Supporting Information for

Speciation and Kinetic Study of Iron Promoted Sugar Conversion to 5-Hydroxymethylfurfural (HMF) and Levulinic Acid (LA)

Yuan Jiang,ab Linan Yang,ab Christine M. Bohn,ab Guannan Li,a Dong Han,f Nathan S. Mosier,bde Jeffrey T. Miller,c Hilkka I. Kenttämäa,ab Mahdi M. Abu-Omarabc

a Brown Laboratory, Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907, United States.
b The Center for direct Catalytic Conversion of Biomass to Biofuels (C3Bio), Purdue University, Discovery Park, 1203 West State Street, West Lafayette, IN 47907, United States
c Department of Chemical Engineering, Purdue University, 480 Stadium Mall Dr., West Lafayette, IN 47907, United States
d School of Agricultural and Biological Engineering, Purdue University, West Lafayette, IN 47907, United States
e Laboratory of Renewable Resources Engineering, Purdue University, West Lafayette, IN 47907, United States
f Maurice J. Zucrow Laboratories, School of Mechanical Engineering, Purdue University, 500 Allison Road, West Lafayette, IN 47907, United States

E-mail: mabuomar@purdue.edu
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Characterization of Iron Species as Determined by MS, UV-Vis and XANES

Mass Spectra of Iron and Fructose Reactions at Elevated Temperature

![Mass spectra](image)

Figure S1. Mass spectra of (a) 0.25 M fructose and 0.10 M FeCl$_3$ in water, (b) after microwave heating at 140 °C for 1 s, and (c) 0.25 M glucose and 0.10 M FeCl$_2$ in water.

UV-Vis Spectra of Iron Fructose Solutions and Comparison of HMF Peak

As shown in the UV-Vis results, Fe$^{III}$ in fructose solution shows characteristic absorption band at 300 nm, while the UV-Vis spectrum of Fe$^{II}$ in fructose solution is featureless. The rising peak at 280 nm in the spectra for reaction mixtures at 1 s, 1 min, and 5 min reaction times indicated the formation of HMF at elevated temperature (Figure S2 a). When mixed with HMF, the absorbance of Fe$^{III}$ overlaps with that of HMF at 280 nm. However, shoulder at about 300-360 nm is characteristic of Fe$^{III}$ in the mixture and can be utilized to confirm presence of Fe$^{III}$ (Figure S2 b).
Figure S2. (a) UV-Vis spectra of 0.25 M fructose and 0.10 M FeCl₃ in water (red), after 1 s at 140°C (blue), after 1 min at 140°C (green), and after 5 min at 140°C (black). Pink spectrum is a solution of 0.25 M fructose and 0.10 M FeCl₂ in water for comparison. (b) Comparison of spectra of FeCl₃ (red), HMF (blue), and the combination of FeCl₃ and HMF (green).

Differentiate Glucose and Fructose by CAD Experiments

Figure S3. CAD spectra of (a) m/z 414 for Fe³⁺-glucose, (b) m/z 414 for Fe³⁺-fructose, (c) m/z 451 for Fe²⁺-glucose, and (d) m/z 451 for Fe³⁺-fructose. Condition: 0.10 M iron salts (FeCl₃ or FeCl₂) and 0.25 M sugar (glucose or fructose) in water.
Quantification of Fe$^{III}$ Reduction by XANES

Figure S4. (a) Fe K-edge XANES from 7.09 to 7.16 keV for 0.10 M FeCl$_3$ and 0.25 M fructose (red), after thermal heating at 140 °C for 16 min (blue), and 0.10 M FeCl$_2$ and fructose (green) for comparison. (b) Fraction of Fe$^{III}$ and Fe$^{II}$ in the reaction samples at elevated temperature. Condition: 0.10 M FeCl$_3$ and 0.25 M fructose under microwave (M) or thermal (T) heating at 140 °C from 0 to 16 min.$^2$

Identification of Unknown Solids by XRD Experiments

Figure S5. XRD spectrum of the solids obtained from 0.25 M glucose and 0.10 M FeCl$_3$ after 1 s reaction at 140 °C (red), and Akaganéite spectrum from database (blue).
Control Experiments for Speciation Study

Water and Microwave Effect

In order to eliminate the possibility that water and microwave heating alone results in the reduction of Fe$^{\text{III}}$ to Fe$^{\text{II}}$, reactions without sugars have been performed. The Mass spectra of iron salts alone in water show that there is no reduction of Fe$^{\text{III}}$ to Fe$^{\text{II}}$ after microwave heating (Figure S5 a, b, and c). Additionally, when adding glucose to the solution of FeCl$_3$ in water that has been heated for 1 min at 140 ºC, only peak m/z 414 is shown in the MS and peak m/z 451 is not in the spectrum, which indicates that iron in the solution is still Fe$^{\text{III}}$ (Figure S5 d). Furthermore, after putting reaction samples of FeCl$_3$ and sugars (glucose or fructose) at room temperature without microwave heating for very long time (16 days), there is small amount of Fe$^{\text{III}}$ reduced to Fe$^{\text{II}}$ (Figure S5 e and f). These control experiments prove that water and microwave heating alone do not result in Fe$^{\text{III}}$ reduced to Fe$^{\text{II}}$, but microwave heating facilitates the reduction of Fe$^{\text{III}}$. 

![Mass spectra images](image-url)
Figure S6. Mass spectra of (a) FeCl₃ (0.10 M) in water, (b) after microwave heating at 140 °C for 1 min, (c) FeCl₂ (0.10 M) in water, (d) the addition of glucose (0.25 M) to the solution of FeCl₃ (0.10 M) in water heated for 1 min at 140 °C, (e) glucose (0.25 M) and FeCl₃ (0.10 M) solution at RT for 16 days, and (f) fructose (0.25 M) and FeCl₃ (0.10 M) solution at RT for 16 days.

Change of Iron Salts

Other than iron chloride, iron sulfate also shows similar reduction behavior. Mass spectrum of solution of Fe₂(SO₄)₃ and glucose has a dominant Fe³⁺ peak at m/z 414, which corresponds to [Fe³⁺ + 2glucose – 2H⁺]⁺, as discussed above. In comparison, mass spectrum of solutions of FeSO₄ and glucose has a dominant ion of m/z 464, which corresponds to [Fe²⁺ + 2glucose + 2SO₄²⁻]⁺. Upon microwave heating of Fe³⁺-glucose solution for 2 min, mass spectrum shows that the abundance of ion of m/z 414 decreases and that m/z 464 (corresponding to Fe²⁺) increases.
Figure S7. Mass spectra of (a) glucose (0.25 M) and Fe$_2$(SO$_4$)$_3$ (0.05 M) in water, (b) after microwave heating at 140 ºC for 2 min, and (c) glucose (0.25 M) and FeSO$_4$ (0.10 M) in water for comparison.

**Iron and HMF Reactions at Elevated Temperature**

Figure S8. Mass spectra of (a) HMF (0.25 M) and FeCl$_3$ (0.05 M) in water, (b) after microwave heating at 140 ºC for 1 s, and (c) HMF (0.25 M) and FeCl$_2$ (0.10 M) in water for comparison.

**Testing of Mixture Solutions**

In the solution of fructose (0.25 M), FeCl$_3$ (0.05 M) and FeCl$_2$ (0.05 M), the dominant ion is m/z 451 (Fe$^{II}$-fructose), while ion abundance for m/z 414 (Fe$^{III}$-fructose) is very low (less than 5% relative abundance), suggesting that fructose favors coordination
with Fe\textsuperscript{II} over Fe\textsuperscript{III} in MS (Figure S9 a). In the solution of glucose (0.25 M), FeCl\textsubscript{3} (0.05 M) and FeCl\textsubscript{2} (0.05 M), the dominant ion is m/z 451 (Fe\textsuperscript{II}-glucose), while ion abundance for m/z 414 (Fe\textsuperscript{III}-glucose) is low (about 35% relative abundance), suggesting that glucose also favor coordination with Fe\textsuperscript{II} over Fe\textsuperscript{III} in MS, but to a less extend than fructose (Figure S9 b). Not like MS, in the solution of glucose (0.25 M), FeCl\textsubscript{3} (0.05 M) and FeCl\textsubscript{2} (0.05 M), UV-Vis shows the absorption of Fe\textsuperscript{III} at about half of that of solution of glucose (0.25 M) and FeCl\textsubscript{3} (0.10 M), indicating that the amount of Fe\textsuperscript{III} in the solution detected by UV-Vis is not influenced by sugars or the instrument. In summary, MS favors Fe\textsuperscript{II}-sugar (glucose or fructose) complexes to some extent in a mixture solution containing both Fe\textsuperscript{II} and Fe\textsuperscript{III}. However, MS results can still be used to demonstrate the reduction of Fe\textsuperscript{III} to Fe\textsuperscript{II} qualitatively. In addition, UV-Vis absorption which reflects the amount of Fe\textsuperscript{III} present in the mixture solution confirms the reduction of Fe\textsuperscript{III} to Fe\textsuperscript{II} upon microwave heating in the catalytic reaction solutions.

Figure S9. Mass spectra of (a) fructose (0.25 M), FeCl\textsubscript{3} (0.05 M), and FeCl\textsubscript{2} (0.05 M) mixture in water, (b) glucose (0.25 M), FeCl\textsubscript{3} (0.05 M), and FeCl\textsubscript{2} (0.05 M) mixture in water.
Figure S10. Overlay of UV-Vis Spectrum of 0.25 M glucose, 0.05 M FeCl\textsubscript{3} and 0.05 M FeCl\textsubscript{2} in water (red), 0.25 M glucose and 0.1 M FeCl\textsubscript{2} in water (blue), and 0.25 M glucose and 0.1 M FeCl\textsubscript{3} in water (green).

**Sugar Conversion Comparison**

Table 1. Comparison of 0.25 M sugar (glucose or fructose) conversion catalyzed by 0.10 M FeCl\textsubscript{3}, versus 0.10 M FeCl\textsubscript{2} and HCl, and versus HCl at the same pH (pH = 1), same temperature (140 °C), and same reaction time (60 min for glucose and 15 min for fructose).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Glucose Conversion</th>
<th>Fructose Conversion</th>
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</thead>
<tbody>
<tr>
<td>FeCl\textsubscript{3}</td>
<td>22 %</td>
<td>94 %</td>
</tr>
<tr>
<td>FeCl\textsubscript{2}, HCl</td>
<td>21 %</td>
<td>94 %</td>
</tr>
<tr>
<td>HCl</td>
<td>13 %</td>
<td>89 %</td>
</tr>
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</table>
Kinetic Profiles

Kinetic Modelling Using Different Iron Concentrations

Figure S11. (a) Kinetic profiles for HMF conversion to LA and FA. (b) Kinetic profiles for reaction of fructose. (c) Kinetics profiles for reaction of glucose. Conditions: The reaction of 0.25 M substance and 0.025 M FeCl$_3$ at 140 ºC. Points are data and solid lines represent kinetic modeling fits. Simulation starts from the point that after temperature reaches 140 ºC. $^{3,4}$
Kinetic Modeling in a Biphasic System

Figure S12. (a) Kinetic profiles for HMF conversion to LA and FA. (b) Kinetic profiles for reaction of fructose. Conditions: The reaction of 0.25 M substance and 0.025 M FeCl₃ at 140 ºC in a water:MeTHF (1:3) biphasic system. Points are data and solid lines represent kinetic modeling fits. Simulation starts from the point that after temperature reaches 140 ºC.

Characterization of Solvent Decomposition by GC-MS
Figure S13. (a) GC-MS spectrum of the first unknown peak. (b) GC-MS spectrum of (Z)-3-penten-1-ol from GC-MS library database. (c) GC-MS spectrum of the second unknown peak. (d) GC-MS spectrum of 1,4-Pentanediol from GC-MS library database. Reaction condition: 0.10 M FeCl₃ in 1 ml H₂O and 3 ml MeTHF at 200 ºC microwave heating for 5 min.

References


