Supplementary Information

Comparative study of the solvolytic deconstruction of corn stover lignin in batch and flow-through reactors

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Equation S1: *Formulas for semiquantitative analysis of HSQC NMR results*

$$C_9 \text{ (Total Phenylpropane units)} = [I(S_{2,6}) + I(S'_{2,6})]/2 + [I(G_2)]$$

$$\beta\text{-O-4 \%} = [A(\alpha)]/C_9 \times 100$$

$$\beta\text{-O-4 (pCA)\%} = [A\text{-}\gamma \text{ (}\gamma\text{- pCA) }]/C_9 \times 100$$

$$\beta\text{-O-4 (pCA)/ }\beta\text{-O-4 \%} = A\text{-}\gamma \text{ (}\gamma\text{- pCA)/ } [A(\alpha) + A\text{-}\gamma \text{ (}\gamma\text{- pCA) }] \times 100$$

$$S/G = [I(S_{2,6}) + I(S'_{2,6})]/[2 \times I(G_2)]$$

Equation S2: *Normalized phenolic monomers yield obtained from fast pyrolysis after pretreatment*

$$Norm.Yield\ (wt\%) = \sum_{i=Time\ point} Yield\ of\ phenolics\ (wt\ \%) * (Mass\ \%\ of products\ obtained\ after\ pretreatment)$$

Table S1: Molecular weights (Mn and Mw) and polydispersity (PD) of the samples collected as a function of time during corn stover lignin deconstruction in batch and flow-through reactors at 250° C, 85 bar.

	Reaction conditions			
Time (min)	**MeOH – Batch (Mn, Mw, PD)**	**MeOH – Flow-through (Mn, Mw, PD)**	**EtOH – Batch (Mn, Mw, PD)**	**MeOH – Flow-through (Mn, Mw, PD)**
0	395 Da, 612 Da, 1.55		386 Da, 593 Da,1.54	
30	364 Da, 520 Da, 1.43	603 Da, 1338 Da, 2.22	363 Da, 514 Da, 1.42	637 Da, 1249 Da, 1.96
50		633 Da, 1383 Da, 2.18		656 Da, 1378 Da, 2.1
60	347 Da, 477 Da, 1.37		355 Da, 488 Da, 1.37	
70		668 Da, 2028 Da, 3.04		730 Da, 1777 Da, 2.44
90	337 Da, 453 Da,1.35	680 Da, 2138 Da, 3.14	347 Da, 468 Da, 1.35	771 Da, 1923 Da, 2.5
110		706 Da, 2355 Da, 3.34		828 Da, 2268 Da, 2.62
120	341 Da, 441 Da, 1.31		340 Da, 449 Da, 1.32	
130		703 Da, 2366 Da, 3.37		931 Da, 2499 Da, 2.68

Table S2*:* NMR integral analysis.

Nature of Fragments	**Assignment**	**Lignin**	**170°C, 30 bar, EtOH**	**250°C, 85 bar, EtOH**	**170°C, 30 bar, MeOH**	**250°C, 85 bar, MeOH**
-OCH3	55.6/3.73	1	1	1	1	1
A- γ	60.1/3.73 and 60.1/3.40	0.0307	0.0484	0.0533	0.0459	0.0621
A-γ (γ- pCA)	63.3/4.42 and 63.3/3.94	0.0445	0.0323	0.0281	0.0264	0.0365
A-G (α)	71.3/4.87	0.0267	0.0218	0.0198	0.0243	0.0313
A-H (α)	71.3/4.87					
A-S (α)	71.3/4.87					
A-H/G (α)	84.4/4.39 and 83.9/4.45	0.0037	0.0034	0.0035	0.0041	0.005
S (2,6)	103.7/6.73	0.116	0.1259	0.1201	0.1203	0.1392
S'(2,6)	106.7/7.24	0.0065	0.0084	0.0083	0.0087	0.0105
FA (2)	111.1/7.36	0.0187	0.0227	0.023	0.0232	0.0267
G (2)	110.8/7.02	0.0293	0.0318	0.0336	0.0319	0.0428
G (5,6)	115.2/6.90	0.2584	0.2928	0.2874	0.3204	0.3264
pCA(3,5)	115.8/6.84	0.1927	0.1873	0.204	0.192	0.1568
pCA (2,6)	130.2/7.49	0.1461	0.1567	0.158	0.1669	0.1848
pCA and FCA (7)	144.9/7.53	0.0772	0.0886	0.0878	0.0922	0.1

Table S3: List of calibration standards used for fast pyrolysis and catalytic fast pyrolysis.

Fast Pyrolysis (Vendor/Assay)	Catalytic Fast Pyrolysis (Vendor/Assay)
CO (Airgas)	Ethane (Airgas, Mixture 2 mole% in He)
CH_4 (Airgas)	Ethylene (Airgas, Mixture 2 mole% in He)
$CO\ (Airgas)_2$	Propane (Airgas, Mixture 2 mole% in He)
Phenol (Sigma Aldrich, >99%)	Propylene (Airgas, Mixture 2 mole% in He)
Guaiacol (ACROS Organics, >99%)	Benzene (Sigma Aldrich, >99%)
o-Cresol (Sigma Aldrich, >99%)	Toluene (Fisher Scientific, >99%)
p-Cresol (ACROS Organics, >99%)	m-Xylene (Fisher Scientific, >99%)
p-Methylguaiacol (Sigma Aldrich, >98%)	1,4 Diethyl Benzene (Alfa Aesar, >98%)
4-Ethylphenol (Sigma Aldrich, >99%)	Mesitylene (Sigma Aldrich, >98%)
4-Ethylguaiacol (Alfa Aesar, >98%)	Naphthalene (ACROS Organics, >99%)
4-Vinyl Phenol (ACROS Organics,95%, 10% solution in propylene glycol)	
4-Vinyl Guaiacol (Frontier Scientific, 98%)	
Eugenol (Sigma Aldrich, 99%)	
Isoeugenol (ACROS Organics, 98% (cis+trans))	
1,3,5-Trimethoxybenzene (Sigma Aldrich, >99%)	
Vanillin (Sigma Aldrich, >99%)	
3',5'-Dimethoxyacetophenone (Alfa Aesar, 97%)	
2,6-Dimethoxy-4-allylpheno (Sigma Aldrich, > 95%)l	

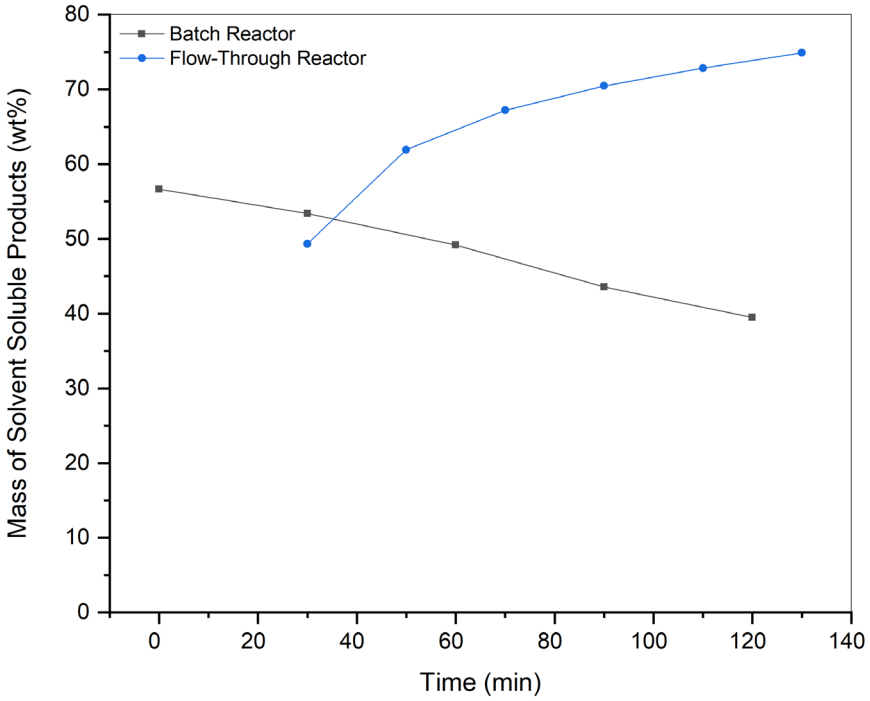

Figure S1: Mass of solvent-soluble products (wt %) obtained as a function of time after treating lignin in batch and flow-through systems at 250 °C, 85 bar, EtOH.

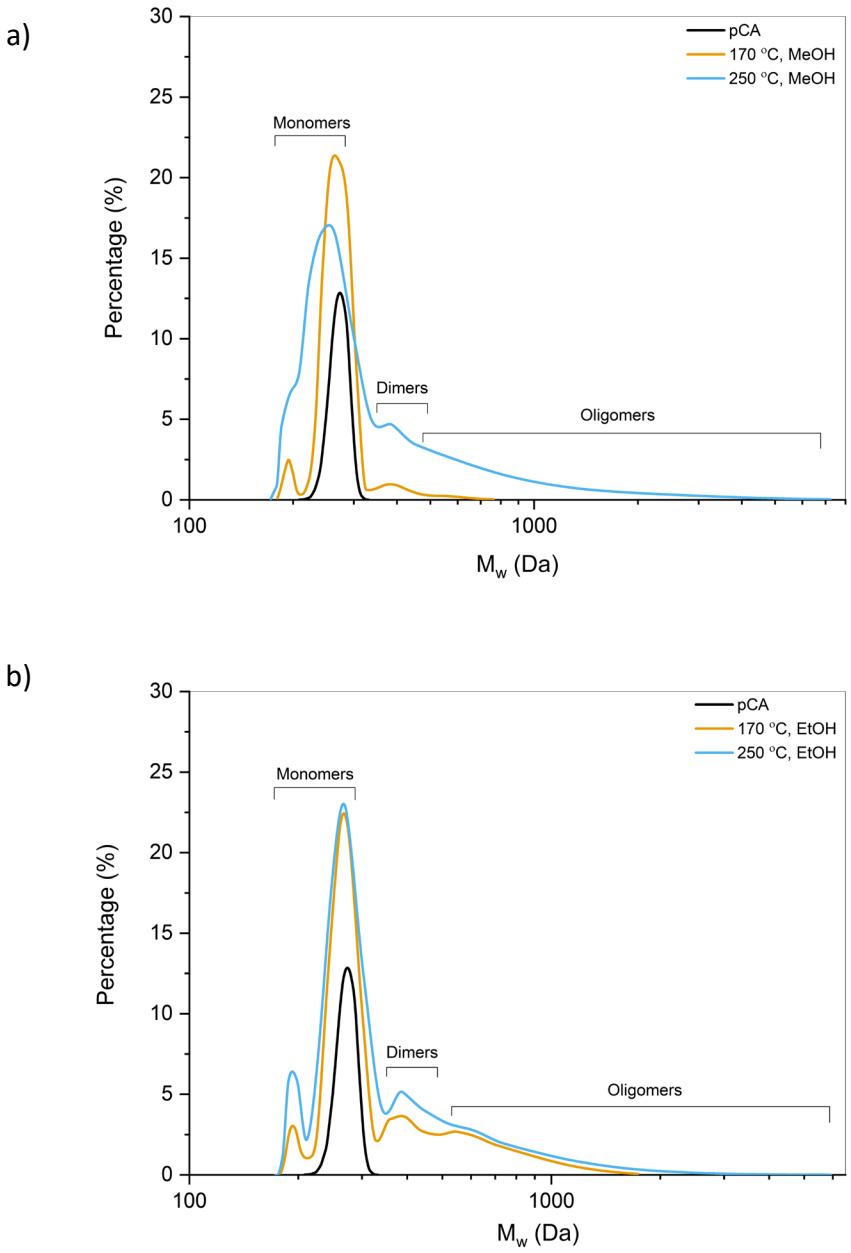

Figure S2. Molecular weight distributions of the products obtained after a 30 min treatment of a 1:1 w/w mixture of *p*-coumaric and ferulic acids (total mass of 10 mg) in 2 mL of solvent under various conditions in **(a)** MeOH and **(b)** EtOH. The regions corresponding to monomers, dimers, and oligomers have been labeled for clarity. The result obtained for *p*-coumaric acid (pCA) is provided as a reference.

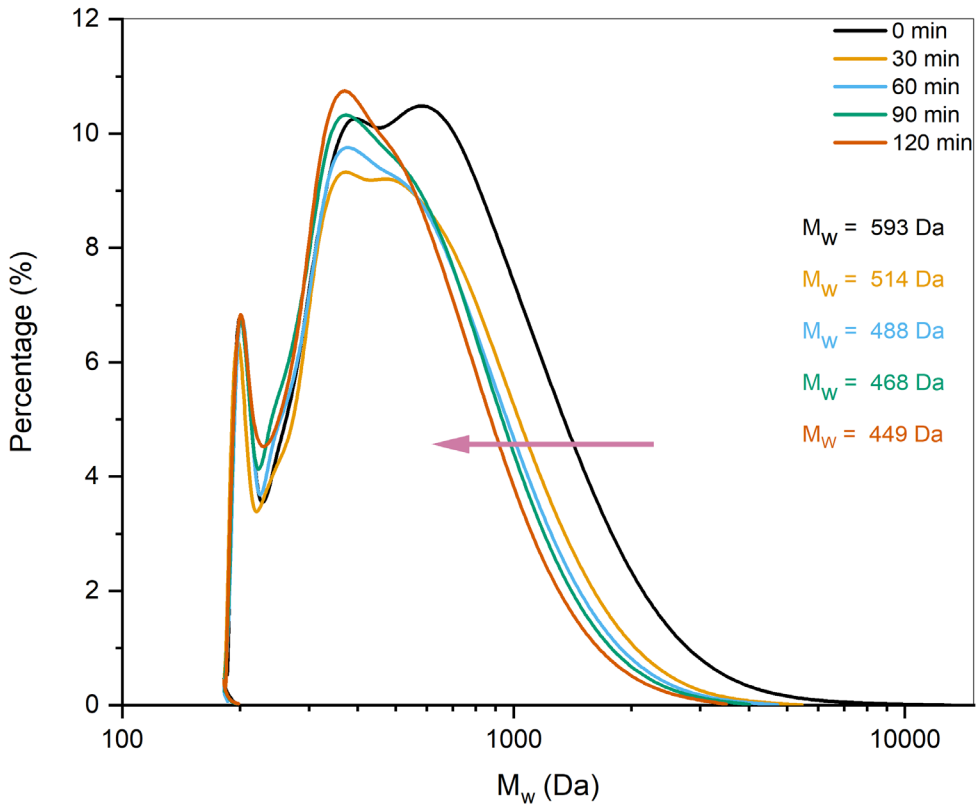

Figure S3: Molecular weight distributions of solvent-soluble products obtained as a function of time using a batch reactor at 250 °C, 85 bar, EtOH.

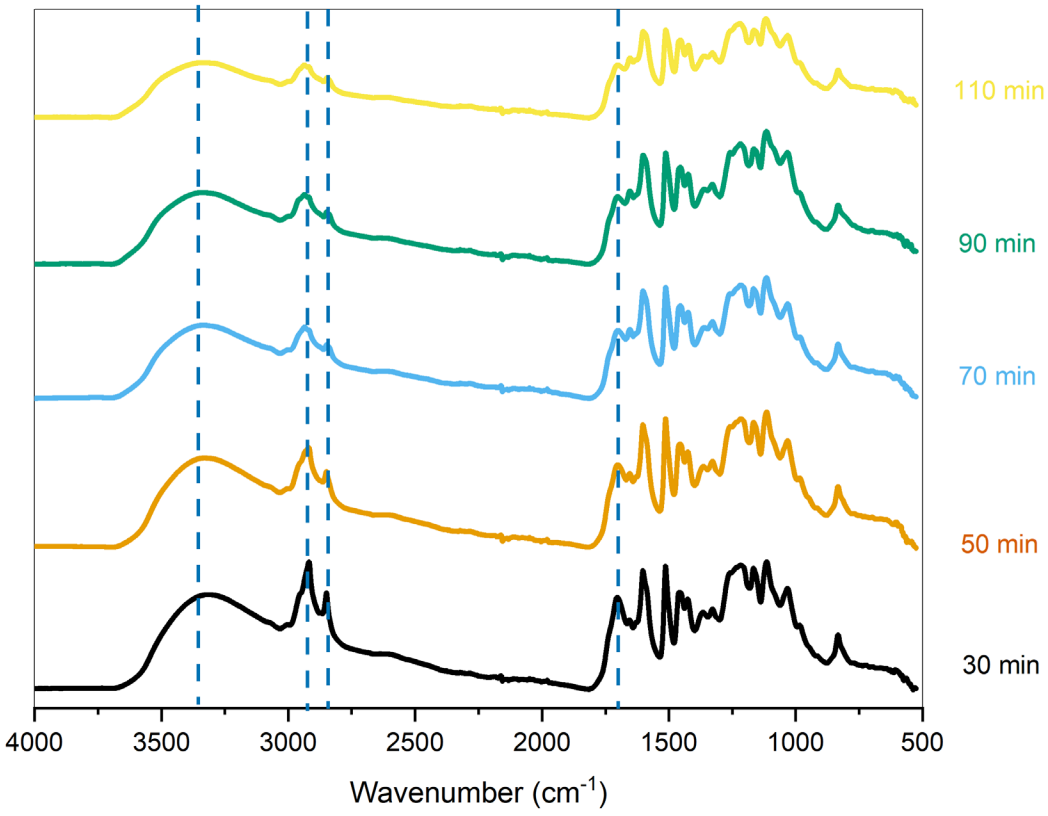

Figure S4: FTIR spectra of solvent-soluble products collected as a function of time at 250 °C, 85 bar, EtOH using a flow-through reactor.

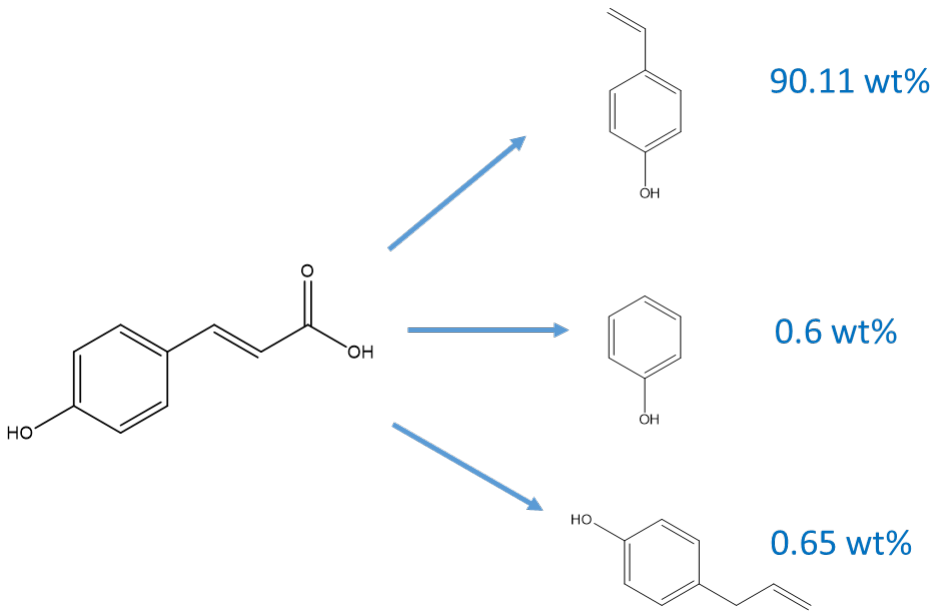

Figure S5: Yields (wt%) of phenolic monomers obtained from the fast pyrolysis of *p*-coumaric acid at 500 °C.

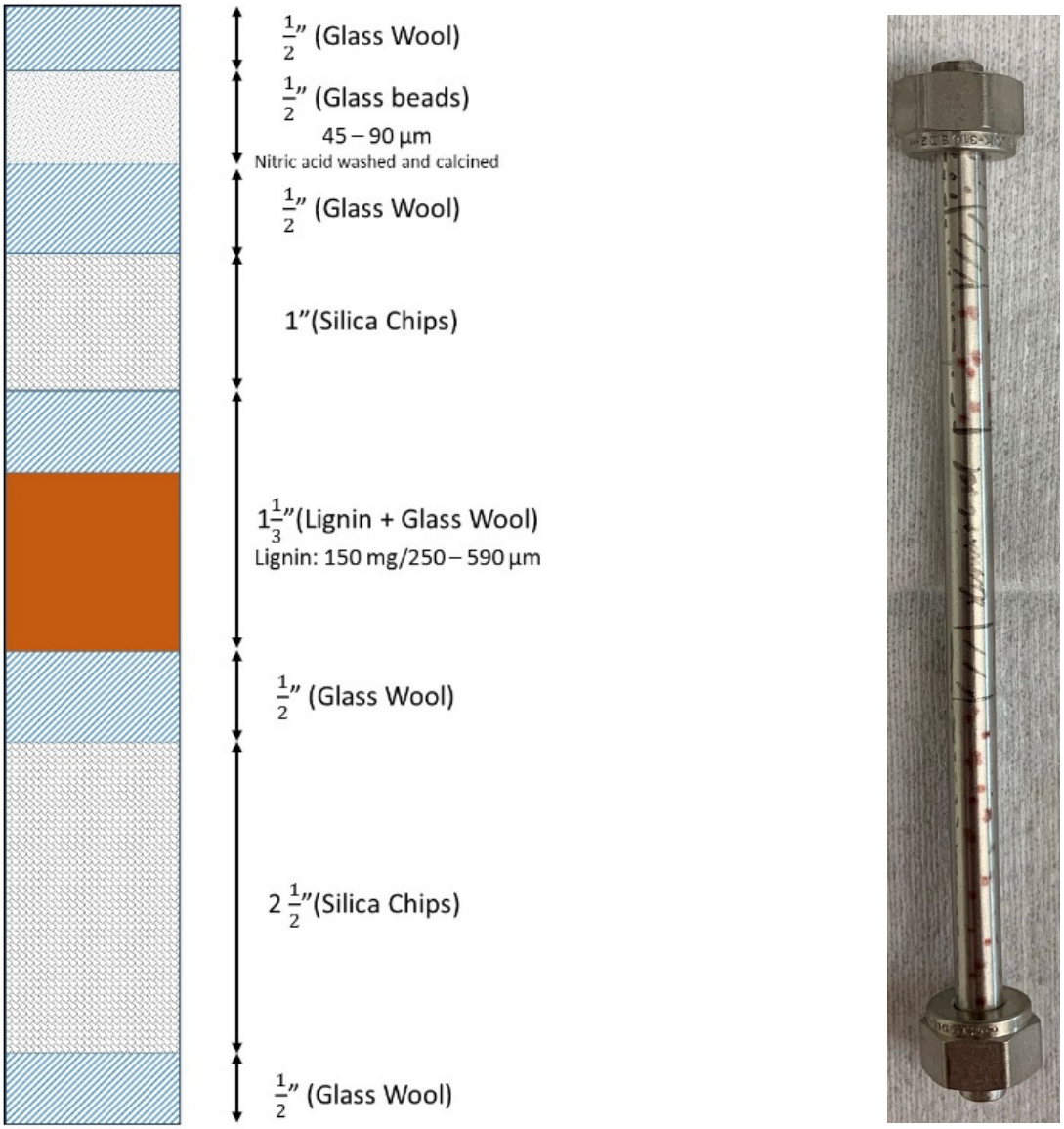

Figure S6: Schematic of the packed reactor used for the flow-through experiments.

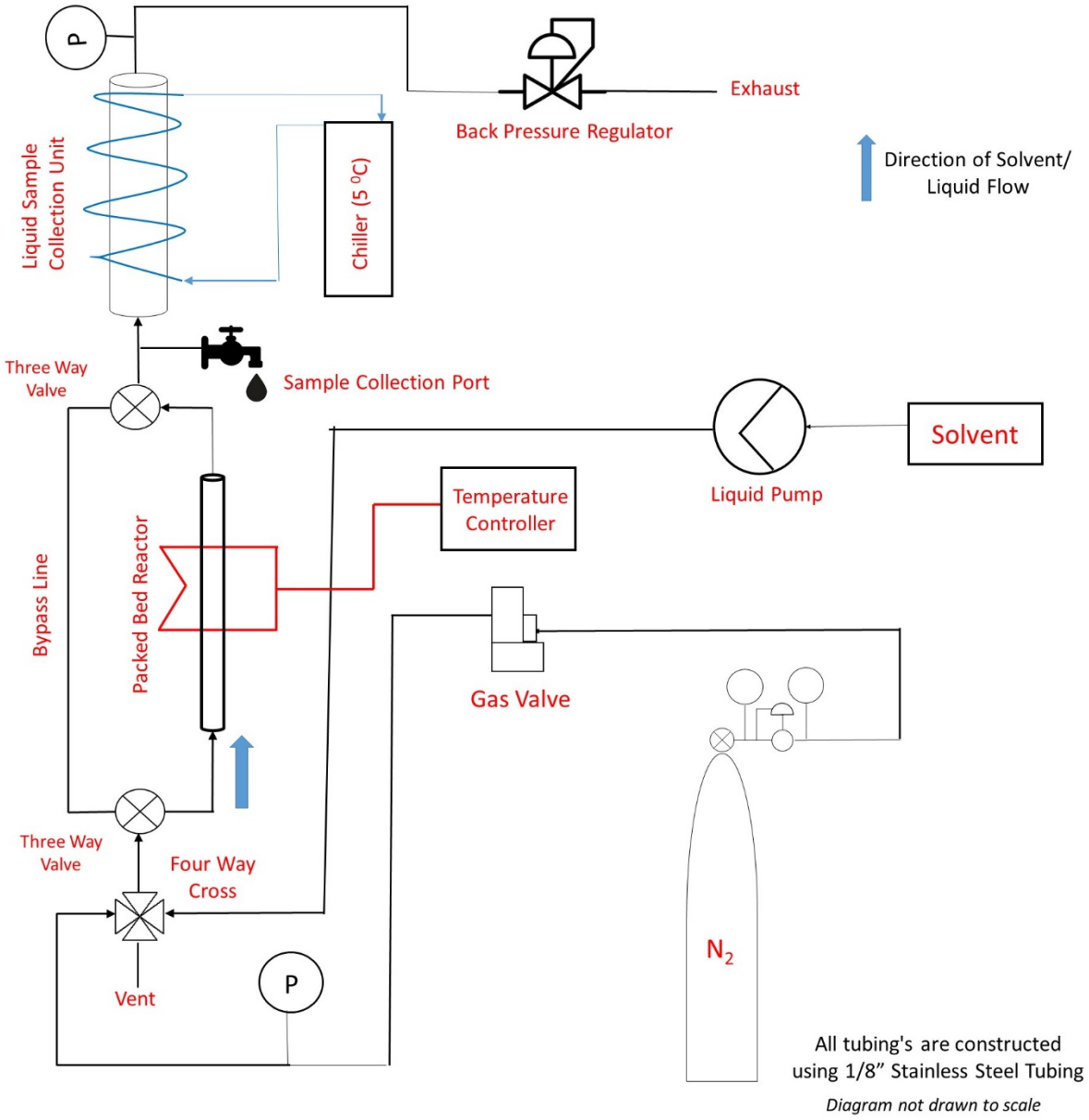

Figure S7: Schematic of the flow-through reactor setup.

a)

b)

Figure S8: a) Stainless-steel reactor and b) industrial fluidized bed used for the model compound reactivity study.

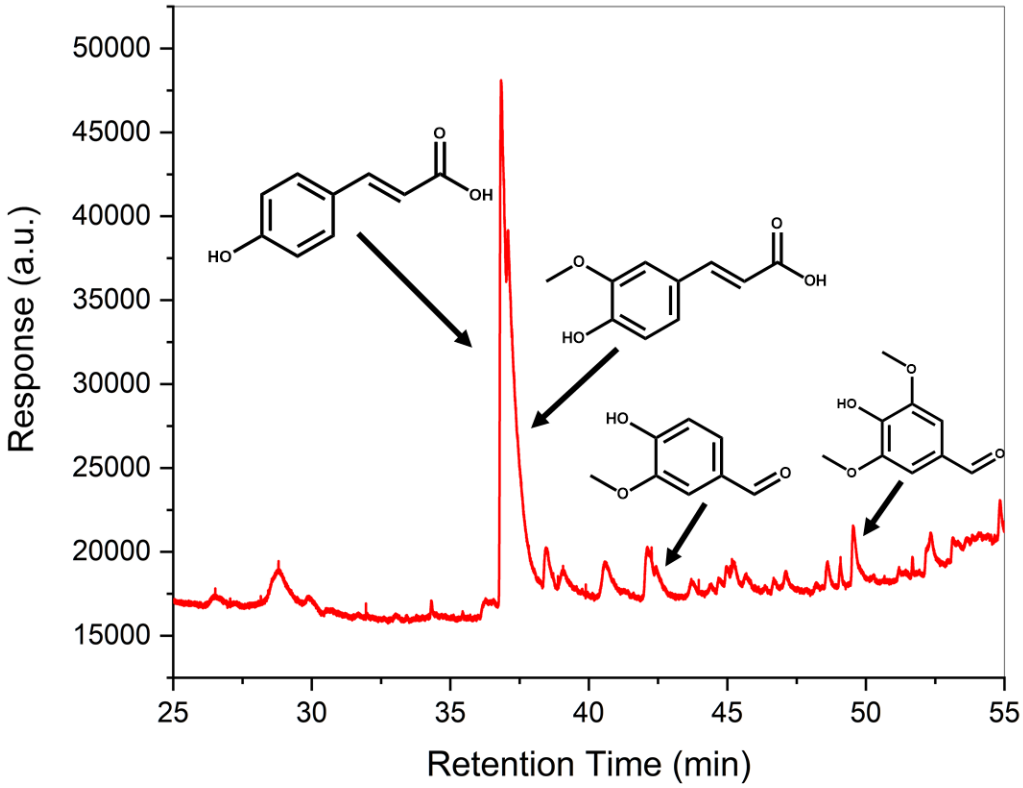

Figure S9: Representative GC-FID chromatogram. The detected products were quantified by comparing the peak areas to five-point calibrations using the corresponding pure compounds. Regression coefficients higher than 0.99 were achieved for each calibration. The yield of each monomer was subsequently calculated as follows:

$$Yield\ \ (wt\%) = \frac{Concentration\ \left(\frac{mg}{mL}\right) \times Volume\ of\ sample\ collected\ \ (mL)}{Weight\ of\ lignin\ (mg)} \times 100$$

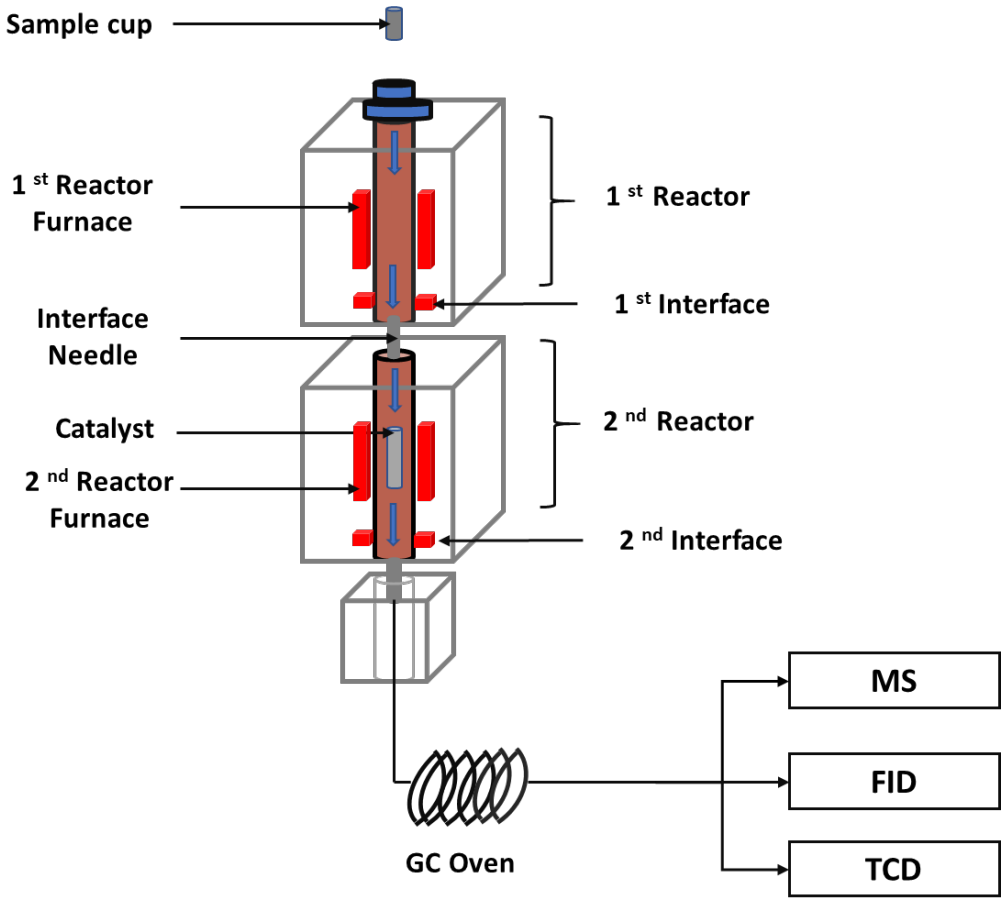

Figure S10: Schematic view of the single-shot tandem micro-pyrolyzer/reactor.