

Supporting information

Catalytic conversion of carbohydrate-derived oxygenates over HZSM-5 in a tandem micro- reactor system

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1. Characterization of synthesized HMF

To verify the successful synthesis of ^{13}C HMF, the spectrum of the two synthesized HMF was compared with the standard spectrum of HMF. The position of ^{13}C in the HMF could be determined by its mass spectrum shown in figure S1, which is obtained by using NIST data base. Comparing to standard HMF, the molecular ion of the synthesized HMF from D-Glucose-1- ^{13}C or D-Glucose-6- ^{13}C has m/z of 127 instead of 126, suggesting the synthesized HMF contains one ^{13}C atom. The position of ^{13}C could be inferred by the m/z of base peak. For HMF, the base peak represents the fragment ion left over by loss of CO from C-1. Therefore, the standard HMF has m/z of 97 as base peak. The m/z of base peak being 97 is expected for 1- ^{13}C HMF due to the loss of labeled ^{13}C as ^{13}CO , which is the case as shown in figure S1 (b). Therefore, 1- ^{13}C HMF was successfully synthesized by using D-Glucose-1- ^{13}C as precursor. Differently, the m/z for base peak is 98 in figure S1 (c), suggesting the ^{13}C is not the first carbon in the HMF when D-Glucose-6- ^{13}C was used as precursor for synthesis. Furthermore, considerable amount of m/z of 32 appears in figure S1 (c), which is ion fragment of $^{13}\text{CH}_2\text{OH}$. The m/z of corresponding fragment in figure S1 (a) and figure S1 (b) is 31, which represents $^{12}\text{CH}_2\text{OH}$. This demonstrates the location of labeled carbon is at C-6 for the HMF synthesized from D-Glucose-6- ^{13}C .

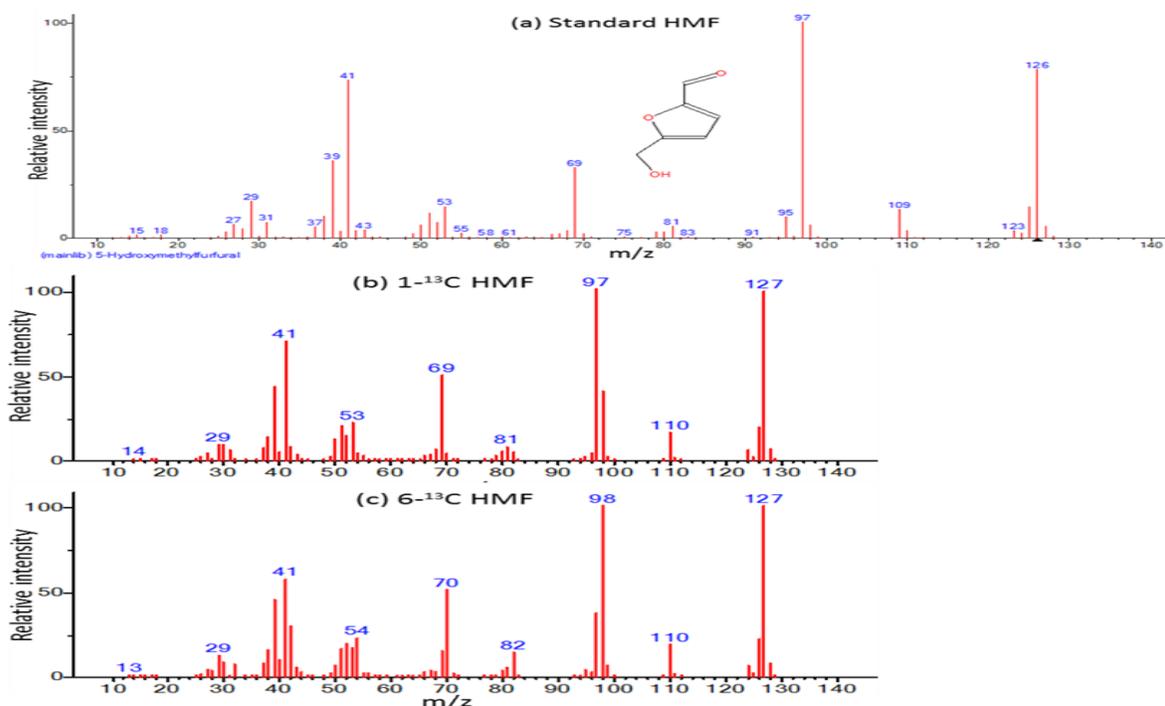


Figure S1. Mass spectrum of (a) standard HMF, (b) synthesized 1-¹³C HMF, and (c) synthesized 6-¹³C HMF.

Purity of the synthesized isotope labeled HMF was quantified using the Tandem micro-reactor system described in section 2.2. The temperatures for both two reactors were kept at 300°C to volatilize the synthesized HMF. Volatilized HMF vapors was identified by MS and quantified by FID. The calibration shows that the purity of synthesized HMF was 78.7 wt%.

2. Gradient of coke deposition in the catalyst bed

Table S1 shows the coke distribution in the spent catalyst from furfural conversion. It indicates that entrance region of the fixed catalyst bed was more heavily coked compared to other regions of the bed.

Table S1. Carbon distribution in the spent catalyst from Tandem micro-reactor system (feedstock: furfural; catalyst loading: 30 mg; 1st reactor temperature: 300°C; 2nd reactor temperature: 600°C)

	5 mg (entrance region)	10 mg (middle region)	15 mg (bottom region)
Coke content*, wt.%	2.11	0.90	0.48

*assuming coke contains 85 wt.% carbon

3. Carbon source determination for CO, CO₂ and aromatics from isotopic labeled glucose and HMF

Figure S2 shows how C-1 and C-6 on glucose distributed in major aromatic products. Generally there is no significant difference between C-1 and C-6 since both of them showed random distribution within aromatics. The results suggest both C-1 and C-6 on glucose molecule undergo hydrocarbon pool theory during which they lose their identity.

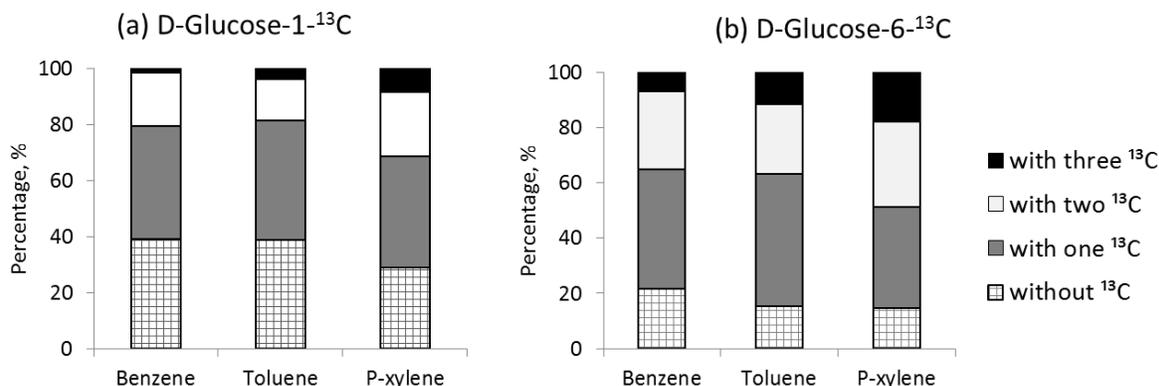


Figure S2. Molar distribution of aromatic products from catalytic reaction of isotopically labeled glucose over HZSM-5 according to the number of ¹³C atoms (a) D-Glucose-1-¹³C and (b) D-Glucose-6-¹³C; data are in terms of mole percentage (*ex-situ* catalysis; pyrolysis temperature for glucose = 500°C; catalyst temperature = 600 °C; reactant loading = 0.5 mg; catalyst CBV 3024 loading = 10mg).

Figure S3 (a) shows carbon source for CO and CO₂ from catalytic fast pyrolysis of isotopically labeled glucose and HMF. The results suggest except for C-1 and C-6, other carbon on glucose and HMF molecules could also form CO and CO₂. The difference between glucose and HMF is that the C-1 on HMF is more involved in CO and CO₂ formation, which is also evident in figure S3 (b) that more than 80% C-1 in HMF ended up with CO and CO₂.

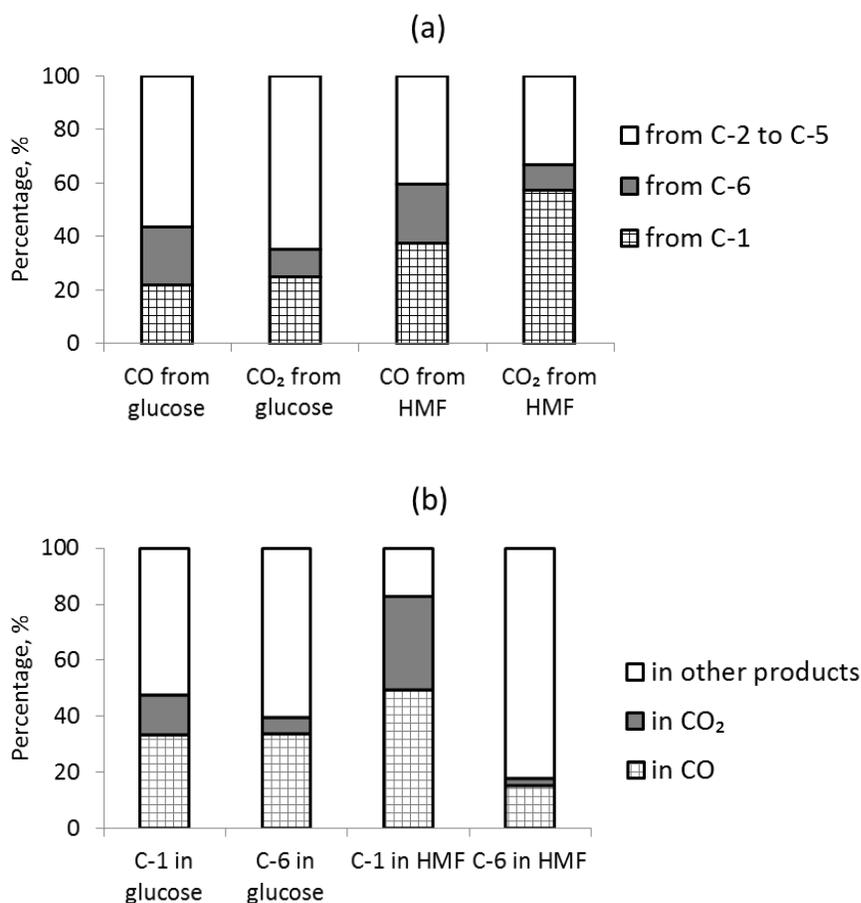


Figure S3. (a) Carbon source for CO/CO₂ formation during catalytic fast pyrolysis of glucose and HMF; (b) distribution of C-1 and C-6 on glucose and HMF within catalysis products; data are in terms of mole percentage (*ex-situ* catalysis; vaporize temperature for HMF = 500°C; catalyst temperature = 600 °C; reactant loading = 0.5 mg; catalyst CBV 3024 loading = 10mg).

4. Non-catalytic pyrolysis of glucose

Pyrolysis of glucose was conducted in the Tandem micro-reactor system. The second reactor was empty of catalyst. The temperature for both reactors was kept at 500°C and temperature for both interfaces was kept at 350°C to prevent condensation of pyrolysis vapor.

For the calibration, standard solutions of the products from glucose pyrolysis (except for those discussed subsequently) were prepared by dissolving the standard chemicals in acetone, which eliminated the interaction between solute and solvent.[1] The levoglucosan calibration was carried out by pyrolyzing a known amount of levoglucosan in the Tandem system, resulting in a single peak corresponding to levoglucosan as determined by MS. For the glycolaldehyde calibration, glycolaldehyde dimer was pyrolyzed at 300 °C, which gave a sharp peak in its chromatogram proven to be glycolaldehyde by MS. For MW 86, the calibration curve of 2 (5H) furanone was used for its quantification due to similar mass spectrum between them. For dianhydro-xylose (DAXP 2 and other DAXP 2), a calibration curve of a similar compound - 4-hydroxy-5-methyl-3-furanone was applied to determine their yields. Both DAXP and 4-hydroxy-

5-methyl-3-furanone have molecular weight of 114. For anhydro-xylopyranose (other AXP), dianhydro-glucofuranose and levoglucosan-furanose, a calibration curve of levoglucosan was used to estimate their yields due to their similarity in functional groups [2]. Pyrolysis product distribution is summarized in Table S2.

Table S2. Product distribution from fast pyrolysis of glucose at 500 °C

	carbon yield, %	Std. Dev.
Formaldehyde	0.41	0.02
Acetaldehyde	0.96	0.06
Methanol	0.30	0.07
Furan	0.26	0.02
Propenal (acrolein)	0.29	0.03
Acetone	0.16	0.02
Methyl glyoxal	3.07	0.11
2-methyl furan	0.17	0.04
Methyl vinyl ketone	0.42	0.05
Glycolaldehyde	20.38	1.59
Acetic acid	0.32	0.02
Acetol	1.37	0.05
MW 86	0.57	0.02
Furfural	3.59	0.34
2 furanmethanol	0.19	0.01
3 furanmethanol	0.09	0.01
2-hydroxy cyclopent-2-en-1-one	0.54	0.03
5-methyl furfural	0.24	0.08
2(5H) furanone	0.35	0.05
DAXP 2	0.44	0.04
Methyl cyclopentenolone	0.24	0.02
Other DAXP 2	1.18	0.15
Levoglucosenone	0.88	0.12
Cyclic hydroxyl lactone	0.97	0.06
1,4,3,6-dianhydro- α -dglucofuranose	0.47	0.05
5-hydroxy methyl furfural	9.87	0.22
Dianhydro glucofuranose	0.53	0.10
Other AXP	0.28	0.03
Levoglucosan	11.67	0.38
Levoglucosan-furanose	4.72	0.36
CO	3.32	0.26
CO ₂	3.58	0.14
Olefin	0.32	0.05
Overall volatiles and gases	72.14	0.40

5. Grouping rules of glucose pyrolysis product

Based on similarity on functional group and molecular size, the vapor products from glucose pyrolysis were classified into five groups, as shown in Table S3.

Table S3. Grouping for oxygenated intermediates from glucose pyrolysis

Groups	Products included
Acetic acid group	Acetic acid
Glycolaldehyde group	Formaldehyde, acetaldehyde, Methanol, Propenal, Acetone, methyl glyoxal, methyl vinyl ketone, glycolaldehyde, acetol
Furfural group	Furan, 2-methyl furan, MW 86, furfural, 2 furanmethanol, 3 furanmethanol, 2-hydroxy cyclopent-2-en-1-one, 2(5H) furanone
HMF group	5-methyl furfural, methyl cyclopentenolone, HMF
Levoglucofan group	MW 114 DAXP 2, other DAXP 2, Levoglucosenone, cyclic hydroxyl lactone, 1,4,3,6-dianhydro-a-d-glucopyranose, dianhydro glucopyranose, other AXP, levoglucosan, levoglucosan-furanose

Reference

- [1] P.R. Patwardhan, J.A. Satrio, R.C. Brown, B.H. Shanks, Product distribution from fast pyrolysis of glucose-based carbohydrates, *Journal of Analytical and Applied Pyrolysis*, 86 (2009) 323-330.
- [2] P.R. Patwardhan, R.C. Brown, B.H. Shanks, Product distribution from the fast pyrolysis of hemicellulose, *ChemSusChem*, 4 (2011) 636-643.