

## Supporting Information

### **Green aromatic aldehydes production from biomass via catalytic fractionation and ozonolysis**

Tianyu Ren,<sup>a</sup> Peidong Li,<sup>a</sup> Zhuo He,<sup>a</sup> Xinfeng Pan,<sup>a</sup> Yutao Yang,<sup>a</sup> Yuhe Liao,<sup>a</sup> Haiyong Wang,<sup>a</sup> Yanbin Cui,<sup>a,\*</sup> Chenguang Wang<sup>a,\*</sup>

<sup>a</sup> CAS Key Laboratory of Renewable Energy, Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences. Tianhe District, Guangzhou 510640, China.

Supporting Information Contents:

Number of pages: 16

Number of Figures: 22

Number of Tables: 2

Number of Notes: 1

\*Corresponding author

E-mail address: [cuiyb@ms.giec.ac.cn](mailto:cuiyb@ms.giec.ac.cn), [wangcg@ms.giec.ac.cn](mailto:wangcg@ms.giec.ac.cn)

**S1 Main materials**

**S2 Experimental procedure**

**S3 Supplementary Figures and Tables**

**S4 References**

## **S1 Main materials**

Macklin chemical company: tetrahydrofuran (99%), acetonitrile (AR and HPLC), methanol (99.5%), ethanol (99.7%), trifluoroacetic acid (99%), ethyl acetate (99%), 1,4-dioxane (99%),  $\gamma$ -valerolactone (98%), propanol (99.5%), isopropanol (99.5%), ethylene glycol (99%), methyl isoeugenol (98%), isoeugenol (97%), molybdenum (IV) oxide (99%), p-benzoquinone (99%), methanol-d4 (D, 99.8%), acetonitrile-d3 (D, 99.8%);

Aladdin chemical company: butanol (99%); vanillin (99%)

Bide pharm: coniferyl alcohol (98%);

Alfa Aesar: molybdenum (IV) oxide (99%);

Energy Chemistry company: ethanol-d6 (D, 99%);

Lebo Chemical company: coniferyl aldehyde (95%), sinapyl alcohol (97%);

Air Liquid: Oxygen (99.9995%).

Poplar, birch, and pine were used without pre-extracted. In small experiments, poplar powder with a size of roughly 0.1 – 0.3 mm were used. In scale-up experiments, sawdust of poplar, birch, and pine with a size of 1-10 mm were used.

## **S2 Experimental procedures**

### **S2.1 Catalytic fractionation**

In small experiments, typically, 300 mg poplar powder and 60 mg MoO<sub>2</sub> were dispersed in 10 mL methanol in a stainless-steel reactor bottle (CHEM NS6-20D-SS1, 20 mL). After replacing air and pressurizing 2 MPa N<sub>2</sub>, the mixture was heated to 180 °C and stirred with a magnetic bar at 500 rpm. After reaching designated time, the reactor was quenched in water. Then, a sample of the product were taken and filtrated. 1 mL of the filtrate and 0.1 mL solution of internal standard (n-dodecane) were transferred into a GC sample bottle and analyzed with GC-FID and GC-MS.

GC-FID conditions: Shimazu GC 2014 equipped with a HP-5 column (0.32 mm × 0.25 μm × 30 m); oven temperature: 70 °C holding for 2 min, then, increase to 310 °C at 10 °C/min, and holding for 5 min; column flow: 1.5 mL/min; injector temperature: 280 °C; injection volume: 2 μL; FID temperature: 320 °C.

GC-MS conditions: ThermoFisher TRACE 1300 - ISQ QD equipped with VF-5ms (0.25 mm × 0.25 μm × 30 m); same oven temperature program and injector temperature with GC-FID.

The quantitative analysis of monomers was based on internal standard method. The relative correction factors of monomers to the internal standard were measured using authentic samples or estimated by effective carbon number method (for MP-G and MP-S). The total amount of other monomer products was estimated by adding up all peaks of by-products within monomer region (10 – 20 min) in GC-FID spectra.

In scale-up experiments, 24 g poplar sawdust, 4.8 g MoO<sub>2</sub>, and 800 mL methanol (or 18 g poplar sawdust, 3.6 g MoO<sub>2</sub>, and 600 mL methanol) were mixed in a stainless-steel reactor (CHEM, MS11000, 1 L). After replacing air and pressurizing 2.5 MPa N<sub>2</sub>, the mixture was heated to 175 °C and stirred with a mechanic stirrer at 500 rpm. During the reaction, samples were taken through a sampling tube equipped with a filter. For each sampling, ~2 mL liquid was taken and discarded, then another ~2 mL liquid was taken for analysis.

### **S2.2 Ozonolysis and overoxidation**

O<sub>3</sub>/O<sub>2</sub> flow was produced via a O<sub>3</sub> generator (Longevity EXT-C5) using pure O<sub>2</sub> as feedstock. The output gas was detected with a O<sub>3</sub> concentration monitor (Tonglin 3S-J5000, 0 – 100 mg/L). By adjusting the flowrate and power level of the O<sub>3</sub> generator, the O<sub>3</sub>/O<sub>2</sub> flow was typically set at O<sub>3</sub> concentration of 60 mg/L at 300 or 50 mL/min before entering substrate solution.

In a typical ozonolysis or overoxidation experiment, 0.1 mL 4-propenyl-G or 0.1 g vanillin were dissolved in 5 mL solvents in a centrifuge tube of 10 mL. Each tube was bubbled with 50 mL O<sub>3</sub>/O<sub>2</sub> gas flow. After reaching designated time, 1 mL solution of internal standard (4-propylguaiacol) was added into the product. Then, 0.1 mL of the mixture was taken and diluted into 1 mL ethanol, followed by HPLC analysis.

HPLC conditions: ELITE EClassical 3200 equipped with a PDA (190 – 800 nm) detector and an Agilent XDB-C18 column (4.6×250 mm 5 μm). 5 μL was injected by an auto-injector for each sample. Mobile phases were acetonitrile and 0.1% aqueous solution of trifluoroacetic acid. Acetonitrile phase started at 20% at 0 – 2 min, then increase to 60% at 8 min, maintained at 60% until 14.0 min, then decreased to 20% at 14.5 min, and

maintained to 40 min. The signal at 280 nm was used for quantitative analysis. The relative correction factors of 4-propenyl-G and vanillin to the internal standard were determined using authentic samples.

In NMR studies, reactions were conducted in deuterated solvents with similar procedures. However, during the reaction, ~0.5 mL of the solution was sampled at different time into a NMR tube and analyzed with a Bruker Advance III 400 MHz spectroscopy at 22 °C. <sup>1</sup>H NMR spectra were scanned 16 times and the spectra were processed with MestReNova software.

### **S2.3 CF-ozonolysis cascade processes**

Typically, after the scale-up experiments, the product was filtrated and the residual were washed with methanol. All solutions were combined and concentrated to ~30 mL via a rotary evaporator. For poplar, the solvent was completely removed, and the residual oil was redissolved in 60 mL of ethanol (this is for comparison of methanol and ethanol). For birch, the concentrated solution was diluted to 60 mL using methanol. Afterward, 30 mL of the concentrated solutions of poplar, birch, and pine were transferred into a glass bottle of 40 mL and used for ozonolysis study. In addition, the carbohydrate residuals were dried at 100 °C and collected for composition analysis.

Ozonolysis of the CF products were conducted by using 300 mL O<sub>3</sub>/O<sub>2</sub> gas flow at 60 mg/L O<sub>3</sub> concentration. Before and during the reaction, ~0.3 mL of the solution was sampled at different time. After the reaction and taking all samples, 0.1 mL of each sample and 0.1 mL solution of internal standard were diluted into 1 mL methanol. Then, the mixtures were subjected to GC analysis.

In consideration of the stability of MP-G and MP-S, we also tried to immediately ozonolyze liquid CF product to minimize product loss during workup. In this case, after CF reaction, the product solution was filtrated without washing the residual. The solution was immediately oxidized with 300 mL O<sub>3</sub>/O<sub>2</sub> gas flow at 30 mg/L O<sub>3</sub> concentration. During the reaction, 1 mL samples were taken and analyzed by GC after adding with 0.1 mL solution of internal standard.

For composition analysis, the carbohydrate residual was hydrolyzed in 72% H<sub>2</sub>SO<sub>4</sub> for 1 h. Then, the solution was diluted to a concentration of 4% and reacted at 121 °C for 2 h. After cooling down, the mixture was filtrated. The solid residual was weight for calculating lignin content, while the filtrated was analyzed by HPLC for cellulose and hemicellulose contents. In addition, the ash contents were determined by calcination at 600 °C for 2 h.

### S3 Supplementary Figures and Tables

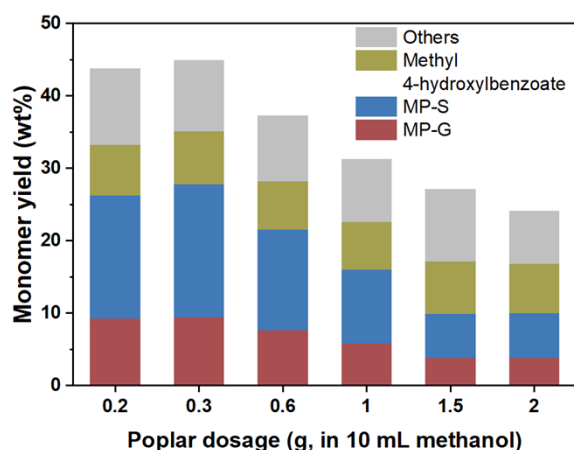


Fig. S1 CF of poplar with different dosage. Reaction conditions: 0.2 - 2 g poplar powder, 10 mL methanol, 20% (60mg) MoO<sub>2</sub>, 2 MPa N<sub>2</sub>, 180 °C, 500 rpm. Note that: in reactions with 1 – 2 g poplar, the stir bar was unable stir throughout the reaction due to too much biomass used. In the reaction with 0.6 g poplar, the stir bar was unable to stir at beginning until partial lignin was depolymerized.

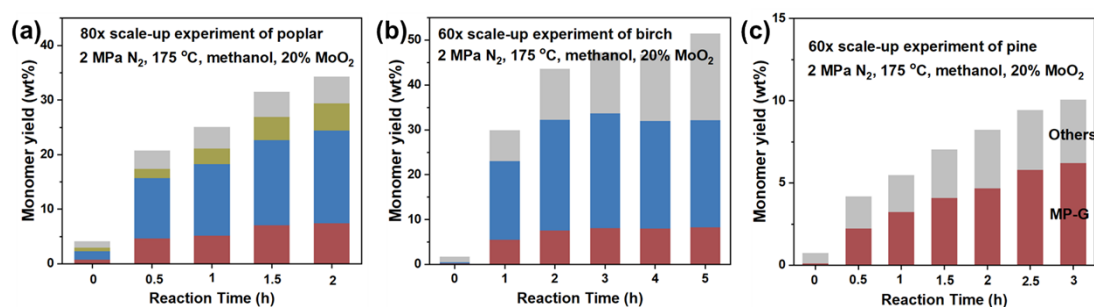


Fig. S2 Scale-up CF of (a) poplar, (b) birch, and (c) pine. Reaction conditions: 24g poplar or 18 g birch/pine sawdust, 600 (800 for poplar) mL methanol, 3.6 (4.8 for poplar) g MoO<sub>2</sub>, 2.5 MPa N<sub>2</sub>, 175 °C, 500 rpm.

Table S1 Composition of poplar and its residual after scale-up CF conversion.

	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Ash (wt%)	Mass (g)
Poplar	40.8	13.9	20.2	1.85	24.0
CF residual	43.8	15.1	- <sup>a</sup>	17.3 <sup>a</sup>	20.9
Recovery	93.5	94.6	-	-	-

a: The residual after CF reaction was mixed with MoO<sub>2</sub>. After hydrolyzing the carbohydrate, the unhydrolyzed solid accounted for 27.2 wt%. However, we cannot identify the percentage of lignin and MoO<sub>2</sub> and other impurities. If considering the content of MoO<sub>2</sub> equals to the ash content, then the lignin content would be roughly estimated to be 9.9 wt%.

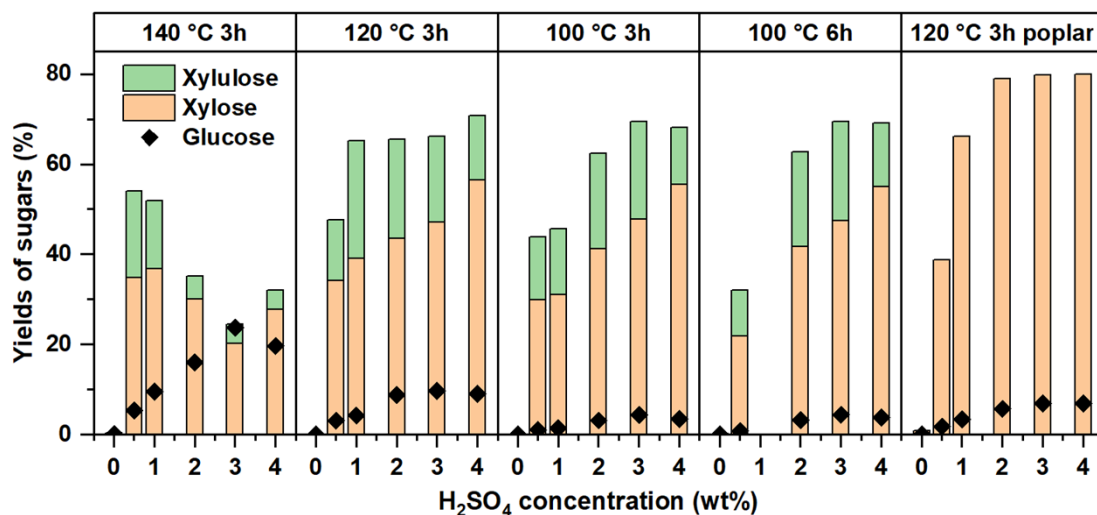


Fig. S3 Hydrolysis of carbohydrate residual of CF. Reaction conditions: 0.3 g residual (poplar 2 h, reaction conditions found in Fig. S2a) or poplar, 4 mL aqueous diluted H<sub>2</sub>SO<sub>4</sub> with concentrations of 0 – 4 wt%, 100 – 140 °C, 3 or 6 h.

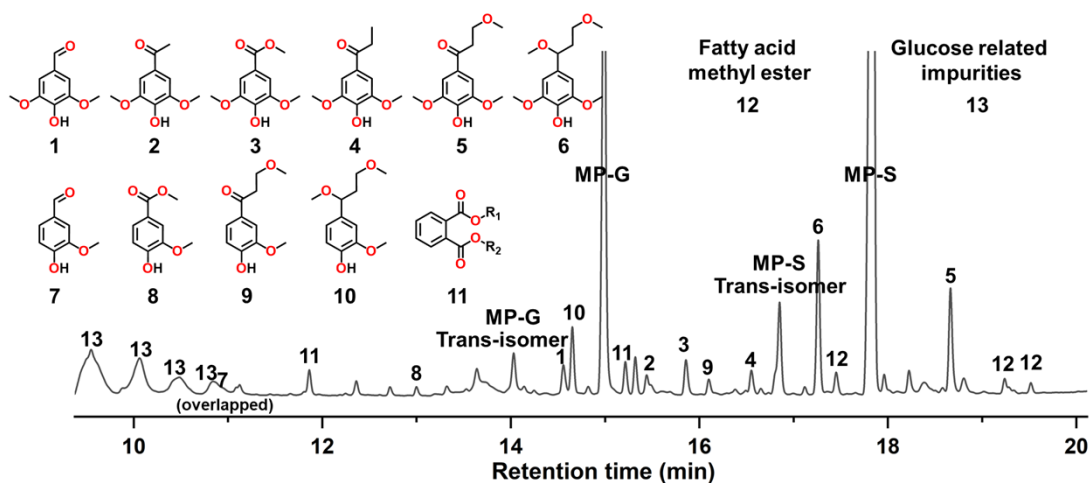


Fig. S4 Analysis of by-products after CF reaction. The GC spectrum is the monomer region of GC spectrum labeling “starting solution” in Fig. S21. In other word, the GC sample was from CF of birch (Fig. S2b) and ready to be ozonolysis.

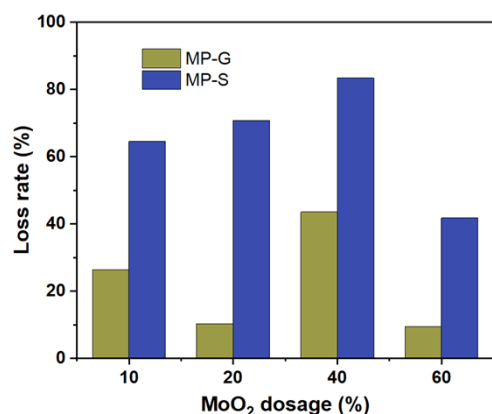


Fig. S5 Loss of MP-G and MP-S after 4 days storage. The samples were those shown in Fig. 1a. After 4 days storage, we detected them again and found partial MP-G and MP-S were missing. We speculate this is due to the oxidation by air.

#### Note S1 Discussion on the stability of MP-G and MP-S

As shown in Fig. S5, MP-G and MP-S are unstable probably due to exposure to air. MP-S is more reactive. Currently, the reason is unclear. We also found that after we concentrated the CF product, some flocculent precipitate formed within 1 h storage. This happened even though the samples were carefully capped (avoiding air) and stored in fridge (4 °C). When the precipitate formed, we found the contents of MP-G and MP-S began to decrease. We are not sure if the precipitate is from MP-G and MP-S or from oligomers. The results demonstrate that high concentration leads to precipitation. This situation was not observed when we handle with other lignin depolymerization products. Thus, we speculate that the instability of MP-G and MP-S and the precipitation are related to the  $C_{\alpha}=C_{\beta}$  unsaturated structures. Therefore, the samples were unable to be studied by 2D NMR which takes long testing time and requires high concentration.

Table S2 Literature reports of conversion of isoeugenol to vanillin by ozonolysis

Entry	Typical conditions	Vanillin yield (%)	Ref.
1	0.5-0.7 M isoeugenol in aqueous 2 wt% Coolade, 500 mL/min O <sub>3</sub> /O <sub>2</sub> , rt, 2.5 h; product reduced with 5.0 equiv of dimethyl sulfide.	50	1
2	Film-shear reactor. 0.1 M isoeugenol in ethyl acetate (10 mL/min) and water (10 mL/min) pumped into the reactor. 0.8 L/min O <sub>3</sub> /O <sub>2</sub> at 77 mg O <sub>3</sub> /L.	49	2
3	0.03 M isoeugenol in dichloromethane, 250 mL/min O <sub>3</sub> /O <sub>2</sub> , rt, 30-40 min; product reduced with 5.0 equiv of dimethyl sulfide.	89	3
4	6 mmol substrate, 50% acetonitrile reaching total volume of 20 mL, 300 mL/min O <sub>3</sub> /O <sub>2</sub> flow with 60 mg/L O <sub>3</sub> concentration, 20 min; product treated with MnO <sub>2</sub> .	60.2	4

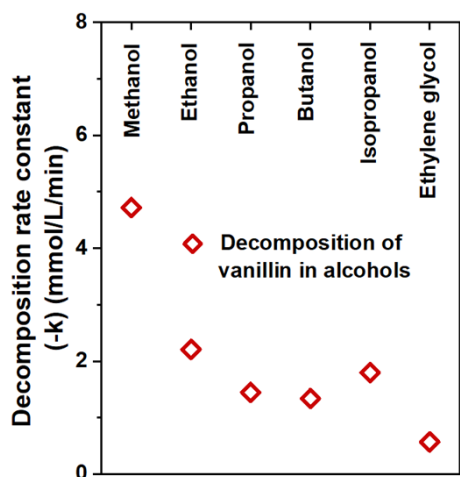


Fig. S6 Decomposition rates of vanillin after ozonolysis of 4-propenyl-G in different alcohol solvents. The decomposition rates are the slopes of the fitted lines of overoxidation branches of 4-propenyl-G ozonolysis (Fig. 2b and 2c).

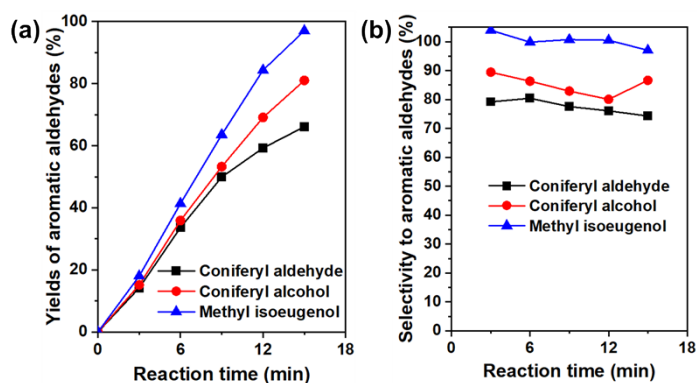


Fig. S7 Ozonolysis of lignin-related alkene-functionalized monomers. (a) Yield and (b) selectivity of aromatic aldehydes. Ozonolysis conditions: 0.13 M substrate in 5 mL ethanol, 50 mL/min  $O_3/O_2$  gas flow at a  $O_3$  concentration of 60 mg/L.

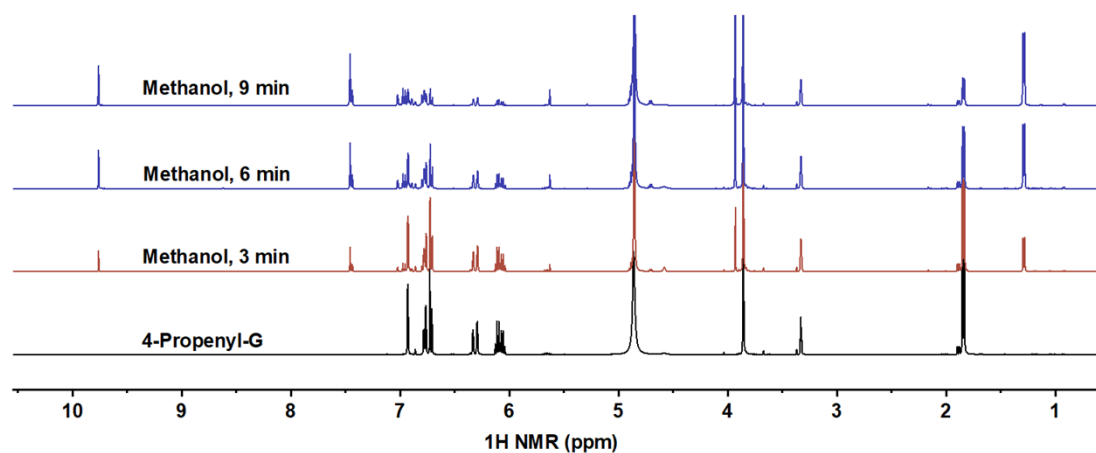


Fig. S8  $^1H$  NMR spectra of ozonolysis of 4-propenyl-G in methanol- $d_4$ .



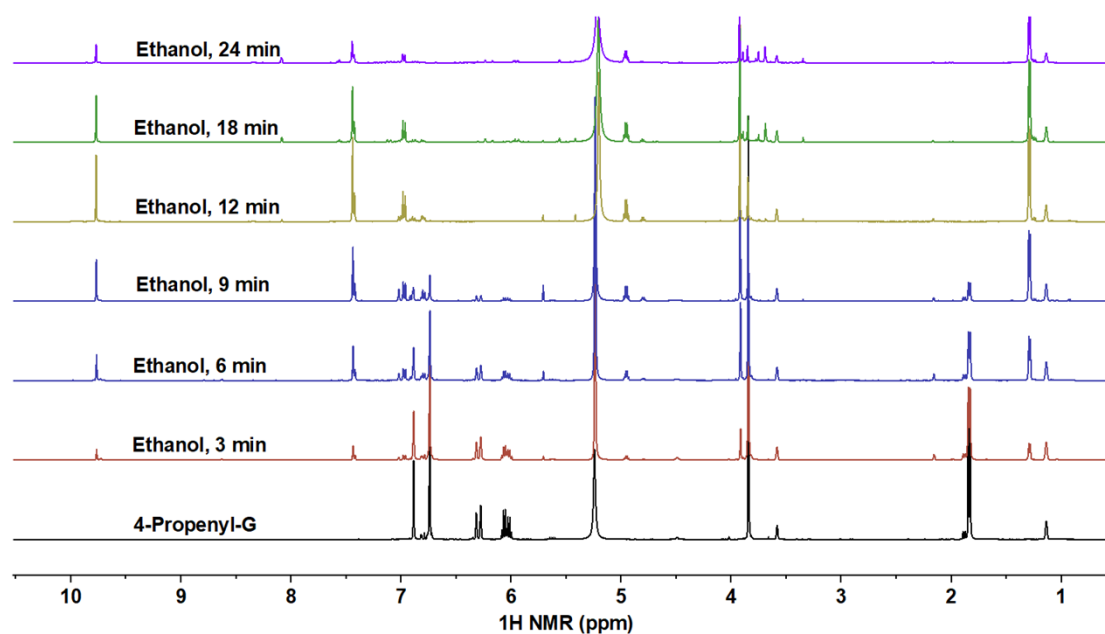


Fig. S9 <sup>1</sup>H NMR spectra of ozonolysis of 4-propenyl-G in ethanol-d<sub>6</sub>.

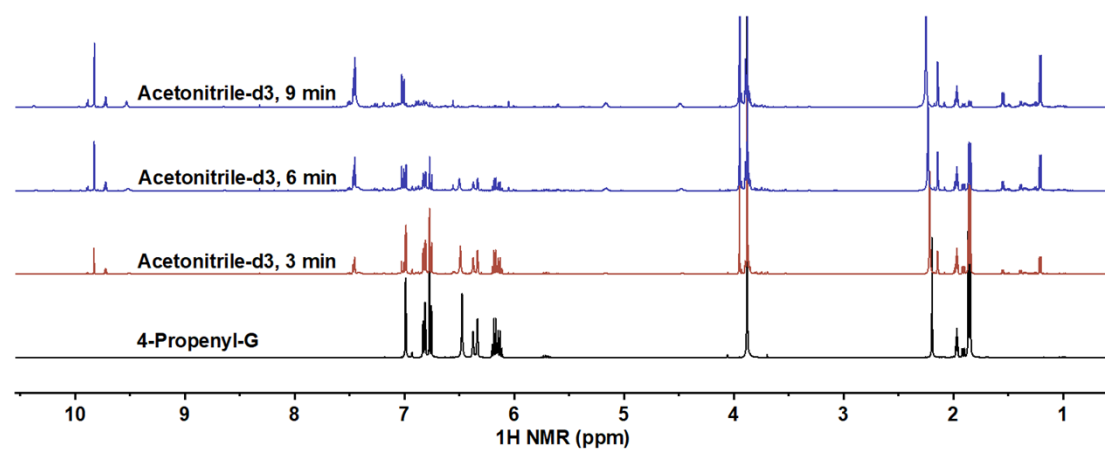


Fig. S10 <sup>1</sup>H NMR spectra of ozonolysis of 4-propenyl-G in acetonitrile-d<sub>3</sub>.

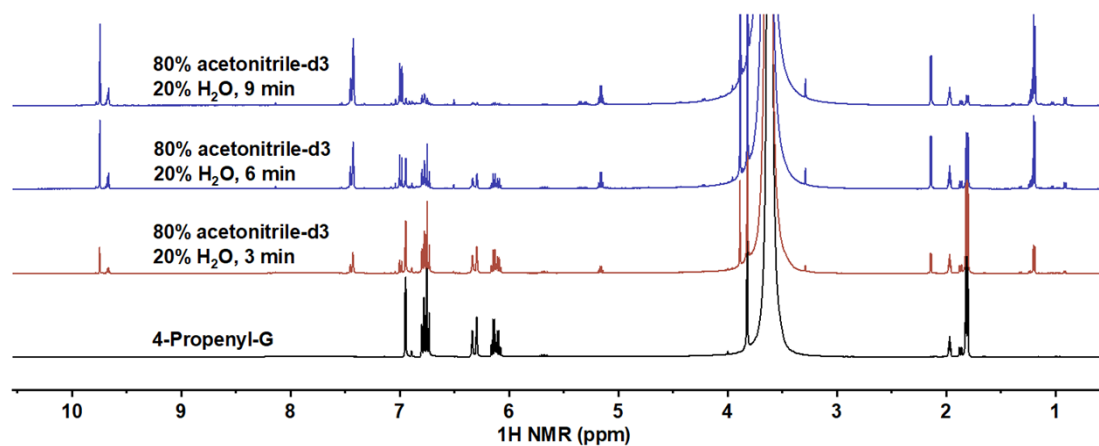


Fig. S11 H NMR spectra of ozonolysis of 4-propenyl-G in 80% acetonitrile-d<sub>3</sub> – 20% H<sub>2</sub>O.

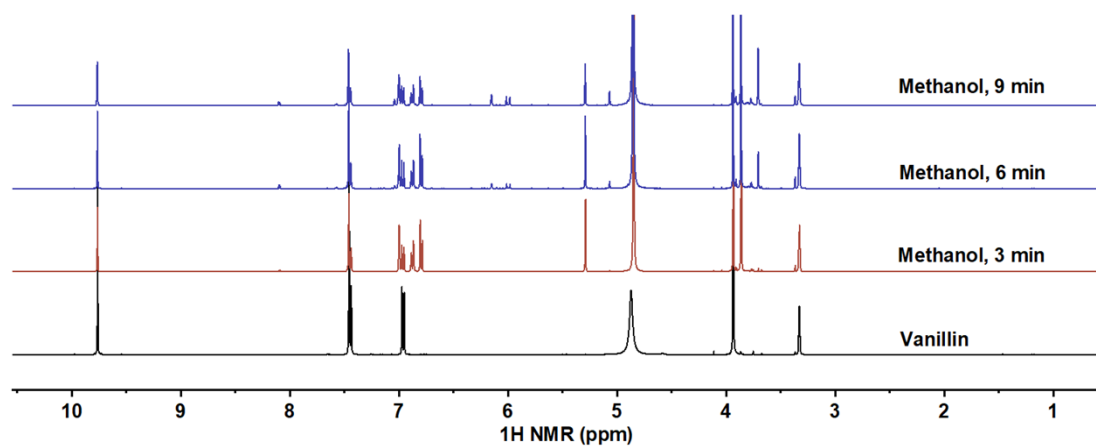


Fig. S12 H NMR spectra of overoxidation of vanillin in methanol-d<sub>4</sub>.

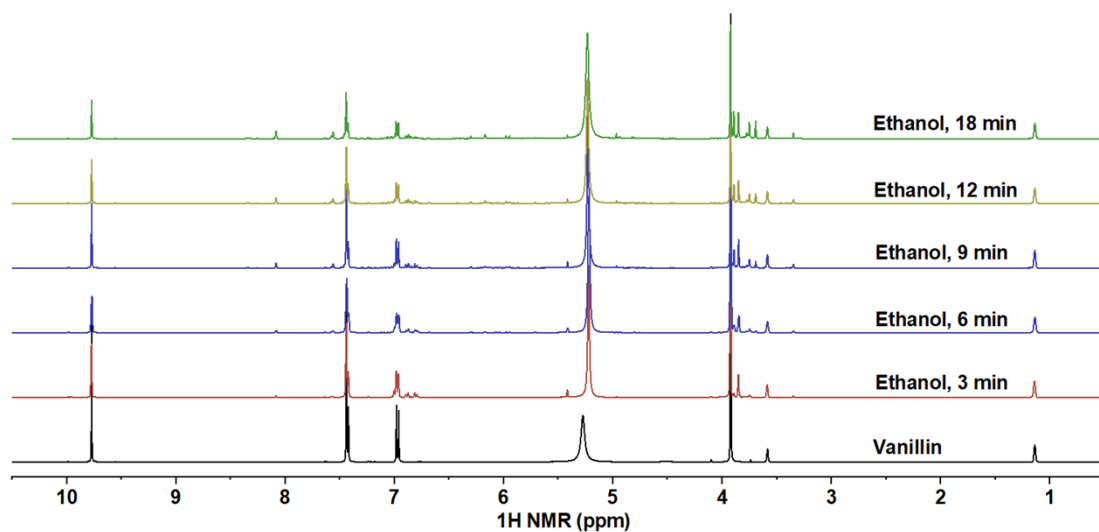


Fig. S13 H NMR spectra of overoxidation of vanillin in ethanol-d<sub>6</sub>.

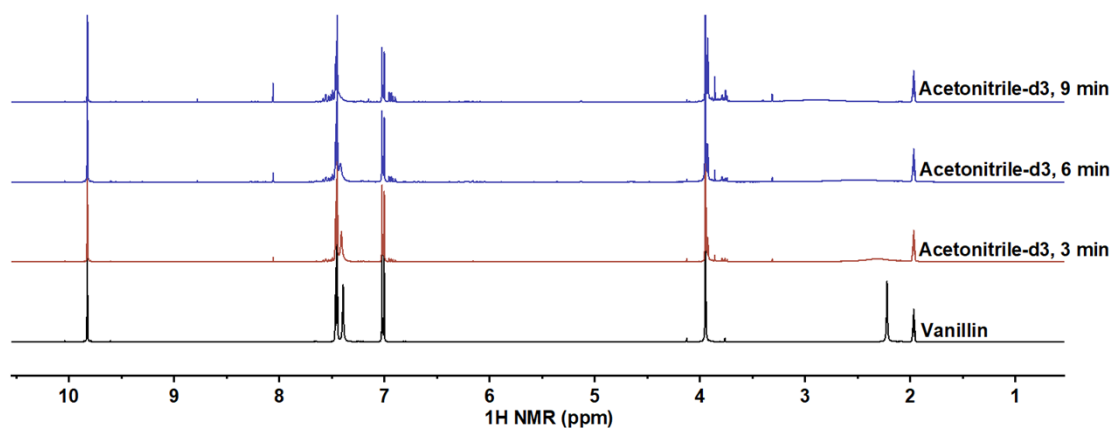


Fig. S14 <sup>1</sup>H NMR spectra of overoxidation of vanillin in acetonitrile-d<sub>3</sub>.

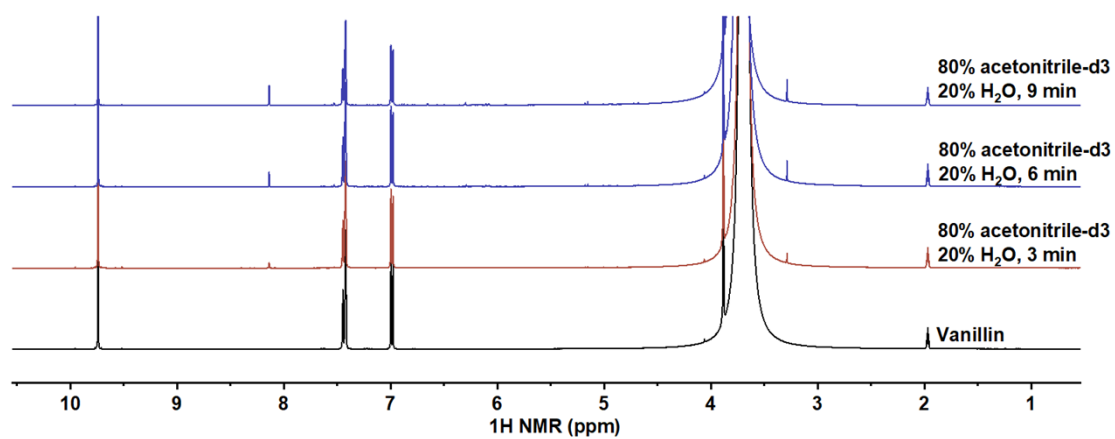


Fig. S15 <sup>1</sup>H NMR spectra of overoxidation of vanillin in 80% acetonitrile-d<sub>3</sub> – 20% H<sub>2</sub>O.

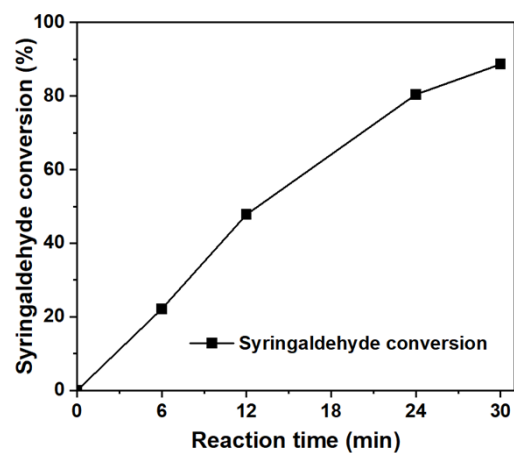


Fig. S16 Fast overoxidation of syringaldehyde. Reaction conditions: 0.572 g syringaldehyde, 30 mL ethanol, 300 mL/min O<sub>3</sub>/O<sub>2</sub> gas flow at a O<sub>3</sub> concentration of 60

mg/L. Samples were taken at designated time.

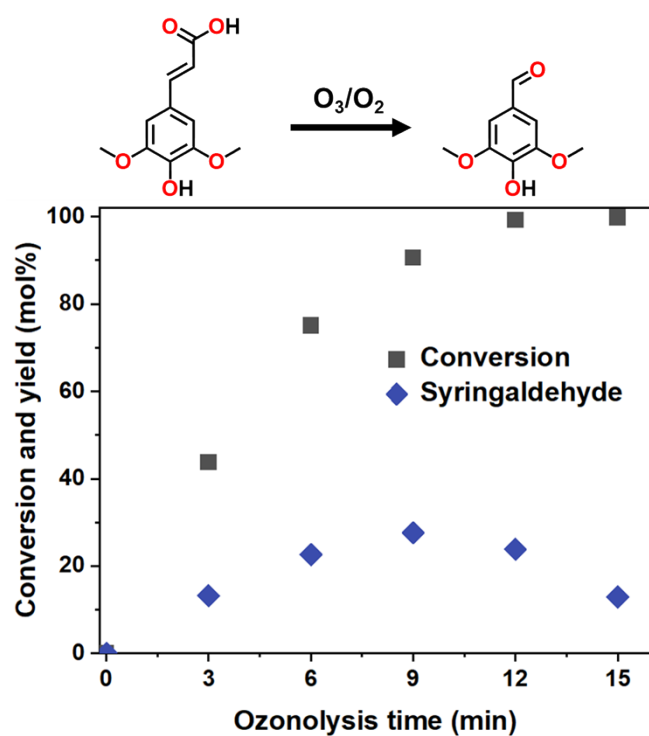


Fig. S17 Ozonolysis of sinapic acid. Reaction conditions: 0.1 g sinapic acid, 5 mL ethanol, 50 mL/min  $O_3/O_2$  gas flow at a  $O_3$  concentration of 60 mg/L.

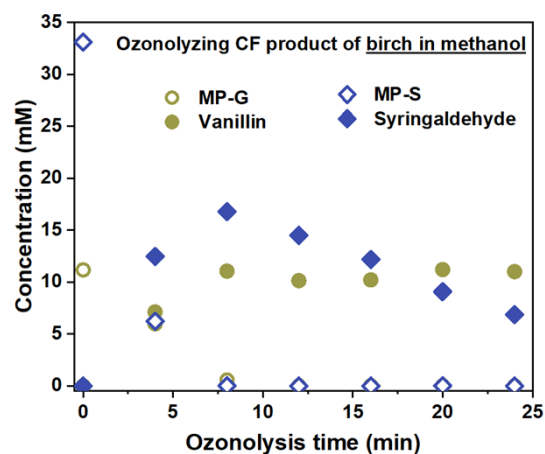


Fig. S18 Ozonolysis of CF products of birch. CF conditions: 18 g birch sawdust, 600 mL methanol, 3.6 g  $MoO_2$ , 2.5 MPa  $N_2$ , 175 °C, 500 rpm. The liquid product was concentrated and bubbled with  $O_3/O_2$  flow. Ozonolysis conditions: 30 mL substrate solution, 300 mL/min  $O_3/O_2$  gas flow at a  $O_3$  concentration of 60 mg/L.

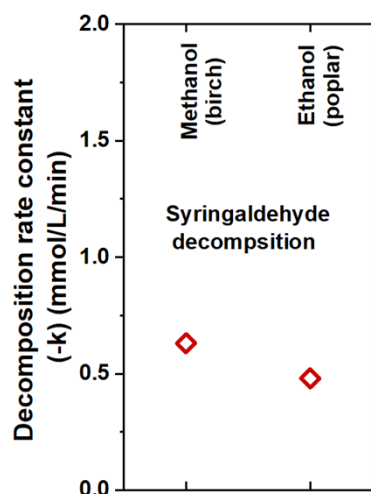


Fig. S19 Decomposition rates of syringaldehyde during overoxidation period in ozonolysis of CF products of birch (in methanol) and poplar (in ethanol). Reaction results and conditions can be found in Fig. 4a and S18.

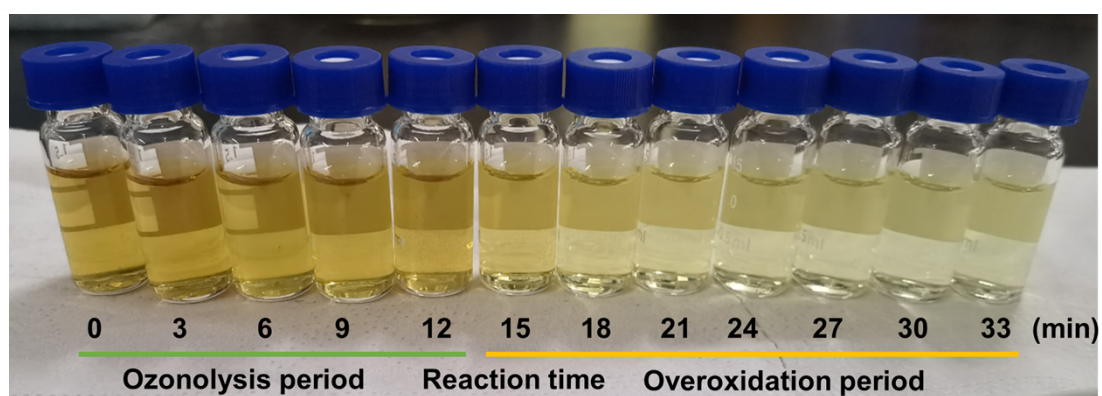


Fig. S20 Color change of samples of CF-ozonolysis of poplar. The samples were diluted ~11 times from the reaction solution of ozonolysis. The reaction conditions and product distribution can be found in Fig. 4a.

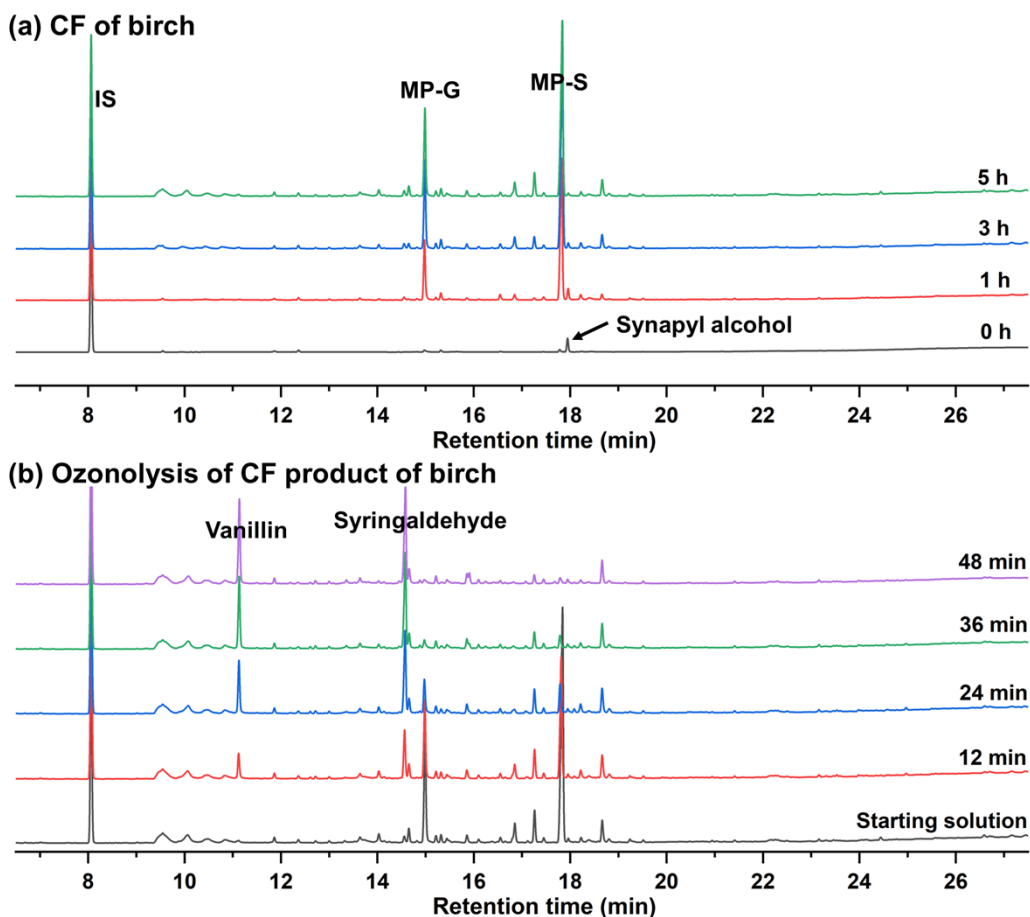


Fig. S21 GC spectra of (a) CF of birch and (b) ozonolysis of the CF product over time. The yield results of (a) and (b) can be found in Fig. S2b and Fig. 4c, respectively. Reaction conditions: CF conditions: 18 g birch sawdust, 600 mL methanol, 3.6 g MoO<sub>2</sub>, 2.5 MPa N<sub>2</sub>, 175 °C, 500 rpm; ozonolysis conditions: all liquid CF product, 300 mL/min O<sub>3</sub>/O<sub>2</sub> gas flow at a O<sub>3</sub> concentration of 30 mg/L.

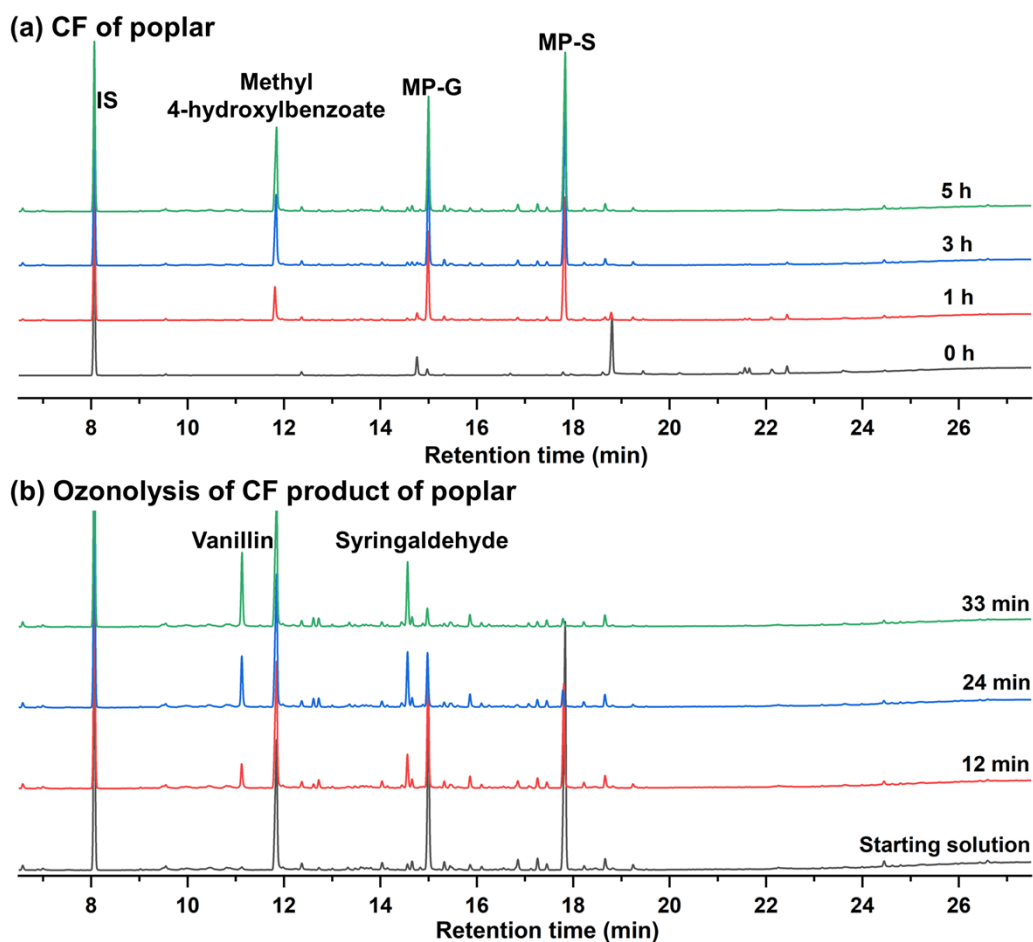


Fig. S22 GC spectra of (a) CF of poplar and (b) ozonolysis of the CF product over time. The yield results of (a) can be found in Fig. 1f. Reaction conditions: CF conditions: 18 g poplar sawdust, 600 mL methanol, 3.6 g MoO<sub>2</sub>, 2.5 MPa N<sub>2</sub>, 175 °C, 500 rpm; ozonolysis conditions: all liquid CF product, 300 mL/min O<sub>3</sub>/O<sub>2</sub> gas flow at a O<sub>3</sub> concentration of 30 mg/L.

## S4 References

1. S. Buntasana, J. Hayashi, P. Saetung, P. Klumphu, T. Vilaivan and P. Padungros, *J. Org. Chem.*, 2022, **87**, 6525-6540.
2. A. J. Kendall, J. T. Barry, D. T. Seidenkranz, A. Ryerson, C. Hiatt, C. A. Salazar, D. J. Bryant and D. R. Tyler, *Tetrahedron Letters*, 2016, **57**, 1342-1345.
3. S. Buntasana, P. Seankongsuk, T. Vilaivan and P. Padungros, *Asian Journal of Organic Chemistry*, 2021, **10**, 1141-1152.
4. T. Ren, Y. Luo, X. Chen and C. Wang, *ACS Sustainable Chem. Eng.*, 2024, DOI: 10.1021/acssuschemeng.4c05462.