Electronic Supplementary Material (ESI) for Green Chemistry.

The Use of Calcium Hydroxide Pretreatment to Overcome Agglomeration of Technical Lignin during Fast Pyrolysis

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-Supplemental Tables and Figures

Table S1. Ultimate and proximate analysis of lignin.

Ultimate analysis (wt%)	
Carbon	61.34
Hydrogen	4.67
Nitrogen	2.00
Sulfur	0.20
Oxygen*	31.79
Proximate analysis (wt%)	
Moisture content	3.87
Volatiles	62.52
Fixed carbon	27.55
Ash	6.07

*Determined by difference

Table S2. Compositional analysis of bio-oil by GC/MS.

	Temperature (°C)			
Compound (% per lignin)	450	500	550	600
Acetic acid	4.81 ± 0.31	3.71 ± 0.11	3.99 ± 0.07	4.12 ± 0.31
Acetol	0.26 ±0.01	0.19 ± 0.18	0.17 ± 0.02	0.14 ± 0.02
Acetol acetate	0.09 ± 0.01	0.07 ± 0.00	0.07 ± 0.00	0.05 ± 0.01
Phenol	0.33 ± 0.01	0.34 ± 0.03	0.36 ± 0.02	0.41 ± 0.04
2-Methoxy-Phenol	0.28 ± 0.06	0.26 ± 0.01	0.17 ± 0.01	0.17 ± 0.05
P-Cresol	0.19 ± 0.00	0.21 ± 0.02	0.22 ± 0.01	0.25 ± 0.01
Creosol	0.19 ± 0.01	0.17 ± 0.02	0.14 ± 0.00	0.14 ± 0.01
4-Ethyl-phenol	0.22 ± 0.02	0.20 ± 0.01	0.17 ± 0.03	0.16 ± 0.01
4-Ethyl-2-methoxy-phenol,	0.18 ± 0.01	0.16 ± 0.02	0.14 ± 0.02	0.06 ± 0.00
4-Vinyl-Phenol	2.79 ± 0.23	2.64 ± 0.17	2.53 ± 0.17	2.08 ± 0.07
2-Methoxy-4-vinylphenol	1.29 ± 0.10	1.12 ± 0.07	0.69 ± 0.02	0.50 ± 0.01
2,6-Dimethoxy-Phenol	0.25 ± 0.01	0.22 ± 0.04	0.12 ± 0.01	0.06 ± 0.00
Isoeugenol	0.14 ± 0.01	0.13 ± 0.01	0.11 ± 0.00	0.11 ± 0.01
1,2,4-Trimethoxybenzene	0.10 ± 0.00	0.08 ± 0.00	0.04 ± 0.00	0.01 ± 0.00
Vanillin	0.15 ± 0.01	0.12 ± 0.01	0.09 ± 0.01	0.06 ± 0.02
1,2,3-Trimethoxy-5-methyl- Benzene	0.05 ± 0.00	0.04 ± 0.02	0.03 ± 0.00	0.02 ± 0.01
3',5'-Dimethoxyacetophenone	0.20 ± 0.01	0.17 ± 0.02	0.11 ± 0.01	0.07 ± 0.03
2,6-Dimethoxy-4-(2-propenyl)- phenol	0.16 ± 0.01	0.10 ± 0.01	0.06 ± 0.00	0.04 ± 0.00

Table S3. Properties of heavy oil and light oil.

Temperature (°C)		450	500	550	600
Bio-oil yield (%)	Heavy oil	20.93	22.53	20.28	18.25
	Light oil	16.49	15.84	18.03	18.78
Water (%)	In heavy oil	5.48	3.24	2.44	3.67
	In light oil	65.17	75.59	69.89	54.06
	Based	11.89	12.70	12.71	10.83
Molecular weight distribution	Heavy oil				
	Mw (Da)	288	297	290	300
	Mn (Da)	181	182	180	180
	PD	1.59	1.63	1.61	1.67
	Light oil				
	Mw (Da)	224	239	187	153
	Mn (Da)	119	131	134	109
	PD	1.88	1.82	1.40	1.40
MAN (mg KOH/g)	Heavy oil	38.99	34.70	32.85	37.48
	Light oil	221.73	204.47	214.05	250.48
Elemental composition (%)	Heavy oil				
	C	67.98	68.89	69.39	69.94
	H	6.99	6.97	6.87	6.06
	O*	23.05	21.85	21.31	21.47
	N	1.93	2.25	2.39	2.50
	S	0.05	0.04	0.04	0.03
	Light oil				
	C	13.33	13.88	12.66	14.59
	H	6.82	8.38	6.81	7.02
	O*	78.89	76.75	79.24	76.82
	N	0.95	0.98	1.27	1.55
	S	0.01	0.01	0.02	0.02
Heating value (MJ/kg)**	Heavy oil	28.90	29.31	29.4	28.38
	Light oil	4.97	4.61	1.54	2.81

*by difference; ** calculated based on the formula provided in reference.[42]

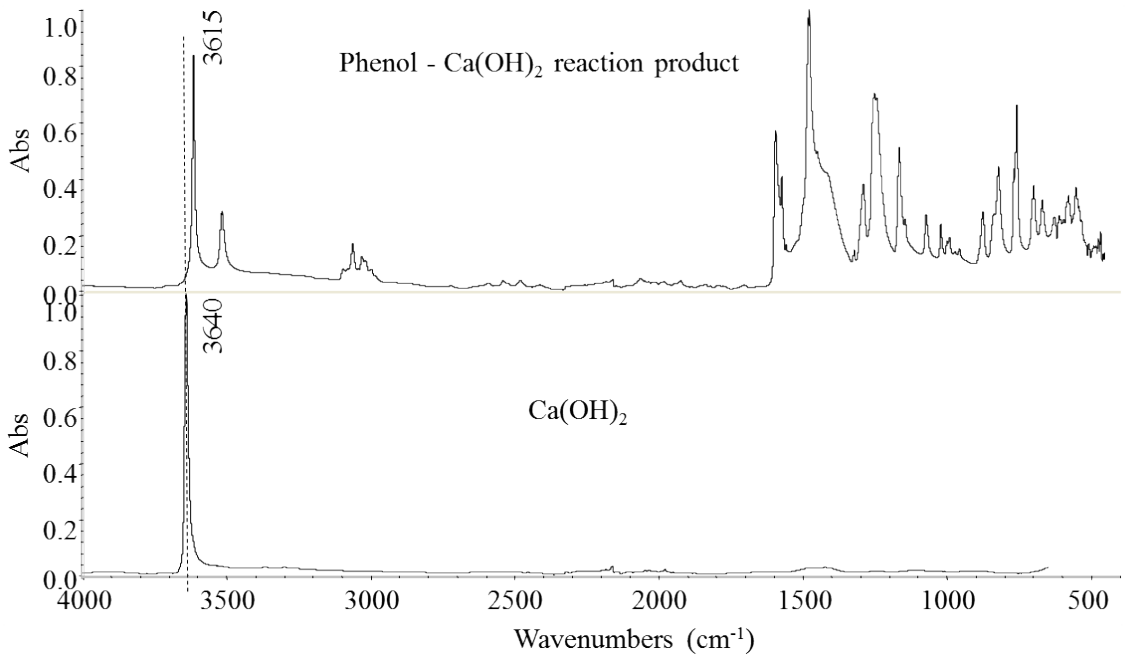

Fig. S1. FTIR spectrum of the $Ca(OH)_2$ treated phenol at 50 ^{0}C (top) compared to the spectrum of $Ca(OH)_2$ (bottom). According to reference [40], the peak at 3615 cm^{-1} and several smaller peaks with the wavenumbers below 700 cm^{-1} do not appear at the spectrum of calcium diphenoxide but they appear for hydroxycalcium phenoxide.

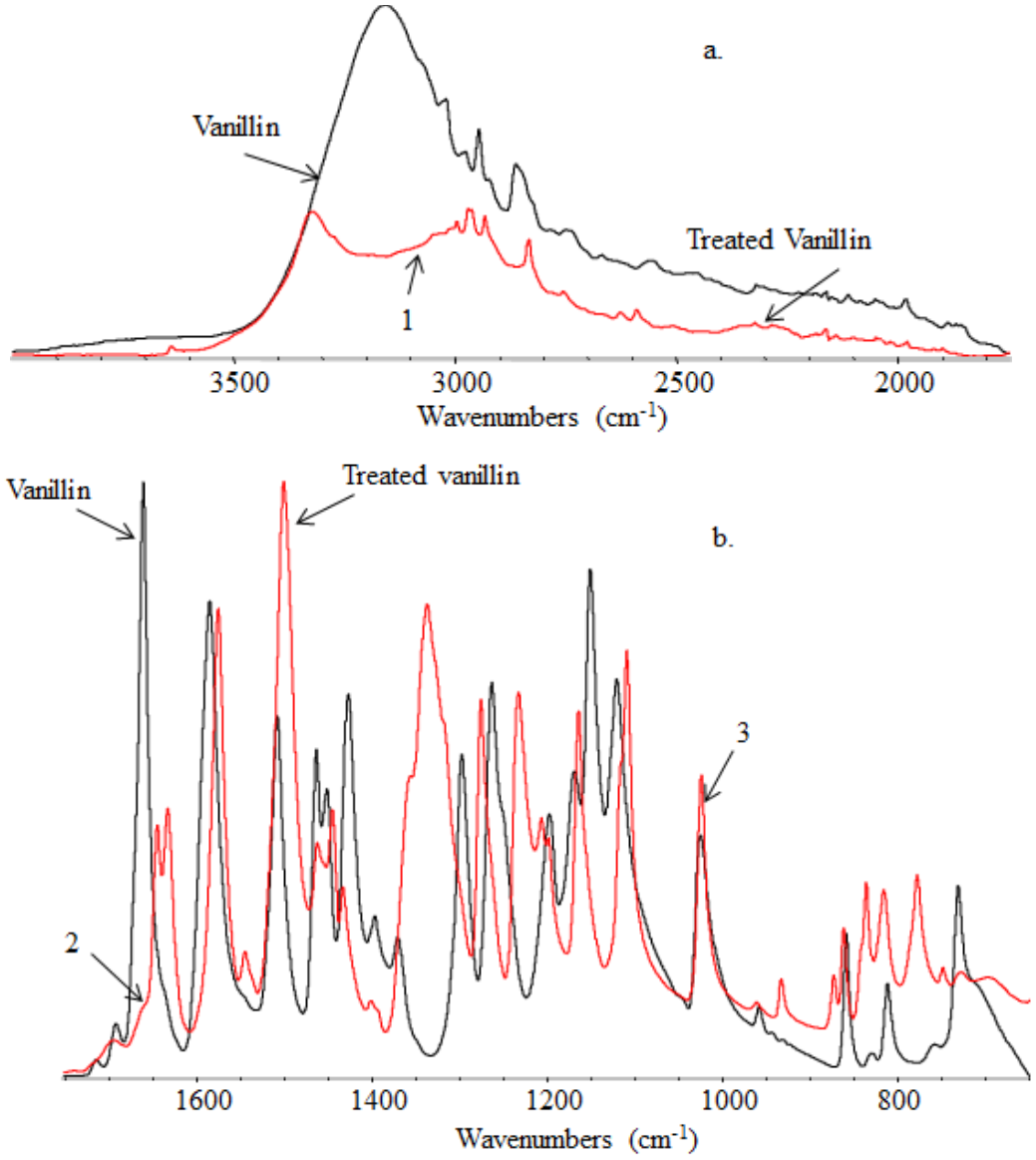

Fig. S2. Comparison of FTIR spectrum of vanillin and $Ca(OH)_2$ treated vanillin; a. 1750-4000 cm^{-1}; b. 650-1750 cm^{-1};1. Reduced OH group; 2. Reduced aldehyde group; 3. Formation of alcohol group.