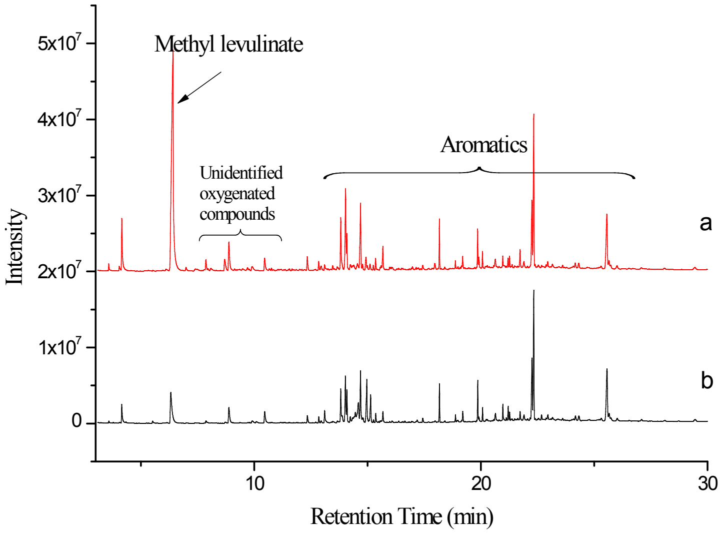


Fig. S1 The components changes with in aromatic product (3) from pine tree.(a. aromatic 3 obtained from the liquefaction product at 240 ℃; b. aromatic 3 obtained from the liquefaction product at 200 ℃). It can be seen that the side product, methyl levulinate, is miscible with the aromatic product, which great affect the purity of the aromatics. The efficient solution for high purity aromatic production is preventing the side reactions during the liquefaction, e.g. decomposition of cellulose fragments.

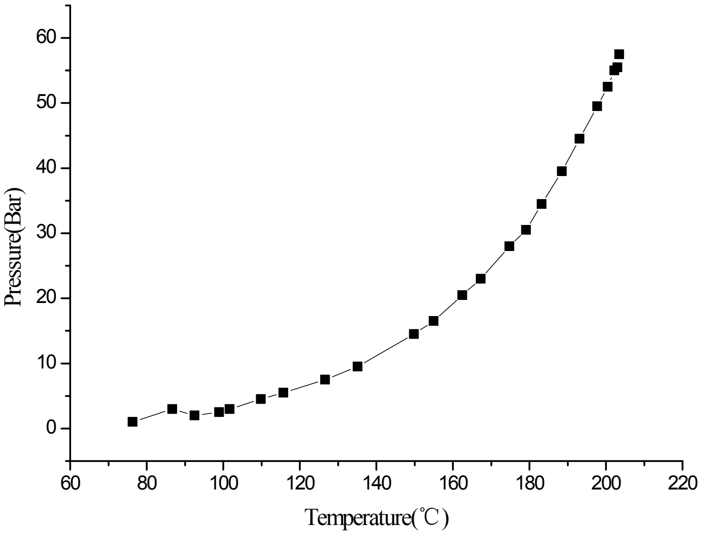
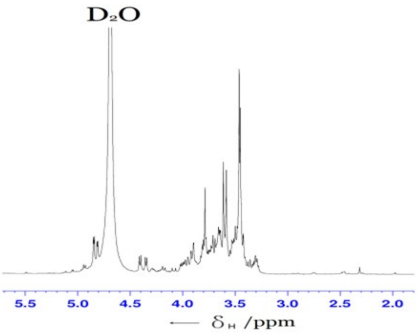
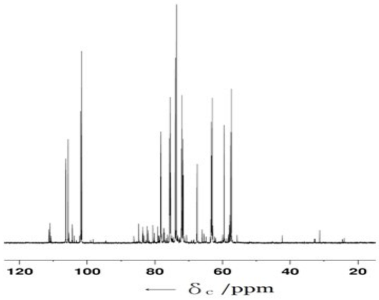


Fig. S2 Pressure and temperature profile during the directional liquefaction. It was found that the increment of the pressure became faster at a high temperature, which indicate decomposition of the biomass. The decomposed products have low molecular weight and high vapor pressure, greatly increase the traction pressure.



(a)



(b)

Fig.S3 Spectra of the sugar derivatives fractionated from liquefied product (a) 1H NMR and (b) 13C NMR. The ^{1}H NMR spectrum indicated that a large amount of protons were aliphatic H adjacent to oxygen (3.0-4.5 ppm) in sugar derivatives. There was no peak observed from 6.0-8.0 ppm (Aromatics). This also indicated sugar derivatives are mainly composed of saturated oxygenated compounds with plenty of hydroxyl groups. The ^{13}C NMR spectrum showed two groups of multiple peaks at the chemical shift of 60-80 and 100-110 ppm, which indicated the C atoms are adjacent to one and two O atoms.

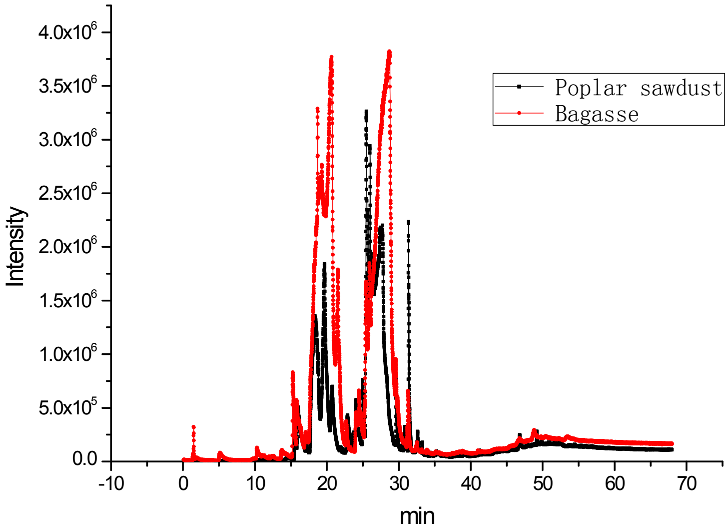


Fig. S4. The sugar products liquefied from other lignocellulosic biomass. All the samples indicate that the purity of the sugars is over 90 % by area normalization method in GC. These sugar products are obtained from different spices of biomass by directional liquefaction, followed by stepwise fractionation, which indicate that this methodology can be applied to most of the lignocellulosic biomass.

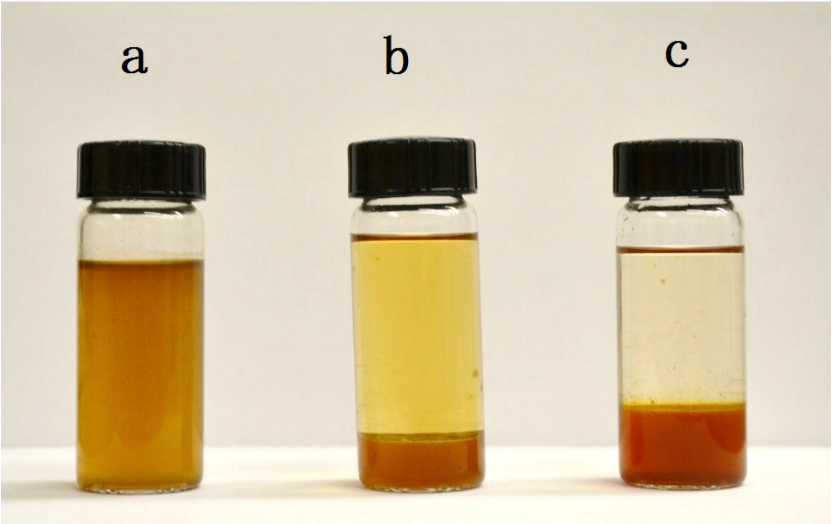


Fig.S5. Solubility of the sugar products in conventional solvents. (a. water; b. methanol; c. ethyl acetate) They are easily soluble in water, partially soluble in methanol and insoluble in hydrophobic solvent such as ethyl acetate.

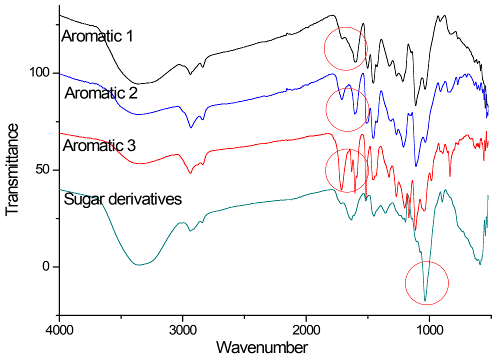
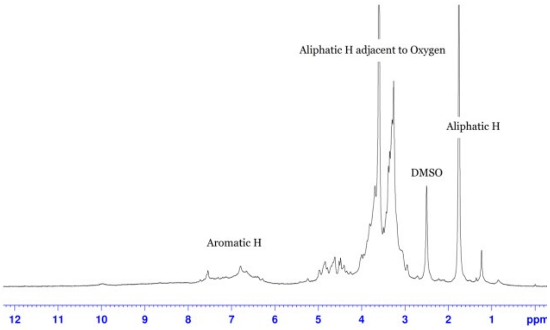
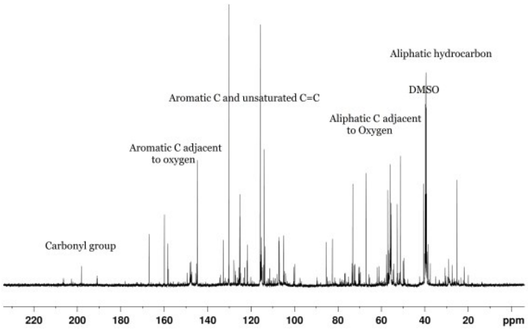


Fig. S6 FT-IR spectra of aromatic and sugar products separated from stepwise precipitation.

FT-IR spectra were used as well to analyse the fractionated products. A broad peak range around 3400 cm^{-1} represents the OH groups from either cellulose or lignin. The peak around 2922 cm^{-1} represents the C-H, a symmetric stretching in aliphatic methyl. A band at approximately 1636 cm^{-1} is characteristic to C=C stretching vibration in the aromatic skeletal of lignin. A band at approximately 1458 cm^{-1} is due to bending vibration of C-H of methylene group (scissoring vibration). An obvious difference between aromatic and sugar products could be recognized at 1100 cm^{-1}, which was due primarily to a large proportion stretching vibration of C-O in sugar rings. There were changes of C=O vibrations in aromatic products. Aromatic 3 presented the highest absorption in the wave number of 1700 cm^{-1} (C=O vibrations), because of the following two reasons: (1) transformation of the molecular structure during the liquefaction, and (2) increment of by-products such as MMF and MLA in the aromatic products. The liquefied lignin products tend to dehydrogenate and form the phenolics with ketone groups such as 2,4'-Dihydroxy-3'- methoxyacetophenone and 3-(4-hydroxyphenyl)-2-Propenoic acid methyl ester, which increase the amount of carbonyl groups in the depolymerized lignin. The by-products from decomposition of sugar derivatives mainly contain carbonyl groups, which also increase the absorption with a peak at 1700 cm^{-1}.



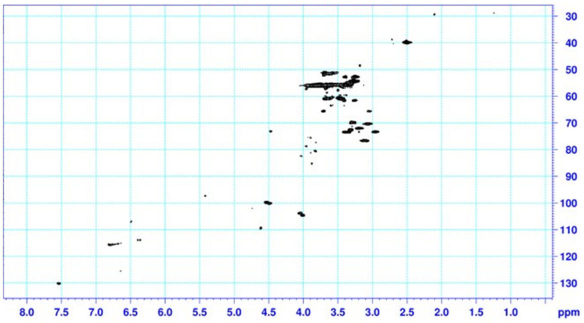
(a)



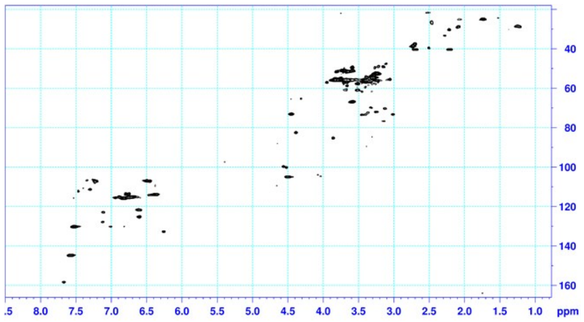
(b)

Fig. S7 NMR analysis of the fractionated aromatic products, (a) ^{1}H NMR, (b) ^{13}C NMR.

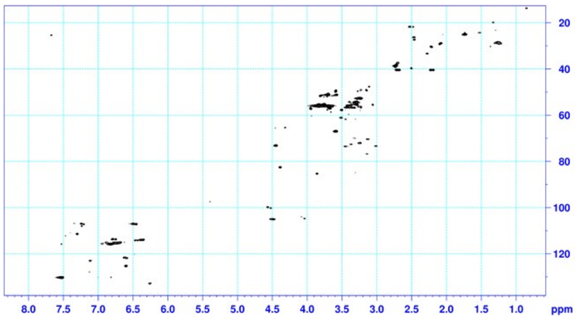
Routine 1D ^{1}H NMR and ^{13}C NMR spectra were recorded for the chemical shift of hydrogen and carbon atoms in aromatic and sugar products (Fig. 12). The ^{1}H NMR spectrum indicated that a large amount of protons were aliphatic H adjacent to oxygen (3.0-4.5 ppm). A chemical shift from 3.0-4.5 ppm showed the aliphatic H in the structure of aromatics. Moreover, protons of aromatic compounds (6.0-8.0 ppm) were observed in the spectra, which were largely aromatic due to the decomposition of lignin.The chemical shift in ^{13}C NMR spectrum was divided into several groups. Aliphatic C was observed at the chemical shift between 20-40ppm, which indicated a side chain connected to the aromatic rings. The aliphatic C adjacent to oxygen atoms (60-80 ppm) was attributed to the dominated linkages such as β-O-4, 4-O-5, and dibenzodioxocin units. There were a large amount of C atoms with the chemical shift between 110-140ppm, which indicated a sufficient amount of aromatic rings. We also noticed that the aromatic C atoms adjacent to the oxygen atoms were from the phenolics. The chemical shift around 200 ppm suggested carbonyl groups in the samples.



Aromatic 1



Aromatic 2



Aromatic 3

Fig. S8. HSQC NMR analysis in the aromatic products fractionated from liquefied bamboo. Three sample present similar spectra both in the aliphatic region and aromatic region. There are much more chemical groups identified in the liquefied product, e.g. aliphatic carbon chain, compared with the previous reports. The decomposition of the biomass disclose the chemical groups inside the plant cell structures, which provide more structure information.

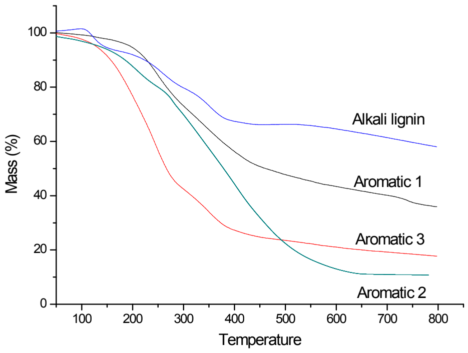
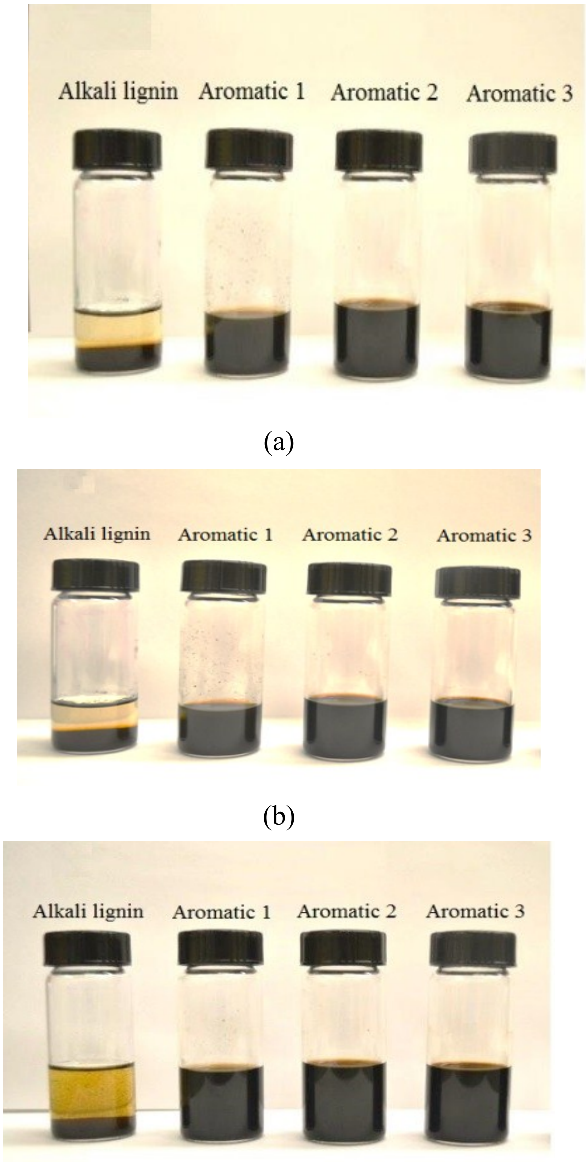


Fig. S9 TGA curves for alkali lignin, aromatic products subject to stepwise fractionation from the liquefied fuel at reaction conditions of methanol, 350 mL; bamboo, 40 g; temperature, 200 ℃; reaction time, 10 min.



(a)

(b)

(c)

Fig. S10 Solubility of phenolic products in different organic solvents at ambient temperature; (a) All the aromatic products (1, 2, 3) in methanol; (b) in acetone; (c) in THF.