Sonochemical oxidation of technical lignin to obtain nanoparticles with enhanced functionality

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Table S1. Estimated effects for Z Potential

FACTOR	ESTIMATED	STANDARD ERROR	V.I.F.
MEAN	-31.7408	1.16813	
A:TEMP	5.19333	1.27962	1.0
B:TIME	-3.35417	1.27962	1.0
C:PEROXYDE	4.72111	1.04481	1.0
AA	-8.05	2.21637	1.0
AB	-1.13	1.56721	1.0
AC	-5.26167	1.27962	1.0
BB	-0.7075	2.21637	1.0
BC	0.7575	1.27962	1.0

*Standard errors based on the total error with 9 g/L

This table shows the estimations for each of the experimental factors and the interactions. It also shows the standard error of every factor, which measures the error of the sampling. The highest variance inflation factor (V.I.F.), is equal to 1.0. for a perfectly orthogonal design, all the factors would be 1. Factors of 10 or more are interpreted as seriously confusing indicatives between the effects.

Table S2. Analysis of Variance for Z potential

SOURCE	SUM OF SQUARES	GL	MEAN SQUARES	F-REASON	P- VALUE
A:TEMP	80.9121	1	80.9121	16.47	0.0028
B:TIME	33.7513	1	33.7513	6.87	0.0278
C:PEROXYDE	100.3	1	100.3	20.42	0.0014
AA	64.8025	1	64.8025	13.19	0.0055
AB	2.5538	1	2.5538	0.52	0.4892
AC	83.0554	1	83.0554	16.91	0.0026
BB	0.500556	1	0.500556	0.10	0.7568
BC	1.72142	1	1.72142	0.35	0.5684

TOTAL ERROR	44.2108	9	4.91231
TOTAL (CORR.)	411.808	17	

Square-R = 89.2642 %
Square-R (adjusted for g.l.) = 79.7213 %
Standard error of the est. = 2.21637
Absolute mean error = 1.33045
Durbin-Watson statistic = 1.70916 (p=0,2060)
Residual autocorrelation of lag 1 = 0.116644

The ANOVA table divides the variability of the size into separate segments for each of the effects. This proves the statistical significance of each effect comparing its least square against an estimate of the experimental standard error. In this case, 5 effects have a p-value below 0.05, thus indicating that they are significantly different from zero with a confidence level of 95.0%.
The statistic Square-R indicates that the model, fitted like that, explains 89.2642% of the variability in the Z Potential. The fitted statistic R-square, which is the most suitable for comparing models with the different numbers of independent variables, is 79.7213%. The standard error for the estimated shows that the standard deviation is 2.21637. The absolute mean error (MAE)of 1.33045 is the mean value of the residues. The Durbin-Watson (DW) statistic tries the residues to determine if there is any significant correlation based on the order in which the data is presented in the file. Since the value of P is higher than 0.5%, there is no signal of serial autocorrelation in the residues with a significance value of 5.0%.

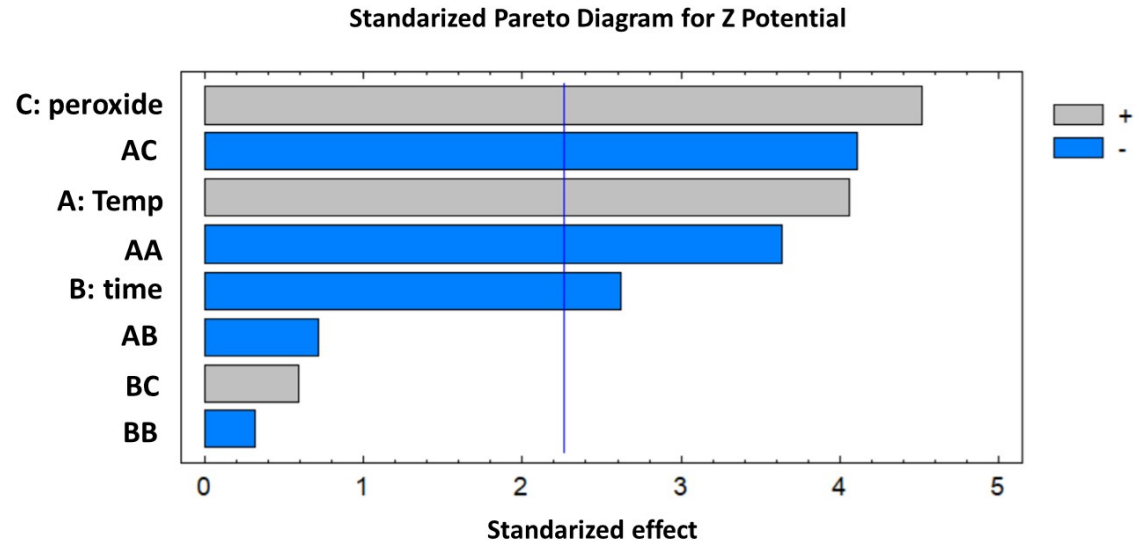


Figure S1. Standarized Pareto Diagram for Z Potential

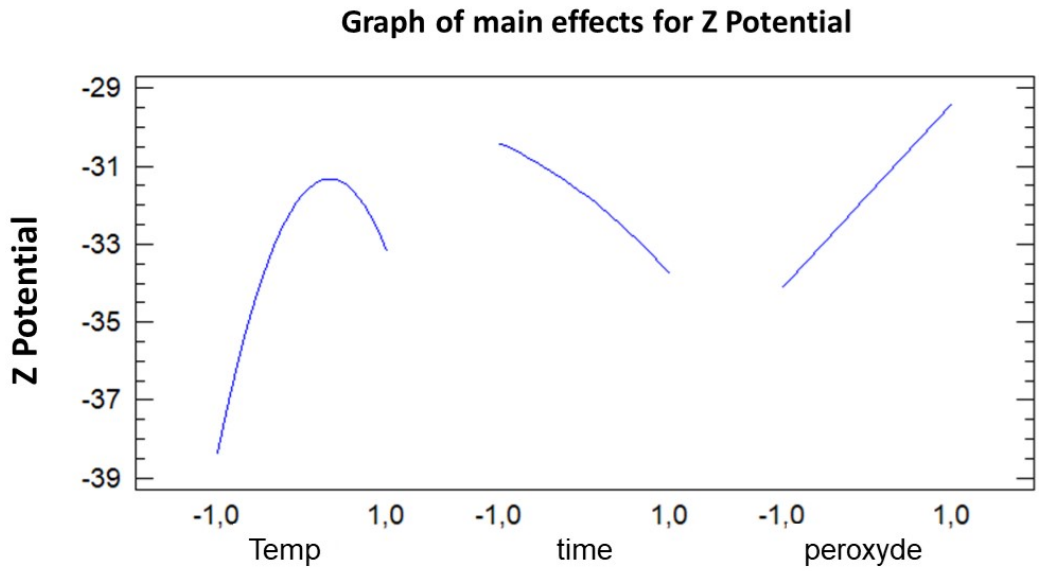


Figure S2. Graph of main effects for Z Potential

Table S3. Yield, total energy delivered to the system, and change in pH during the reaction for the different oxidative conditions.

SAMPLE	YIELD (%)	E (KJ)	PH CHANGE
USOX1	76.65	50.54	-0.59
USOX2	74.62	100.00	-0.63
USOX3	75.92	209.45	-0.06
USOX4	72.18	58.40	-0.95
USOX5	72.83	95.70	-1.88
USOX6	74.72	194.00	-1.64
USOX7	74.03	60.39	-0.22
USOX8	76.29	133.61	-0.30
USOX9	68.48	201.60	-0.47
USOX10	76.29	54.83	-1.51
USOX11	74.73	113.20	-2.24
USOX12	74.99	238.12	-2.35
USOX13	71.94	45.95	-0.63
USOX14	73.49	87.09	-0.26
USOX15	71.30	180.56	-0.32
USOX16	66.55	89.28	-3.15
USOX17	69.31	171.1	-2.59
USOX18	73.36	188.84	-2.93

Table S4. Chemical composition of oxidized lignins.

SAMPLE	AIL (%)	ASL (%)	CA (%)	ASH (%)
KL	73.94 ± 0.93	18.99 ± 0.25	1.03 ± 0.21	6.04 ± 1.06
USOX1	87.97 ± 2.67	7.61 ± 1.03	2.89 ± 0.11	1.53 ± 0.97
USOX2	87.78 ± 4.80	6.92 ± 0.04	3.49 ± 0.93	1.81 ± 0.33
USOX3	87.41 ± 1.82	8.00 ± 0.23	3.08 ± 0.16	1.51 ± 0.08
USOX4	86.78 ± 1.32	8.43 ± 1.06	3.09 ± 0.08	1.70 ± 0.68

USOX5	88.92 ± 1.36	6.05 ± 0.25	2.79 ± 0.23	2.24 ± 2.30
USOX6	88.37 ± 3.36	6.91 ± 0.07	3.14 ± 0.02	1.58 ± 0.43
USOX7	89.32 ± 2.53	5.92 ± 0.07	3.65 ± 0.46	1.11 ± 0.09
USOX8	89.75 ± 2.53	5.99 ± 0.22	3.07 ± 0.06	1.19 ± 0.17
USOX9	91.23 ± 0.85	4.29 ± 0.25	3.59 ± 0.48	0.89 ± 0.01
USOX10	89.25 ± 0.67	5.99 ± 0.31	3.88 ± 0.71	0.88 ± 0.20
USOX11	88.20 ± 1.66	6.79 ± 0.43	4.11 ± 0.48	0.90 ± 0.12
USOX12	87.41 ± 0.59	6.42 ± 0.25	4.36 ± 0.46	1.81 ± 0.88
USOX13	92.60 ± 0.32	6.29 ± 0.11	0 ± 0.00	1.11 ± 0.07
USOX14	89.25 ± 1.24	5.40 ± 0.34	3.59 ± 4.88	1.76 ± 0.45
USOX15	85.75 ± 2.05	4.78 ± 0.18	8.48 ± 0.62	0.99 ± 0.79
USOX16	84.02 ± 2.36	5.67 ± 0.30	8.91 ± 0.58	1.40 ± 0.33
USOX17	86.03 ± 0.84	5.50 ± 0.30	7.76 ± 1.18	0.71 ± 0.02
USOX18	85.68 ± 1.00	4.65 ± 0.13	8.70 ± 0.17	0.97 ± 0.10

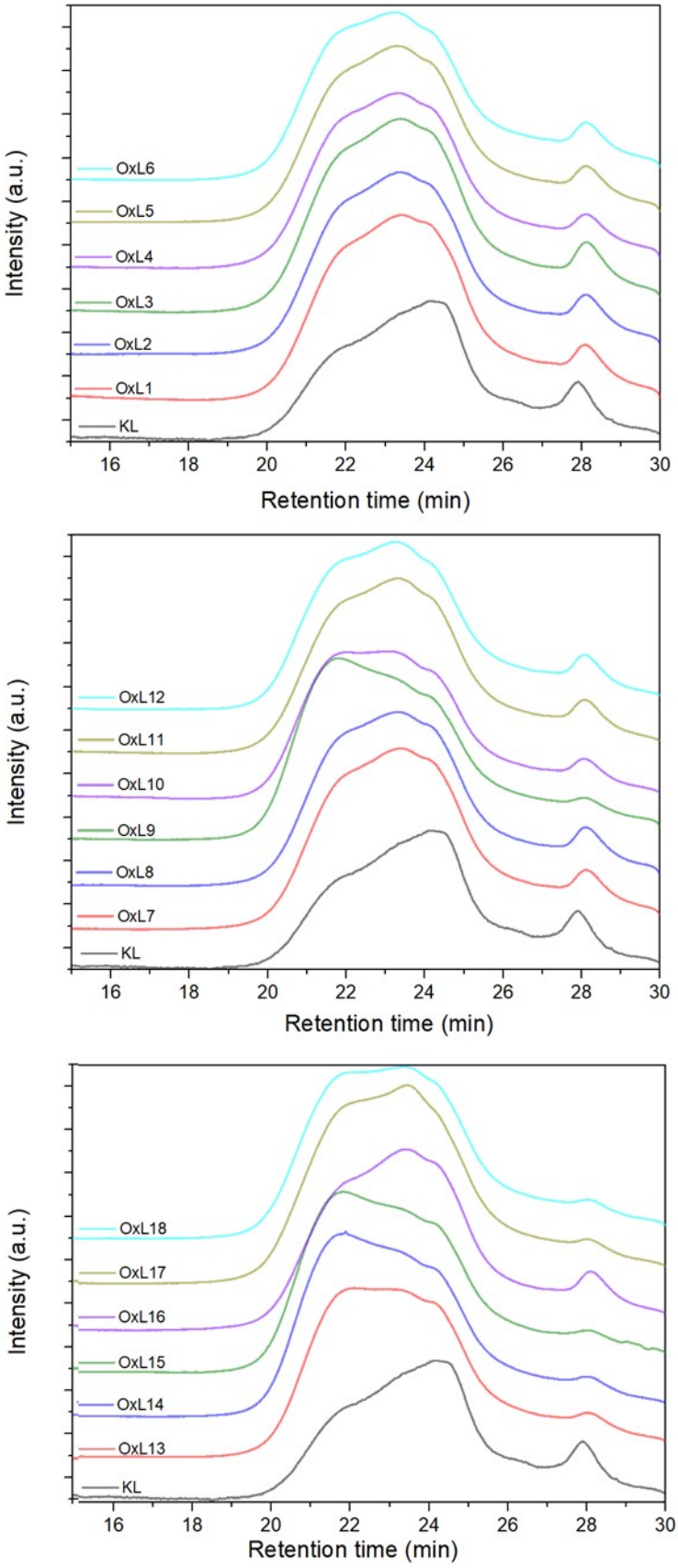


Figure S3. Chromatogram curves of KL and its oxidized samples.

Table S5. Elemental analysis results

	C	*H*	*N*	*S*	*O*
KL	62.44 ± 0.38	5.20 ± 0.02	0.31 ± 0.03	5.07 ± 0.16	26.98 ± 0.54
OxL1	64.97 ± 0.13	5.69 ± 0.19	0.32 ± 0.02	5.43 ± 0.11	23.60 ± 0.40
OxL2	64.87 ± 0.63	5.51 ± 0.16	0.30 ± 0.02	5.47 ± 0.09	23.84 ± 0.85
OxL3	64.71 ± 0.18	5.47 ± 0.03	0.33 ± 0.03	6.08 ± 0.05	23.41 ± 0.28
OxL4	64.59 ± 0.50	5.45 ± 0.03	0.30 ± 0.04	4.91 ± 0.15	24.75 ± 0.66
OxL5	64.49 ± 0.18	5.38 ± 0.06	0.31 ± 0.02	5.04 ± 0.05	24.79 ± 0.26
OxL6	63.53 ± 0.54	5.26 ± 0.08	0.28 ± 0.01	5.14 ± 0.05	25.80 ± 0.66
OxL7	64.48 ± 1.08	5.28 ± 0.08	0.30 ± 0.02	5.19 ± 0.16	24.75 ± 1.32
OxL8	65.25 ± 0.49	5.34 ± 0.05	0.30 ± 0.02	5.46 ± 0.08	23.64 ± 0.63
OxL9	66.41 ± 0.76	5.22 ± 0.09	0.33 ± 0.01	4.39 ± 0.16	23.64 ± 1.00
OxL10	64.00 ± 0.09	5.68 ± 0.05	0.31 ± 0.01	4.63 ± 0.03	25.39 ± 0.16
OxL11	63.53 ± 0.65	5.55 ± 0.04	0.28 ± 0.03	4.88 ± 0.13	25.76 ± 0.84
OxL12	63.45 ± 0.44	5.37 ± 0.12	0.30 ± 0.02	5.03 ± 0.06	25.86 ± 0.54
OxL13	66.03 ± 0.33	5.45 ± 0.04	0.33 ± 0.01	4.51 ± 0.09	23.68 ± 0.47
OxL14	66.00 ± 0.47	5.32 ± 0.05	0.32 ± 0.02	4.34 ± 0.09	24.02 ± 0.58
OxL15	66.37 ± 0.62	5.46 ± 0.01	0.34 ± 0.03	4.32 ± 0.18	23.50 ± 0.83
OxL16	64.79 ± 0.16	5.48 ± 0.02	0.28 ± 0.02	4.99 ± 0.07	24.45 ± 0.16
OxL17	65.83 ± 0.61	5.40 ± 0.03	0.32 ± 0.01	4.07 ± 0.08	24.39 ± 0.67
OxL18	65.78 ± 0.63	5.38 ± 0.01	0.31 ± 0.02	3.93 ± 0.11	24.60 ± 0.77

Table S6. FTIR assignments for each frequency range

Absorption frequency range (cm-1)	*Assignment*
3400	ν(O-H) stretching of phenolic hydroxyl and aliphatic hydroxyl groups
2940 and 2840	ν(C-H) methyl (-CH3) and methylene (-CH2-) groups
1708	ν(C=O) stretching of unconjugated ketones, conjugated aldehydes and carboxylic acids
1610 and 1515	Aromatic skeletal vibrations (guaiacyl-syringyl)
1460	δ(C-H) methyl (-CH3) and methylene (-CH2-) groups
1425	Aromatic skeletal vibrations combined with δ(C-H) (in-plane)
1329	ν(C-O) syringyl
1217	ν(C-O) guaiacyl
1150	ν(C-O) aliphatic ethers
1033	ν(C-O-C) ether linkage and phenolic hydroxyl groups
910	δ(C-H) (out-of-plane) aromatic
835	ν(C-O) aliphatic ethers

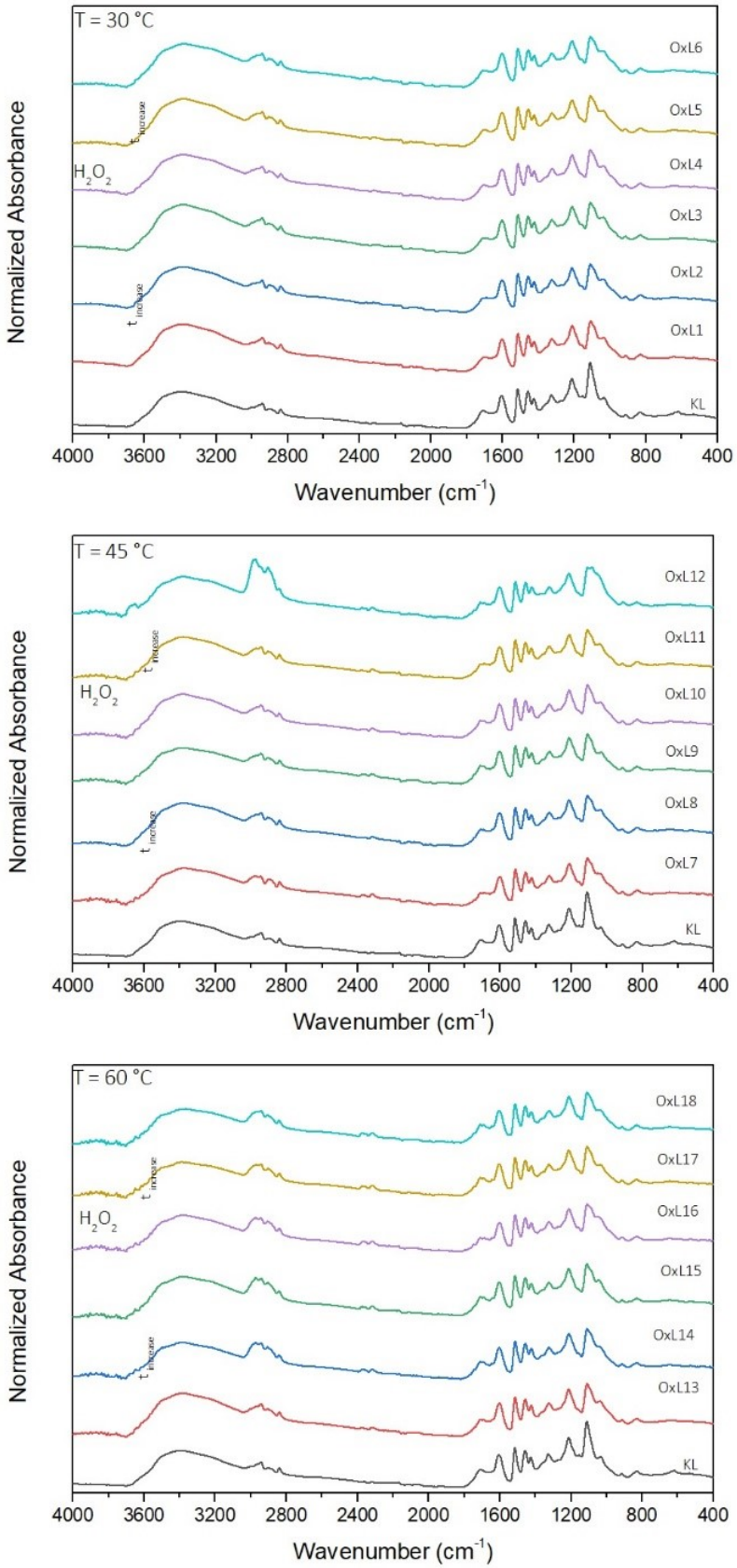


Figure S4. FTIR spectra of KL and oxidized lignin samples.

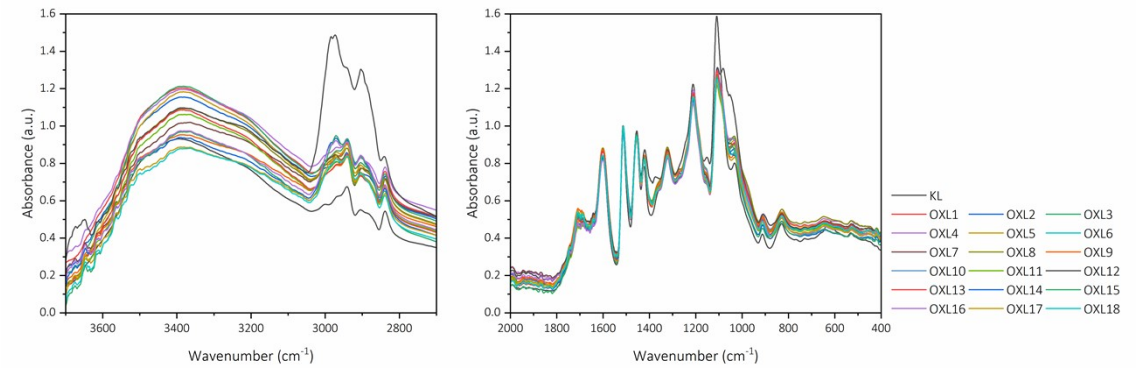
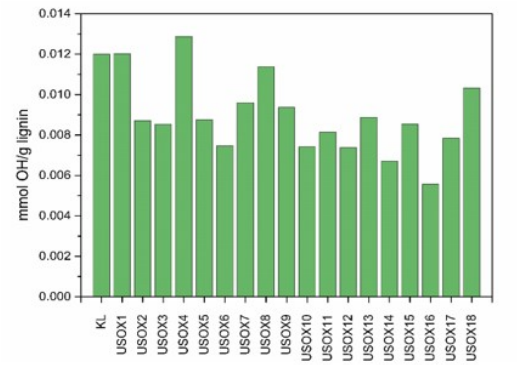
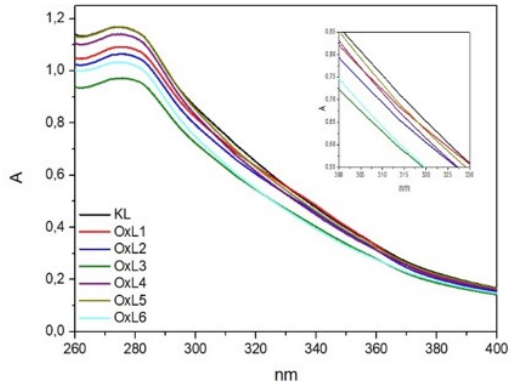
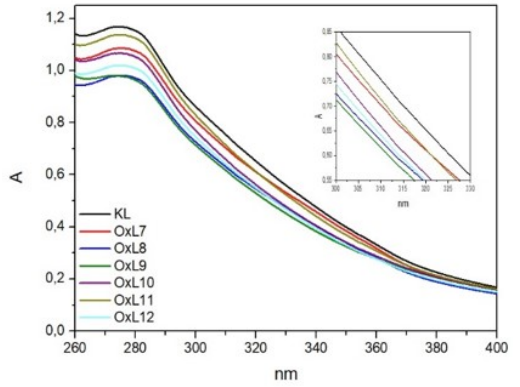


Figure S5. A close-up look to the characteristic bands of the oxidized samples.







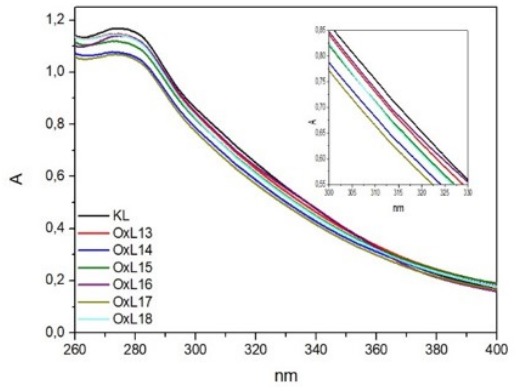


Figure S6 Total Phenolic Content (TPC) and conjugated and non-conjugated OH groups

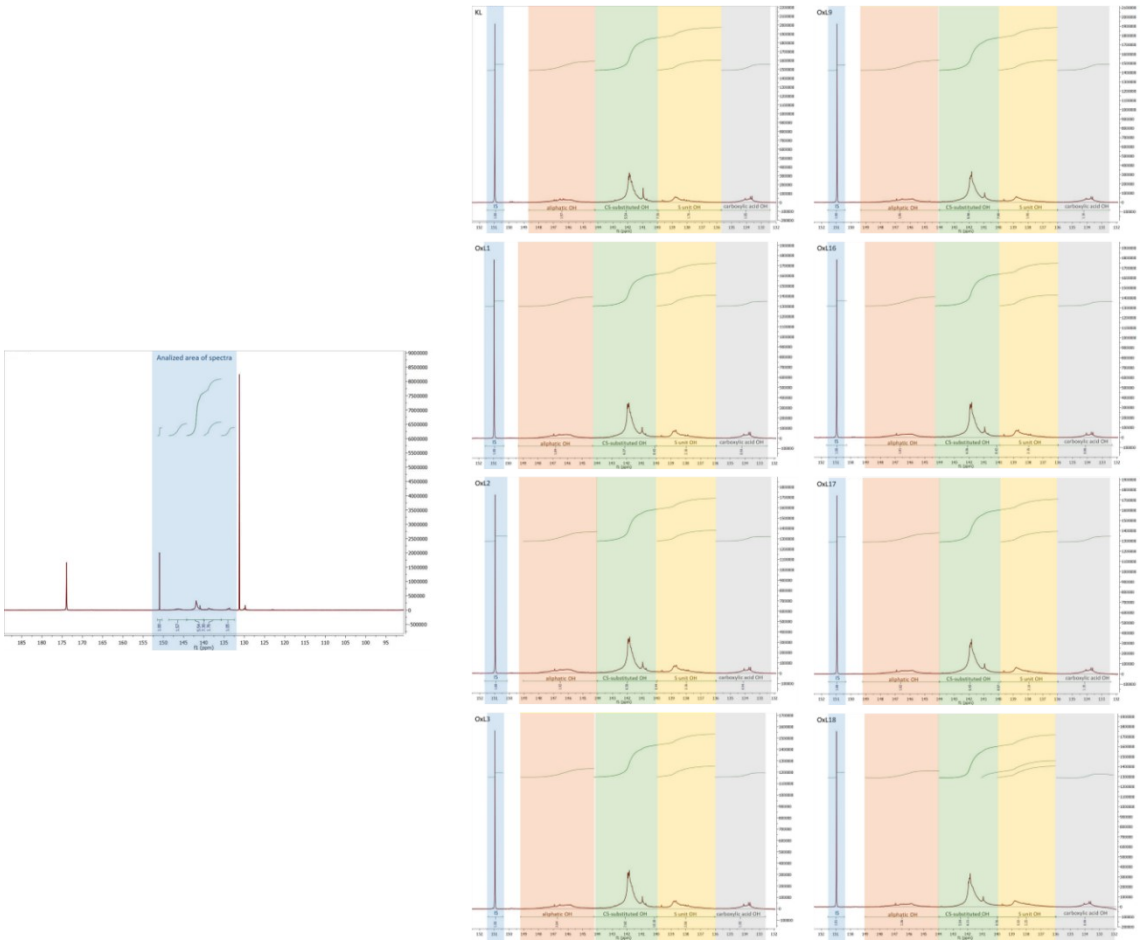


Figure S7. 31P NMR spectra of KL, OxL1, OxL2, OxL3, OxL9, OxL16, OxL17, and OxL18

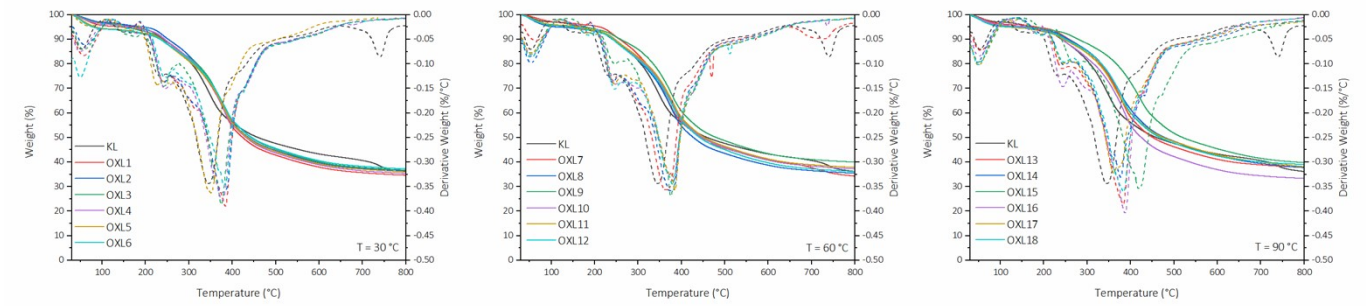


Figure S8. TG and DTG curves obtained for KL and its oxidized samples.

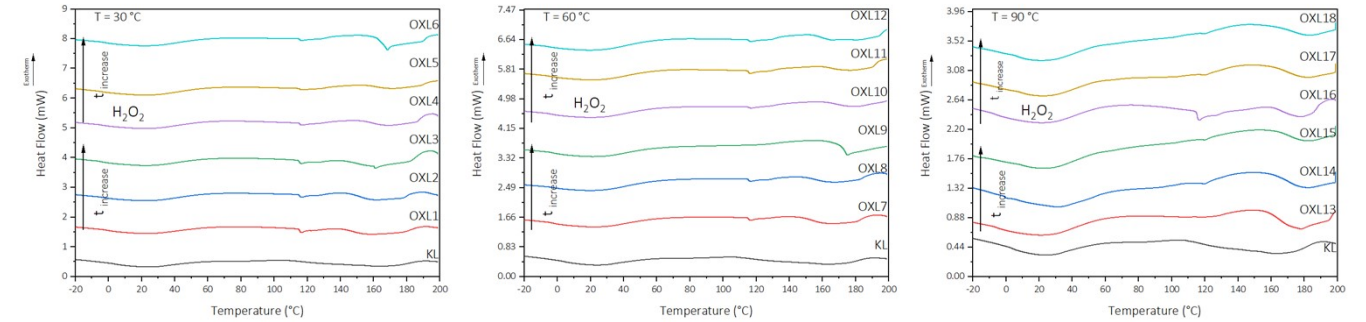


Figure S9. DSC curves of KL and its oxidized samples.

Table S7. Mass loss at 5% and 50% ($T_{5\%}$ and $T_{50\%}$), degradation stages of KL and oxidized samples, and glass transition temperatures (T_g).

	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	Degradation stages (°C)	Char (%)	Tg (°C)
KL	175	460	**50**/150/175/**225**/**350**/425/550/**740**	**36.05**	**116.4**
OxL1	150	425	**60**/160/**240**/320/**375**/425/525/600	**34.59**	**116.6**
OxL2	175	440	**60**/160/**240**/300/**375**/425/525/600	**36.40**	**116.8**
OxL3	150	445	**60**/150/175/**240**/**375**/425/525/600	**36.67**	**116.6**
OxL4	200	540	**60**/175/225/**300**/360/**460**/525/650	**40.31**	**116.9**
OxL5	75	440	**60**/160/**225**/250/275/**350**/375/475/650	**35.94**	**117.3**
OxL6	75	445	**50**/150/175/**250**/300/**375**/425/525/600	**37.16**	**116.9**
OxL7	200	450	**70**/175/**220**/**375**/425/**475**/575/**725**	**34.20**	**116.8**
OxL8	100	425	**50**/190/**220**/290/310/**375**/425/525/700	**35.43**	**116.9**
OxL9	175	475	**50**/**200**/**250**/**375**/430/525/600	**39.94**	**100.0**
OxL10	150	450	**50**/150/**190**/**250**/300/**375**/425/525/600/730	**37.16**	**117.0**
OxL11	150	450	**50**/150/**190**/**250**/280/**390**/425/525/600/700	**37.77**	**116.6**
OxL12	150	450	**50**/150/**190**/**250**/275/**390**/425/510/600/700	**36.05**	**117.0**
OxL13	180	450	**50**/125/190/**220**/**390**/425/525/600/700	**37.76**	**117.8**
OxL14	150	475	**50**/**200**/**220**/**375**/420/525/600	**37.69**	**97.1**
OxL15	150	520	**50**/220/**260**/**420**/475/600/725	**38.89**	**97.0**
OxL16	150	425	**50**/150/175/250/300/**390**/425/525/675	**33.28**	**116.7**
OxL17	100	475	**50**/125/190/**220**/**375**/425/525/600/675	**38.05**	**97.2**
OxL18	100	475	**50**/200/**250**/300/**390**/425/525/600/700	**38.95**	**97.2**

*In red and bold the temperatures in which the main degradation occurred. In black bold the other significant degradations.

Table S8. Particle aggregation type and size, and particle size in mm of KL and oxidized samples.

Sample	Particle aggregation type	Average particle size range (nm)
KL	Big agglomerations	124.1 ± 34.6
OxL1	Small agglomerations	153.0 ± 39.9
OxL2	Medium aggregates	25.9 ± 2.8
OxL3	Free particles	25.8 ± 4.0
OxL9	Small aggregates	17.8 ± 2.7
OxL16	Small agglomerates	144.0 ± 25.5
OxL17	Free particles	123.5 ± 71.0
OxL18	Big aggregates	103.7 ± 67.8