

# **Direct valorization of lignocellulosic biomass into value-added chemicals by polyoxometalate catalyzed oxidation under mild condition**

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### **Composition analysis of lignocellulosic biomass**

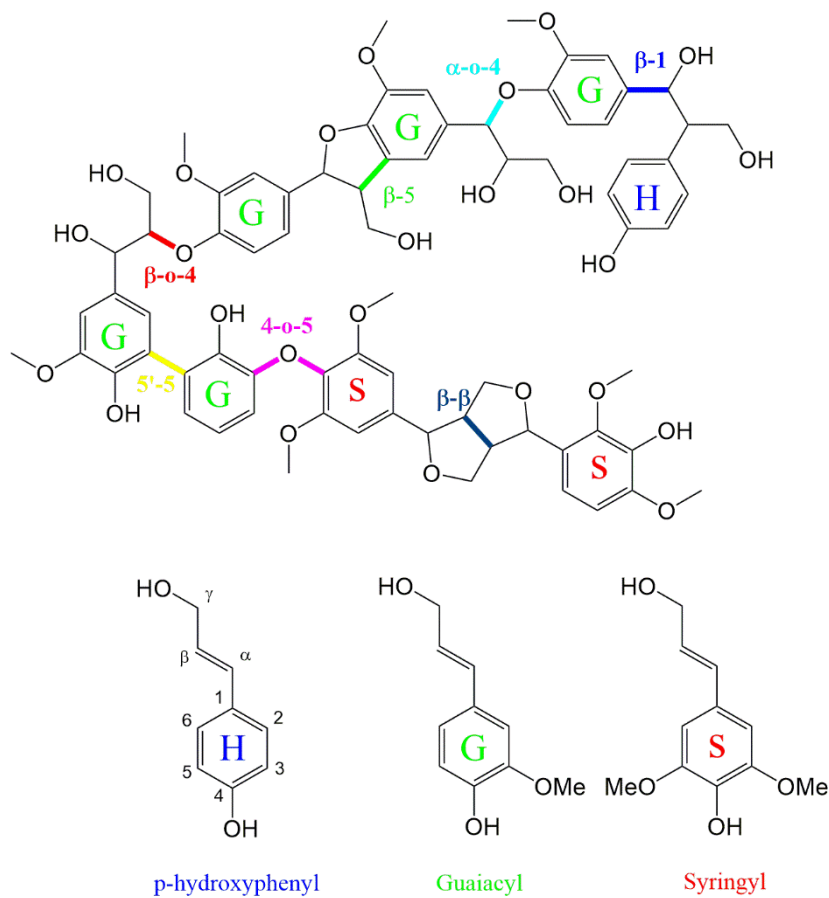
According to a standard TAPPI method, the composition analysis of wood biomass was conducted. The moisture content of wood biomass was determined by calculating the mass loss of wood powder samples before and after drying at 105 °C overnight. 0.5 g wood powders were loaded into 25 mL beakers with the addition of 10 mL 72 wt% H<sub>2</sub>SO<sub>4</sub>. The mixture was left at room temperature for 2 h and stirred with a glass rod every 10 min. Water were added to dilute the slurry to reach a 4 wt% H<sub>2</sub>SO<sub>4</sub>. Then the mixture was treated for 6 h under reflux conditions. The residual was washed with water and dried at 70 °C for 24 h and weighed to determine klason lignin. The acid soluble lignin (ASL) was determined by UV spectra by measuring the absorbance of the resulting liquid at 205 nm. The resulting liquid was used for the determination and quantification of monomeric sugars by high performance liquid chromatography (HPLC). The mass of cellulose and hemicellulose was calculated according to the concentrations of monomeric sugars in the hydrolysate. The resulting liquid was also used for calculating organic carbon of cellulose and hemicellulose components by TOC analysis.



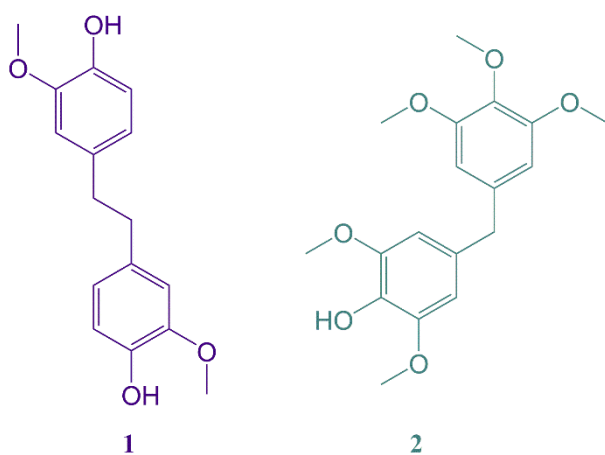
**Table. S1** Compositions of the lignocellulosic biomass.

Samples	Moisture content (%)	Cellulose (%)	Hemicellulose (%)	Total Lignin (%)
Hardwood	7.3	41.9	17.8	25.7
Softwood	4.6	37.2	21.1	30.9

## Lignin structure



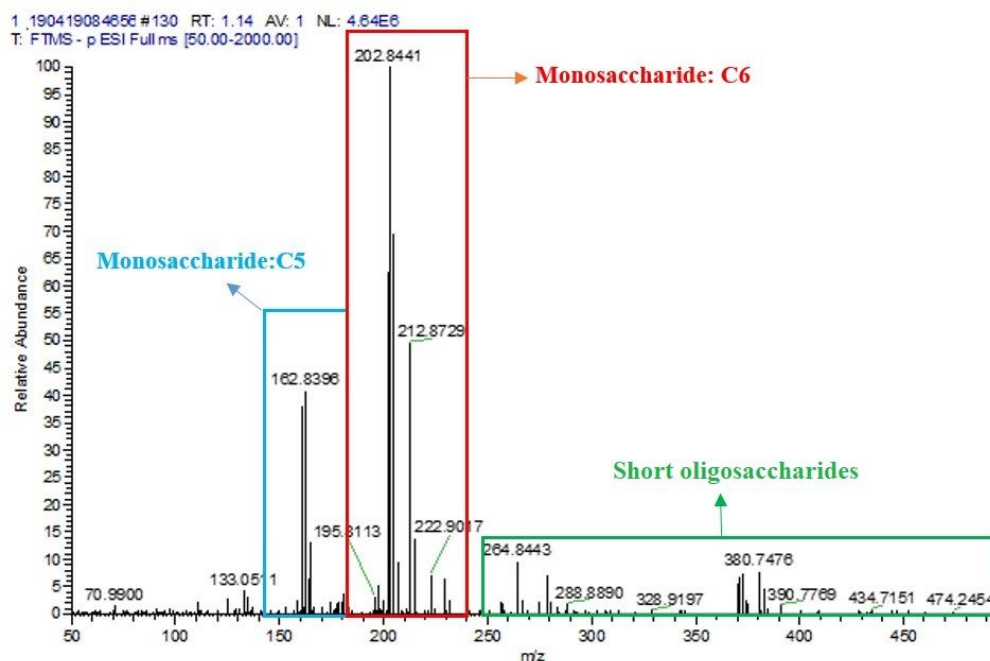
**Fig. S1** Wood lignin structure with three building structure (H, G, S types) and the typical  $\beta$ -O-4, 5'-5,  $\beta$ -5,  $\alpha$ -O-4,  $\beta$ -1, 4-O-5,  $\beta$ - $\beta$  linkages<sup>1-3</sup>.



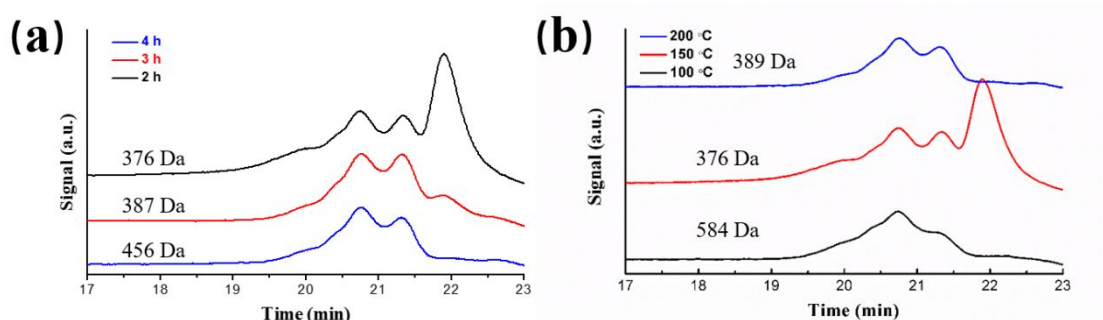
**Fig. S2** Typical condensed structures formed during kraft pulping process<sup>4</sup>.

**Table. S2** Detailed products distribution of the gas products obtained from the oxidative degradation of lignocellulosic biomass with vary times and temperatures

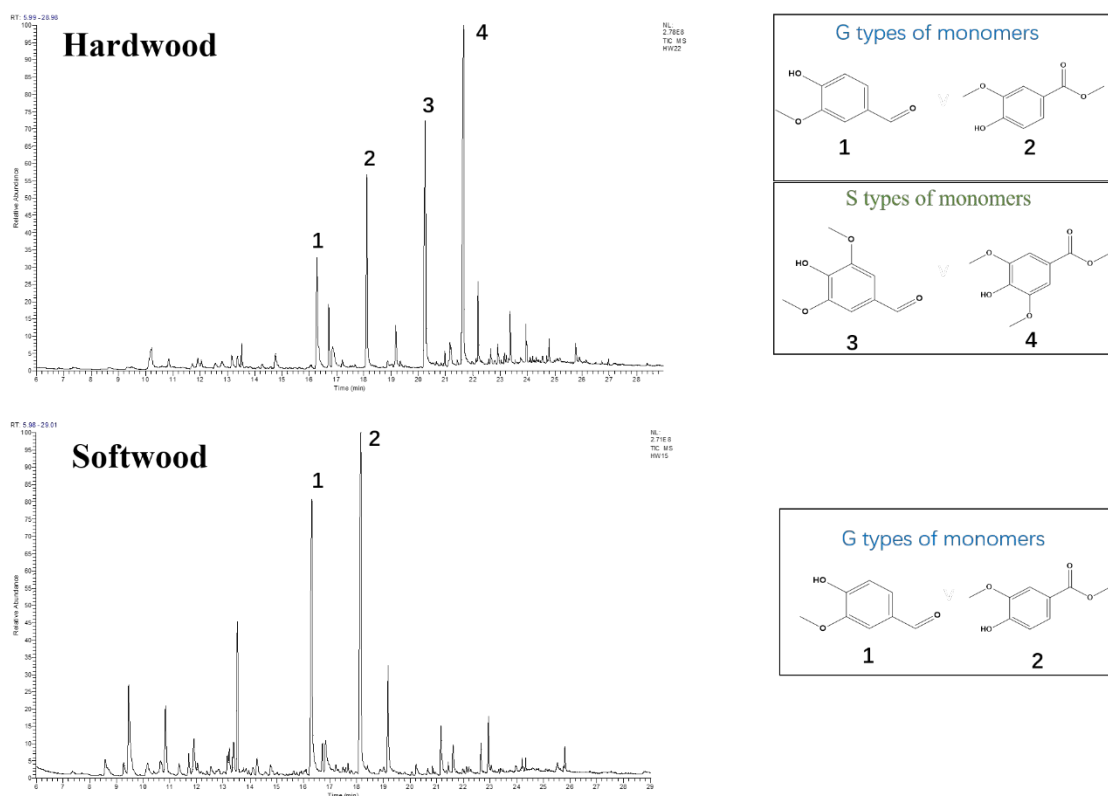
Entry	t (h)	T (°C )	CO ( % )	CO <sub>2</sub> ( % )	Sum ( % )
1	2	150	0.1	0.5	0.6
2	3	150	1.0	5.4	6.4
3	4	150	1.6	9.0	10.6
4	2	100	0.1	0.4	0.5
5	2	200	1.8	10.0	11.8



**Figure S3.** Mass spectrum of water-soluble products obtained from the oxidative depolymerization under 150 °C for 2 h.



**Figure S4.** GPC analysis of extractable lignin oil obtained from the oxidation degradation of hardwood under vary reaction times (a), and vary reaction temperatures (b).



**Figure S5.** GC-MS chromatograms of the extractable lignin oil obtained from the oxidative depolymerization for Hardwood and Softwood. The details of main aromatic monomer products were shown.

1. J. Zakzeski, P. C. Bruijninx, A. L. Jongerius and B. M. Weckhuysen, *Chemical reviews*, 2010, **110**, 3552-3599.

2. C. Li, X. Zhao, A. Wang, G. W. Huber and T. Zhang, *Chem. Rev*, 2015, **115**, 11559-11624.
3. D. Fengel and G. Wegener, *Walter de Gruyter*, 1984, **613**, 1960-1982.
4. J. S. Gratzl and C.-L. Chen, ACS Publications, 2000.