Supplementary Information

Experimental

Chemicals

For this study, bamboo particles was collected from a local farm in Jiangsu Province, China. All materials were passed through a 250–425 μm sieve and dried to a constant weight for 24 h at 105 °C. The absolute-dried particles were kept in a desiccator until used.

Analytic methods

Gas chromatography (GC) mass spectrometry (MS) (Agilent 5975C VL MSD) analysis was used a HP-5 fused capillary column (*l*= 30 m, *i d*= 0.32 mm, *t*= 0.25 μm) with poly dimethyl siloxane with 5% phenyl methyl substitution as the stationary phase. The injection mode was split at a rate of 35. The carrier gas was He at a flow rate of 1.5 mL min^{-1}. The program of column heating was kept at 30 °C maintained for 2 min, at a rate of 10 °C/min heated to 240 °C and held for 10 min. The injector temperature was held at 240 °C. The mass spectra were recorded in electron ionization mode for *m/z* 50–550. The components in the liquefied products were confirmed and identified by using the pre-established criteria for data analysis and total ion chromatograms and fragmentation pattern.

The yields of target products (levulinates and furfurals) in the liquefied products were analyzed by GC with a flame ionization detector (GC, Shimadzu 2010plus) and a HP-5 fused capillary column (film thickness 0.25 μm) to quantify. The following temperature program was used under the following conditions: kept at 30 °C maintained for 2 min, at a rate of 10 °C/min heated to 230 °C and held for 20 min. The injector temperature was held at 240 °C. Helium was used as the carrier gas at a flow rate of 1.0 mL/min. The absolute contents of target products (methyl levulinate) and intermediate products (furfurals) were calculated by comparison with an internal standard solvent as the reference sample (*n*-octanol). The MLA and *n*-octanol relevant line equation is y=2.06543x–0.02107 (coefficient of correlation R^2 =0.9998), the intermediate products (such as MMF) and *n*-octanol relevant line equation is y=1.9657x+0.0612 (coefficient of correlation R^2 = 0.9996).

The High Performance Liquid Chromatography HPLC instrument (Shimadzu LC–10ATVP, Aminex HPX–87H column) with a RID-20A detector was used to quantitative analyzed the methyl pentose glycosides (C5-Gly) and methyl hexose glucosides (C6-Gly). Used 0.005 mmol sulfuric acid (sonication, deaeration) in water as the mobile phase and the flow rate was of 0.5 mL/min, and the column temperature was kept at 45 °C for 30 min. The standard curve of concentration of C5-Gly is y=(4.51e-6)x+0.00426 (coefficient of correlation R^2=0.9999) and C6-Gly is y=(3.96e-6)x+0.00510 (coefficient of correlation R^2=0.9999).

Eq. (1) was used to measure the mass conversion of biomass, and Eq. (2) was used to identify the yield of MLA from biomass. Eq. (3) was used to calculate the mass yield of MMF (5-methoxymethylfurfural and methyl glycosides). Eq. (4) and Eq. (5) were used to identify the mass yield of C6-Gly and C5-Gly from biomass. Eq. (6) was used to identify the yield of recycled matching solvents. Eq. (7) and Eq. (8) were used to identify the molar yield of C6-Gly and C5-Gly from biomass. Eq. (9) was used to identify the molar yield of MLA from cellulose and hemicellulose in biomass. Eq. (10) was used to identify the yield of furans (include furfural, 5-hydroxymethylfurfural(HMF), 5-methoxymethylfurfural(MMF), 2-(dimethoxymethyl)-furan (DOF), 5-(hydroxymethyl)-2-(dimethoxymethyl)-furan(HDF), and 2-(dimethoxymethyl)-5-(methoxymethyl)-furan (DMF)) from cellulose and hemicellulose in biomass.

$$\text{Conversion of bamboo (wt\%)} = \frac{m(\text{liquefaction product})}{m(\text{bamboo})} \times 100\% \quad (1)$$

$$\text{MLA yield (wt\%)} = \frac{m(\text{liquefaction product}) \times \text{mass yield of MLA (measured by GC)}}{m(\text{bamboo})} \times 100\% \quad (2)$$

$$\text{MMF yield (wt\%)} = \frac{m(\text{liquefaction product}) \times \text{mass yield of (MMF)(measured by GC)}}{m(\text{bamboo})} \times 100\% \quad (3)$$

$$\text{C6-Gly yield (wt\%)} = \frac{m(\text{liquefaction product}) \times \text{mass yield of (C6-Gly)(measured by HPLC)}}{m(\text{bamboo})} \times 100\% \quad (4)$$

$$\text{C5-Gly yield (wt\%)} = \frac{m(\text{liquefaction product}) \times \text{mass yield of (C5-Gly)(measured by HPLC)}}{m(\text{bamboo})} \times 100\% \quad (5)$$

$$\text{Recycled matching solvent yield (\%)} = \frac{m(\text{recycled co-solvents})}{m(\text{initial co-solvents})} \times 100\% \quad (6)$$

$$\text{Molar yield of C5-Gly (mol\%)} = 100\% \times \frac{m(\text{C5-Gly}) \times \text{mass yield of C5-Gly(measured by HPLC)(wt\%)} / 176(\text{molecular weight of C5-Gly})}{m(\text{material}) \times \text{hemicellulose content(wt\%)} / 132(\text{molecular weight of hemicellulose})} \quad (7)$$

$$\text{Molar yield of C6-Gly (mol\%)} = 100\% \times \frac{m(\text{C6-Gly}) \times \text{mass yield of C6-Gly(measured by HPLC)(wt\%)} / 194(\text{molecular weight of C6-Gly})}{m(\text{material}) \times \text{cellulose content(wt\%)} / 162(\text{molecular weight of cellulose})} \quad (8)$$

$$\text{Molar yield of MLA (mol\%)} = 100\% \times \frac{m(\text{MLA}) \times \text{mass yield of MLA (measured by GC)(wt\%)} / 130(\text{molecular weight of MLA})}{m(\text{material}) \times \text{cellulose content(wt\%)} / 162(\text{molecular weight of cellulose}) + m(\text{material}) \times \text{hemicellulose content(wt\%)} / 132(\text{molecular weight of hemicellulose})} \quad (9)$$

Molar yield of various furans (mol%) = 100%×

$$\frac{m(\text{furfurals})\times\text{mass yield of all furfurals (measured by GC)(wt\%)}/_{\text{M(molecular weight of furans)}}}{m(\text{material})\times\text{cellulose content(wt\%)}/_{162(\text{molecular weight of cellulose})}+m(\text{material})\times\text{hemicellulose content(wt\%)}/_{132(\text{molecular weight of hemicellulose})}} \quad (10)$$

Molar conversion of Cellulose and Hemicellulose (mol%) = Molar yield of (C5-Gly+ C6-Gly+ MLA+ various furans) (11)

However, as we think the molar yield data is not particularly accurate relative to the mass yield. When calculate the molar yield of C6-Gly, we regard the C6 sugars as were all derived from cellulose, however hemicellulose also contains a certain amount of C6 sugars. MLA and furans were also derived from both cellulose and hemicellulose degradation products. Moreover, lignin is partially converted into phenolic compounds during liquefaction. Since the structure of lignin with various phenolic compounds cannot be determined, the mass yield of phenolic compounds can be calculated, and the calculation of molar yield is not accurate enough.

Directional liquefaction and fractionation of lignocellulosic biomass

In our experiment, the liquefaction of lignocellulosic biomass was operating in a Parr 4843 pressure sealed reactor system fitted with a thermocouple, stirring device, a pressure gauge and 100 mL capacity. The liquefaction mixtures were consisted of 5 g of biomass material, 50 g of solvent and a certain concentration (0.2–0.6 wt% of solvent amount) of acid catalyst. The reactants were heated with a rate of 3 °C/min in an autoclave at a designated temperature (120–220 °C) and kept for a specified time (0–150 min). After the liquefaction, the reactor was cooled to room temperature in about 30 min with cooling water running through a coil installed inside the reactor. After that, the reactor was opened. The liquid products and solid residue were collected and separated with filter paper. The solid residue was dried at 105 °C for 12 h to constant weight to measure the amount of insoluble residue. The weight of residue (dry basis) can be used to calculate the conversion of biomass material during the liquefaction.

The liquid products were distilled at 40 °C under vacuum to remove and recycle the DMM and methanol. And DMM/methanol solvent can be separated with using extractive distillation with N,N-dimethylformamide (DMF) as an entrainer (Fig. S8). Subsequently, the liquefied products were successively separated from liquefied filtrate mixtures with stepwise precipitation and extraction. The detail stepwise process (Fig. S6) included: 1) adding water into the liquid product with the mass ratio of 3:1; 2) insoluble phase with methyl levulinate and phenols was separated from soluble phase with glycoside compounds; 3) adding CH_2Cl_2 into the insoluble phase with the mass ratio of 2:1 at room temperature and atmospheric pressure; 4) the mixtures were separated into a paste-like phase and a CH_2Cl_2 soluble phase; 5) and the CH_2Cl_2 soluble phase was evaporated under vacuum (-0.1 MPa) to remove the CH_2Cl_2 at 30 °C, and achieve the methyl levulinate with high-purity. The glycoside compounds were obtained by removal of the water under vacuum (-0.1 MPa) at 60 °C from the aqueous solution using a rotary evaporator. In the process of evaporated transpiration of water or CH2Cl2, the water or CH2Cl2 was separated and recovered by condensing using a rotary evaporator with a cryogenic coolant cycle pump (Fig. S6(b)).

Abbreviation

MLA: methyl levulinate
DMM/METH: Dimethoxymethane/methanol
HMF: 5-hydroxymethylfurfural
MMF: 5-methoxymethylfurfural
DOF: 2-(dimethoxymethyl)-furan
HDF: 5-(hydroxymethyl)-2-(dimethoxymethyl)-furan
DMF: 2-(dimethoxymethyl)-5-(methoxymethyl)-furan
MCC: microcrystalline cellulose
Furans include furfural, 5-hydroxymethylfurfural (HMF), 5-methoxymethylfurfural (MMF), 2-(dimethoxymethyl)-furan (DOF), 5-(hydroxymethyl)-2-(dimethoxymethyl)-furan (HDF), and 2-(dimethoxymethyl)-5-(methoxymethyl)-furan (DMF).

Supporting Tables and Figures

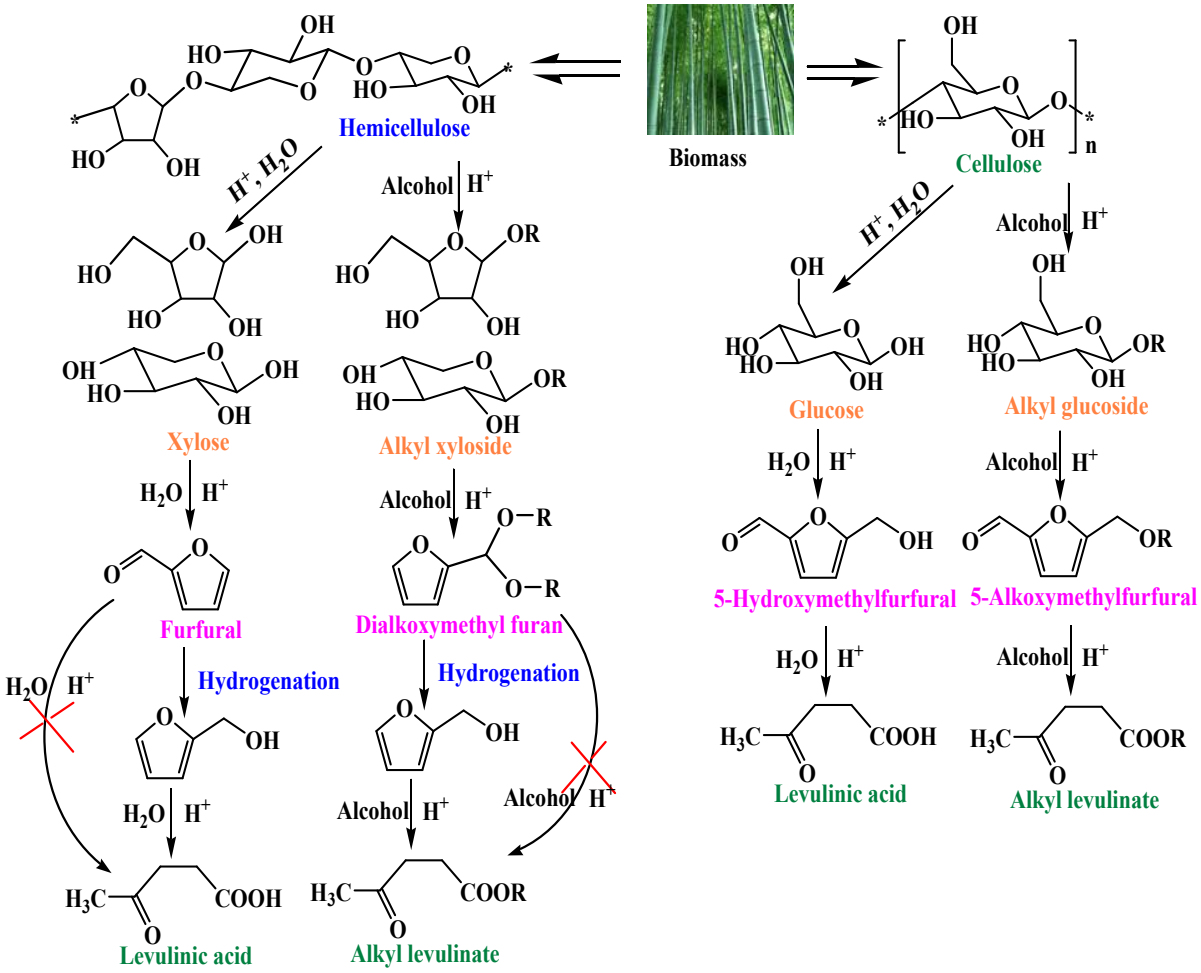

Fig. S1. Reaction pathway for conventional acid-catalyzed hydrolysis and alcoholysis of cellulose and hemicellulose.

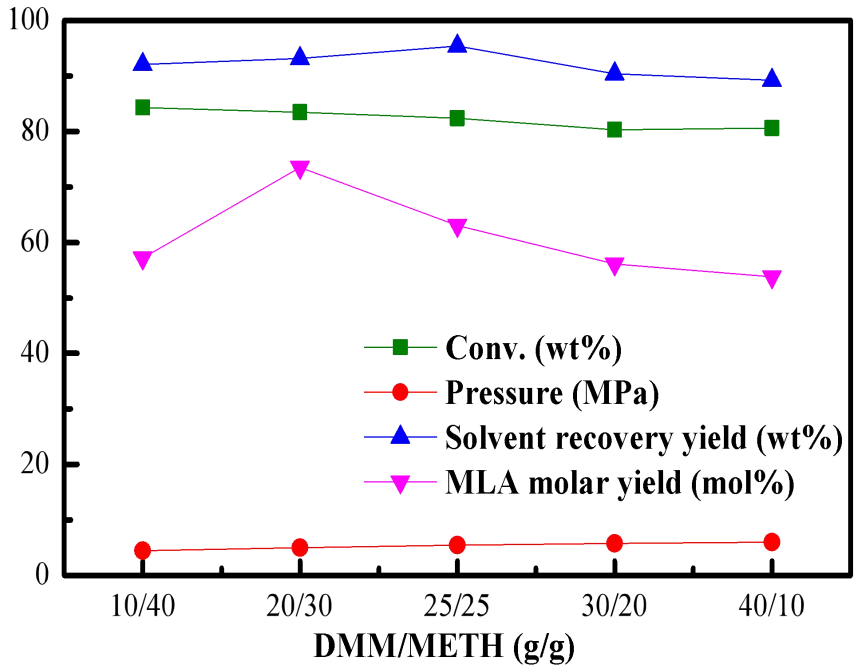

Fig. S2. Effect of composite solvent ratio on the liquefaction of bamboo.

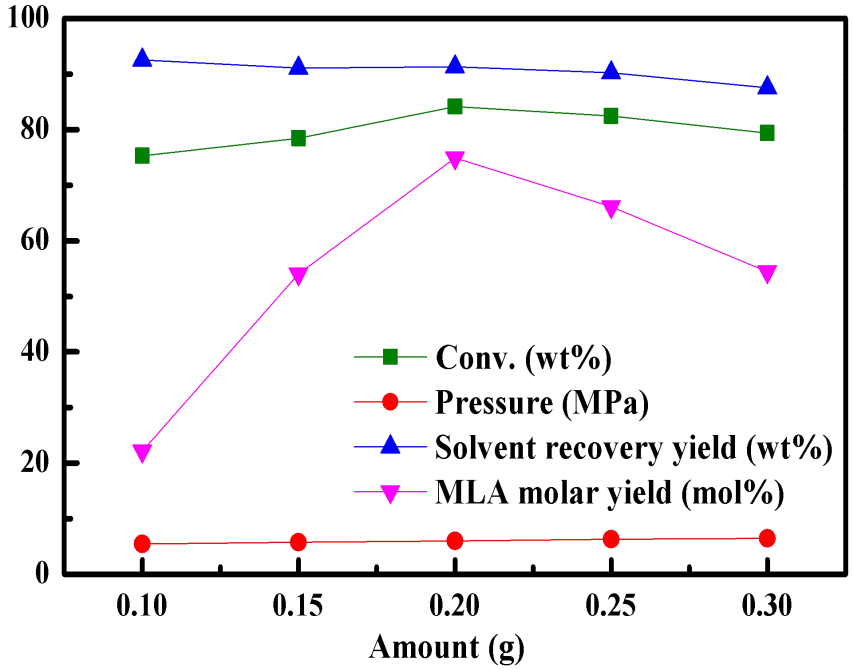

Fig. S3. Effect of catalyst loading on the liquefaction of bamboo.

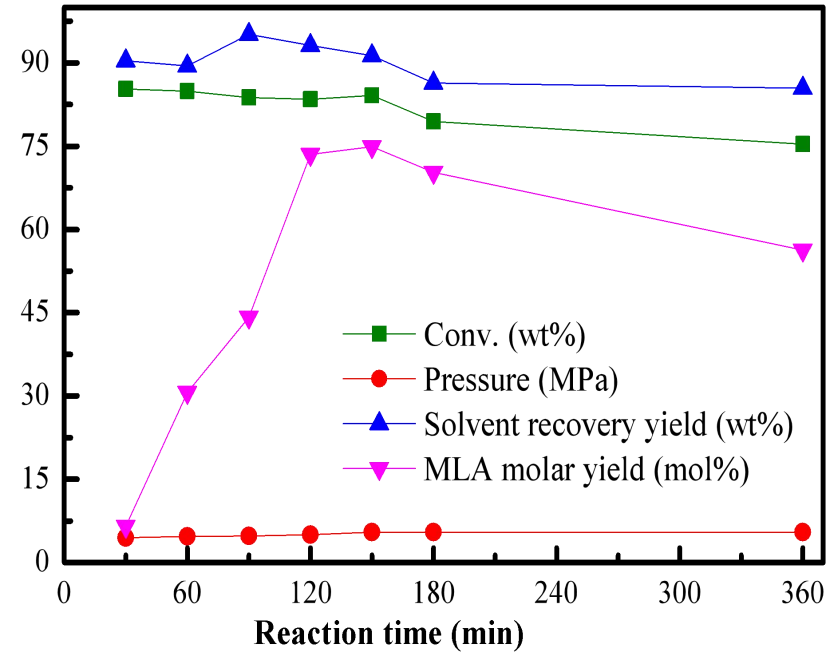

Fig. S4. Effect of reaction time on the liquefaction of bamboo.

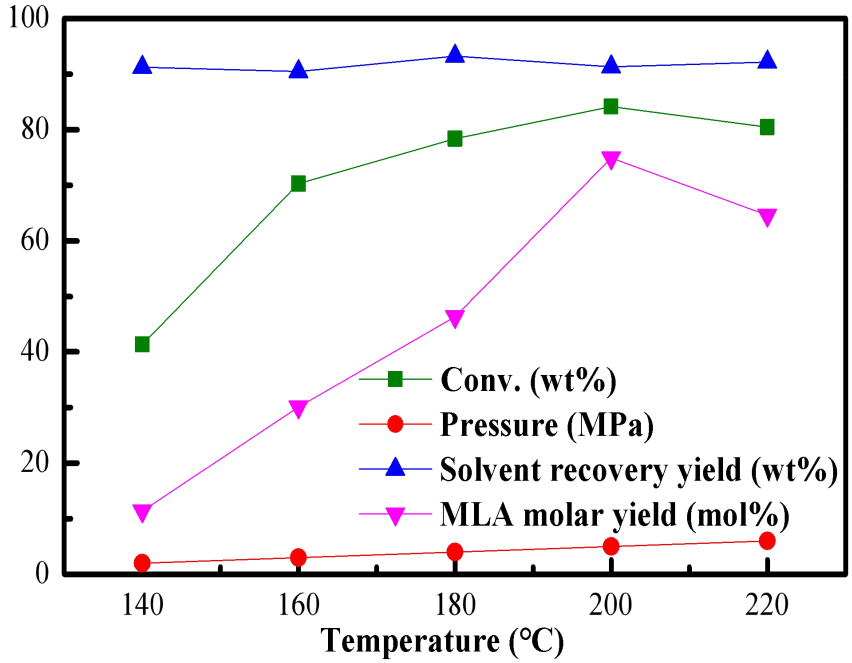

Fig. S5. Effect of reaction temperature on the liquefaction of bamboo.

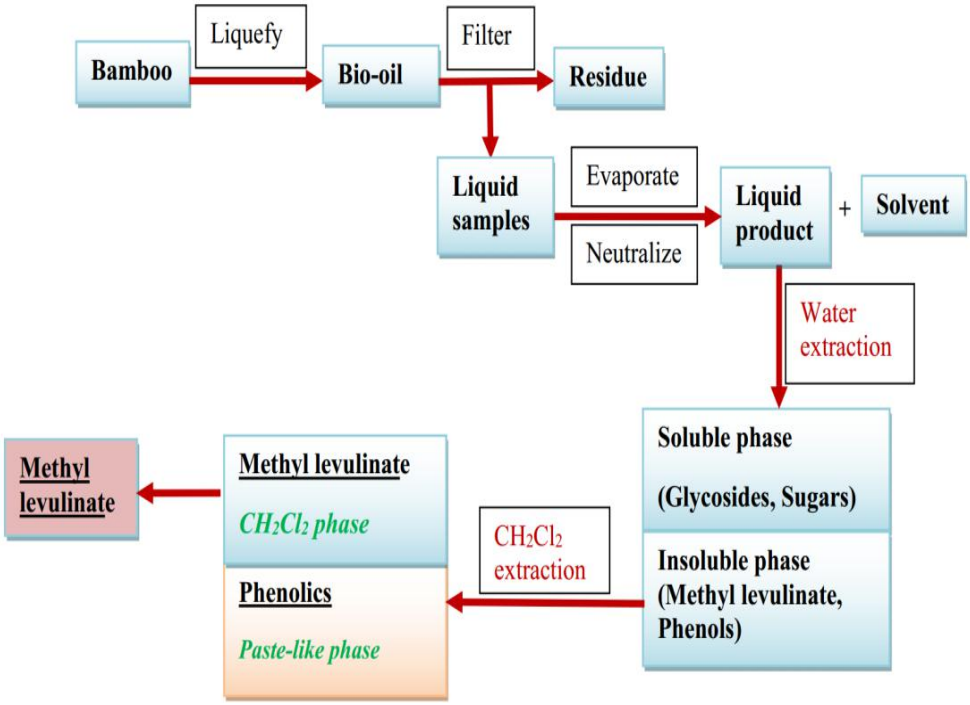

Fig. S6(a). The production and separation of methyl levulinate via its extraction from liquefied product derived from bamboo.

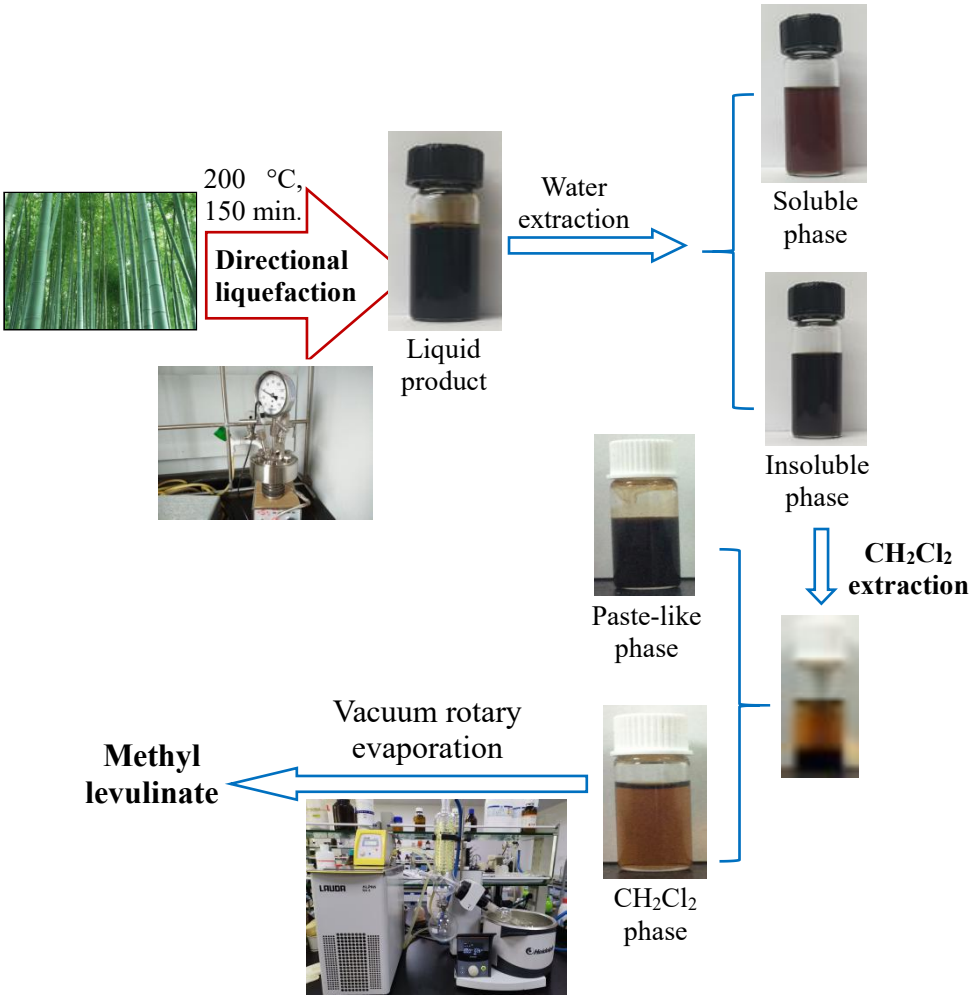

Fig. 6(b). Formation process of methyl levulinate from liquefied product derived from bamboo.

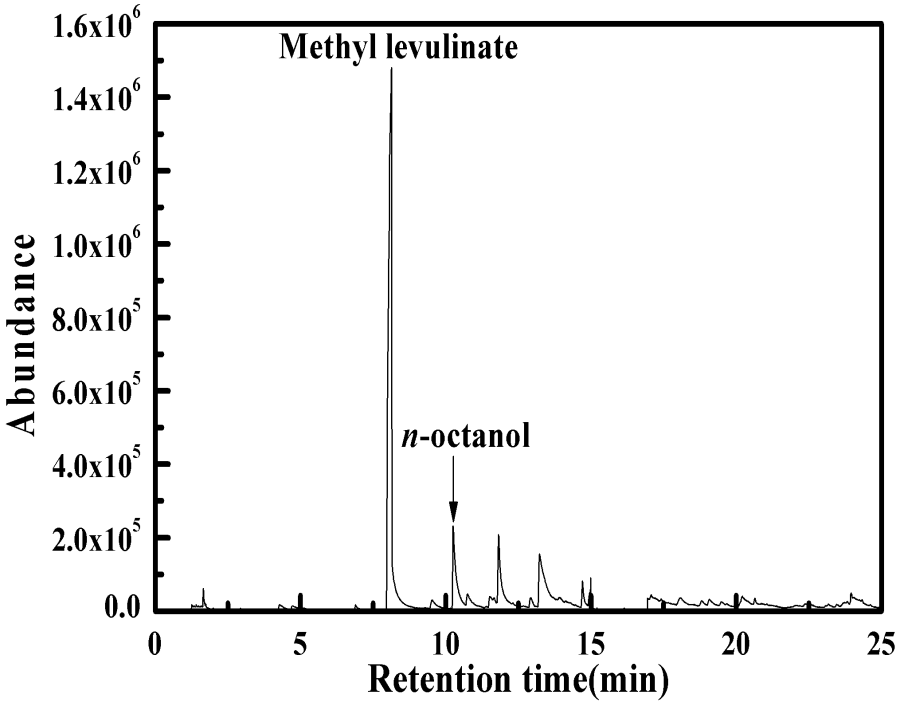

Fig. S7. The GC result for the extracted MLA. (The MLA content was calculated using the internal standard method by comparison with an authentic *n*-octanol reference sample.)

It is difficult to separate MLA from liquefied products effectively using distillation as their boiling points are close. Extraction is a potential way to obtain the end product as the polarities of chemicals are distinct. Commonly used extraction solvent agents are methyl isobutyl ketone (MIBK), methyl-tetrahydrofuran (MTHF), dichloromethane (DCM), 2-butanol and tetrahydrofuran (THF).[S1] The CH_2Cl_2 were used as the solvent to extract methyl levulinate and levulinic in some reported studies,[S2] these literatures were mainly about convert the biomass-derived glucose, xylose and furfurals to methyl levulinate and levulinic acid in biphasic solvents systems (such as H_2O_2/CH_2Cl_2). In this study, the liquefied product was a brown liquid obtained by rotary evaporation. The liquefied product can be separated into two phases when a certain amount of polar water is added. The insoluble phase products were mostly composed of MLA and phenols (decomposed from lignin). The MLA can be further separated via extraction with CH_2Cl_2 (Fig. S6). As a result, the content of the extracted MLA was up to 88.9% (measured by GC with internal standard method). The GC result for the MLA extracted with *n*-octanol (internal standard substance of MLA) is shown in Fig. S7.

The mass balances of directional liquefaction product yields are shown in Table S1. The total feed subjected to liquefaction was 55.2 g, which consisted of 5 g bamboo, 50 g co-solvents and 0.2 g C_7H_7-SO_3H. Although the reaction mixture was taken out from the autoclave as quickly as possible some methanol, losses were unavoidable, but were all less than 2 %. The liquefied product yield was more than 80% when averaged over three runs. As the tests involved repeated data points, average values for the data were obtained by repeating the experiments three times.

Table S1 The balances for the directional liquefaction of bamboo in METH/DMM.

	Input (g)[a]			Output							
				Liquefied product from bamboo (%)			Solvent recovery (g)[b]				
Entry	Bamboo	DMM/METH	H_2SO_4	MLA	Glycosides	Phenols	METH	DMM	Residue (%)	Loss (%)	CH_2Cl_2 recovery yield(%)
1	5.03	20.02/30.00	0.20	40.98	10.69	35.25	28.14	16.37	11.85	1.23	87.5
2	5.01	20.00/30.01	0.21	40.35	12.21	33.42	27.65	17.21	13.24	0.78	91.5
3	5.00	20.00/30.02	0.20	39.87	11.33	34.85	27.30	18.02	12.67	1.48	89.3

[a] Reaction conditions: bamboo 5 g, DMM/METH was 20 g/30 g, C_7H_7-SO_3H 0.2 g, 200 °C, 150 min. [b] The composition of recovered solvents were determined with GC and total mass of recovered matching-solvents.

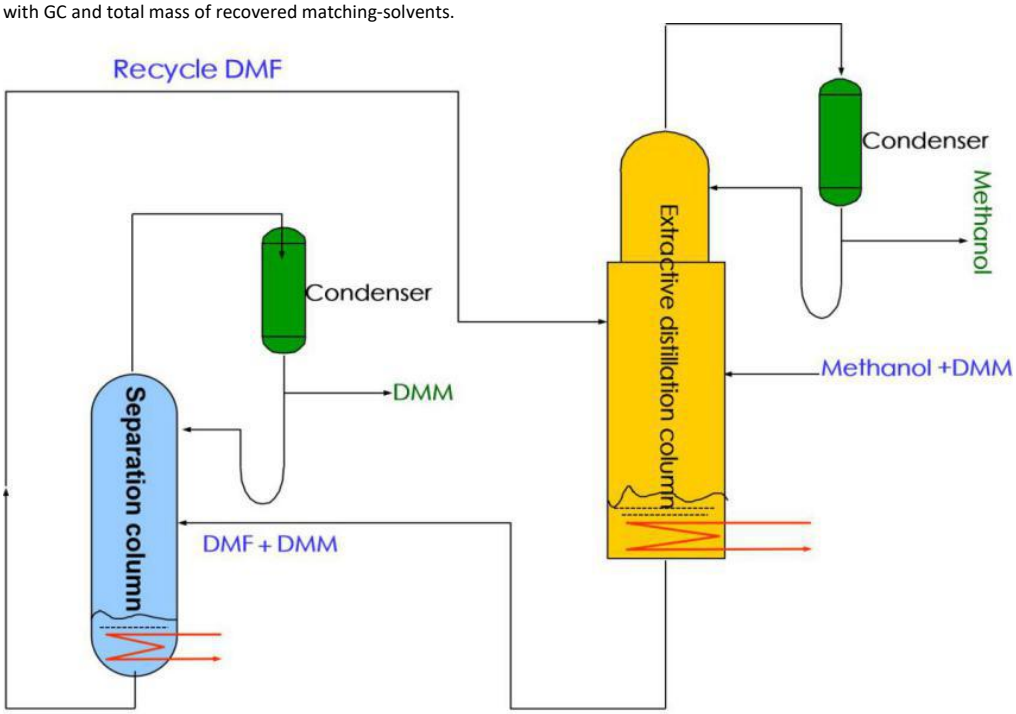

Fig. S8. DMM/METH matching-solvents separation using extractive distillation with N,N-dimethylformamide(DMF) as an entrainer.

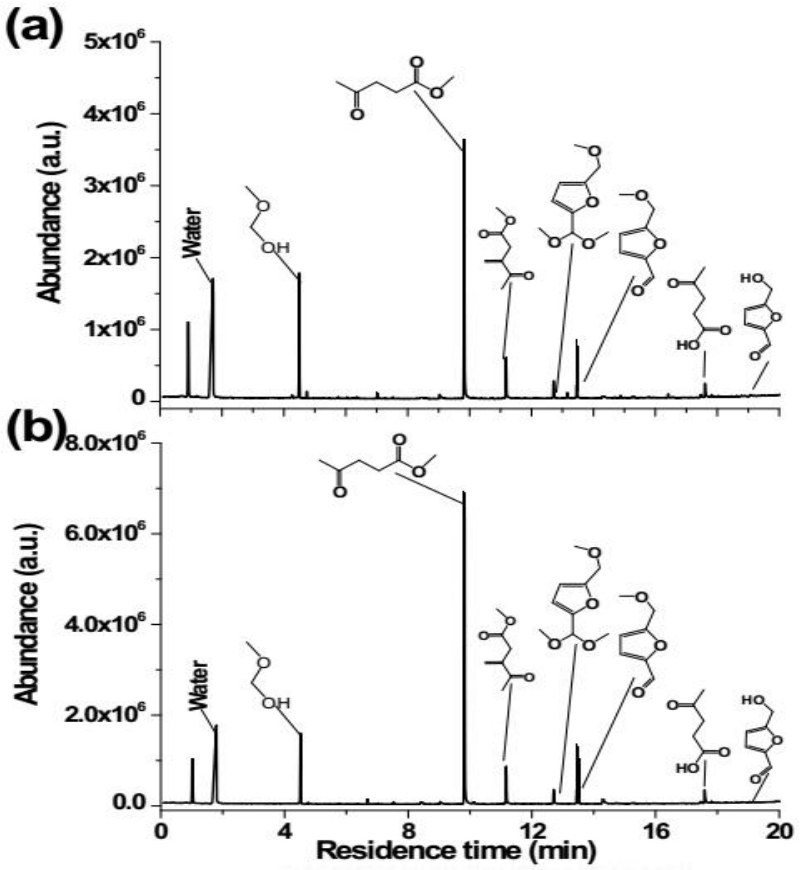

Fig. S9. Typical mass spectrum for the conversion of (a) glucose and (b) HMF in DMM/methanol.

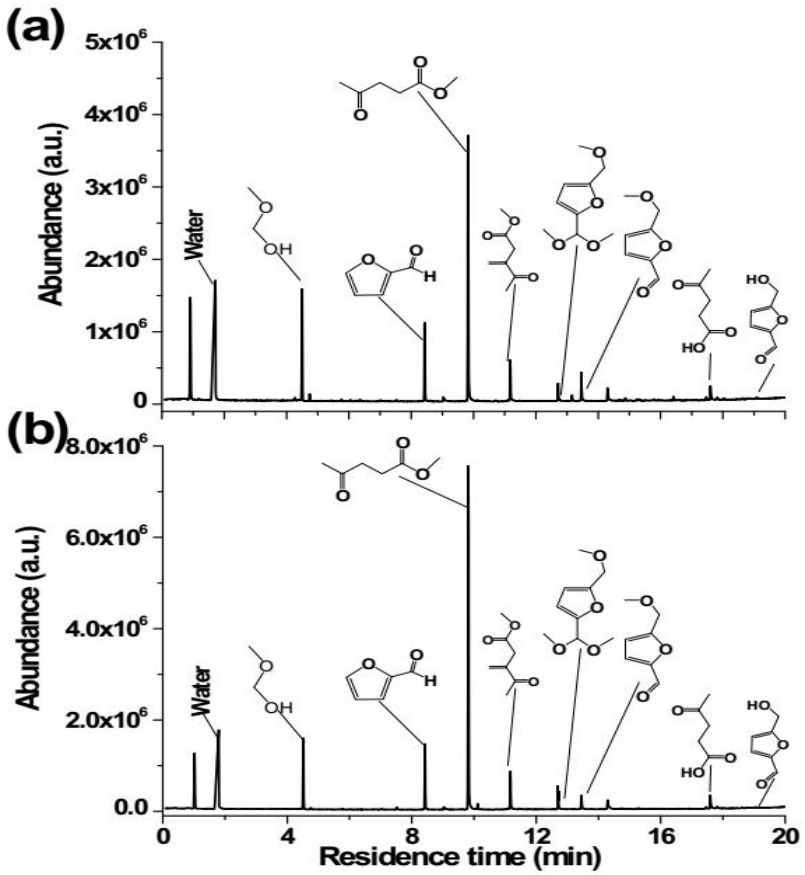

Fig. S10. Typical mass spectrum for the conversion of (a) xylose and (b) furfural in DMM/methanol.

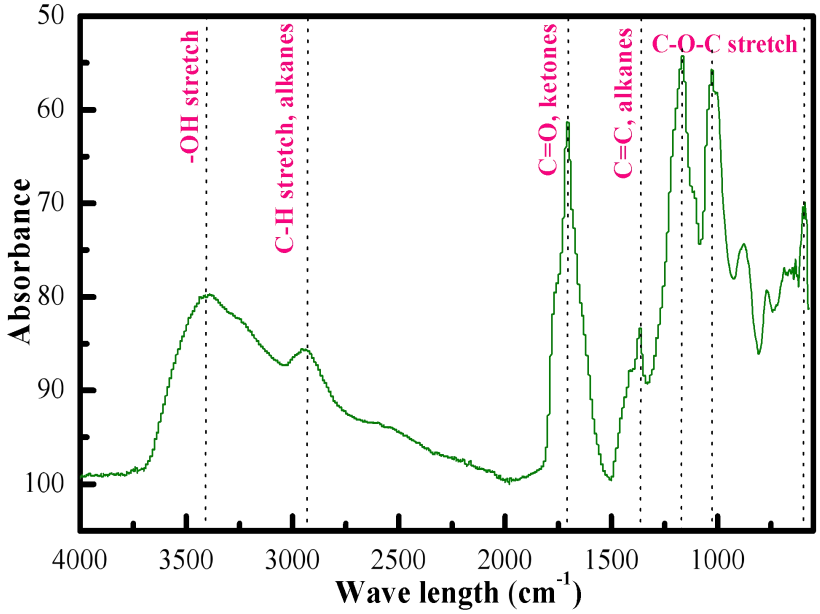

Fig. S11. FT-IR characterization of directional liquefaction of xylose/glucose in DMM/METH.

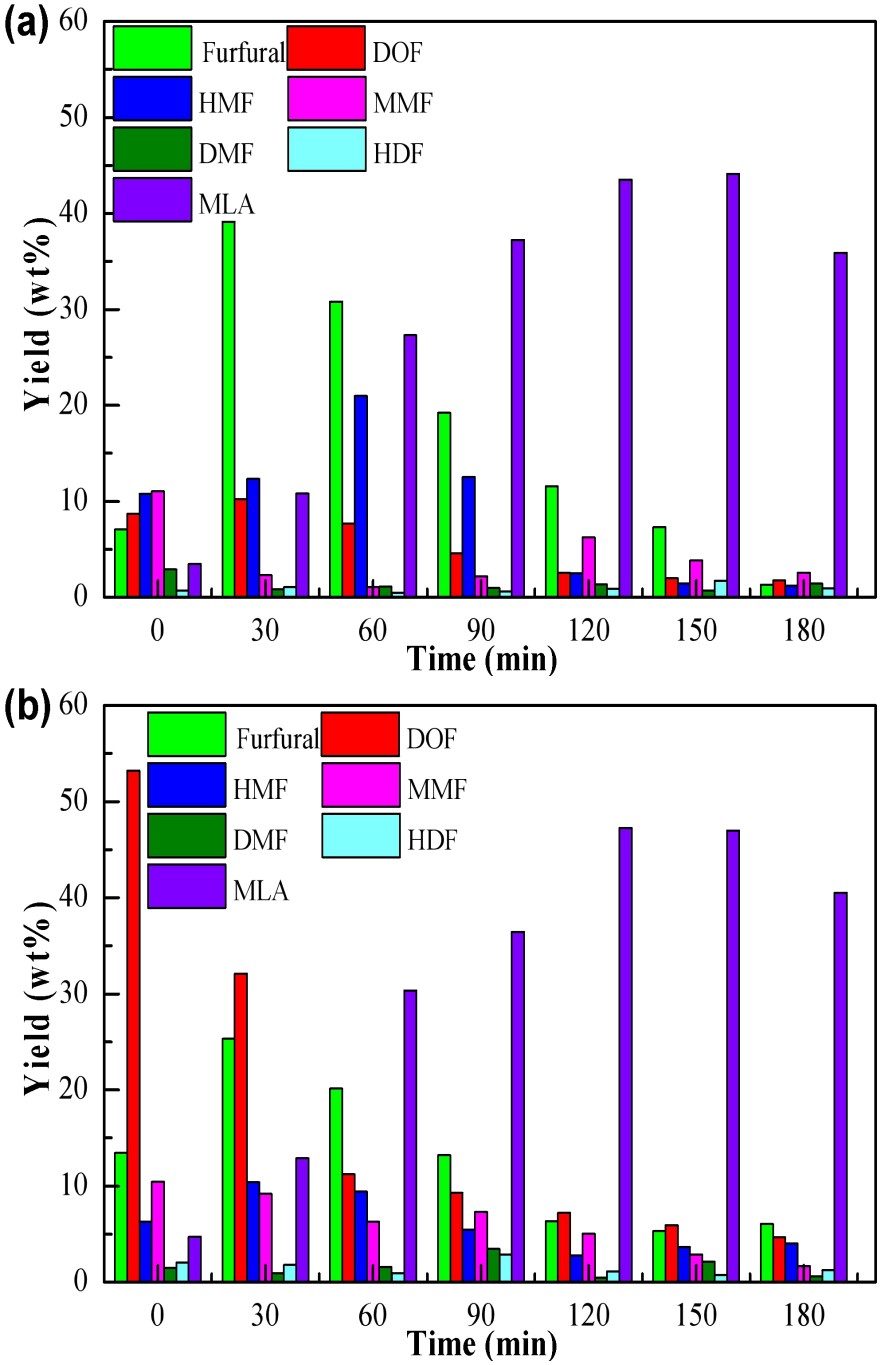

Fig. S12. Product distributions in the directional liquefaction of xylose (a) and furfural (b) in DMM/methanol solvents. Reaction conditions: xylose or furfural 5 g, C_7H_7-SO_3H 0.2 g, DMM 25 g, methanol 25 g, 160 °C.

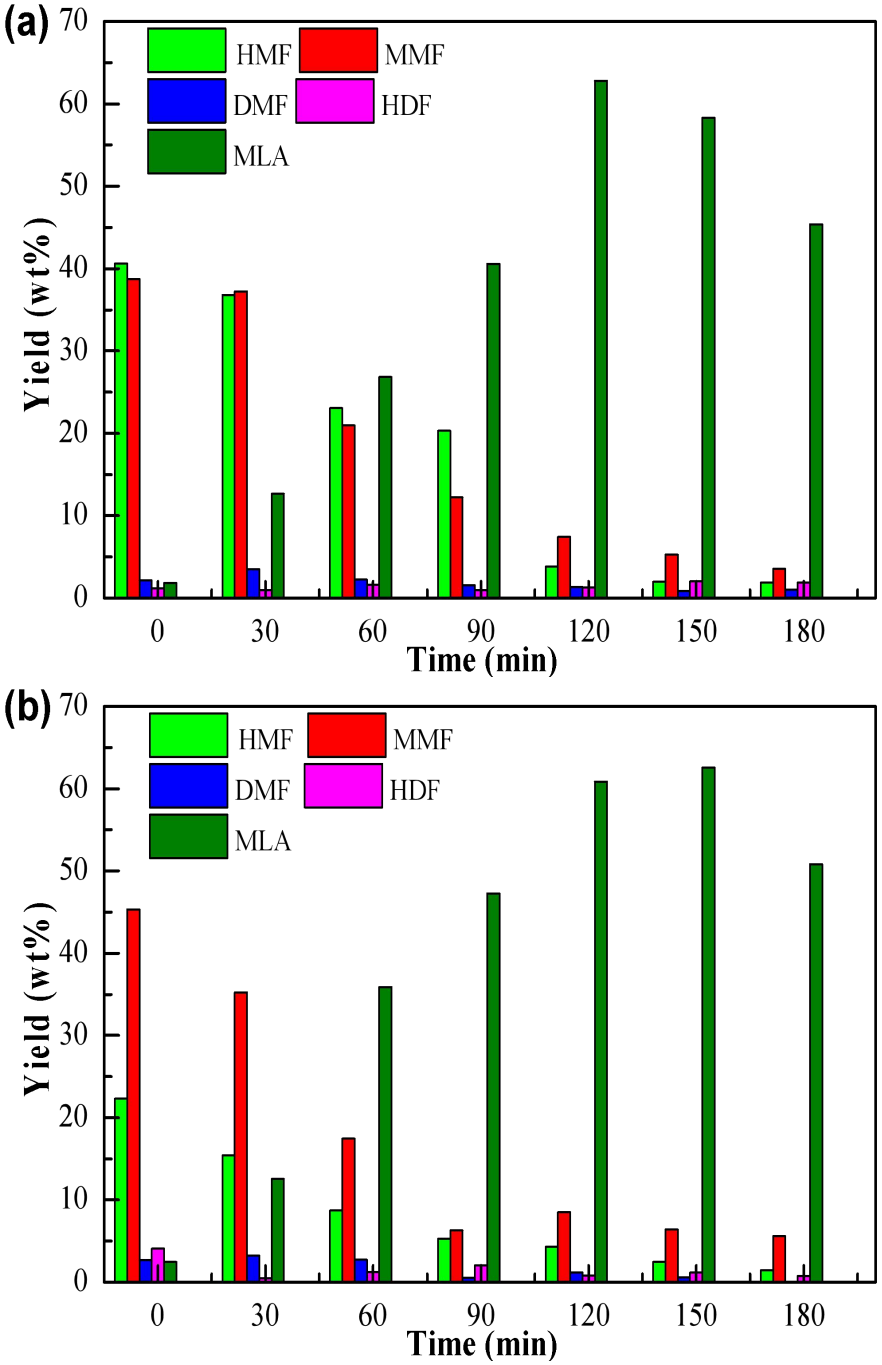

Fig. S13. Product distributions in the directional liquefaction of glucose (a) and HMF (b) in DMM/methanol solvents. Reaction conditions: glucose or HMF 5 g, C_7H_7-SO_3H 0.2 g, DMM 25 g, methanol 25 g, 160 °C.

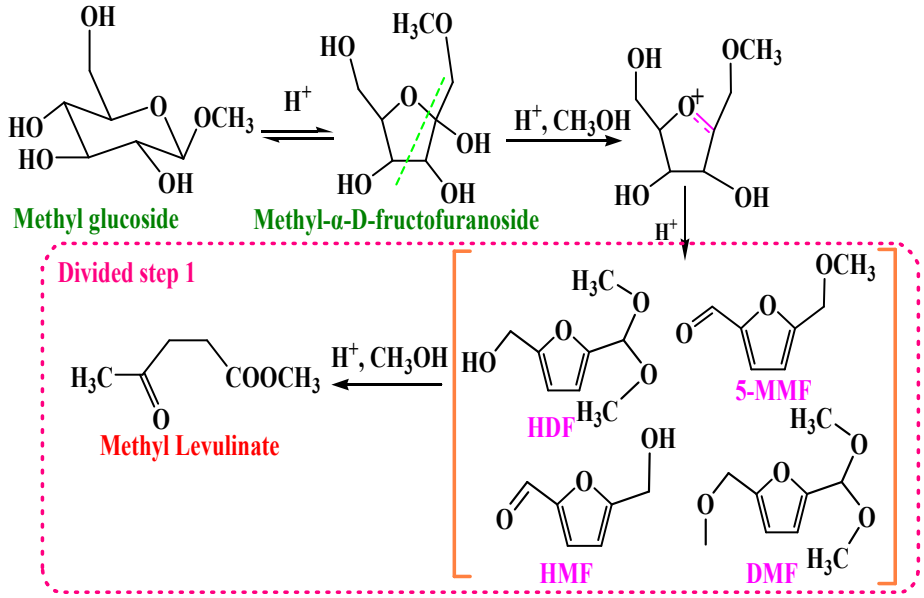

Fig. S14. Conversion of glucose to levulinic acid/ester in DMM/METH. All products were detected with GC-MS.

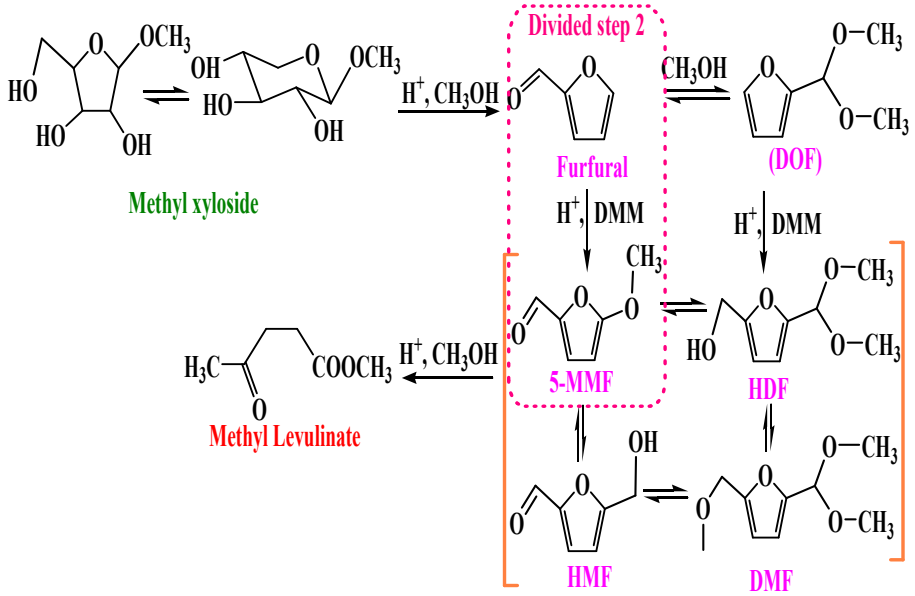

Fig. S15. Conversion of xylose to levulinic acid/ester in DMM/METH. All products were detected with GC-MS.

Supporting Notes and references

S1 S. Elumalai, B. Agarwal, T. M. Runge, R. S. Sangwan. Carbohydrate polymers, 2016, 150, 286-298.

S2 J. Romo, N. Bollar, C. Zimmermann, S. Wettstein. ChemCatChem, 2018, 10(21), 4805-4816.