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# Supplementary Information

## Direct transformation of carbohydrates to the biofuel 5-ethoxymethylfurfural by solid acid catalysts

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**Table S1.** Conversion of fructose with various solid acid catalysts.

| Catalyst | Conversion (%) | Product Yield (%) | | | | |
|---|---|---|---|---|---|---|
| | | HMF | EMF | EDFF | ELevu | EMFda |
| H-Y (2.6) | 80 | 4 | 16 | 23 | 10 | <1 |
| H-USY (6) | 77 | 3 | 15 | 31 | 9 | <1 |
| H-USY (30) | 74 | 2 | 8 | 21 | 3 | <1 |
| H-beta (12.5) | 80 | 3 | 17 | 25 | 10 | <1 |
| H-beat (19) | 78 | 3 | 17 | 22 | 7 | <1 |
| Amberlyst-15 | 97 | 8 | 61 | 6 | 13 | <1 |
| $SO_3H$-SBA-15 | 94 | 8 | 50 | 4 | 21 | 1 |
| Dowex 50WX8-100 | 97 | 8 | 51 | 6 | 13 | <1 |
| Nafion NR50 | 96 | 10 | 36 | 4 | 15 | <1 |
| (3.9 wt%)$SO_4$-$ZrO_2$ | 72 | 16 | 17 | 20 | 11 | <1 |

Reaction conditions: Fructose (0.15 g), catalyst (100 mg), T = 96 ± 1 ºC, t = 11 h, ethanol (5 mL). HMF: 5-Hydroxymethylfurfural, EMF: 5-Ethoxymethylfurfural, EDFF: Ethyl-D-fructofuranoside, ELevu: Ethyl levulinate, EMFda: 5-Ethoxymethylfurfural diethyl acetal.

**Table S2.** Conversion of glucose with various solid acid catalysts.

| Catalyst | Conversion (%) | Product Yield (%) | | | | Bio-HEs Yield (%) |
|---|---|---|---|---|---|---|
| | | HMF | EMF | ELevu | EMFda | |
| H-Y (2.6) | 80 | 4 | 4 | 3 | 0.2 | 11 |
| H-USY (6) | 81 | 2 | 6 | 1 | 0.1 | 9 |
| H-USY (30) | 73 | <0.5 | 1 | <0.5 | 0 | 2 |
| H-beta (12.5) | 80 | 2 | 2 | 2 | <1 | 7 |
| H-beta (19) | 75 | 2 | 3 | 1 | 0 | 6 |
| Sn-beta | 76 | 2 | 2 | <1 | 0.3 | 5 |
| Amberlyst-15 | 98 | <0.5 | <0.1 | 1 | 0 | 2 |

Reaction conditions: Glucose (0.15 g), catalyst (100 mg), T = 96 ± 1 ºC, t = 11 h, ethanol (5 mL). HMF: 5-Hydroxymethylfurfural, EMF: 5-Ethoxymethylfurfural, EDFF: Ethyl-D-fructofuranoside, ELevu: Ethyl levulinate, EMFda: 5-Ethoxymethylfurfural diethyl acetal. Bio-HEs denote HMF, EMF, ELevu and EMFda (5-ethoxymethylfurfural diethyl acetal).

**Table S3.** Catalytic conversion of glucose with various solid acid catalysts.

| Catalyst | Conversion (%) | Product Yield (%) | | | | Bio-HEs Yield (%) |
|---|---|---|---|---|---|---|
| | | HMF | EMF | ELevu | EMFda | |
| H-Y (2.6)+Amberlyst-15 | 86 | 2 | 27 | 4 | 1 | 34 |
| H-USY (30)+Amberlyst-15 | 83 | 2 | 10 | 1 | 0 | 13 |
| H-beta (12.5)+Amberlyst-15 | 86 | 4 | 28 | 3 | <1 | 36 |
| H-beta (19)+Amberlyst-15 | 83 | 4 | 304 | 24 | <0.5 | 36 |

Reaction conditions: Glucose (0.15 g), catalyst (100 mg), T = 96 ± 1 ºC, t =11 h, ethanol (5 mL). One-pot, two-step process with successive addition of zeolite (75 mg) for 5 h followed by Amberlyst-15 (25 mg) for 6 h. HMF: 5-Hydroxymethylfurfural, EMF: 5-Ethoxymethylfurfural, EDFF: Ethyl-D-fructofuranoside, ELevu: Ethyl levulinate, EMFda: 5-Ethoxymethylfurfural diethyl acetal. Bio-HEs denote HMF, EMF, ELevu and EMFda (5-ethoxymethylfurfural diethyl acetal).

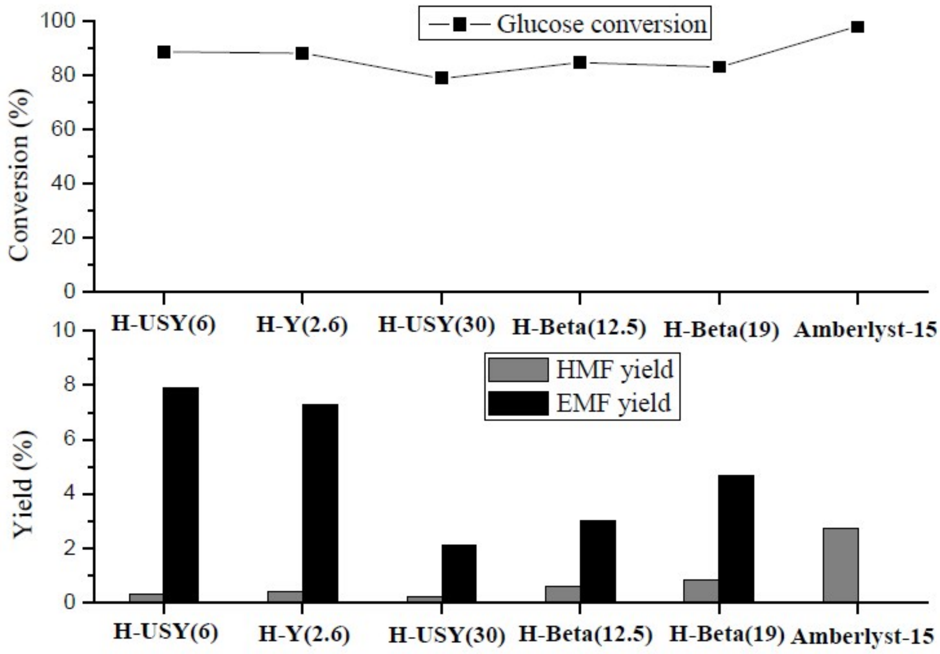



**Figure S1.** Catalytic conversion of glucose to EMF/HMF with different solid acids (Reaction conditions: 0.150 g glucose, 100 mg catalyst, 5 mL ethanol, T = 110 ±1 ºC, t = 6 h).

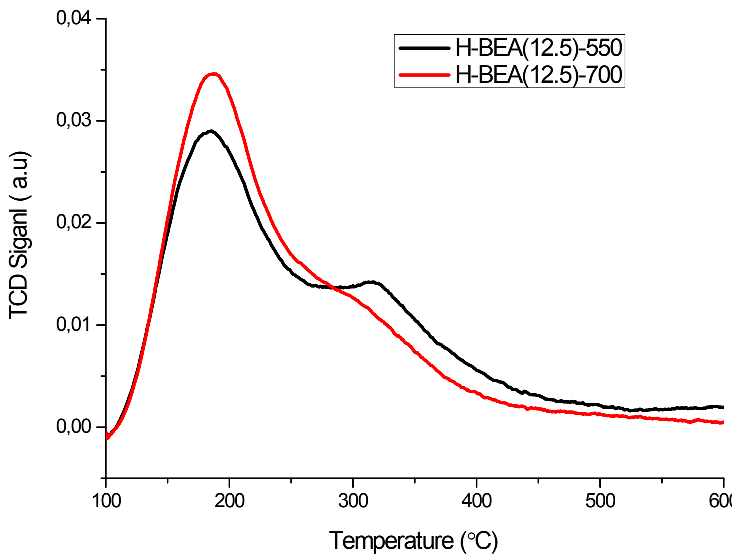



**Figure S2**. $NH_3$-TPD profiles of H-beta (12.5) and DeAl-H-beta (12.5)-700.

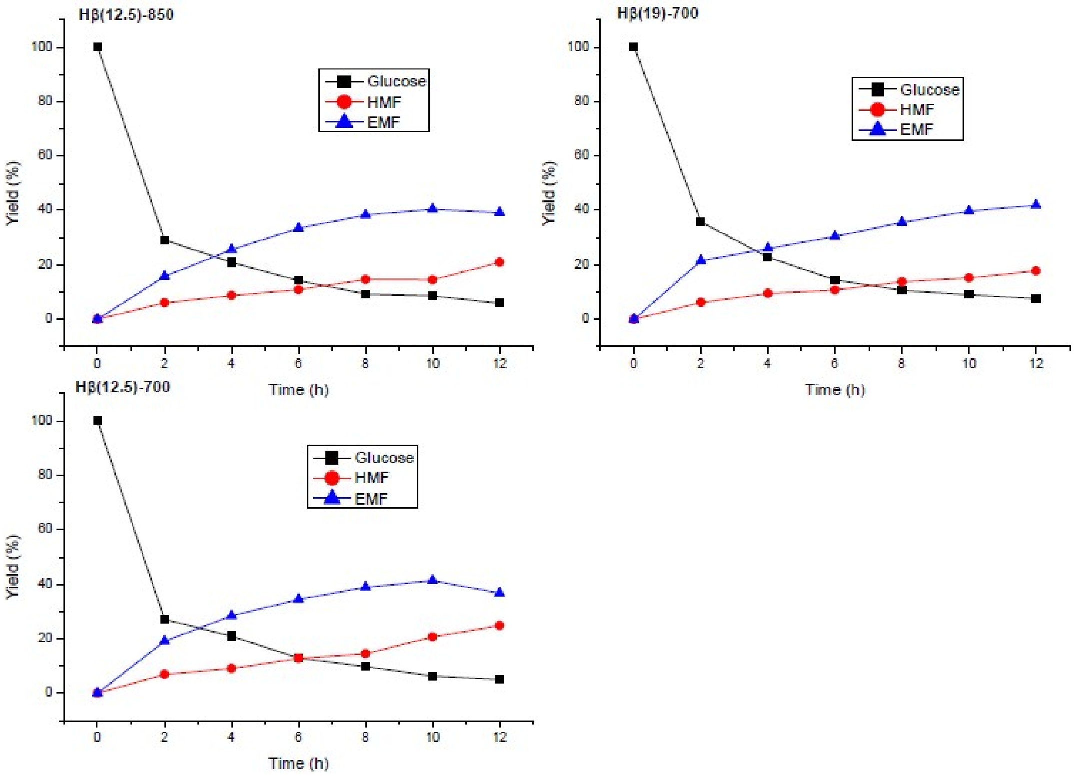
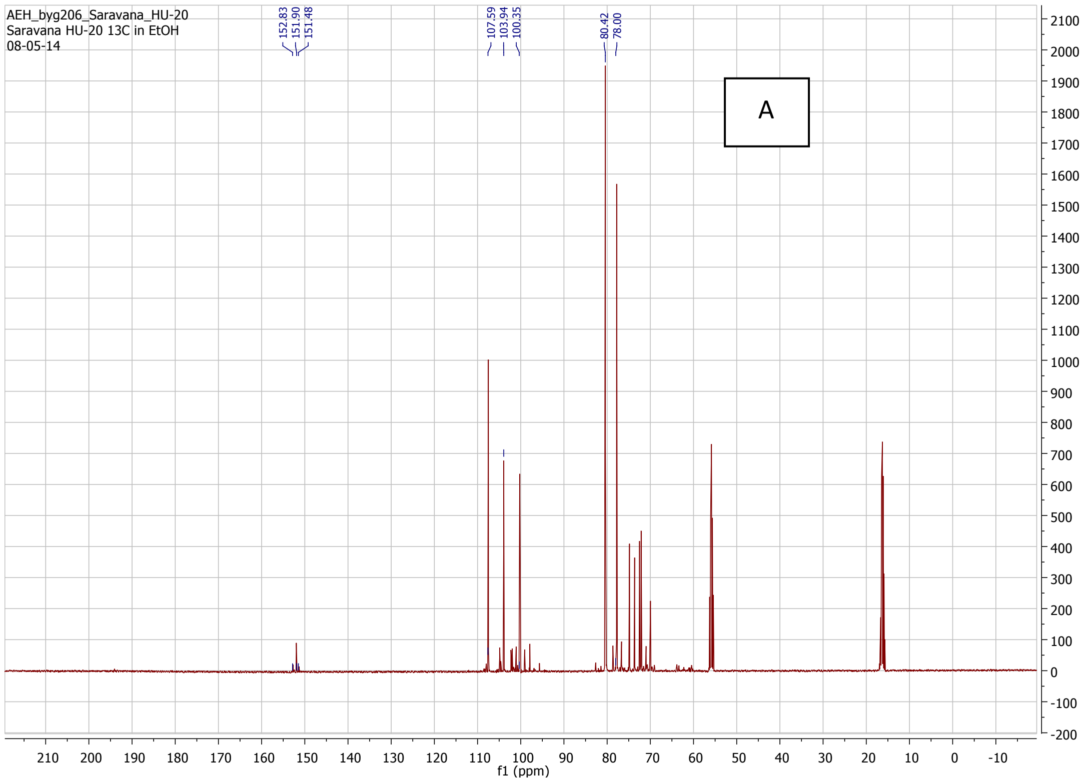



**Figure S3.** Effect of reaction time on the yield of HMF/EMF from conversion of glucose with DeAl-H-beta (12.5). (Reaction conditions: 0.15 g Glucose, 100 mg catalyst, 5 mL ethanol, T = 125 ± 1 ºC).



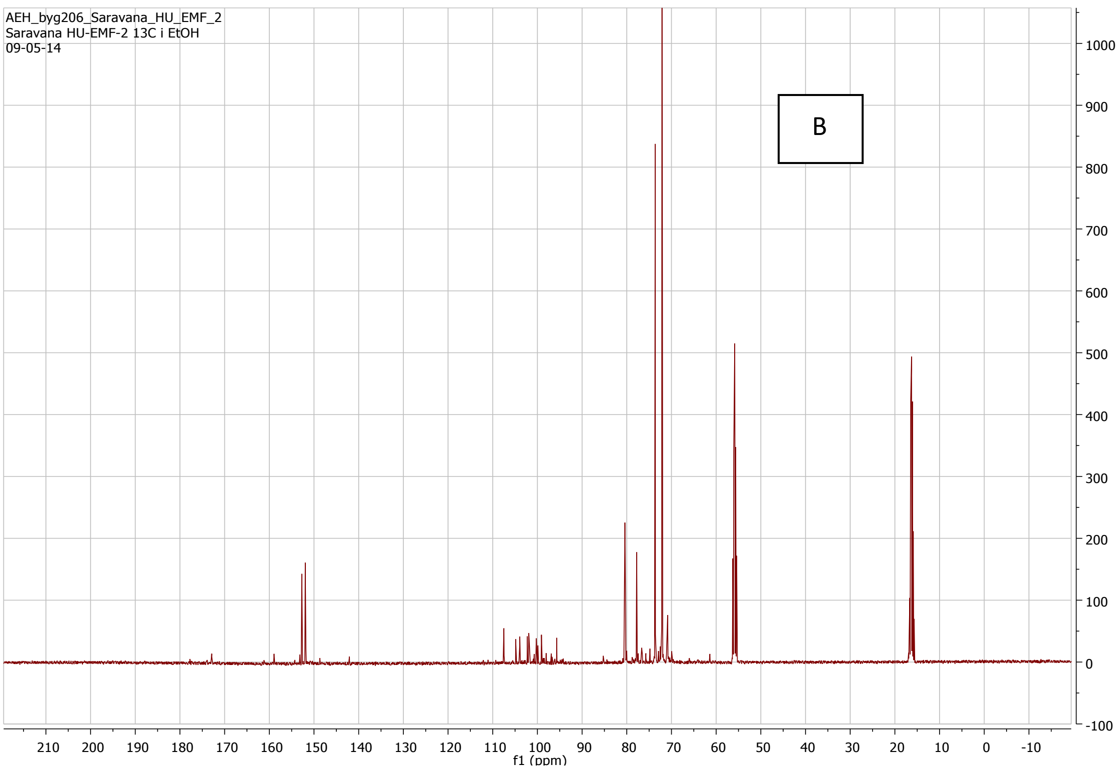




**Figure S4**. $^{13}C$ NMR spectra of the reaction mixture in the conversion of 2-$^{13}C$-glucose in ethanol-$d_6$ with DeAl-H-β(12.5)-700 after a) the first reaction step at 110 ±1 $^oC$ for 1 h and b) the second reaction step at 125 $^oC$ for 3 h.

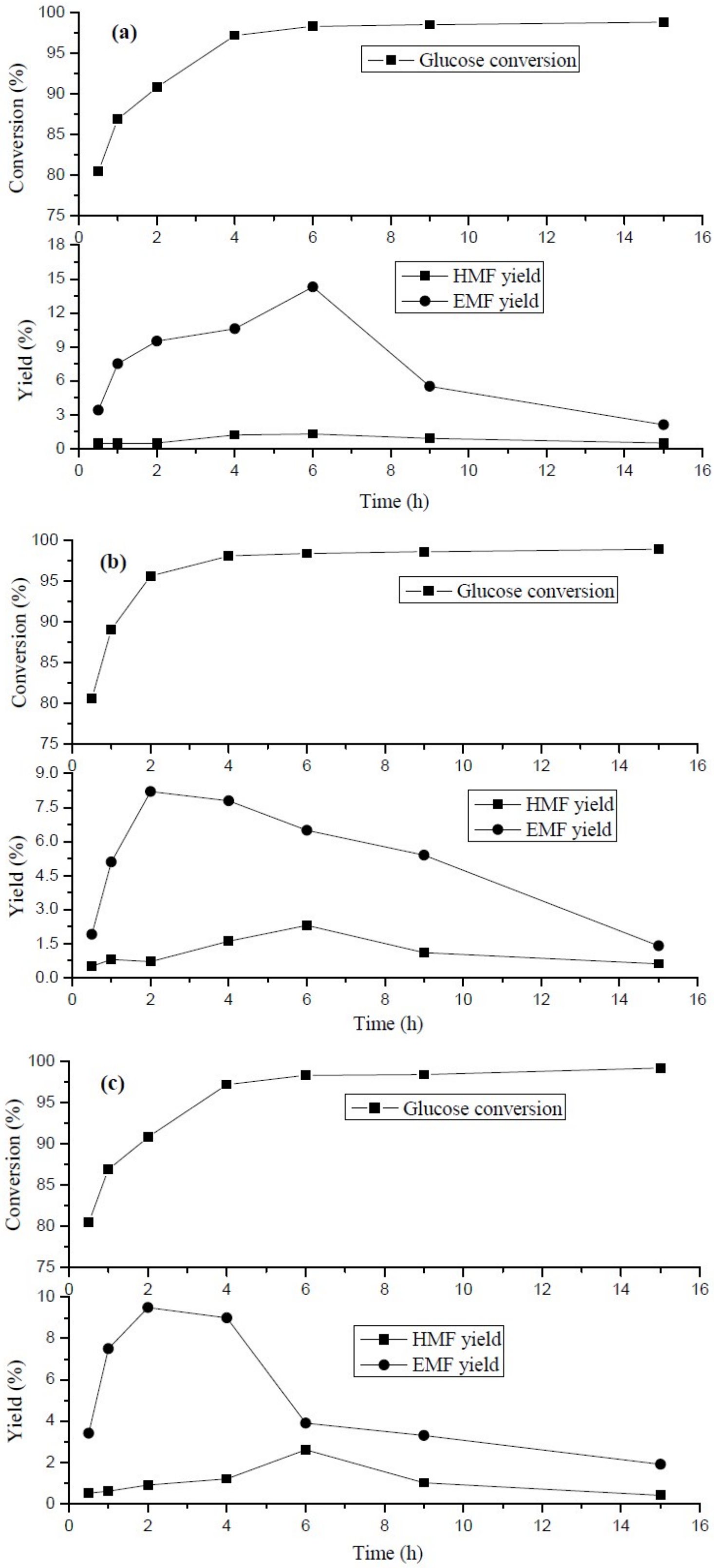



**Figure S5.** Catalytic conversion of glucose to EMF/HMF with (a) H-USY (6)/Amberlyst-15 (3:1), (b) H-USY (6)/Amberlyst-15 (1:1) and (c) H-USY (6)/Amberlyst-15 (1:3) (Reaction conditions: 0.15 g glucose, 100 mg catalyst, 5 mL ethanol, T = 110 ±1 ºC).

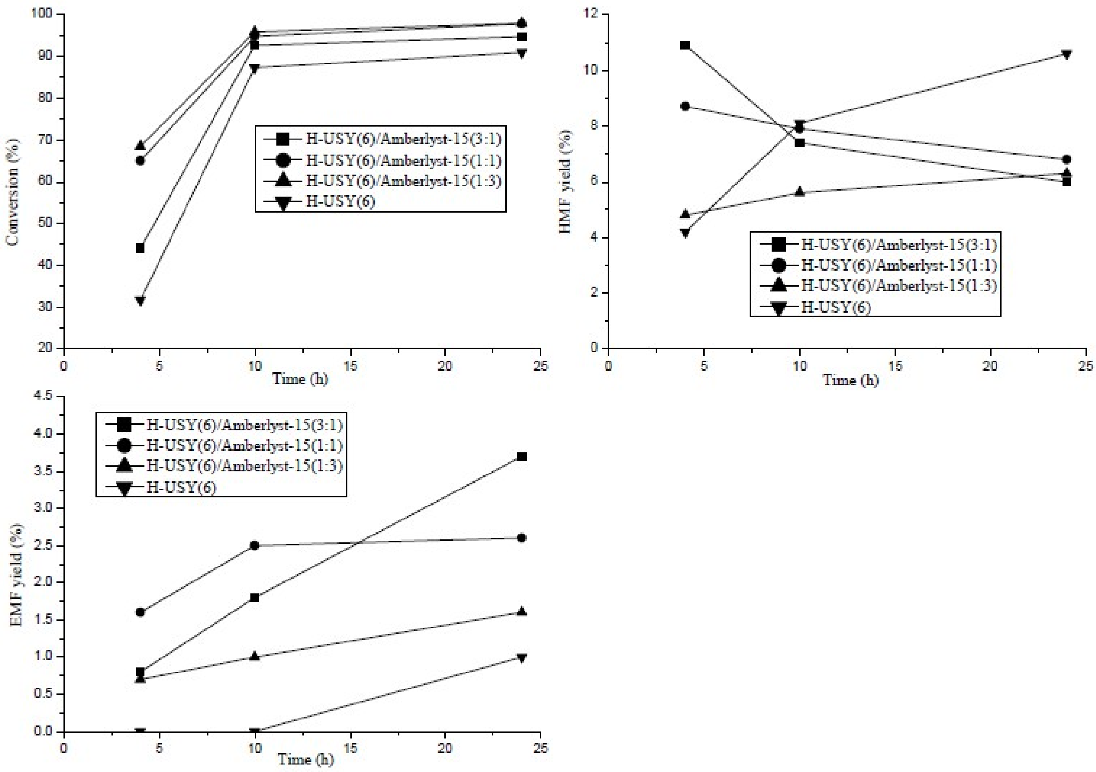



**Figure S6.** Effect of reaction time, catalyst ratio and co-solvent on catalytic conversion of glucose to EMF/HMF with H-USY (6)/Amberlyst-15 (Reaction conditions: 0.15 g glucose, 100 mg catalyst, 5 mL DMSO/ethanol (3:7), T = 110 ±1 ºC).

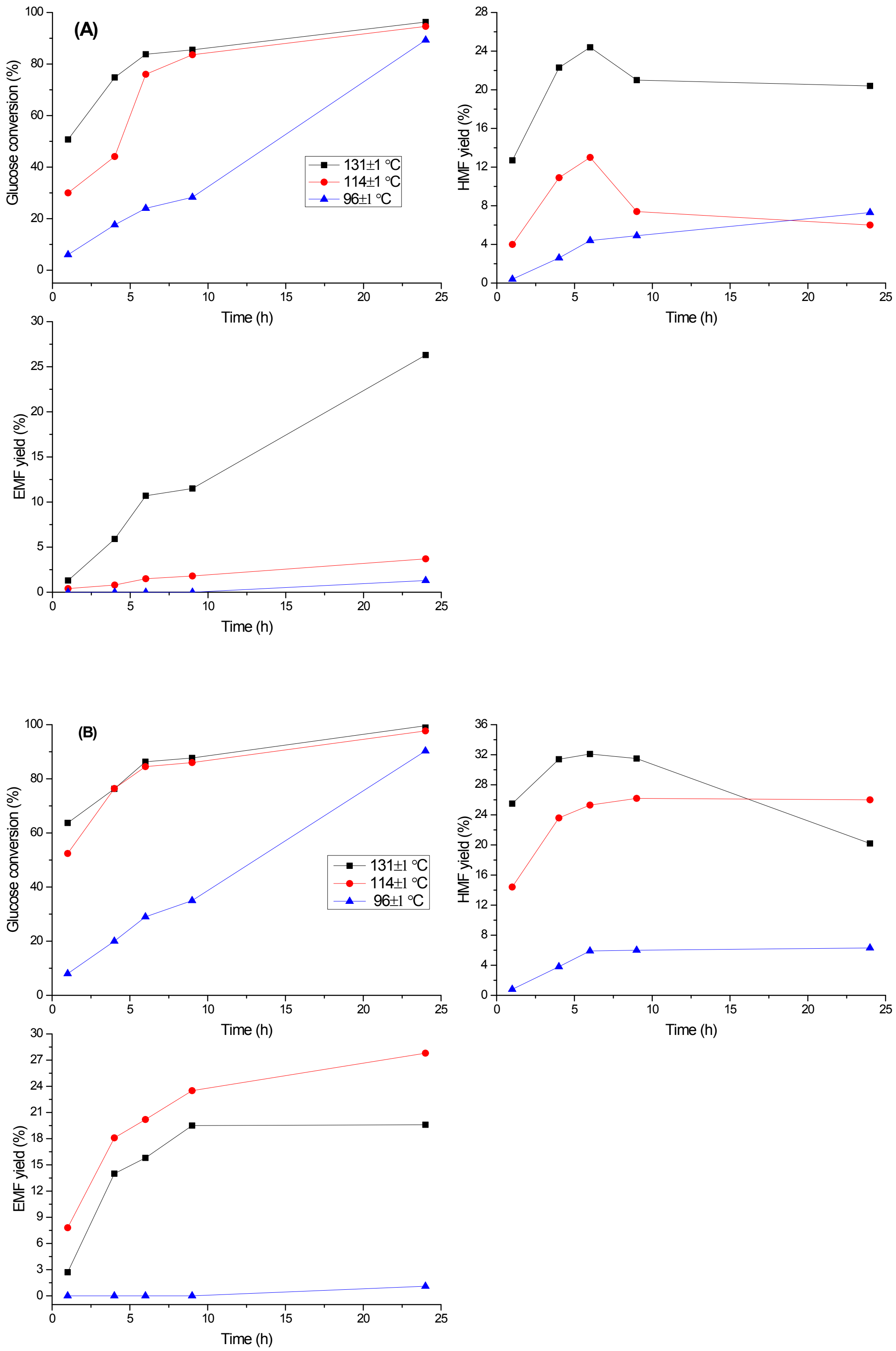



**Figure S7.** Optimization of reaction temperature and time for glucose-to-EMF conversion in DMSO/ethanol via (A) single-step and (B) two-step catalytic process ($t_1 + t_2 = t$, $t_1 = 1$) in one-pot. (Reaction conditions: 0.15 g glucose, 75 mg H-USY (6), 25 mg Amberlyst-15, 5 mL DMSO/ethanol (3:7)).

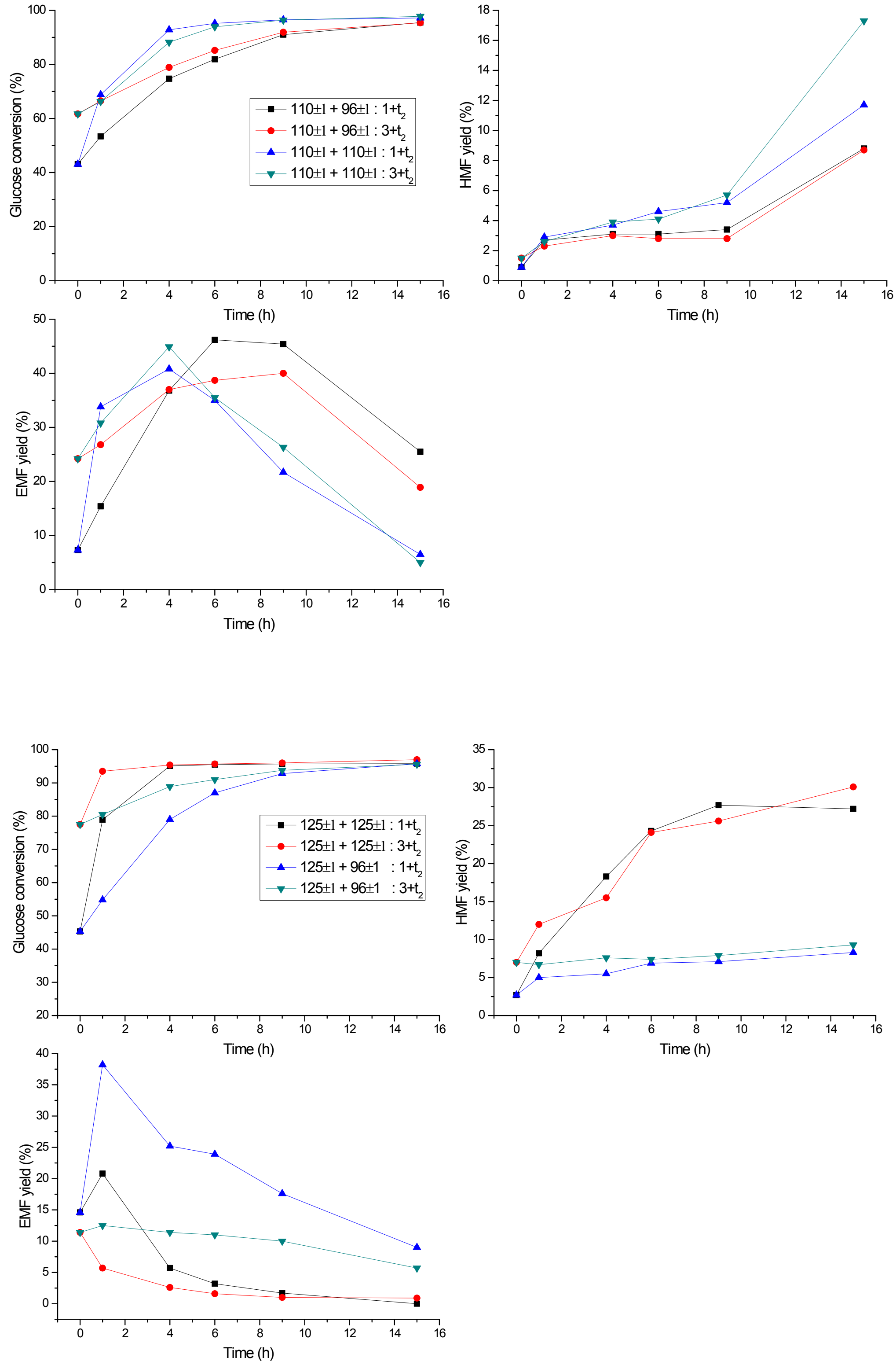



**Figure S8.** Optimization of reaction temperature and time for glucose-to-EMF conversion in ethanol via two-step catalytic process ($t_1 + t_2 = t$, $t_1 = 1$, 3 h) in one-pot (Reaction conditions: 0.15 g glucose, 75 mg H-USY (6), 25 mg Amberlyst-15, 5 mL ethanol).

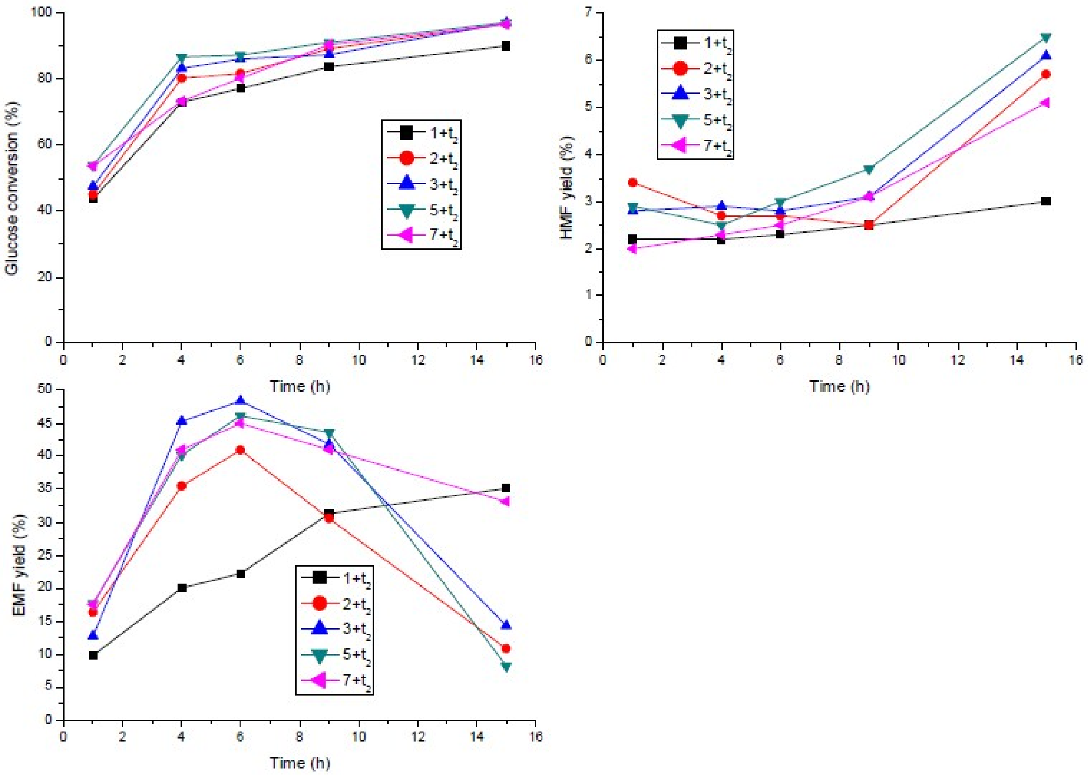



**Figure S9.** Optimization of reaction time for glucose-to-EMF conversion in ethanol via two-step ($t_1 + t_2 = t$, $t_1 = 1$, 2, 3, 5, 7 h) one-pot catalytic process with H-USY (6)/Amberlyst-15 (3:1) (Reaction conditions: 0.15 g glucose, 100 mg catalyst, 5 mL ethanol, T = 96 ± 1 ºC).