Biomass-derived magnetic amorphous carbon as an efficient catalyst in the

conversion of fructose into 5-hydroxymethylfurfural

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Section 1: Chemical and equipment

Iron (III) chloride (\geq 97%), sodium hydroxide (\geq 99%), hydrochloric acid (36%), oxalic acid (\geq 99%), *D*-glucose monohydrate (\geq 99%), dioxane (\geq 99%), methyl isobutyl ketone (MIBK) (\geq 99%), *D*-fructose (\geq 99%), dimethylformamide (\geq 99%) were obtained from Merck. 2,5-Diformylfuran (>99%), 2,5-furandicarboxylic acid (>99%), 5–(hydroxymethyl)furfural (>99%) furfural (>99%), levulinic acid (>99%), deuterochloroform (>99%), dimethyl sulfoxide (>99%) were supplied by Sigma–Aldrich. All chemicals were utilized without any additional purification.

Analytical techniques

The NMR spectra were obtained using a Bruker Advance 500 MHz nuclear magnetic resonance (NMR) spectrometer, with D-chloroform serving as the solvent. A thorough examination was carried out using Fourier transform-infrared spectroscopy (FTIR) on KBr pellets utilizing a Bruker Vertex 70 system. The reaction products were measured using a high-performance liquid chromatography system with a diode array detector at a specific wavelength. A particular type of column, called InertSustain C18, was used in the experiment to efficiently separate the different components in the reaction mixture. The temperature of the column was kept at 30 °C. A solution of methanol and sulfuric acid was utilized as the eluent, flowing at a rate of 0.7 mL.min⁻¹.

 $H\% = (The number of 5-HMF moles)/(The initial number of fructose moles) \times 100\%$ (1)





Figure S2-2. ¹³C–NMR spectrum of HMF

Section 3: Titration of catalyst



Figure S3-1. The titration curves of 100-4 with pH/V (orange line) and Δ pH/V (blue line)



Figure S3-2. The titration curves of 200-4 with pH/V (orange line) and $\Delta pH/V$ (blue

line)



Figure S3-3. The titration curves of 300-4 with pH/V (orange line) and Δ pH/V (blue line)



Figure S3-4. The titration curves of 350-4 with pH/V (orange line) and $\Delta pH/V$ (blue

line)



Figure S3-5. The titration curves of 400-4 with pH/V (orange line) and $\Delta pH/V$ (blue

line)



Figure S3-6. The titration curves of 400-4R4 with pH/V (orange line) and $\Delta pH/V$ (blue line)



Figure S3-7. The titration curves of 500-1 with pH/V (orange line) and Δ pH/V (blue line)



Figure S3-8. The titration curves of 500-2 with pH/V (orange line) and Δ pH/V (blue line)



Figure S3-9. The titration curves of 500-3 with pH/V (orange line) and Δ pH/V (blue line)



Figure S3-10. The titration curves of 500-4 with pH/V (orange line) and Δ pH/V (blue line)



Figure S3-11. The titration curves of 500-5 with pH/V (orange line) and $\Delta pH/V$ (blue

line)



Figure S3-12. The titration curves of Blank with pH/V (orange line) and Δ pH/V (blue line)

Section 4: HPLC chromatography

Figure S4-1: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 30 minutes at 120 °C.



Figure S4-2: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 1 hour at 120 °C.

Data File D:\DATA\2022\Thang 5\12-05-HMF\2022-12-05-HMF 2022-05-12 16-48-03\MT 15.D Sample Name: MT 15



Figure S4-3: HPLC chromatography of 5-HMF in investigating catalytic performance.

Reaction conditions: Fructose (1mmol), DMSO, for 3 hours at 120 °C.

Sample Name: MT 16

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                                             Inj Volume : 10.000 µl
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   Aca. Method
                  150 hat nho.M
   Last changed
               : 4/19/2022 4:56:47 PM by SYSTEM
   Analysis Method : D:\METHOD\HMF_cot 150_hat nho_KQ.M
               : 5/14/2022 2:06:57 PM by SYSTEM
   Last changed
   Additional Info : Peak(s) manually integrated
          DAD1 A, Sig-210,4 Ref-360,100 (D:\DATA\20...Thang 5\12-05-HMF\2022-12-05-HMF 2022-05-12 16-48-03\MT 16.D)
                                      5-HME
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      2000
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8.532
8.843
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                  Area
                          Amt/Area
                                    Amount Gro Name
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   [min]
                                     [ppm]
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    8,700
                                               Levulinic acid
    9.747 BV R 9574.73145 1.23625e-1 1183.67713
                                               HMF
    10.487 VB E
               637.41016 5.79379e-2 36.93020
                                               DFF
                 14.78250 0.00000 0.00000
30.35662 8.31934e-2 2.52547
    11.193 BB
                                               FDCA
    11.598 BV
                                               Furfural
                                                                              Page 1 of 2
HPLC-DAD 5/17/2022 11:58:30 PM SYSTEM
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Figure S4-4: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 6 hours at 120 °C.



Figure S4-5: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 8 hours at 120 °C.



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Figure S4-6: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 9 hours at 120 °C.



Figure S4-7: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 10 hours at 120 °C.

Data File D:\DATA\2022\Thang 5\12-05-HMF\2022-12-05-HMF 2022-05-12 16-48-03\MT 20.D Sample Name: MT 20



HPLC-DAD 5/18/2022 12:03:38 AM SYSTEM

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Figure S4-8: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 11 hours at 120 °C.

Data File D:\DATA\2022\Thang 5\12-05-HMF\2022-12-05-HMF 2022-05-12 16-48-03\MT 21.D Sample Name: MT 21



HPLC-DAD 5/18/2022 12:04:13 AM SYSTEM

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Figure S4-9: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 120 °C.



Figure S4-10: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 13 hours at 120 °C.

Data File D:\DATA\2022\Thang 5\12-05-HMF\2022-12-05-HMF 2022-05-12 16-48-03\MT 23.D

Sample Name: MT 23 _____ Acq. Operator : SYSTEM Seq. Line : 42 Acq. Instrument : HPLC-DAD Location : P1-E-06 Injection Date : 5/13/2022 5:12:45 AM Inj: 1 Inj Volume : 10.000 µl Acq. Method : D:\DATA\2022\Thang 5\12-05-HMF\2022-12-05-HMF 2022-05-12 16-48-03\HMF_cot 150_hat nho.M Last changed : 4/19/2022 4:56:47 PM by SYSTEM Analysis Method : D:\METHOD\HMF_cot 150_hat nho_KQ.M Last changed : 5/14/2022 2:06:57 PM by SYSTEM Additional Info : Peak(s) manually integrated DAD1 A, SIg=210,4 Ref=360,100 (D:\DATA\20...Thang 5\12-05-HMF\2022-12-05-HMF 2022-05-12 16-48-03\MT 23.D) mAU -1 5-HMF 2000 1500 · 248 1000 9 10.817 500 189 ĝ 뚏 3.547 3.871 4.256 d e 0. 16 10 12 DAD1 B, Sig-285.4 Ref-360.100 DATA\20...Thang 5\12-05-HMF\2022-12-05-HMF 2 2-05-12 16-48 23 D) mAU ; 2500 2000 -1500 1000 10.540 28 8.156 8.526 8.838 500 18 S 0 _____ External Standard Report _____ Sorted By . Signal Calib. Data Modified : 5/13/2022 1:43:08 AM Multiplier : 1.0000 Dilution . 1.0000 Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=210,4 Ref=360,100

RetTime Type Area Amount Grp Name Amt/Area [mAU*s] [min] [ppm] 2.34893 12.00479 3.547 BB 5.11074 Formic acid 8,700 Levulinic acid 9.748 BV R 9428.64746 1.23623e-1 1165.59609 HMF 10.493 VV E 317.50110 5.41227e-2 17.18401 DFF 10.817 VB E 81.47691 1.62233e-1 13.21824 FDCA 16.65361 6.40537e-2 1.06673 Furfural 11.599 BB

HPLC-DAD 5/18/2022 12:05:04 AM SYSTEM

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Figure S4-11: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 30 minutes at 120 °C.



Figure S4-12: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 1 hour at 120 °C. Data File D:\DATA\2022\Thang 5\12-05-HMF\2022-12-05-HMF 2022-05-12 16-48-03\MT 26.D Sample Name: MT 26



Figure S4-13: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 3 hours at 120 °C.



Figure S4-14: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 6 hours at 120 °C.



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Figure S4-15: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 8 hours at 120 °C.



Figure S4-16: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 9 hours at 120 °C.



Figure S4-17: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 10 hours at 120 °C.



Figure S4-18: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 11 hours at 120 °C.



Figure S4-19: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 120 °C.



Figure S4-20: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 13 hours at 120 °C.



Figure S4-21: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 30 minutes at 120 °C.



Figure S4-22: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 1 hour at 120 °C.



Figure S4-23: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 3 hours at 120 °C.



Figure S4-24: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 6 hours at 120 °C.



Figure S4-25: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 8 hours at 120 °C.



Figure S4-26: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 9 hours at 120 °C.



Figure S4-27: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 10 hours at 120 °C.



Figure S4-28: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 11 hours at 120 °C.



Figure S4-29: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 120 °C.



Figure S4-30: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 13 hours at 120 °C.



Figure S4-31: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at room temperature.



Figure S4-32: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 40 °C.



Figure S4-33: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 60 °C.



Figure S4-34: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 80 °C.



Data File D:\DATA\2022\Thang 5\30-05-HMF\2022-03-06-HMF 2022-06-03 16-51-25\MT 49.D Sample Name: MT 49

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12,56385 0,00000

29.78968 8.27507e-2

10.300

11.152 BV

11.599 VB

Page 1 of 2

0.00000

2,46512

DFF

FDCA

Furfural

Figure S4-35: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 100 °C.

Data File D:\DATA\2022\Thang 5\30-05-HMF\2022-03-06-HMF 2022-06-03 16-51-25\MT 50.D Sample Name: MT 50 _____ Acq. Operator : SYSTEM Seq. Line : 70 Acq. Instrument : HPLC-DAD Location : P1-C-07 Inj: 1 Injection Date : 6/4/2022 1:41:11 PM Inj Volume : 10.000 µl : D:\DATA\2022\Thang 5\30-05-HMF\2022-03-06-HMF 2022-06-03 16-51-25\HMF_cot Acq. Method 150_hat nho.M Last changed : 4/19/2022 4:56:47 PM by SYSTEM Analysis Method : D:\METHOD\HMF_cot 150_hat nho_KQ.M : 6/6/2022 7:14:45 AM by SYSTEM Last changed (modified after loading) DAD1 A, Sig=210.4 Ref=360.100 (D:\DATA\20...Thang 5\30-05-HMF\2022-03-06-HMF 2022-06-03 16-51-25\MT 50.D) mAU 7 5-HMF 2000 -1500 -1000 -500 -13.062 3.752 2763 0 DATA\20...Thang 5\30-05-HM 06-03 16-5 MT 50 D DAD1 B. Slo=28 ef-360,100 (D 03-06-HM mAU 3 200 -150 -100 -3.630 50 -820 8 1659 4 0 _____

External Standard Report

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Signal 1: DAD1 A, Sig=210,4 Ref=360,100

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8.700		-	-	-	L	evulinic acid.
9.419	BB	189.97421	1.16391e-1	22.11138	H	MF
10.300		-	-	-		DFF
11.000		-	-	-	F	DCA
11.600		-	-	-	F	Furfural

HPLC-DAD 6/6/2022 7:36:27 AM SYSTEM

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Figure S4-36: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 120 °C.



Figure S4-37: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 140 °C.



HPLC-DAD 6/6/2022 7:37:27 AM SYSTEM

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Figure S4-38: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 40 °C.



Figure S4-39: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 60 °C.



Figure S4-40: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 80 °C.



Figure S4-41: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 100 °C.



Figure S4-42: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 120 °C.



Figure S4-43: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 12 hours at 140 °C.



Figure S4-44: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 3 hours at 120 °C.



Figure S4-45: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 3 hours at 120 °C.



Figure S4-46: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 3 hours at 120 °C.



Figure S4-47: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 3 hours at 120 °C.



Figure S4-48: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 3 hours at 120 °C.



Figure S4-49: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 3 hours at 120 °C.



Figure S4-50: HPLC chromatography of 5-HMF in investigating catalytic performance. Reaction conditions: Fructose (1mmol), DMSO, for 3 hours at 120 °C.

