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Breakdown of lignins, lignin model compounds, and hydroxy-aromatics, to C_1 and C_2 chemicals via metal-free oxidation with peroxide or persulfate under mild conditions

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General Information

All commercially available compounds were purchased and used as received unless otherwise noted. The 31.5 wt% solution of H_2O_2 was kept refrigerated prior to use. Dimer LMCs were synthesized according to literature procedures.[1] Lignin samples were acquired from various sources: Alkali lignin (from Aldrich) (**9**); pyrolytic lignin (**10**); a CH_2Cl_2-soluble fraction Kraft lignin (from Prof. J. Kadla, Faculty of Forestry, University of British Columbia) (**11**); indulin AT Kraft lignin (from MeadWestvaco Corp.) (**12**); and a lignin from Lignol Energy Corp. (**13**).

^{1}H NMR data were collected at 298 K on Bruker AVANCE 300 or 400 MHz spectrometers and were referenced to hexamethylbenzene in benzene-d_6 (δ_H = 2.12) contained in a capillary inside the NMR tube. The integration error is estimated at ± 2% due to excellent peak separation and signal-to-noise ratio. Methoxy content of lignin **11** was calculated by dissolving 15 mg of the lignin and a known amount of pivalic acid in 500 μL of $CDCl_3$.[2] A recycle delay (d1) of 5 seconds was used to ensure complete relaxation of all proton nuclei. The mmols of –OMe were calculated from the ratio of pivalic acid signals to –OMe signals (δ_H = 3.6 – 4.0); the data were converted into a weight and subsequently a percentage (18.7%).

Qualitative ^{13}C NMR data were collected at 298 K on the AVANCE 300 MHz spectrometer (75 MHz for ^{13}C) equipped with a Bruker 5 mm QNP probe at the University of British Columbia. The inverse-gated UDEFT pulse sequence[3] was used in order to increase the signal strength of quaternary carbons, specifically for the low-field formate, carbonate, and oxalate species. At least 10,000 FIDs were accumulated for each experiment resulting in run times of ~12 h. Unfortunately, quantitative data could not be collected from these runs due to instrument sensitivity and time restrictions.

Quantitative ^{13}C NMR data were collected at 298 K on a Bruker AVANCE II 600 MHz spectrometer (150 MHz for ^{13}C) equipped with a Bruker 5 mm QNP cryogenically-cooled probe at Simon Fraser University (Burnaby, BC, Canada) by Dr. Andrew Lewis. Inverse-gated ^{1}H composite pulse decoupling (WALTZ-16) was employed with a recycle delay (d1) of 150 seconds to ensure complete relaxation of all carbon nuclei which was verified using pivalic acid as an internal standard. At least 400 FIDs were accumulated for each experiment (~16 h) in order to ensure a minimum signal-to-noise ratio of 25:1 for the formate, carbonate, and oxalate signals; this resulted in an error of about ± 2% in the integrations of the pivalic acid signals.

Experimental Section

General Procedure for the Breakdown of LMCs and Lignins

The appropriate amount of LMC (0.050 mmol for monomeric models; 0.025 mmol for dimeric models) or lignin sample (15 mg) was added to an NMR tube with a screw-cap closure. 1 mL of 1 M KOH or 1 M K_2CO_3 solution in D_2O was added to the tube *via* syringe. A capillary standard containing hexamethylbenzene in benzene-d_6 was also added. An initial "time zero" ^{1}H NMR spectrum was recorded at 298 K at which point either H_2O_2 (0.50 mmol, 50 μL) or $K_2S_2O_8$ (0.25 mmol, 68 mg) was added. $RuCl_3$•H_2O (0.015 mmol, 3.9 mg) was sometimes added at this stage. The NMR tube was then placed in a pre-heated 60 °C oil-bath for 3 h. The tube was then cooled to ambient temperature before the addition of pivalic acid (0.05–0.10 mmol, 5-10 mg), an internal spectroscopic standard for determination of substrate consumption and product yields. The relevant ^{1}H NMR signals (in basic D_2O) are presented in Table S1.

Table S1 Relevant ^{1}H NMR signals for substrates, products, and standards.

Compound	δ_H (ppm)	Proton	Multiplicity
Guaiacol (**1**)	3.67	OCH_3	singlet
Syringic Acid (**2**)	3.73	OCH_3	singlet
Syringyl Aldehyde (**3**)	3.70	OCH_3	singlet
Syringyl Alcohol (**4**)	3.66	OCH_3	singlet
Veratric Acid (**5**)	3.77	OCH_3	singlet
Vanillic Acid (**6**)	3.73	OCH_3	singlet
LMC Dimer (**7**)[a]	*n/a*	*n/a*	*n/a*
Catechol	6.28-6.53	Ar-*H*	multiplet
Phenol	6.51-7.21	Ar-*H*	multiplet
Methanol	3.30	OCH_3	singlet
Formate	8.45	HCO_2^-	singlet
Pivalic Acid	1.03	CH_3	singlet

[a] The dimer is not fully soluble in the basic aqueous solutions.

Table S2 Reactions of LMCs and lignins in 1 M KOH solution (from ^{1}H NMR data).

Substrate	Oxidant	Consumption (%)	Methanol (mmol)	Formate (mmol)
Guaiacol (**1**)	H_2O_2	61	0.025	0.021
	$K_2S_2O_8$	94	0.028	0.008
Syringic Acid (**2**)	H_2O_2	89	0.073	0.022
	$K_2S_2O_8$	100	0.069[b]	0.002[b]
Syringyl Aldehyde (**3**)	H_2O_2	100	0.096	0.085
	$K_2S_2O_8$	100	0.086	0.016
Syringyl Alcohol (**4**)	H_2O_2	100	0.100	0.093
	$K_2S_2O_8$	100	0.096	0.013
Veratric Acid (**5**)	H_2O_2	40	0.004	0.003
	$K_2S_2O_8$	96	0.020	0.002
Vanillic Acid (**6**)	H_2O_2	4	0.000	0.000
	$K_2S_2O_8$	51	0.025	0.000
LMC Dimer (**7**)[a]	H_2O_2	*n/a*	0.022	0.039
	$K_2S_2O_8$	*n/a*	0.019	0.002
9	H_2O_2	80	0.040	0.046
	$K_2S_2O_8$	84	0.018	0.006
10	H_2O_2	97	0.022	0.031
	$K_2S_2O_8$	95	0.033	0.007
11	H_2O_2	99	0.093	0.050
	$K_2S_2O_8$	89	0.090[c]	0.004[c]
12	H_2O_2	82	0.047	0.054
	$K_2S_2O_8$	82	0.019	0.003
13	H_2O_2	91	0.055	0.033
	$K_2S_2O_8$	78	0.037	0.003

[a] The dimer is not fully soluble in the basic aqueous solutions and consumption cannot be accurately determined.
[b] When $RuCl_3 \cdot 3H_2O$ is added to form RuO_4^{2-}, the values for methanol and formate are 0.034 and 0.012 mmol, respectively.
[c] When $RuCl_3 \cdot 3H_2O$ is added to form RuO_4^{2-}, the values for methanol and formate are 0.029 and 0.005 mmol, respectively.

Table S3 Reactions of LMCs and lignins in 1 M K_2CO_3 solution (from ^1H NMR data).

Substrate	Oxidant	Consumption (%)	Methanol (mmol)	Formate (mmol)
Guaiacol (**1**)	H_2O_2	42	0.013	0.007
	$K_2S_2O_8$	100	0.022	0.000
Syringic Acid (**2**)	H_2O_2	71	0.060	0.007
	$K_2S_2O_8$	100	0.082	0.000
Syringyl Aldehyde (**3**)	H_2O_2	100	0.099	0.083
	$K_2S_2O_8$	100	0.085	0.015
Syringyl Alcohol (**4**)	H_2O_2	99	0.073	0.028
	$K_2S_2O_8$	100	0.070	0.009
Veratric Acid (**5**)	H_2O_2	21	0.006	0.003
	$K_2S_2O_8$	100	0.033	0.000
Vanillic Acid (**6**)	H_2O_2	6.5	0.000	0.000
	$K_2S_2O_8$	12	0.007	0.000
9[b]	H_2O_2	*n/a*	0.017	0.010
	$K_2S_2O_8$	*n/a*	0.019	0.005
10[b]	H_2O_2	*n/a*	0.024	0.022
	$K_2S_2O_8$	*n/a*	0.015	0.006
11[b]	H_2O_2	*n/a*	0.078	0.014
	$K_2S_2O_8$	*n/a*	0.054	0.003
12[b]	H_2O_2	*n/a*	0.021	0.012
	$K_2S_2O_8$	*n/a*	0.023	0.003
13[b]	H_2O_2	*n/a*	0.028	0.007
	$K_2S_2O_8$	*n/a*	0.017	0.001

[a] The dimer is not fully soluble in the basic aqueous solutions and consumption cannot be accurately determined.

[b] Lignins only partially dissolve in the 1 M K_2CO_3 solutions and consumption cannot be accurately determined.

Spectroscopic Data

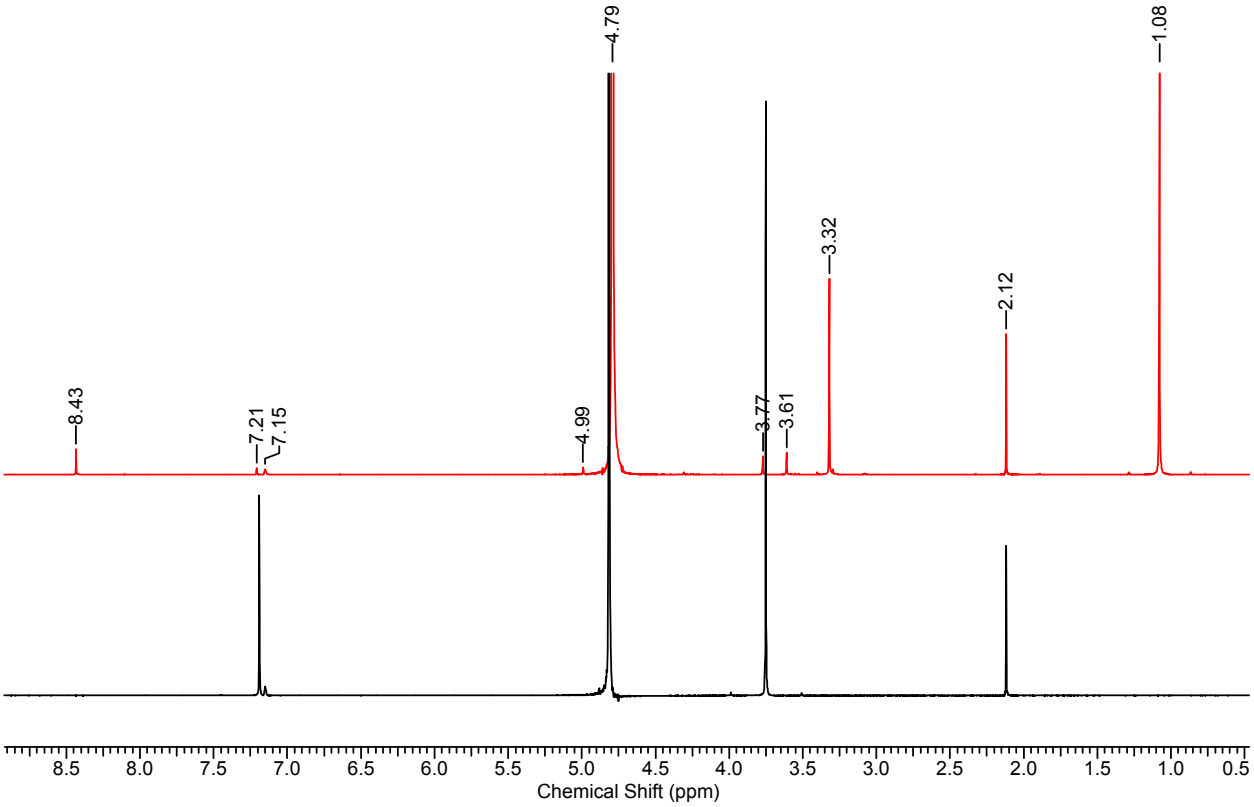

Figure S1 ^{1}H NMR spectra for a typical reaction mixture. In this example, syringic acid (**2**) is reacted with H_2O_2 in 1 M KOH according to the General Procedure. The bottom spectrum (black) is the initial "time zero" spectrum; the top spectrum (red) was taken after 3 h reaction at 60 °C (after addition of pivalic acid). See Table S1 for signal assignment.

In addition to the residual substrate signals and those of methanol and formate, two trace, unassigned signals (δ_H = 3.61 and 4.99) are seen for the syringyl derived substrates (**2**–**4**). ^{1}H–^{13}C NMR spectroscopy (HSQC, Fig. S2) of a completed reaction for syringic acid (**2**) reveals a relationship between the δ_H = 3.61 and δ_C = 55.7 signals. Integrations from quantitative ^{13}C NMR (*vide infra*) and the corresponding ^{1}H NMR data suggest these signals are representative of a CH_3 group. The HSQC spectrum also shows the δ_H = 4.99 and δ_C = 95.0 signals are related; however, the integrations are uninformative about the number of protons attached to the carbon. A COSY ^{1}H–^{1}H NMR experiment (Fig. S3) confirms that the δ_H = 3.61 and 4.99 signals are related, suggesting a molecule with at least a two carbon chain, but this side-product has not yet been identified.

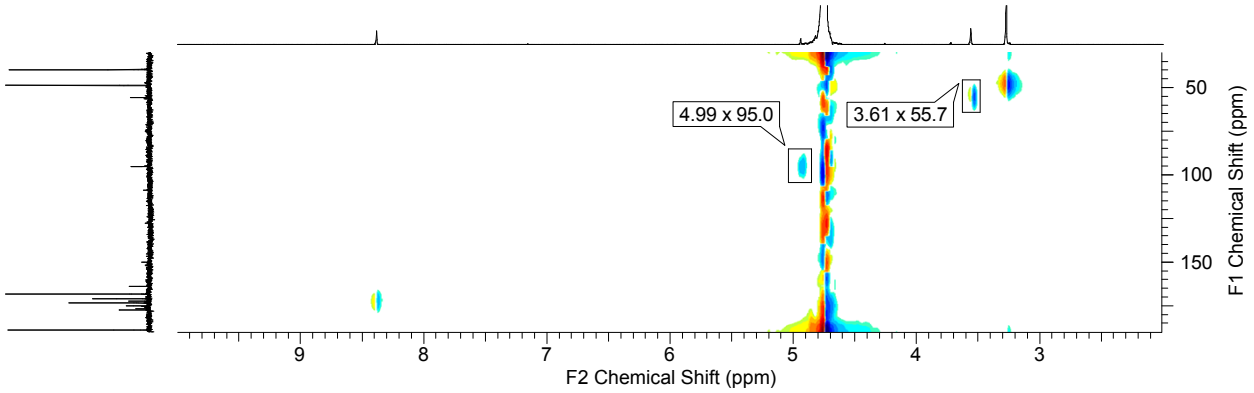

Figure S2 HSQC spectrum for syringic acid (**2**) reacted with H_2O_2 in 1 M KOH according to the General Procedure. The correlations shown from right to left are as follows: δ_H = 3.30 and δ_C = 48.7 (methanol); δ_H = 3.61 and δ_C = 55.7 (unidentified); δ_H = 4.99 and δ_C = 95.0 (unidentified); δ_H = 8.45 and δ_C = 171.0 (formate).

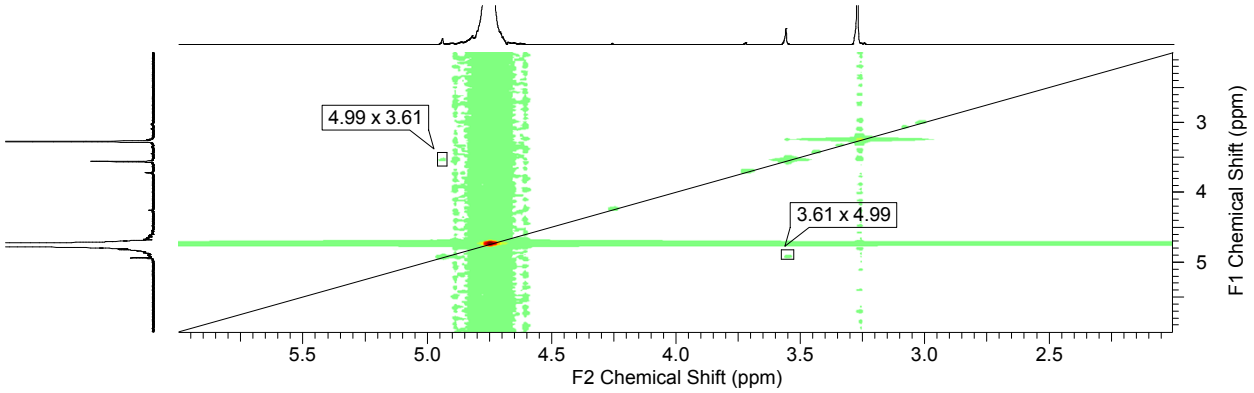

Figure S3 COSY spectrum for syringic acid (**2**) reacted with H_2O_2 in 1 M KOH according to the General Procedure. The relevant off-diagonal signals are highlighted for clarity.

Table S4 Quantitative $^{13}C\{^{1}H\}$ data for the reaction of syringic acid (**2**) with H_2O_2 in 1 M KOH according to the General Procedure.

Compound	δ_C (ppm)	Amount (mmol)	% Total Carbon Present
Pivalic Acid (3 carbons)	27.47	0.214	Internal Standard
Pivalic Acid	39.77	0.074	Internal Standard
Methanol	48.83	0.072	21.6
Unidentified	55.69	0.086	2.6
Unidentified	95.18	0.082	2.5
Unidentified	163.88	0.105	3.2
Carbonate	168.37	0.116	35.1
Formate	171.05	0.029	8.7
Unidentified	172.45	0.010	3.1
Oxalate (2 carbons)	173.44	0.037	11.0
Unidentified	174.98	0.013	3.9
Unidentified	176.76	0.006	1.8
Unidentified	177.43	0.018	5.3
Pivalic Acid	188.93	0.069	Internal Standard

Total Identified Carbon (MeOH + HCO_2^- + CO_3^{2-} + $C_2O_4^{2-}$) = 0.253 mmol
Total Unidentified Carbon (*see italics*) = 0.079 mmol
Total Carbon Present (identified + unidentified) = 0.332 mmol
Expected Carbon = 0.450 mmol

Total Identified / Total Carbon Present = 76.3%
Total Unidentified / Total Carbon Present = 23.7%

Total Carbon / Expected Carbon = 73.7%

Integration of the ^{1}H NMR spectrum (600 MHz) of the same sample gives the following:

0.071 mmol MeOH (1.4% change from ^{13}C data)
0.027 mmol HCO_2^- (6.8% change from ^{13}C data)

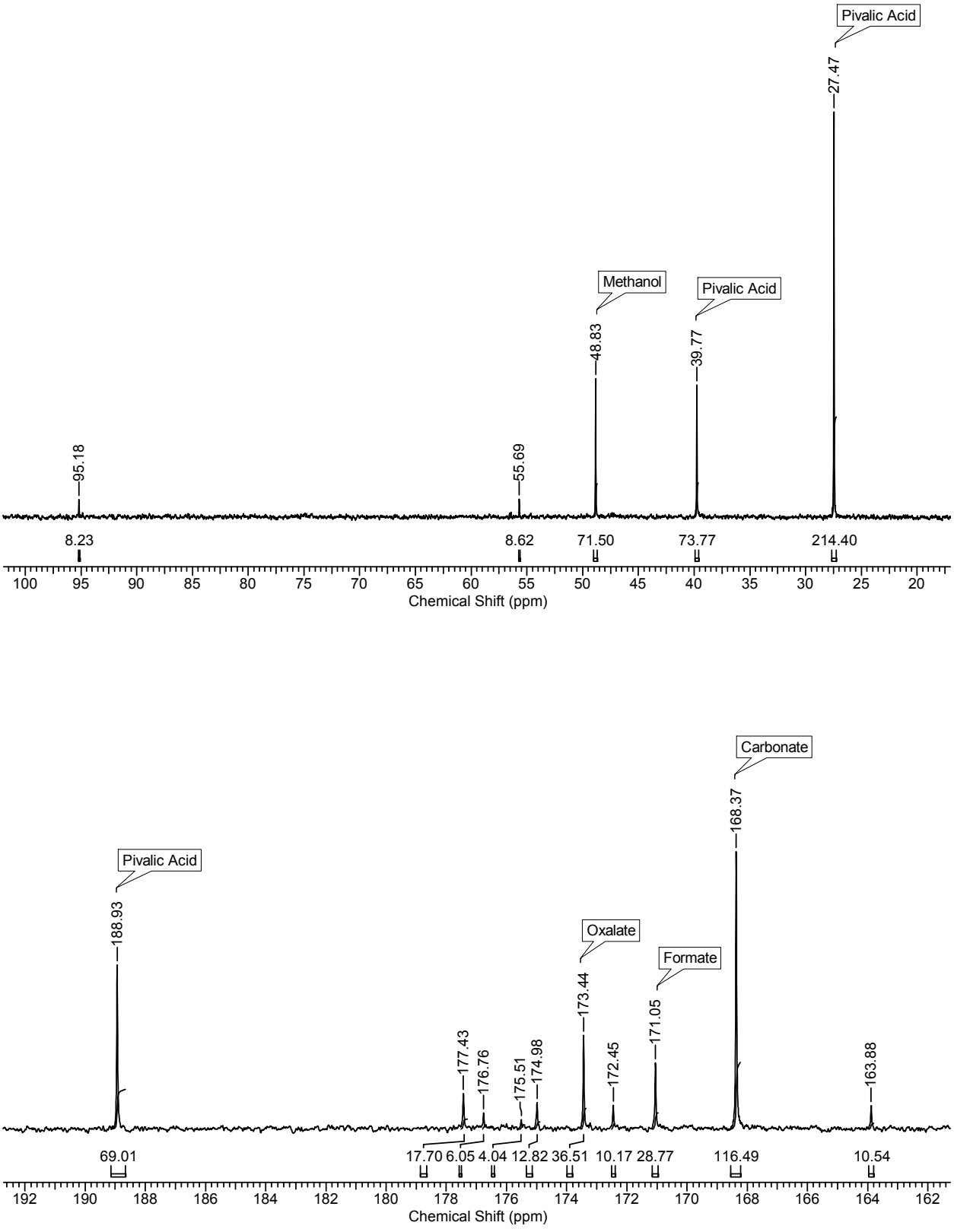

Figure S4 $^{13}C\{^{1}H\}$ spectrum corresponding to the data in Table S4.

Table S5 Quantitative $^{13}C\{^1H\}$ data for the reaction of syringyl aldehyde (**3**) with H_2O_2 in 1 M KOH according to the General Procedure.

Compound	δ_C (ppm)	Amount (mmol)	% Total Carbon Present
Pivalic Acid (3 carbons)	27.48	0.268	Internal Standard
Pivalic Acid	39.77	0.090	Internal Standard
Methanol	48.83	0.080	20.4
Unidentified	55.69	0.014	3.6
Unidentified	95.19	0.012	3.1
Unidentified	163.88	0.013	3.3
Carbonate	168.38	0.079	20.1
Formate	171.05	0.080	20.2
Unidentified	172.46	0.019	4.8
Oxalate (2 carbons)	173.44	0.046	11.7
Unidentified	174.98	0.013	3.4
Unidentified	176.77	0.012	3.0
Unidentified	177.43	0.025	6.4
Pivalic Acid	188.93	0.089	Internal Standard

Total Identified Carbon (MeOH + HCO_2^- + CO_3^{2-} + $C_2O_4^{2-}$) = 0.285 mmol
Total Unidentified Carbon (*see italics*) = 0.108 mmol
Total Carbon Present (identified + unidentified) = 0.393 mmol
Expected Carbon = 0.450 mmol

Total Identified / Total Carbon Present = 72.5%
Total Unidentified / Total Carbon Present = 27.5%

Total Carbon / Expected Carbon = 87.3%

Integration of the ^1H NMR spectrum (600 MHz) of the same sample gives the following:

0.080 mmol MeOH (0.0% change from ^{13}C data)
0.078 mmol HCO_2^- (2.5% change from ^{13}C data)

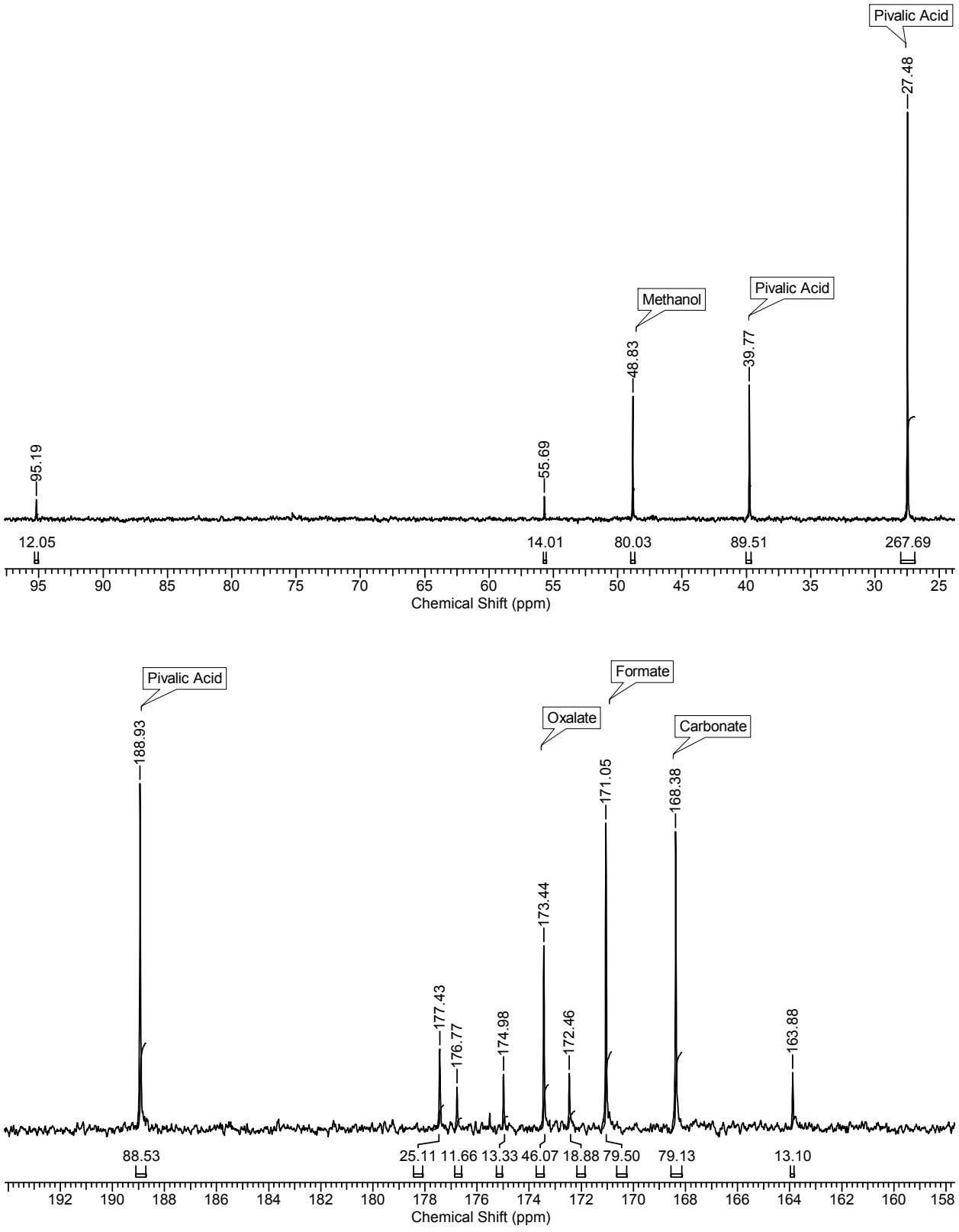

Figure S5 $^{13}C\{^{1}H\}$ spectrum corresponding to the data in Table S5.

Table S6 Quantitative $^{13}C\{^1H\}$ data for the reaction of a CH_2Cl_2-soluble fraction Kraft lignin (**11**) with H_2O_2 in 1 M KOH according to the General Procedure.

Compound	δ_C (ppm)	Amount (mmol)	% Total Carbon Present
Pivalic Acid (3 carbons)	27.47	0.176	Internal Standard
Pivalic Acid	39.77	0.058	Internal Standard
Methanol	48.83	0.081	29.0
Unidentified	55.69	0.004	1.3
Unidentified	95.18	0.006	2.3
Unidentified	163.88	0.003	1.2
Carbonate	168.38	0.082	29.2
Formate	171.05	0.052	18.4
Unidentified	172.46	0.004	1.5
Oxalate (2 carbons)	173.44	0.027	9.8
Unidentified	174.98	0.003	1.2
Unidentified	176.77	0.007	2.5
Unidentified	177.43	0.011	3.8
Pivalic Acid	188.93	0.058	Internal Standard

Total Identified Carbon (MeOH + HCO_2^- + CO_3^{2-} + $C_2O_4^{2-}$) = 0.242 mmol
Total Unidentified Carbon (*see italics*) = 0.038 mmol
Total Carbon Present (identified + unidentified) = 0.280 mmol

Total Identified / Total Carbon Present = 86.4%
Total Unidentified / Total Carbon Present = 13.6%

Integration of the ^1H NMR spectrum (600 MHz) of the same sample gives the following:

0.078 mmol MeOH (3.7% change from ^{13}C data)
0.038 mmol HCO_2^- (26.9% change from ^{13}C data)

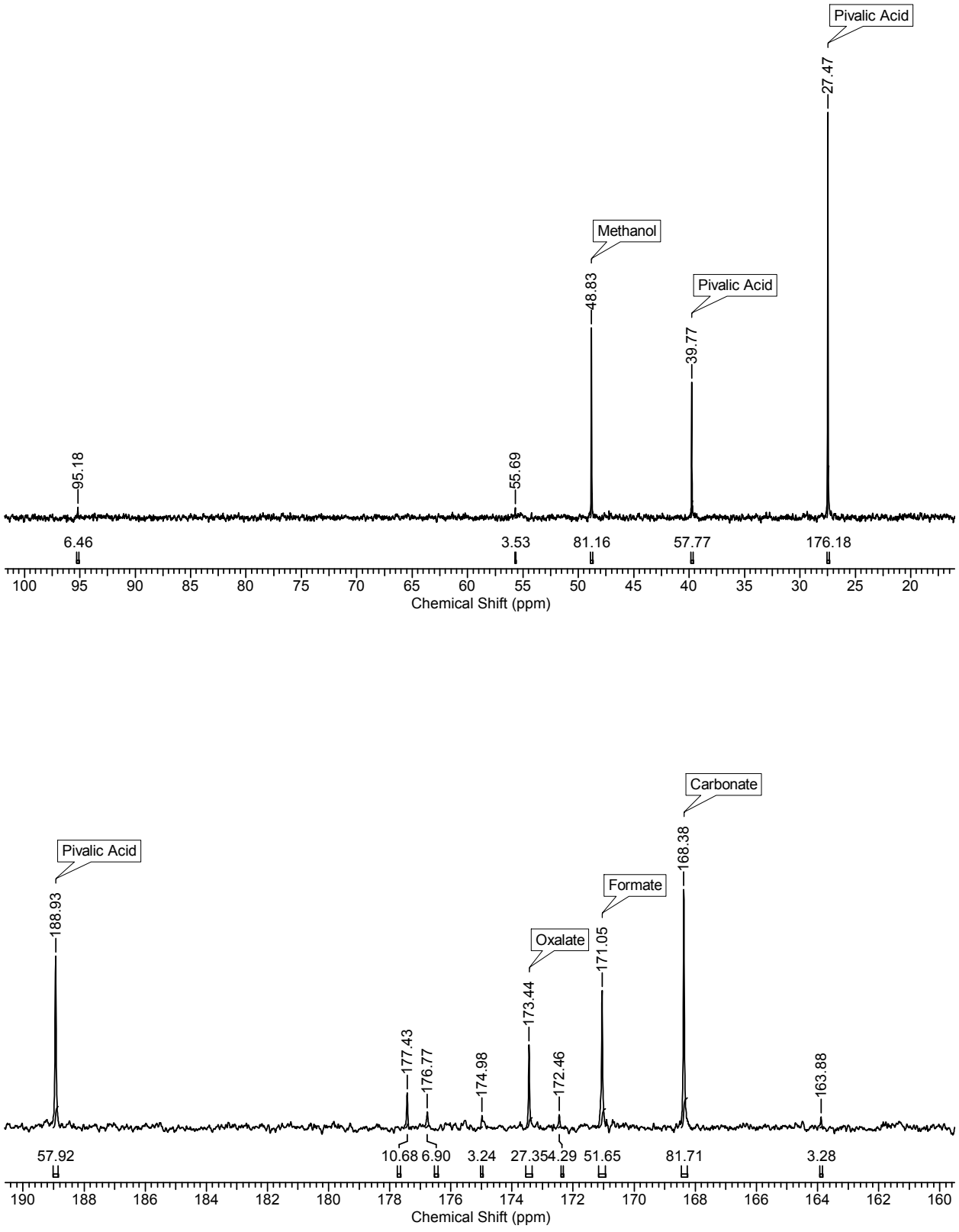

Figure S6 $^{13}C\{^{1}H\}$ spectrum corresponding to the data in Table S6.

Quantitative $^{13}C\{^1H\}$ Integration

The range of total carbon detected by $^{13}C\{^1H\}$ referred to in the main text arises from differences in the integration method of the signals. The spectra were processed using two different software suites (ACD Labs 12.01 and Topspin 2.1) and were integrated by hand and by region definition. Though the values for the larger signals (pivalic acid, methanol, formate, carbonate, oxalate) showed only small variations, the 7 unidentified signals experienced larger deviations due to their size relative to the baseline. The signal-to-noise ratio of 25:1 gives excellent data for the internal standard (± 2%) but is not precise enough to give exact data on the unidentified signals that are just 3 times the baseline height. The values reported in Tables S4, S5, and S6 are integrated by hand using ACD Labs 12.01 and represent the lower threshold of the reported ranges.

Reactivity at Room Temperature

Of note, no substrates signals are present in the quantitative $^{13}C\{^1H\}$ NMR spectra reported herein. This is a result of the r.t. reactivity described in the text. After the 3 h reaction time with H_2O_2 at 60 °C, a ^1H NMR spectrum was taken as outlined in the General Procedure and the substrate consumptions were calculated (94 and 100% for **2** and **3** respectively); consumption of **11** was not calculated due to poor shimming that resulted in overlap between the remaining aromatic signals and the C_6D_6 signal). In the quantitative $^{13}C\{^1H\}$ NMR experiments performed at Simon Fraser University, the samples were allowed to sit at r.t. overnight or even longer depending on availability of the spectrometer. However, before beginning the $^{13}C\{^1H\}$ NMR analysis a ^1H NMR spectrum was taken and these showed no substrate signals, suggesting complete consumption before the quantitative experiments began and thus explaining the lack of corresponding signals in the $^{13}C\{^1H\}$ NMR spectra. Although our studies involving r.t. reactivity of LMCs and lignins are preliminary, the product ratios of MeOH to formate (as determined by ^1H NMR) vary little between reactions at 60 °C and those performed at r.t. Therefore, it is supposed that the values gleaned from the quantitative $^{13}C\{^1H\}$ NMR analysis are accurate as r.t. reactivity accounts for < 10% of the overall substrate consumption.

Decomposition of H_2O_2

In an effort to probe the stoichiometry of reactions, the possibility of determining the amount of H_2O_2 that remained after the 3 h was explored. However, titration of H_2O_2 with standard $KMnO_4$ or iodine solutions requires acidic media whereas the degradation reactions require a basic environment. To this end, 50 μL of 31.5 wt. % H_2O_2 solution was dissolved in 1 mL of 1 M KOH solution and immediately neutralized with 1 M HCl before undergoing titration; such samples had the same [H_2O_2] (within error) as those taken directly from the commercial source. Conversely, H_2O_2 samples that were left in the basic solution for 1 h or shaken vigorously for 5 min had, on average, only ~73% of the value found in untreated samples. Peroxide samples heated at 60 °C for 2 h in the basic solution reveal a dramatic decrease in [H_2O_2], with only ~18% remaining; the findings are consistent with the known H_2O_2 decomposition to O_2 and water at higher pH and/or temperature.[4]

The variable decomposition of the H_2O_2 is considered to be the main source of error (± 15%) in consumption values for the degradation of the LMCs.

References

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