Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

SUPPLEMENTARY INFORMATION

Ozone mediated depolymerization and solvolysis of technical lignins at ambient conditions in ethanol

M.B. Figueirêdo[a], H.J. Heeres[a] and P.J. Deuss*[a]

[a]Department of Chemical Engineering, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, the Netherlands

(*) Corresponding author: p.j.deuss@rug.nl
Tel.: +31 50 3634918

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1. Methods

Mass Balance Calculations. Since the evaluated lignins have very low solubility in ethanol and the solvent participates in the ozonation, the amounts of dissolved lignin and mass incorporation were calculated based on the solids recovered after each reaction (here called insoluble lignin). Hence, these solids were considered unreacted lignin and provided an indication of how much of the initial lignin was solvated during ozonation (*i.e.* dissolved lignin). As an example, calculations with the data obtained from the 20 minutes ozonation experiment with KL are shown below. The initial amount of KL was of 2.02 g, and the amount of solids recovered after ozonation was of 1.46 g. Furthermore, the amount of lignin oil (obtained after removing ethanol from the ozonated solution) was of 1.16 g. From this, an Incorporation ratio (IR) of 2.1 (representing the mass incorporation from ozone and ethanol) can be calculated according to equations S1-S6 as shown below.

$$Dissolved\ lignin\ (g) = Initial\ lignin\ (g) - Insoluble\ lignin\ (g) \tag{Eq. S1}$$

$$Dissolved\ lignin\ (g) = 2.02\ g - 1.46\ g = 0.56\ g \tag{Eq. S1a}$$

$$Dissolved\ lignin\ (wt\%) = \frac{Dissolved\ lignin\ (g)}{Initial\ lignin\ (g)} * 100 \tag{Eq. S2}$$

$$Dissolved\ lignin\ (wt\%) = \frac{0.56\ g}{2.02\ g} * 100 = 28\ wt\% \tag{Eq. S2a}$$

$$Insoluble\ lignin\ (wt\%) = \frac{Insoluble\ lignin\ (g)}{Initial\ lignin\ (g)} * 100 \tag{Eq. S3}$$

$$Insoluble\ lignin\ (wt\%) = \frac{1.46\ g}{2.02\ g} * 100 = 72\ wt\% \tag{Eq. S3a}$$

$$Lignin\ oil\ (wt\%) = \frac{Lignin\ oil\ (g)}{Initial\ lignin\ (g)} * 100 \tag{Eq. S4}$$

$$Lignin\ oil\ (wt\%) = \frac{1.16\ g}{2.02\ g} * 100 = 57\ wt\% \tag{Eq. S4a}$$

$$Mass\ incorporation\ (g) = Lignin\ oil\ (g) - \ Dissolved\ lignin\ (g) \tag{Eq. S5}$$

$$Mass\ incorporation = 1.16\ g - \ 0.56\ g = 0.6\ g \tag{Eq. S5a}$$

$$Incorporation\ ratio\ = \frac{Lignin\ oil\ (g)}{Dissolved\ lignin\ (g)} \tag{Eq. S6}$$

$$Incorporation\ ratio\ = \frac{1.16\ g}{0.56\ g} = 2.1 \tag{Eq. S6a}$$

HSQC NMR. HSQC NMR spectra were integrated with respect to the chemical groups related to each specific region in the spectrum (see Figure S1 for an example). Spectra were processed and analyzed using MestReNova software. Prior to integration, the solvent (*i.e.* DMSO-d_6) was referenced and a manual phase correction was applied.

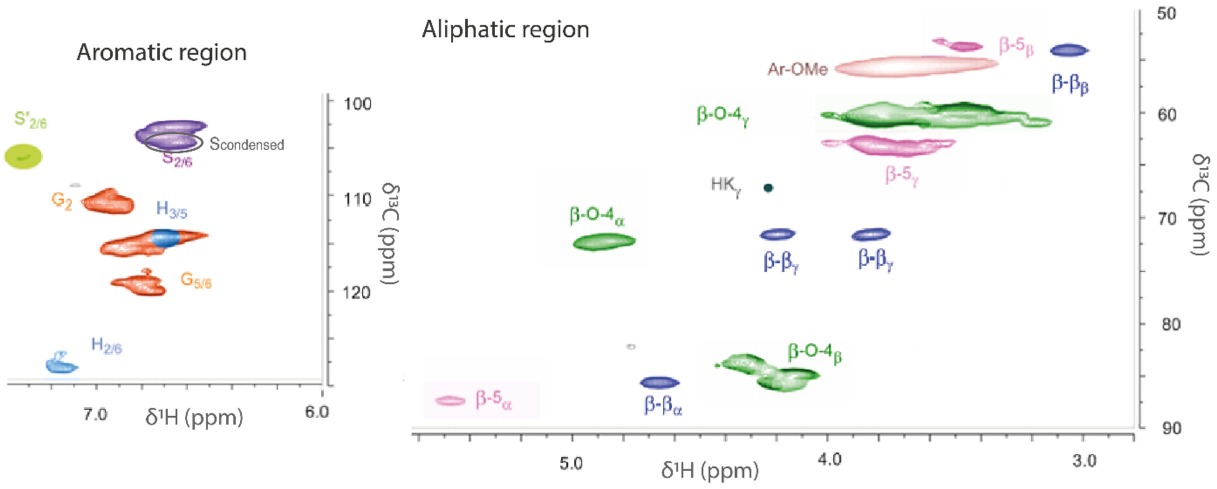

Figure S1. Example of the aromatic and aliphatic lignin regions in a HSQC spectrum. Adapted from[1]

The following calculations were used to determinate the G/S/H ratios in the lignins and the proportion of the different interunit linkages. The total group of aromatics is calculated with Equation S7. The symbols used refer to the integration of the specific aromatic areas as showed in Figure S1.

$$Total\ aromatic = \left(\frac{(S_{2/6} + S'_{2/6})}{2}\right) + \left(\frac{G_2 + G_5 + G_6 - H_{2/6}}{3}\right) + \left(\frac{H_{2/6}}{2}\right) \qquad \text{(Eq. S7)}$$

The aromatic ratios are determined with Equations S8-S10.

$$Ratio\ S = \frac{\left(\frac{(S_{2/6} + S'_{2/6})}{2}\right)}{Total\ aromatic} * 100\% \qquad \text{(Eq. S8)}$$

$$Ratio\ G = \frac{\left(\frac{G_2 + G_5 + G_6 - H_{2/6}}{3}\right)}{Total\ aromatic} * 100\% \qquad \text{(Eq. S9)}$$

$$Ratio\ H = \frac{\left(\frac{H_{2/6}}{2}\right)}{Total\ aromatic} * 100\% \qquad \text{(Eq. S10)}$$

The number of linkages are determined with Equations S11-S13.

$$\beta - O - 4\ linkages\ = \frac{(\beta - O - 4_{\alpha})}{Total\ aromatic} * 100\% \qquad \text{(Eq. S11)}$$

$$\beta - 5\ linkages\ = \frac{(\beta - 5_{\alpha}\ )}{Total\ aromatic} * 100\% \qquad \text{(Eq. S12)}$$

$$\beta - \beta\ linkages\ = \frac{(\beta - \beta_{\alpha})}{Total\ aromatic} * 100\% \qquad \text{(Eq. S13)}$$

The percentage of $S_{condensed}$ units is determined with Equation S14.

$$S_{condensed} = \frac{S_{condensed}}{Total\ aromatic} * 100\% \qquad \text{(Eq. S14)}$$

^{13}C-NMR. ^{13}C-NMR spectra were acquired on a Bruker NMR spectrometer (600 MHz) using a 90° pulse and an inverse-gated decoupling sequence with relaxation delay of 5 seconds, sweep width of 220 ppm and 2048 scans, with a total acquisition time of 3.5 h and TMS as reference. Spectra were processed and analyzed using MestReNova software. Prior to integration, the solvent (*i.e.* DMSO-d_6) was referenced and an exponential apodization (3 Hz) and multipoint baseline correction were applied. When needed, a manual phase correction was performed as well. The relative areas were obtained by integrating spectral regions based on previous literature[2,3] (see Table S1).

Table S1. ^{13}C-NMR integration areas

Group	δ range (ppm)
Aliphatics	0-55
Methoxy groups	55-57
Aliphatic C-O	57-95
Aromatic C-H	95-122
Aromatic C-C	122-139
Aromatic C-O	139-165
Carbonyl groups	165-190

^{31}P-NMR. ^{31}P-NMR analyses followed a procedure described elsewhere[4] and used cyclohexanol as internal standard and $CDCl_3$ as solvent. ^{31}P-NMR spectra were acquired on a Bruker NMR spectrometer (600 MHz) at 293 K using a standard 90° pulse, 256 scans and 5 s of relaxation delay. Spectra were processed and analyzed using MestReNova software. Prior to integration, an exponential apodization (3 Hz) and multipoint baseline correction were applied. When needed, a manual phase correction was performed as well. Chemical shifts were referenced from the signal arising from the reaction product between residual water and 2-chloro-4,4,6,6-tetramethyl-1,3,2-diaxophospholane at 132.2 ppm. The signal related to the internal standard (cyclohexanol) has a chemical shift of 145.15 ppm. The content of hydroxyl groups was obtained by integrating spectral regions based on previous literature[2,4,5] (see Table S2).

Table S2. ^{31}P-NMR integration areas.

Group	δ range (ppm)
Aliphatic OH	145.5 - 152
C_5 substituted and/or condensed phenolic units	140.2 – 144.8
Syringyl phenolic units	142.3 – 143.2
Guaiacyl phenolic units	139 – 140.2
Catechol phenolic units	138.2 – 139
p-Hydroxyphenyl units	137.3 – 138.2
Carboxylic acids	133.6 – 137.3

2. Supplementary Results

Figure S2. Example of a lignin oil (after ethanol removal, *in vacuo*)

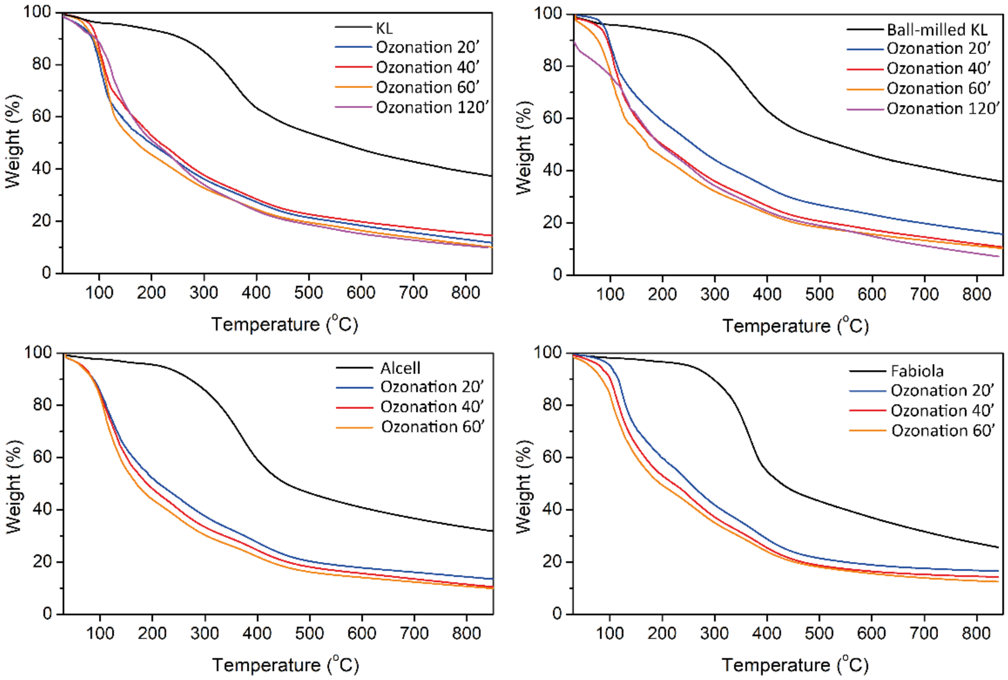

Figure S3. TGA curves of the lignin feeds and their lignin oils after ozonation

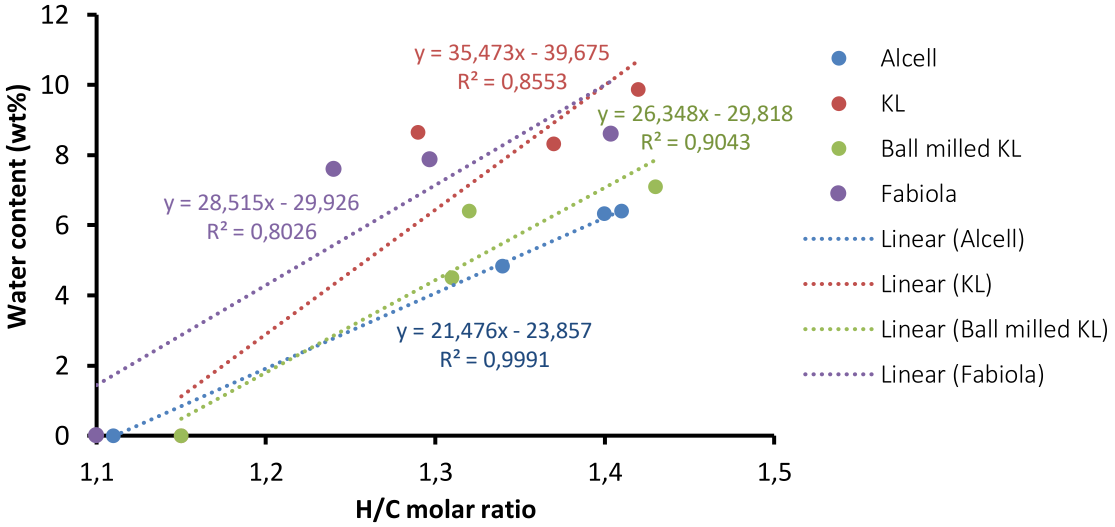

Figure S4. Correlations between H/C ratios and water content of the lignin oils

Table S3. (Di)carboxylic acids identified in the lignin oils by HPLC

Sample	Oxalic (wt%)	Maleic (wt%)	Malonic (wt%)	Formic (wt%)	Acetic (wt%)	Adipic (wt%)	Propanoic (wt%)
KL 20’	2.6	0.6	0.7	5.4	8.4	0.0	0.0
KL 40’	5.1	0.8	1.3	7.0	10.3	1.2	0.8
KL 60’	8.9	1.3	1.7	10.9	13.2	1.0	1.2

KL 120’	6.8	1.8	2.5	9.9	14.2	2.1	0.0
Ball-milled 20’	3.6	0.6	1.2	6.5	5.4	0.9	0.5
Ball-milled 40’	6.3	0.7	1.2	7.5	8.0	1.1	0.6
Ball-milled 60’	9.7	1.5	1.8	10.8	13.2	1.0	1.0
Ball-milled 120’	3.0	0.7	1.2	7.4	9.6	1.6	0.9
Alcell 20’	5.1	0.3	0.6	6.2	6.3	0.8	0.5
Alcell 40’	8.3	0.6	1.2	9.0	9.8	1.2	1.0
Alcell 60’	8.9	0.9	1.2	8.8	10.9	1.1	1.0
Fabiola 20’	4.2	0.5	1.1	5.9	4.9	2.3	0.6
Fabiola 40’	4.1	0.6	1.0	6.0	5.3	1.5	4.4
Fabiola 60’	3.2	0.4	0.9	5.5	4.3	1.1	0.6

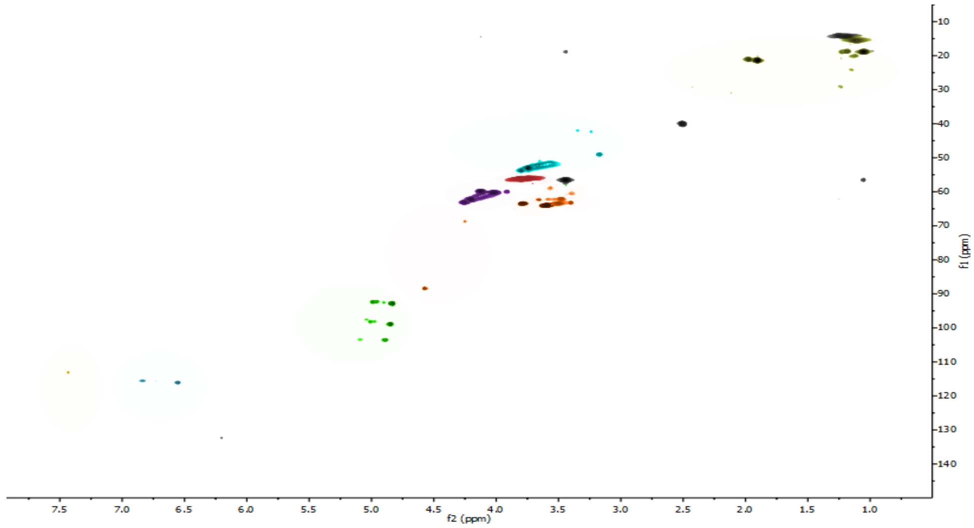

Figure S5. HSQC NMR spectrum of the lignin oil from ball-milled KL (1h ozonation, DMSO-d$_6$)

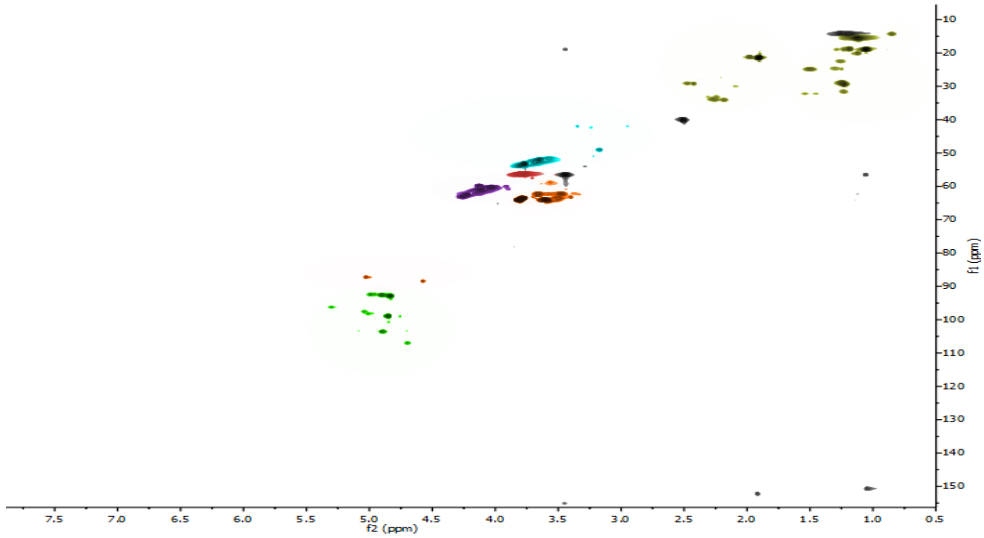

Figure S6. HSQC NMR spectrum of the lignin oil from Alcell lignin (1h ozonation, DMSO-d$_6$)

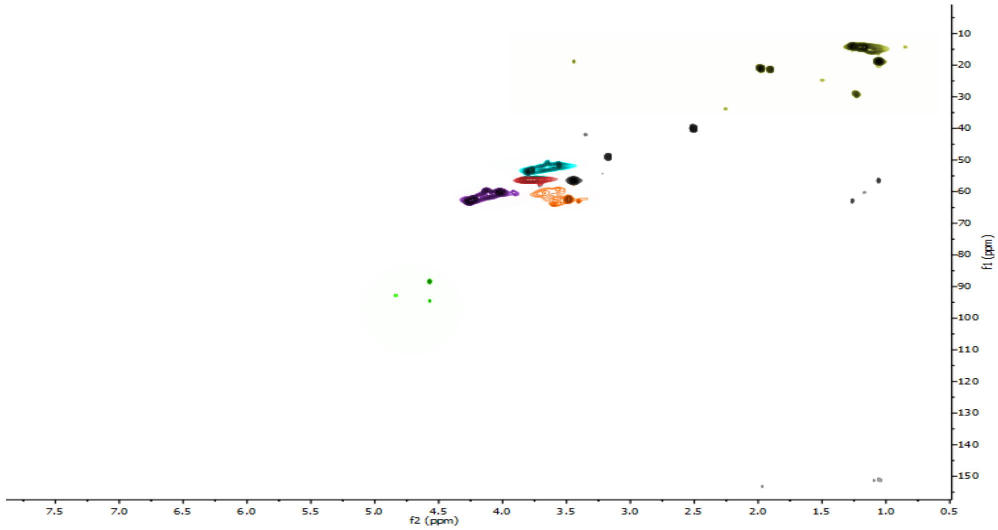

Figure S7. HSQC NMR spectrum of the lignin oil from Fabiola lignin (1h ozonation, DMSO-d_6)

Blank Ozonation Experiments with Ethanol. For the blank experiments, 45 g of ethanol were ozonated for 20, 40 and 60 minutes under room conditions. Ozone (diluted in oxygen) was bubbled in the mixture through a pipette. A flow of 4 L/min of oxygen was fed into the ozone generator (model LAB2B from Ozonia), producing 9.5 g of O_3/h. Stirring was set to 1500 RPM. The product mixtures were diluted with water (15 wt%) and analyzed by HPLC. In addition, the product mixture of the 20 minutes' reaction was directly analyzed by GC-MS. A sample was also diluted in DMSO-d_6 (50 wt%) and analyzed by ^{13}C-NMR and HSQC NMR.

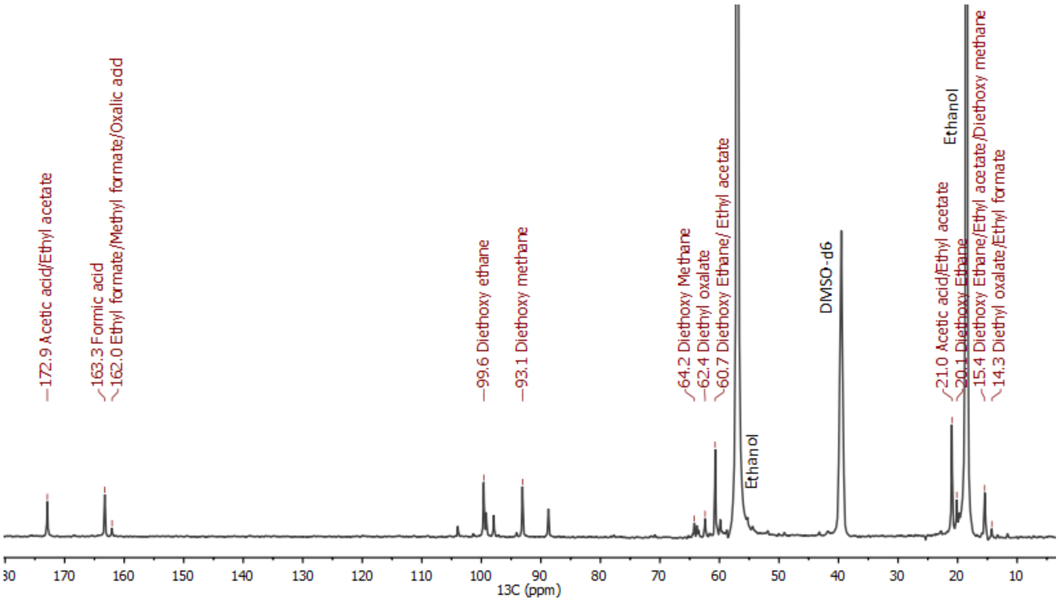

Figure S8. ^{13}C-NMR spectrum of the blank ozonation experiment with ethanol (DMSO-d_6)

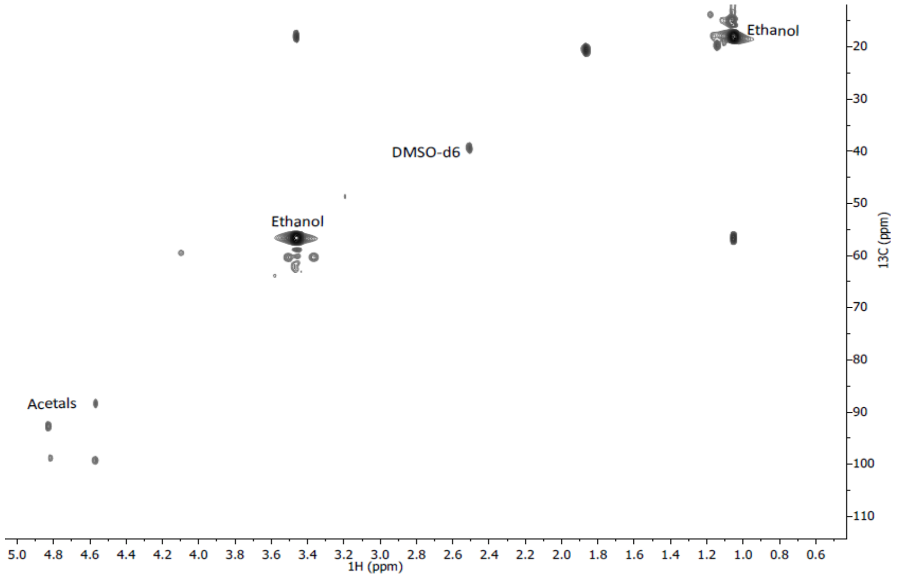

Figure S9. HSQC NMR spectrum of the blank ozonation experiment with ethanol (DMSO-d_6)

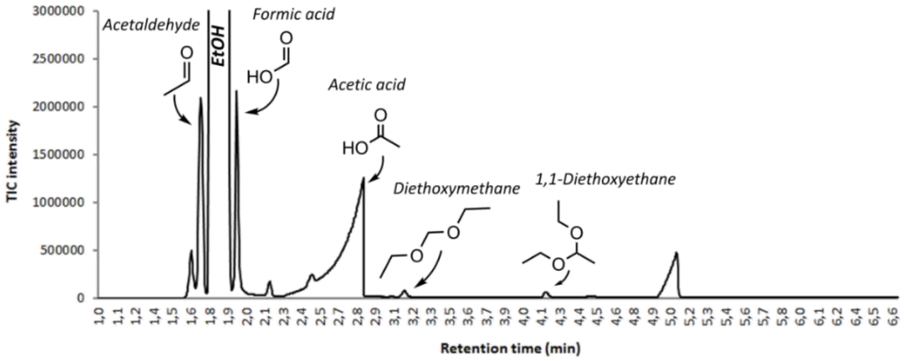

Figure S10. GC-MS chromatogram of the blank ozonation experiment with ethanol

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