of humins from fructose and sorbose (both of which are ketoses) decreased to 33.1% and 35.8%, respectively (Table 2, entry 6–7), while the yield of humins from glucose, xylose, and ribose (all of which are aldoses) increased to 73.1%, 56.6%, and 54.9%, respectively (Table 2, entry 8–10). Obviously, the ketoses yielded less humins in ethyl acetate than in water, while the aldoses are the opposite. The different behavior of ketoses and aldoses could be explained by the different propensity for formation of furfural derivatives. Generally, ketoses such as fructose are presented as furanose form structures in solvents; thus, they could selectively undergo dehydration to form furfural derivatives [30, 31], leading to lower humins and higher volatiles formation in ethyl acetate than in water. On the contrary, the aldoses are generally present as pyranose form structure, so they could not selectively undergo dehydration to generate furfural derivatives [5, 32]. Besides, around 10–20% of non-volatile products were generated from these carbohydrates in both water and ethyl acetate, indicating that the polymerization of the formed intermediates could not be efficiently suppressed in ethyl acetate.

GC-MS analysis also confirmed that fructose can be selectively transformed into furfural derivatives, such as furfural, HMF, (5-formylfuran-2-yl)methyl acetate, and 5,5'-(oxybis(methylene))bis(furan-2-carbaldehyde), while glucose could not be selectively transformed into furfural derivatives (Fig. 2d and e). Except for furfural derivatives, ethyl levulinate, ethyl glucoside, and multiple unidentified by-products were also detected in the degradation

Table 2 Carbon yields of humins and other products from carbohydrates in water and ethyl acetate

Entry	Feed stock ^a	Solvent	Conversion (%)	Carbon yield of products (%)		
				Humins	Non-volatiles	Volatiles
1	Fructose	Water	100	54.1 ± 2.0%	16.2 ± 1.0%	29.7 ± 2.0%
2	Sorbose	Water	100	52.8 ± 2.0%	15.2 ± 1.0%	32 ± 2.0%
3	Glucose	Water	100	60.7 ± 2.0%	13.5 ± 1.0%	25.8 ± 2.0%
4	Xylose	Water	100	42.5 ± 2.0%	12.5 ± 1.0%	45 ± 2.0%
5	Ribose	Water	100	41.0 ± 2.0%	13.2 ± 1.0%	45.8 ± 2.0%
6	Fructose	Ethyl acetate	100	33.1 ± 2.0%	12.9 ± 1.0%	54 ± 2.0%
7	Sorbose	Ethyl acetate	100	35.8 ± 2.0%	12.1 ± 1.0%	52.1 ± 2.0%
8	Glucose	Ethyl acetate	100	73.1 ± 2.0%	12.5 ± 1.0%	14.4 ± 2.0%
9	Xylose	Ethyl acetate	100	56.6 ± 2.0%	19.2 ± 1.0%	24.2 ± 2.0%
10	Ribose	Ethyl acetate	100	54.9 ± 2.0%	16.4 ± 1.0%	28.7 ± 2.0%
11	Glyoxal	Water	100	21.7 ± 2.0%	3.8 ± 1.0%	74.5 ± 2.0%
12	Pyruvaldehyde	Water	100	44.2 ± 2.0%	6.7 ± 1.0%	46.1

Reaction condition, 30 mL H₂O, 493 K, 5 h

^a 0.12 mol carbon atoms contained in raw material

Table 3 The C₃–C₆ α -carbonyl aldehydes, α -hydroxy acids, β,γ -unsaturated- α -carbonyl aldehydes, and β,γ -unsaturated- α -hydroxy acids from furfural derivatives and aldose [24, 29, 34–43]

Aldose	α -Carbonyl aldehydes	α -Hydroxy acids	β,γ -Unsaturated- α -carbonyl aldehydes	β,γ -Unsaturated- α -hydroxy acids
HMF	2,5-Dioxo-6-hydroxy-hexanal	–	–	–
Furfural	2-Oxopentanedial	–	–	–
Glucose	3-Deoxyglucosone	(2R,4S,5R)-2,4,5,6-Tetrahydroxyhexanoic acid	5,6-Dihydroxy-2-oxohex-3-enal	(2R,5S)-2,5,6-Trihydroxyhex-3-enoic acid
Xylose	3-Deoxyxylosone	(2R,4S)-2,4,5-Trihydroxypentanoic acid	5-Hydroxy-2-oxopent-3-enal	(R)-2,5-Dihydroxypent-3-enoic acid
Erythrose	4-Hydroxy-2-oxobutanal	(R)-2,4-Dihydroxybutanoic acid	2-Oxobut-3-enal	(R)-2-Hydroxybut-3-enoic acid
Glyceraldehyde	Pyruvaldehyde	Lactic acid	–	–

products of glucose. It should be noted that ethyl levulinate was not detected from fructose, but it was the main product during the degradation of glucose, suggesting that glucose may generate levulinic acid through a pathway without formation of HMF.

3.3 Discussion on the primary precursors and initial reactions for formation of humins

Generally, HMF and furfural are regarded as the primary precursors for formation of humins. Two routes for formation of humins from HMF/furfural are proposed, one route involves the electrophilic substitution of these compounds without ring opening reaction [23, 33] (Route 1 in Figure 1), and the other route involves the aldol condensation of the chain aldehydes rich in carbonyl group formed by hydrolytic ring opening of HMF/furfural [24, 25] (Route 2 in Figure 1). In this study, the formation of humins from these furfural derivatives in water but the absence of humins in ethyl acetate indicate that water is essential for these furfural derivatives to generate humins, suggesting that the route for formation of humins from furfural derivatives via hydrolytic ring opening of the furfural derivatives followed by aldol condensation of the formed chain aldehydes rich in carbonyl group seemed to be more feasible (Route 2 in Figure 1). On the other hand, the formation of humins from carbohydrates and the absence of humins from furfural derivatives in ethyl acetate suggested that carbohydrates may generate humins with other intermediates in addition to furfural derivatives. Some studies also proposed that reaction between carbohydrates and furfural derivatives through aldol condensation [22] or acetalization [21] could lead to the formation of humins (Route 3 and 4 in Figure 1). However, the formation of large amounts of humins from solely furfural derivatives indicates that those routes could not be main routes for formation of humins. Thus, the results in this study suggested that the proposed routes for formation of humins are incorrect or incomplete, and humins could be formed via other species of primary precursors during the hydrothermal conversion of carbohydrates and furfural derivatives.

Identification of the primary precursor of formation of humins during the degradation of carbohydrate is important for revealing the mechanism of formation of humins. Previous reports have confirmed that hydrolytic ring opening of furfural derivatives could generate chain α -carbonyl aldehydes (Fig. 3) [24, 29]. For example, 2,5-dioxo-6-hydroxy-hexanal could be formed by hydrolytic ring opening of HMF, while 2-oxopentanedial could be formed by hydrolytic ring opening of furfural [29] (Table 3). On the other hand, recent research progresses confirmed that the degradation of aldoses (glucose, xylose, erythrose, and glyceraldehyde) could generate a series of C₃–C₆ α -carbonyl aldehydes, α -hydroxy acids, β,γ -unsaturated- α -carbonyl aldehydes, and β,γ -unsaturated- α -hydroxy acids (Table 3) [34–42]. In particular, Tolborg et al.

identified the products of 3-deoxyglucosone, 3-deoxygluconic acid, *trans*-2,5,6-trihydroxy-3-hexenoic acid, and 3-deoxy- γ -gluconolactone during the hydrothermal degradation of glucose catalyzed by Sn- β [34]. Elliot et al. reported that catalytic degradation of xylose could generate 3-deoxyxylosone, *cis*-3,4-dideoxyxylos-3-enone, *trans*-3,4-dideoxyxylos-3-enone, 2,5-dihydroxy-4-methoxy-pentanoic acid, 3-deoxypentanolactone, and *trans*-2,5-dihydroxy-3-pentenoic acid [36]. Dusselier et al. reported that catalytic degradation of glucose and erythrose could produce 2-hydroxy butenoic acid, α -hydroxy- γ -butyrolactone, and 2,4-dihydroxy butyric acid [40, 41]. Among all these identified chemicals, the chain α -carbonyl aldehydes with several adjacent carbonyl groups, such as 3-deoxyglucosone, 3-deoxyxylosone, 4-hydroxy-2-oxobutanal, and pyruvaldehyde, all could be generated from aldoses through β -elimination reaction followed by keto-enol tautomerism [34–42]. According to the above analysis, we found that the α -carbonyl aldehydes could be formed both from hydrolytic ring opening of furfural derivatives and from β -elimination of carbohydrates. Thus, we suggest that these chain α -carbonyl aldehydes formed during the degradation of carbohydrates may be the primary precursors for formation of humins.

The formation of humins from furfural derivatives and carbohydrates in water and ethyl acetate can be satisfactorily explained by regarding α -carbonyl aldehydes as the primary precursors for formation of humins. As α -carbonyl aldehydes could be formed from dehydration of carbohydrates and hydrolytic ring opening of furfural derivatives (Fig. 3), so humins could be formed from furfural derivatives solely in hot compressed water, or from carbohydrates in both water and ethyl acetate. On the contrary, when decomposition of these furfural

derivatives is carried out in organics such as pure ethyl acetate, the hydrolytic ring opening reaction of these furfural derivatives was suppressed [5, 43, 44], leading to only little α -carbonyl aldehydes and humins being generated. As for the carbohydrates, aldoses (glucose, xylose, and ribose) could easily generate α -carbonyl aldehydes through β -elimination reaction followed by keto-enol tautomerism in both water and ethyl acetate (Fig. 3) [34, 36]; thus, they could yield solid humins in both water and ethyl acetate. As for the ketoses, they could undergo dehydration to form furfural derivatives, thus leading to less formation of humins in ethyl acetate than in water. Because the formation of α -carbonyl aldehydes can explain the formation of humins from all these model compounds, we proposed that α -carbonyl aldehydes are the key primary precursors for formation of humins from furfural derivatives and carbohydrates.

To further confirming that α -carbonyl aldehydes are the key primary precursors for formation of humins, we studied the hydrothermal degradation behavior of glyoxal and pyruvaldehyde, both of which are α -carbonyl aldehydes. The results showed that 21.7% of humins could be formed during the hydrothermal degradation of glyoxal, while pyruvaldehyde could yield 44.2% of humins (Table 2, entry 11–12), further indicating that α -carbonyl aldehydes should be the key primary of formation of humins.

3.4 Degradation behavior of 2-deoxyaldoses in water and ethyl acetate

In the above study, we suggested the humins generated during the degradation of furfural derivatives, ketoses, and aldoses in various solvents with the α -carbonyl aldehydes as the key

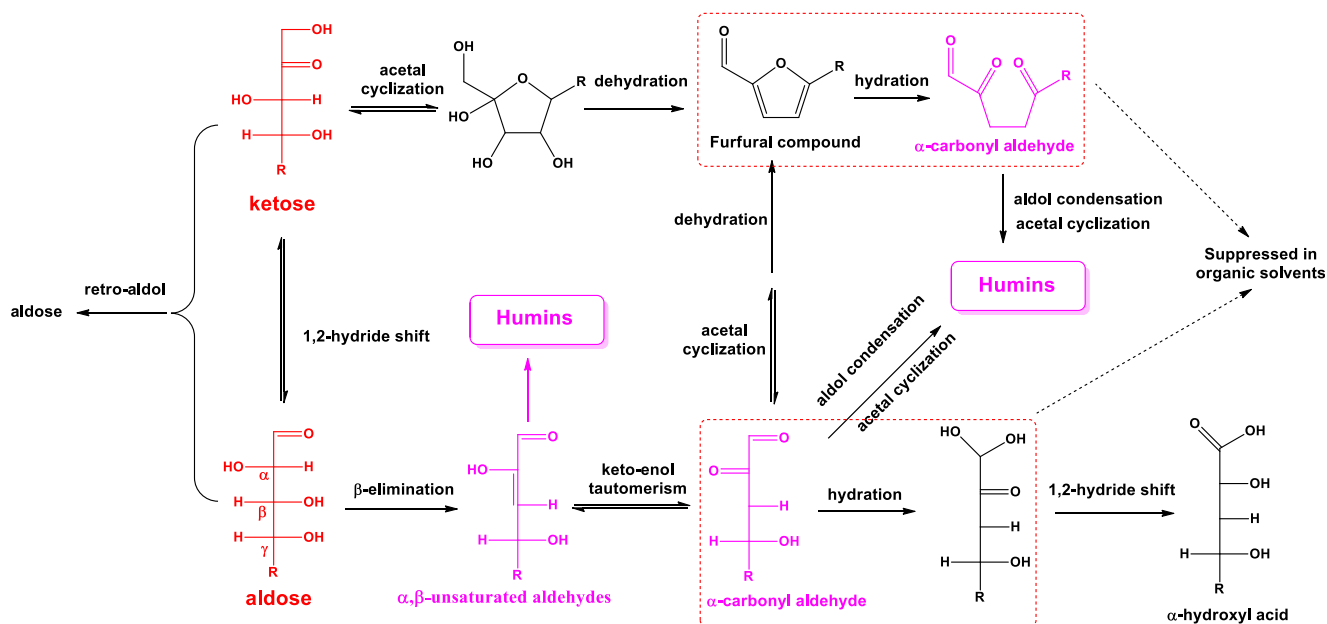
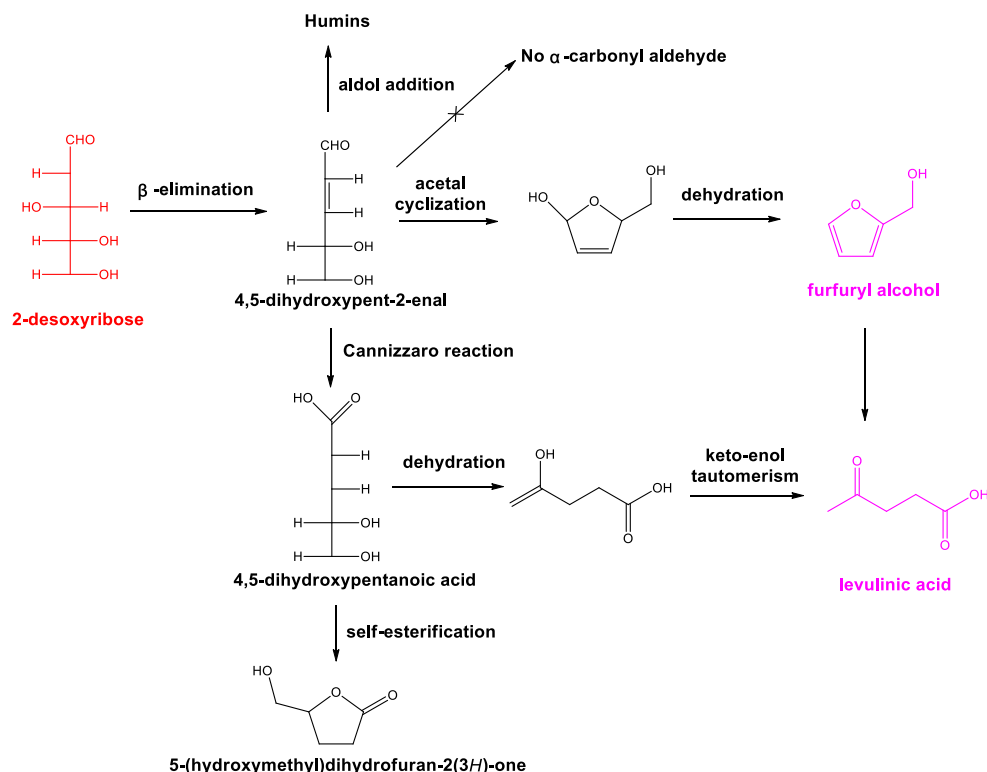


Fig. 3 Plausible pathways in hydrothermal degradation path of ketoses, aldoses, and furfural derivatives

Fig. 4 Plausible hydrothermal conversion pathways of 2-deoxyribose



precursor of humins. Unlike aldoses, 2-deoxyaldoses could hardly generate α -carbonyl aldehydes through the two steps of β -elimination and keto-enol tautomerism during the degradation process (Fig. 4), so we further studied the degradation behavior of 2-deoxyaldoses. However, both of them could generate solid humins in both water and organic solvent, which could not be explained by regarding α -carbonyl aldehydes as the primary precursors of humins (Table 4). Especially, degradation of 2-deoxyglucose and 2-deoxyribose in water can generate as high as 41.2% and 40.6% of humins, respectively. Because these 2-deoxyaldoses all could generate α,β -unsaturated aldehydes with chain structure, we proposed that the α,β -unsaturated aldehydes are also the key precursors of humins production from these 2-deoxyaldoses.

GC-MS analysis confirmed that furfuryl alcohol and furfuryl acetate are the main products formed during 2-deoxyribose degradation in ethyl acetate, indicating that 2-deoxyribose can be easily converted into furfuryl alcohol [45]. Small amounts of 5-(ethoxymethyl)dihydrofuran-2(3H)-one was also detected, which was formed by transesterification of 5-(methyl)dihydrofuran-2(3H)-one with ethyl acetate (Fig. 2(f)). The MS profiles of ethyl levulinate and 5-(ethoxymethyl)dihydrofuran-2(3H)-one are shown in Fig. S8-S9.

The possible formation mechanism of furfuryl alcohol, levulinic acid, and 5-(hydroxymethyl)dihydrofuran-2(3H)-one are shown in Fig. 4. The 2-deoxyribose could undergo β -elimination to generate one α,β -unsaturated aldehyde named 4,5-dihydroxypent-2-enal, which could

Table 4 Carbon yield of humins and other products from 2-deoxyaldoses in water and ethyl acetate

Entry	Feed stock ^a	Solvent	Carbon yield of products (%)		
			Humins	Non-volatiles	Volatiles
1	2-Deoxyglucose	Water	41.2 ± 2.0%	13.7 ± 1.0%	45.1 ± 2.0%
2	2-Desoxyribose	Water	40.6 ± 2.0%	14.4 ± 1.0%	45 ± 2.0%
3	2-Deoxyglucose	Ethyl acetate	1.4 ± 2.0%	21.8 ± 1.0%	76.8 ± 2.0%
4	2-Desoxyribose	Ethyl acetate	28.8 ± 2.0%	16.7 ± 1.0%	54.5 ± 2.0%

Reaction condition, 30 mL H₂O, 493 K, 5 h

^a 0.12 mol carbon atoms contained in raw material

Table 5 Carbon yield of humins from carbohydrates and furfural derivatives in tetrahydrofuran and ethanol

Entry	Feed stock ^a	Carbon yield of humins obtained in various solvents (%)	
		Tetrahydrofuran	Ethanol
1	HMF	N.D.	N.D.
2	5-Methylfurfural	N.D.	N.D.
3	Furfural	N.D.	N.D.
4	Furfuryl alcohol	N.D.	N.D.
5	Fructose	27.4 ± 2.0%	2.1 ± 0.5%
6	Sorbose	28.3 ± 2.0%	1.5 ± 0.5%
7	Glucose	52.6 ± 2.0%	N.D.
8	Xylose	38.7 ± 2.0%	N.D.
9	Ribose	40.4 ± 2.0%	N.D.
10	2-Deoxyglucose	N.D.	N.D.
11	2-Desoxyribose	22.7 ± 2.0%	N.D.

Reaction condition, 30 mL solvents, 493 K, 5 h

N.D., not detected

^a 0.12 mol carbon atoms contained in raw material

further undergo acetal cyclization and dehydration to form furfuryl alcohol [45], or undergo Cannizzaro reaction to generate 4,5-dihydroxypentanoic acid. The formed 4,5-dihydroxypentanoic acid can further undergo dehydration and keto-enol tautomerism to form levulinic acid, or undergo self-esterification to generate 5-(hydroxymethyl)dihydrofuran-2(3H)-one [46].

3.5 Degradation behavior of carbohydrates in other organic solvents

In order to further verify the previous speculation, we further studied the degradation of these model compounds in two common organic solvent of tetrahydrofuran and ethanol (Table 5). Similar with the condition in ethyl acetate, these furfural derivatives still could not generate humins in tetrahydrofuran and ethanol (Table 5, entry 1–4), which further confirmed that water is essential for these furfural derivatives to generate humins.

The yields of humins formed from carbohydrates were all decreased within tetrahydrofuran as reaction media compared with ethyl acetate and water, but the yield of humins generated from aldoses is always higher than those from ketoses and 2-deoxyaldoses (Table 5, entry 5–11). We propose that the tetrahydrofuran played similar role with ethyl acetate, which could suppress the formation of humins from carbohydrates via suppressing the hydrolytic ring opening of the furfural derivatives, but could not suppress the formation of chain α -carbonyl aldehydes and α,β -unsaturated aldehydes from β -elimination of aldoses. Thus, the carbon yields of humins from carbohydrates were decreased compared with the condition with water as reaction media.

When ethanol was employed as reaction media, no humins were formed from aldoses, and only very little humins were formed from ketoses (2.1% from fructose and 1.5% from sorbose), which were consisted with the previous reports [47–49]. The reduced formation of humins could be due to that the ethanol could react with the formed chain α -carbonyl aldehydes through acetalization [48–50], thus suppressed the aldol addition/condensation of the formed α -carbonyl aldehydes and α,β -unsaturated aldehydes.

4 Conclusion

In summary, we studied the degradation behavior of 11 model compounds including aldoses (glucose, xylose, ribose), ketoses (fructose, sorbose), furfural derivatives (furfural, 5-hydroxymethylfurfural, 5-methylfurfural and furfuryl alcohol), and 2-deoxyaldoses (2-deoxyglucose and 2-desoxyribose) in various solvents (water, ethyl acetate, tetrahydrofuran, and ethanol), and the results suggested that the chain α -carbonyl aldehydes and α,β -unsaturated aldehydes should be the key primary precursors for formation of humins. Carbohydrates could undergo β -elimination to form α,β -unsaturated aldehydes, which can undergo keto-enol tautomerism to generate α -carbonyl aldehydes; the carbohydrates could also undergo dehydration to form furfural and related derivatives, which could undergo hydrolytic ring opening to generate α -carbonyl aldehydes. These formed α,β -unsaturated aldehydes and α -carbonyl aldehydes could undergo aldol addition/condensation to generate solid humins. Thus, we propose that humins are formed by aldol condensation/addition of the formed α -carbonyl aldehydes and α,β -unsaturated

aldehydes during the degradation of carbohydrates and furfural derivatives.

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