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Potential of catalytic oxidation of Kraft black liquor for the production of biosourced compounds

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Electronic Supplementary Information

1. Catalyst preparation and characterization

Catalyst preparation. 5%CuO/TiO_2 was synthetized in our group by incipient wetness impregnation employing a copper nitrate as precursor ($Cu(NO_3)_2.2.5H_2O$) in aqueous solution. The catalyst was kept under stirring 4 hours after the impregnation, and then dried at 110°C for one night and calcined at 550°C for 5 hours. Such method showed a good repeatability in the metal charge from one catalyst batch to another (4.9-5%wt).

Chemical analysis (ICP-OES) was carried out by using ICP-OES ACTIVA Jobin Yvon device. Before analysis, mineralization was carried out by a dilution with H_2SO_4, HNO_3 and HF, a subsequent evaporation and then heating process of the residue with HNO_3.

Physisorption N_2. The porosimetry and BET analysis were carried out on an ASAP 2020 of Micromeritics, equipped with two pressure sensors. The analysis were done using nitrogen as physisorption gas at a temperature of -196°C. Desorption pre-treatment was carried out for 3 h at 300°C under vacuum.

X-ray diffraction analysis was carried out in a Bruker D8-Advance with automatic sampler, using a radiation Cu-Kα (0.154184nm).

Table S1. Characterization of CuO/TiO_2 (5%wt Cu)

Analysis	Parameter	Result
ICP	Cu charge	4.9-5 wt.% Homogeneous loading
N_2 Physisorption - BET	Specific surface	32 ± 1 $m^2.g^{-1}$
N_2 Physisorption - BJH	Porosity	Mesopores (2-50 nm) Av. Size: 25 nm
XRD	Phases distribution	TiO_2 Anatase and Rutile CuO Tenorite (minor)

The catalyst specific surface area was rather low (32 $m^2.g^{-1}$). The pores presented an average diameter of 25 nm. The crystalline phases observed by XRD corresponded to the ones of the commercial TiO_2 support, with minor signal corresponding to CuO crystallites.

2. FTIR spectra of Kraft black liquor (KBL), Kraft lignin (KL) and Klason phases (KP)

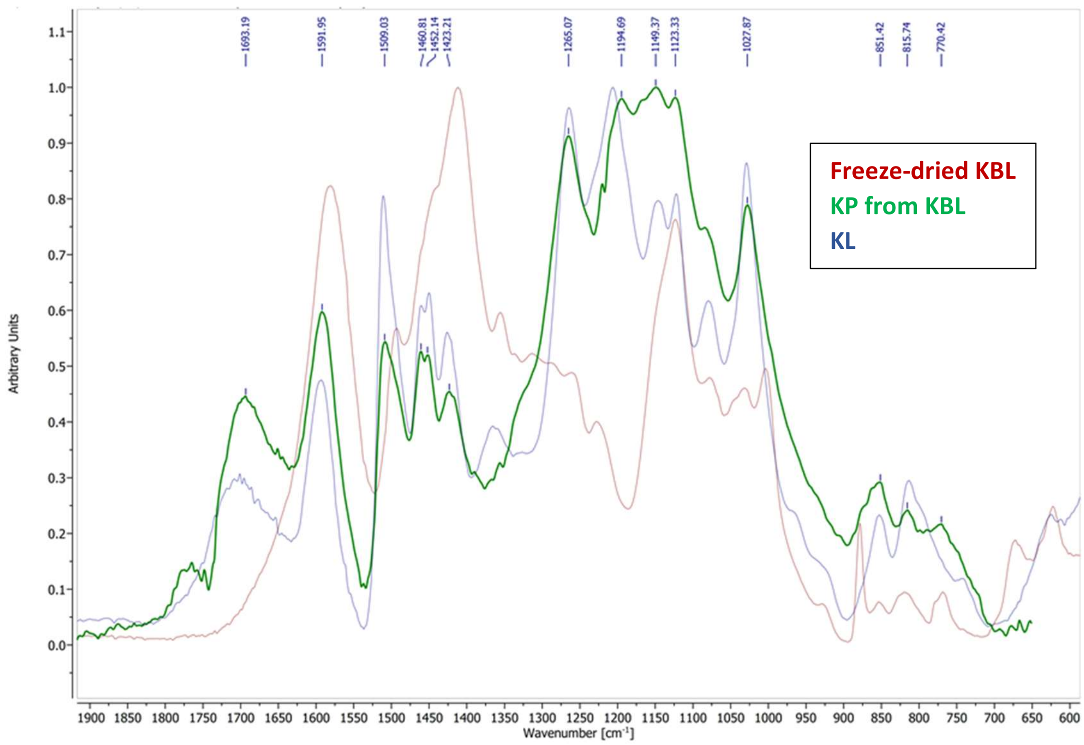

Figure S1. *FTIR spectra of starting materials. KBL after freeze-drying (red), KP extracted from KBL (green) and KL.*

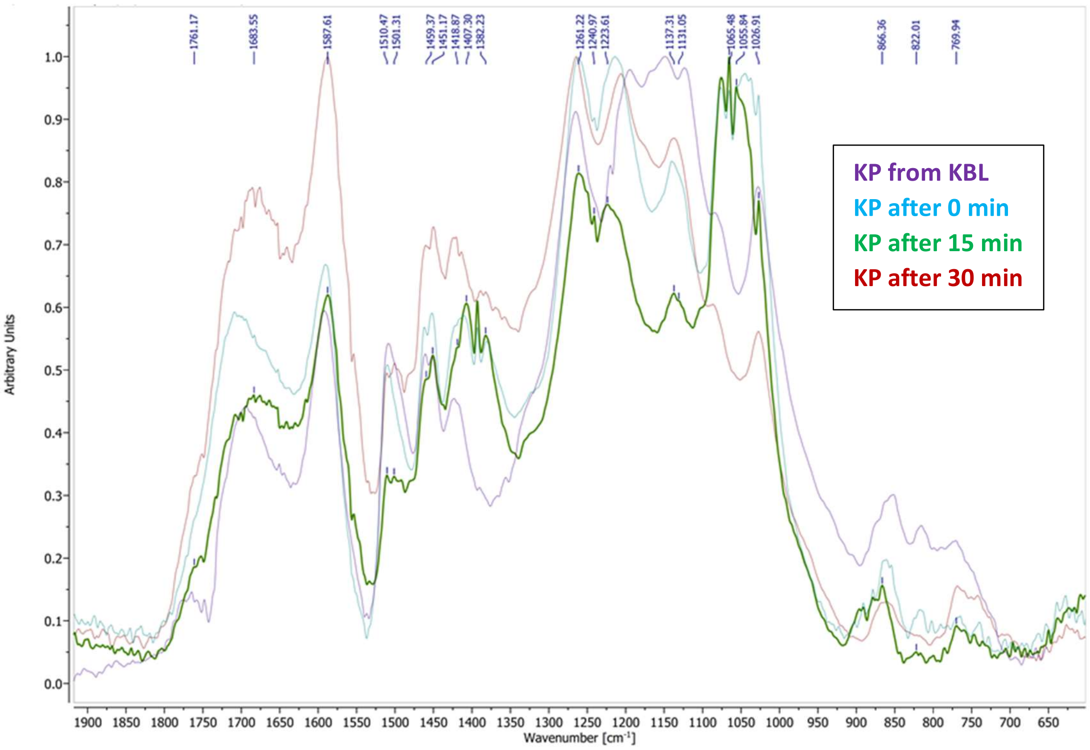

Figure S2. *FTIR spectra of Klason phases after non-catalytic oxidation reactions, in batch mode, 150°C, 20 bar.*

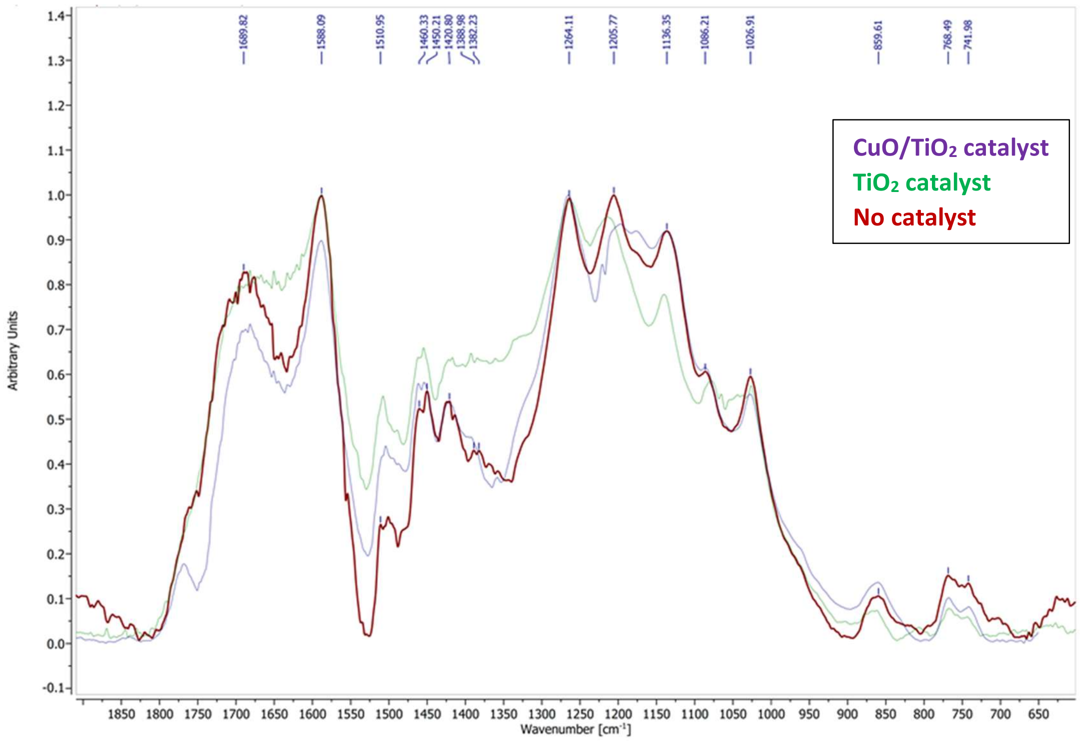

Figure S3. *FTIR spectra of Klason phases after non-catalytic / catalytic oxidation reactions, in batch mode, 150°C, 20 bar, 30 min.*

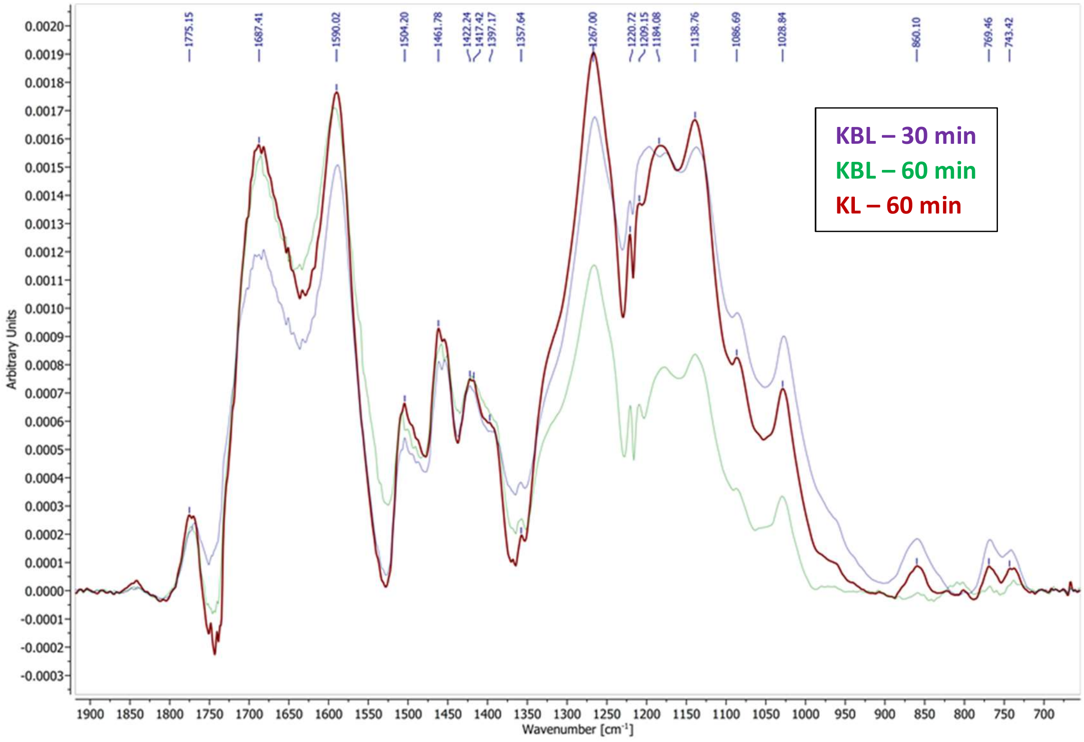

Figure S4. *FTIR spectra of Klason phases after catalytic oxidation reactions, in batch mode, 150°C, 20 bar, catalyst CuO/TiO$_2$, starting material KBL or KL.*

3. HPLC analysis of KBL before reaction

Table S2. Concentration of aliphatic and phenolic compounds measured in HPLC in raw KBL (in gC.L^{-1}). *n.d.: not detected.*

Compound	Raw KBL, not diluted (26 % dry matter)
Oxalic acid	0.095
Tartronic acid	1.943
Glyceric acid	0.118
Glycolic acid	1.308
Formic acid	2.547
Malic acid	n.d.
Malonic acid	n.d.
3-hydroxypropionic acid	1.047
Lactic acid	1.833
Maleic acid	n.d.
Acetic acid	2.705
Fumaric acid	n.d.
Succinic acid	0.189
2-hydroxybutyric acid	0.614
Gallic acid	traces
HMF	traces
Furfural	traces
Catechol	n.d.
p-Benzoquinone	0.110
Protocatechuic acid	0.022
4-Hydroxybenzoic acid	n.d.
Phthalic acid	0.788
Vanillic acid	n.d.
Homovanillic acid	0.364
m-Anisic acid	n.d.
Syringic acid	n.d.
Phenol	0.214
4-Hydroxyacetophenone	n.d.
Vanillin	0.129
Syringaldehyde	n.d.
Acetovanillone	n.d.
Acetosyringone	n.d.
Ferulic acid	n.d.
Guaiacol	0.247
Benzoic acid	0.146
4-Hydroxybenzaldehyde	0.114

4. NMR HSQC and ^{1}H of Kraft black liquor (KBL), Kraft lignin (KL) and Klason phases (KP)

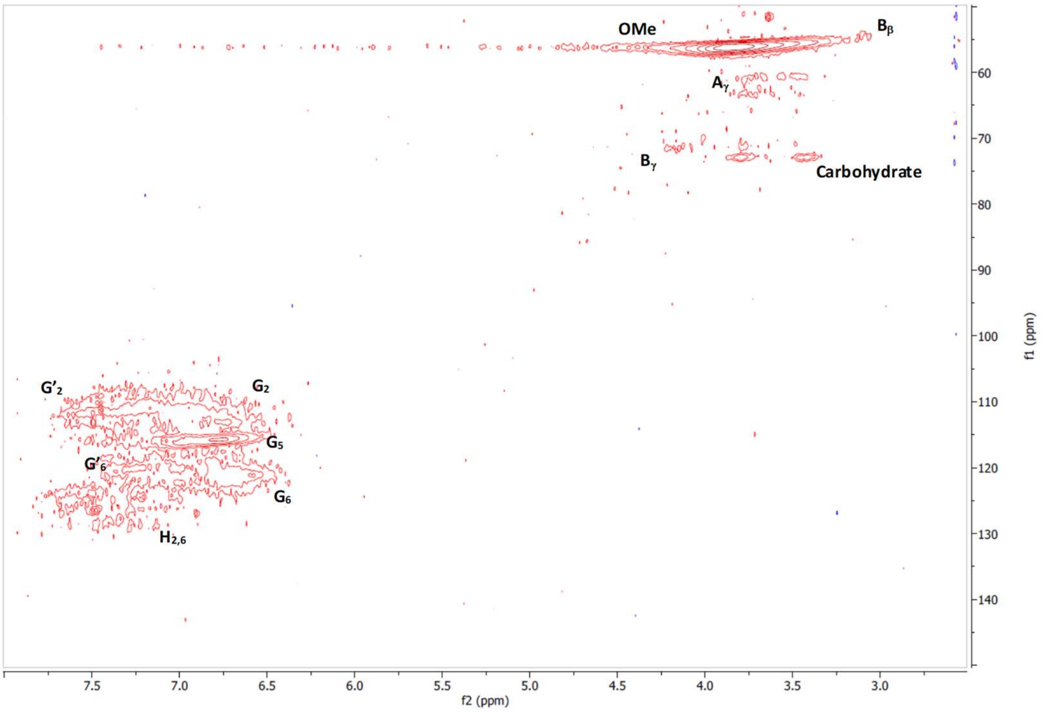

Figure S5. *HSQC spectra of the initial KBL, freeze-dried. Please note the absence of correlations corresponding to inter-unit bonds.*

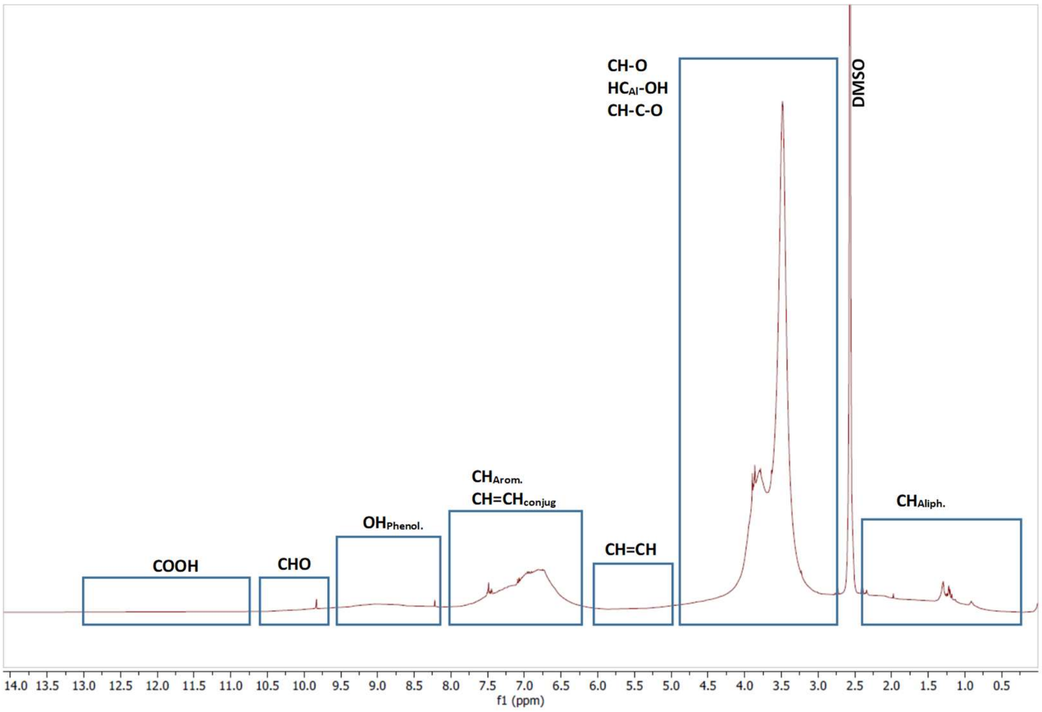

Figure S6. *^{1}H NMR spectra of KBL as obtained from freeze-dried black liquor.*

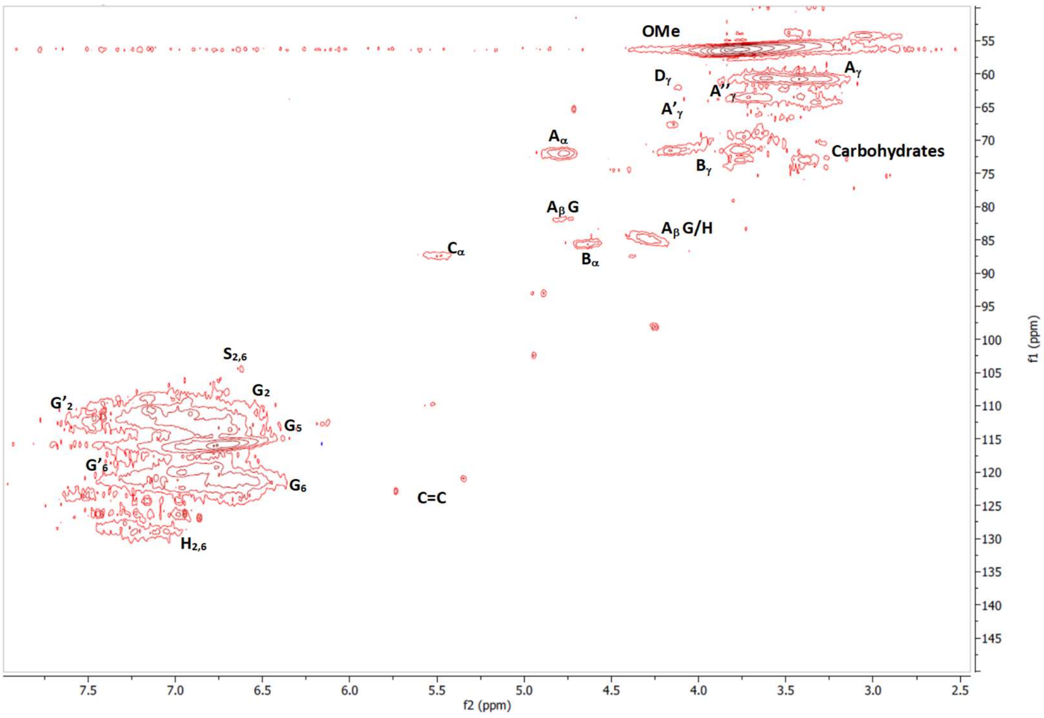

Figure S7. *HSQC spectra of the initial KL.*

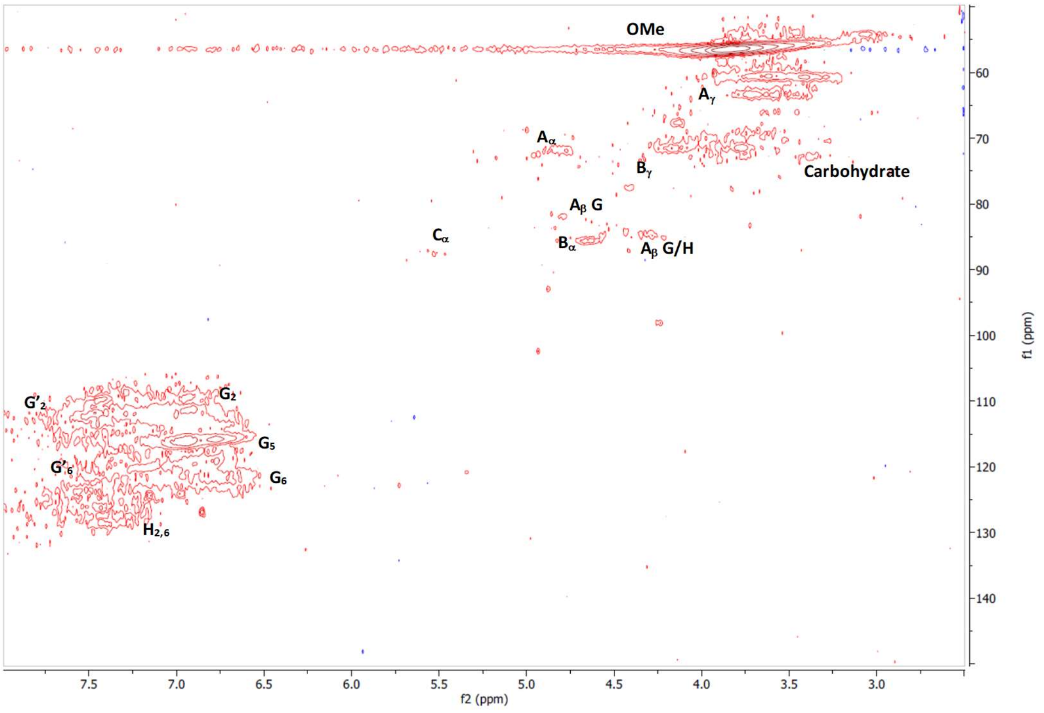

Figure S8. *HSQC spectra of KP after <u>0 min</u> of <u>non catalytic</u> oxidation of KBL in batch mode, 150°C, 20 bar.*

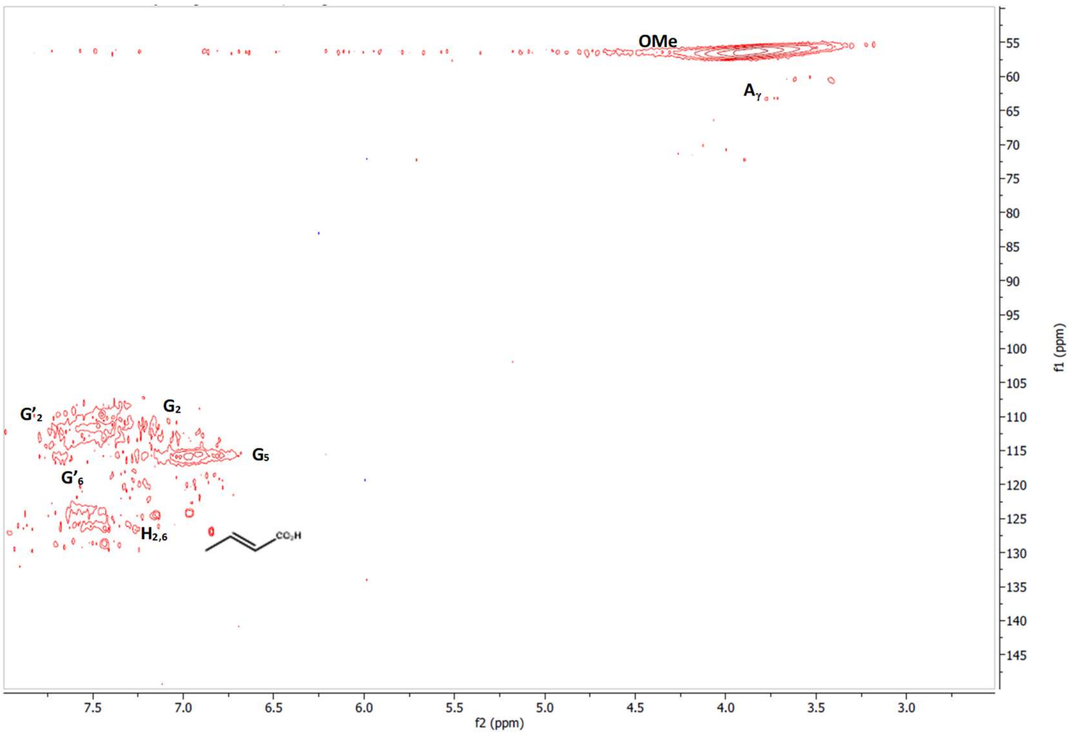

Figure S9. *HSQC spectra of KP after* <u>*15 min*</u> *of* <u>*non catalytic*</u> *oxidation of KBL in batch mode, 150°C, 20 bar.*

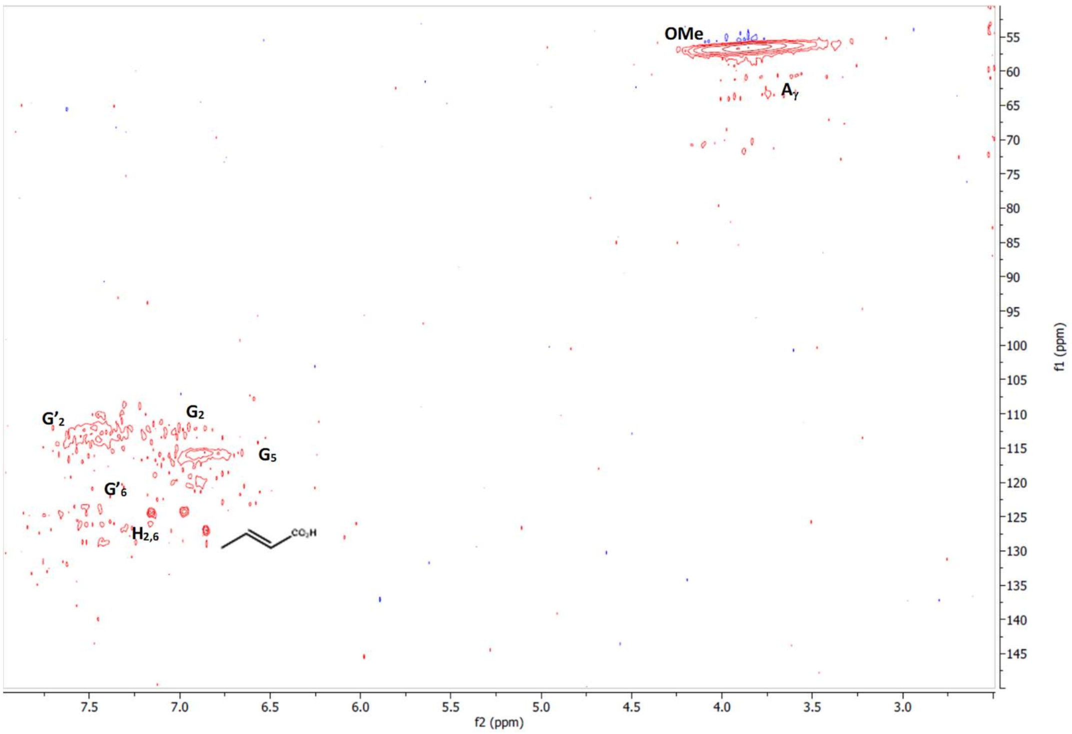

Figure S10. *HSQC spectra of KP after* <u>*30 min*</u> *of* <u>*non catalytic*</u> *oxidation of KBL in batch mode, 150°C, 20 bar.*

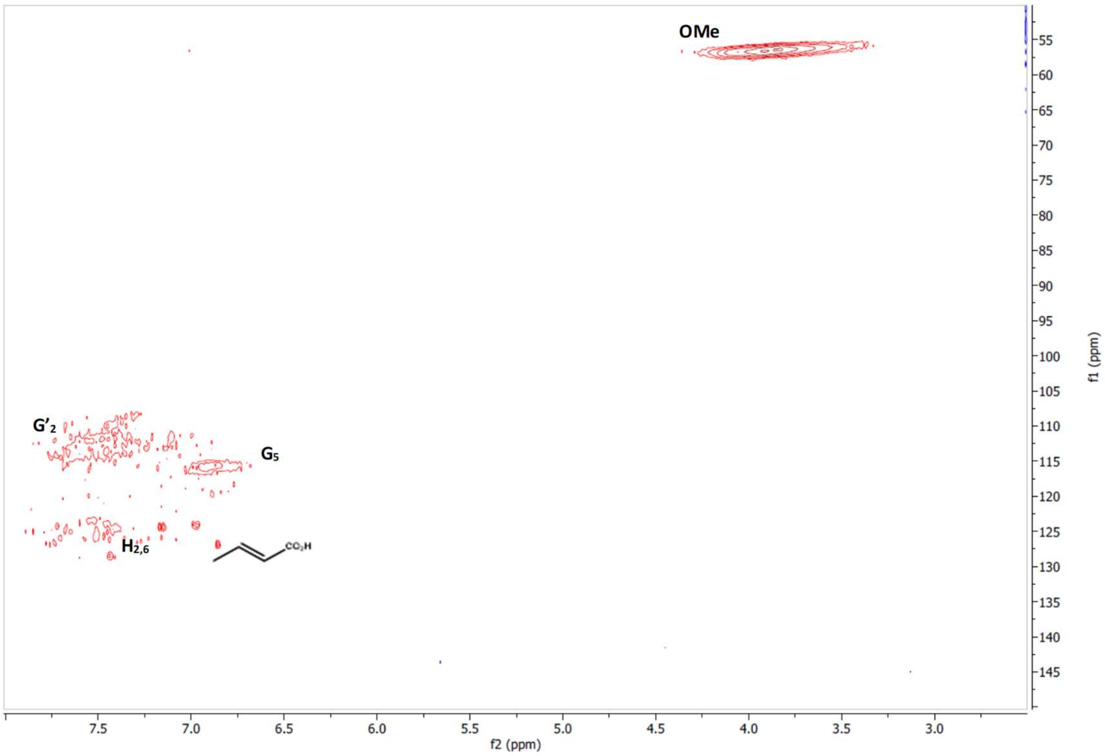

Figure S11. *HSQC spectra of KP after <u>30 min</u> of <u>catalytic</u> oxidation of KBL in batch mode, 150°C, 20 bar, catalyst CuO/TiO₂.*

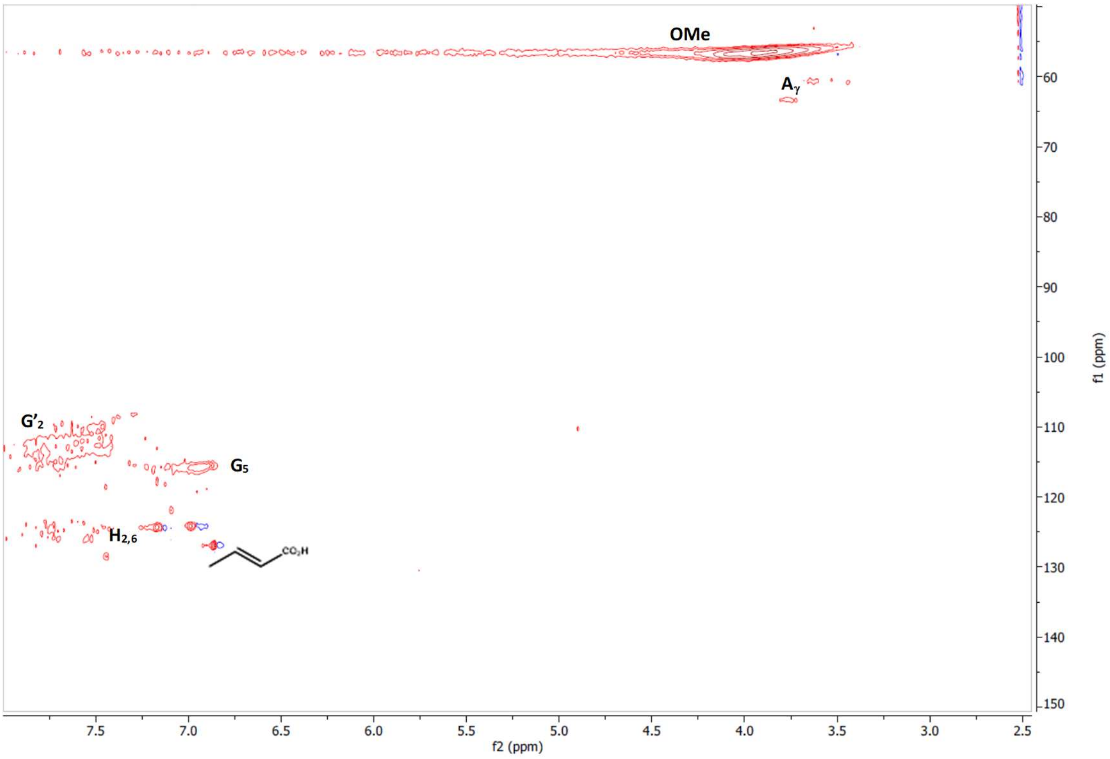

Figure S12. *HSQC spectra of KP after <u>30 min</u> of <u>catalytic</u> oxidation of <u>KL</u> in batch mode, 150°C, 20 bar, catalyst CuO/TiO₂.*

5. Carbon balance during catalytic oxidation of KBL

Total organic carbon was measured after KBL oxidation with a copper catalyst. Results are presented in Figure S133.

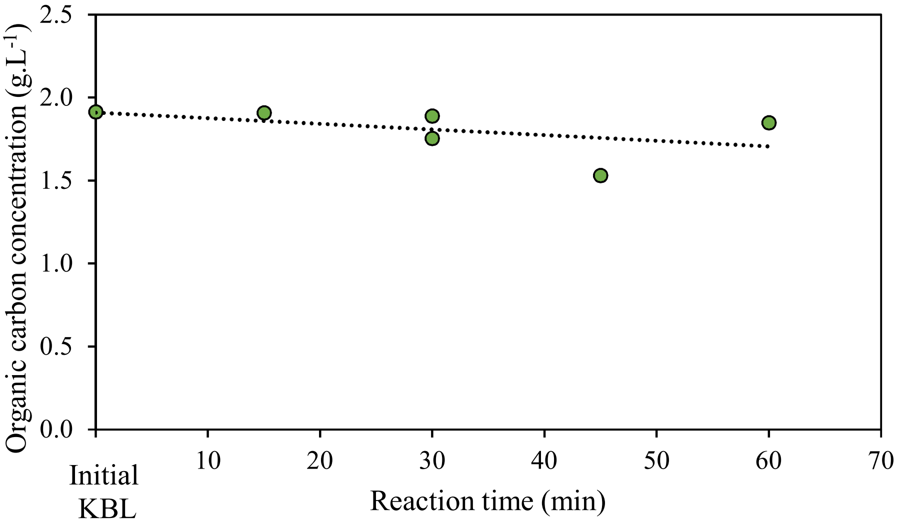

Figure S13. *Carbon concentration in liquid phase during KBL oxidation (150°C, 20 bar, batch mode).*

6. Repeatability test on catalytic oxidation of KBL (batch mode)

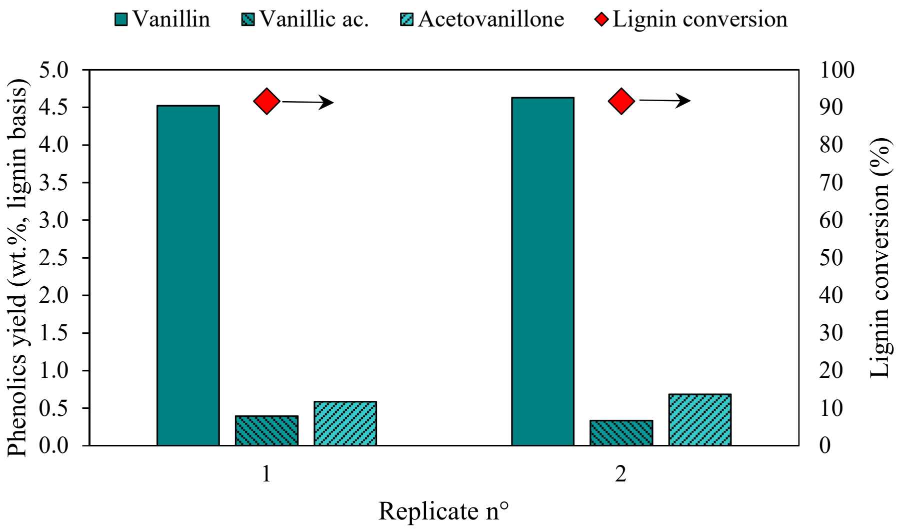

Figure S14. Repeatability of the catalytic oxidation of KBL in batch mode. *Operating conditions: 150°C, 20 bar air, stirring 1800 rpm, 30 min, dry matter concentration 5 g.L*$^{-1}$*, copper/lignin mass ratio 5 %.*

7. Deactivation of the catalyst CuO/TiO_2 (continuous mode)

Figure S15 shows the performances of CuO/TiO_2 catalyst during KBL oxidation in continuous reactor, at 200°C. An absence of deactivation was observed during 2 h on stream.

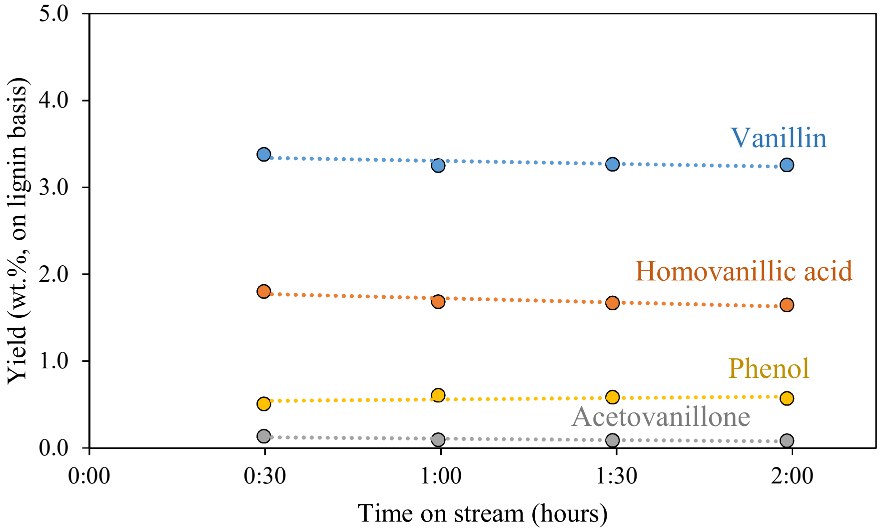

Figure S15. Yields of phenolic compounds during the catalytic oxidation of KBL. *Operating conditions: 200°C, 80 bar, contact time 3.9 min, dry matter concentration 5 g.L*$^{-1}$*, catalyst* CuO/TiO_2.

8. Productivity of various compounds

Table S3. Values calculated for the productivity of various compounds in various operating conditions (in kg.h^{-1}.m^{-3}).

Starting material	Catalyst	Reaction time (min)	Reactor type	Klason phase (lignin)	Vanillin	Phenol	Phenolic mix	Formic acid	Acetic acid	Tartronic acid	Succinic acid	Aliphatic acids mix without volatiles
KL	CuO/TiO$_2$	30	Batch	0.293	*0.0884*	0.055	**0.22**	1.048	0.191	0.000	0.593	**1.30**
KBL	CuO/TiO$_2$	15	Batch	0.681	*0.1981*	0.035	**0.37**	1.74	0.42	1.37	1.20	**3.89**
KBL	CuO/TiO$_2$	30	Batch	0.189	*0.1051*	0.025	**0.19**	1.01	0.24	0.63	0.71	**2.12**
KBL	CuO/TiO$_2$	60	Batch	0.011	*0.0456*	0.023	**0.10**					
KBL	no	15	Batch	0.757	*0.1633*	0.020	**0.33**	1.24	0.50	1.22	1.20	**3.61**
KBL	no	30	Batch	0.143	*0.0825*	0.018	**0.16**	0.94	0.33	0.49	0.77	**2.05**
KBL	CuO/TiO$_2$	Contact time 8 min	Fixed bed	0.828	0.33	0.03	**0.60**	3.37	1.47	2.21	3.27	**10.05**
KBL	CuO/TiO$_2$	Contact time 6 min	Fixed bed	1.89	0.46	0.09	**0.80**	4.20	1.48	11.62	3.77	**17.74**
KBL	CuO/TiO$_2$	Contact time 4 min	Fixed bed	4.61	0.73	0.12	**1.27**	3.91	1.55	11.35	3.75	**17.66**