

Analysis of the Electrochemical Depolymerization of Lignin using Chemometrics



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INTRODUCTION

- The economics of electrochemical depolymerization of lignin are most likely unfavorable without some control over the oxidation mechanism because depolymerization generates many unwanted compounds.
- It is important to understand whether $\cdot\text{OH}$ radicals mediate the oxidation process instead of a direct electrochemical route to depolymerization.
- Control over the depolymerization process can lead to high-yield chemical products like aromatic phenols and carboxylic acids.
- The overall goal is to develop a sustainable, economically viable, and cost-effective method for utilizing lignin by-products.

EXPERIMENTS

1. Electrochemical Oxidation of Lignin Compounds

- The electrochemical oxidation of lignin was done using an electrolytic cell in which Ni-Co served as the working electrode, Pt foil was used as the counter electrode, and Hg/HgO was the reference electrode.
- Dimethyl sulfoxide (DMSO), a radical scavenger, was added to half of the samples, and the products were compared to determine whether a free radical mechanism was involved.

2. Detection

- Using a random block design, each lignin sample were measured five times over the course of five days.
- The lignin was sampled using headspace solid phase micro-extraction (SPME).
- A single quadrupole gas chromatograph-mass spectrometer (GCMS-QP2010 SE) was used to analyze the lignin sample.
- GC-MS Parameters
 - ✓ Total run time: 15 min
 - ✓ Injection temperature: 250 °C
 - ✓ Carrier gas: Helium
 - ✓ Split: 10:1
 - ✓ Mass range: m/z 50-500

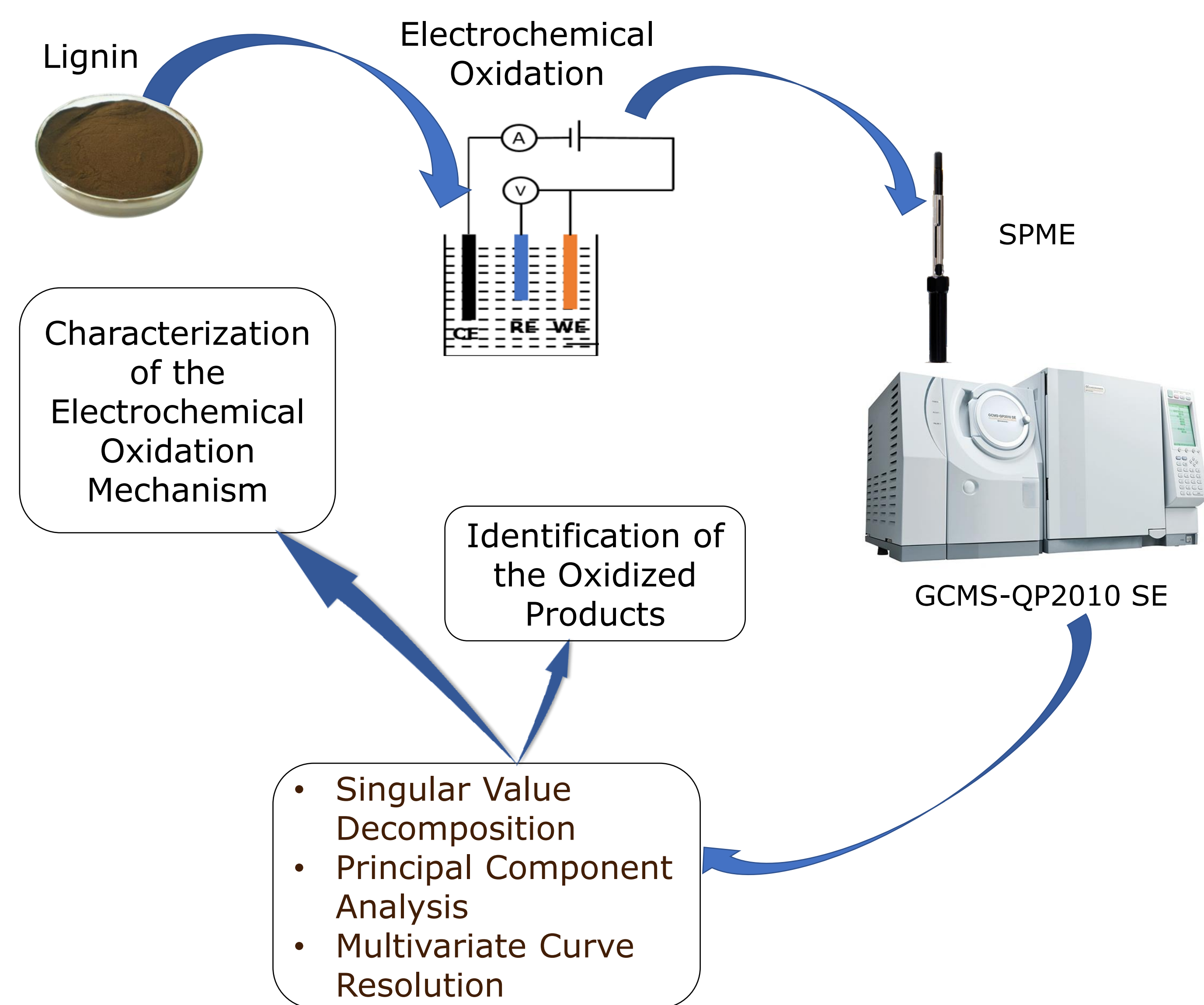
Table 1. GC Temperature Program

Rate ($^{\circ}\text{C min}^{-1}$)	Temperature ($^{\circ}\text{C}$)	Time (min)
-	50	2
20	250	3

3. Analysis

- The spectra obtained from GC-MS were analyzed using chemometric tools: singular value decomposition (SVD), principal component analysis (PCA), and multivariate curve resolution (MCR).

METHODOLOGY



RESULTS

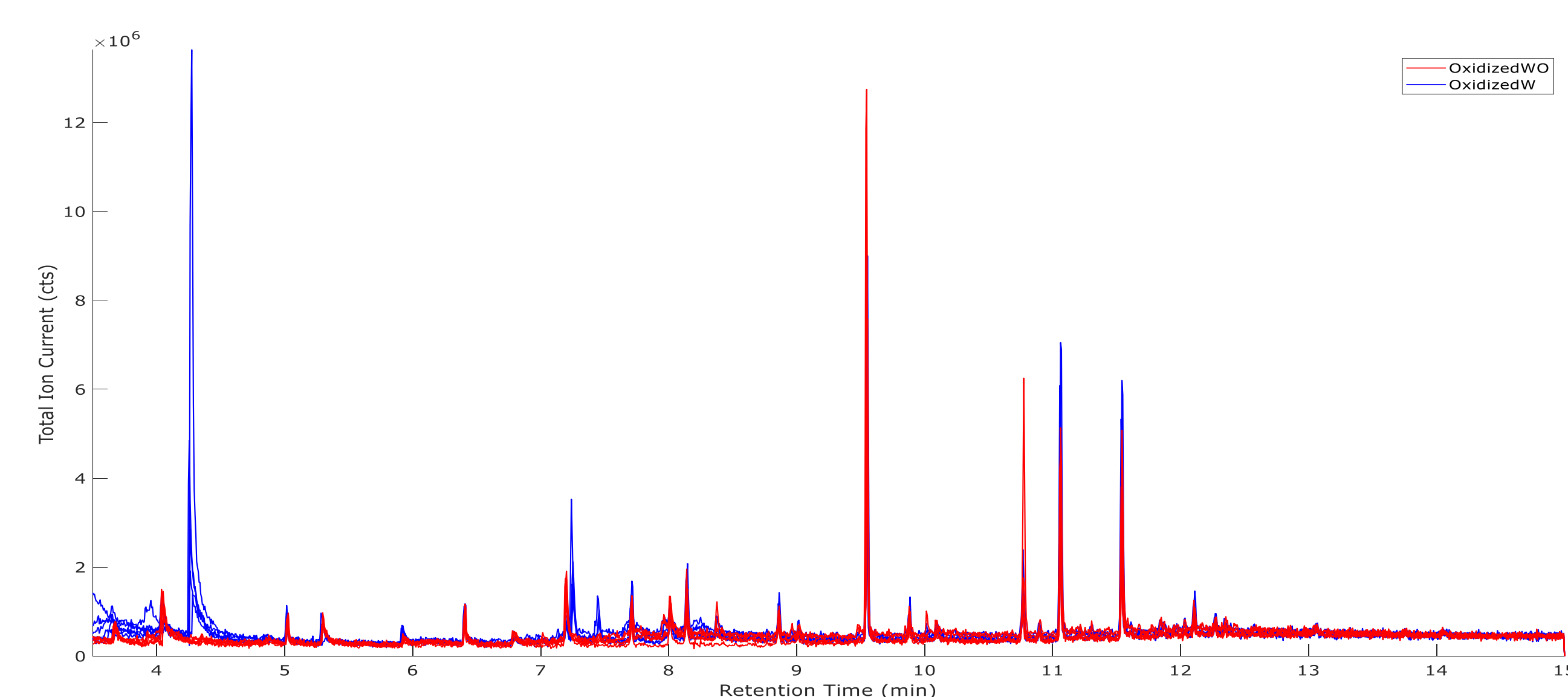


Figure 1. Comparison of TIC (total ion current) of oxidized lignin samples (at 1.0 V vs. Hg/HgO) with (blue) and without (red) DMSO.

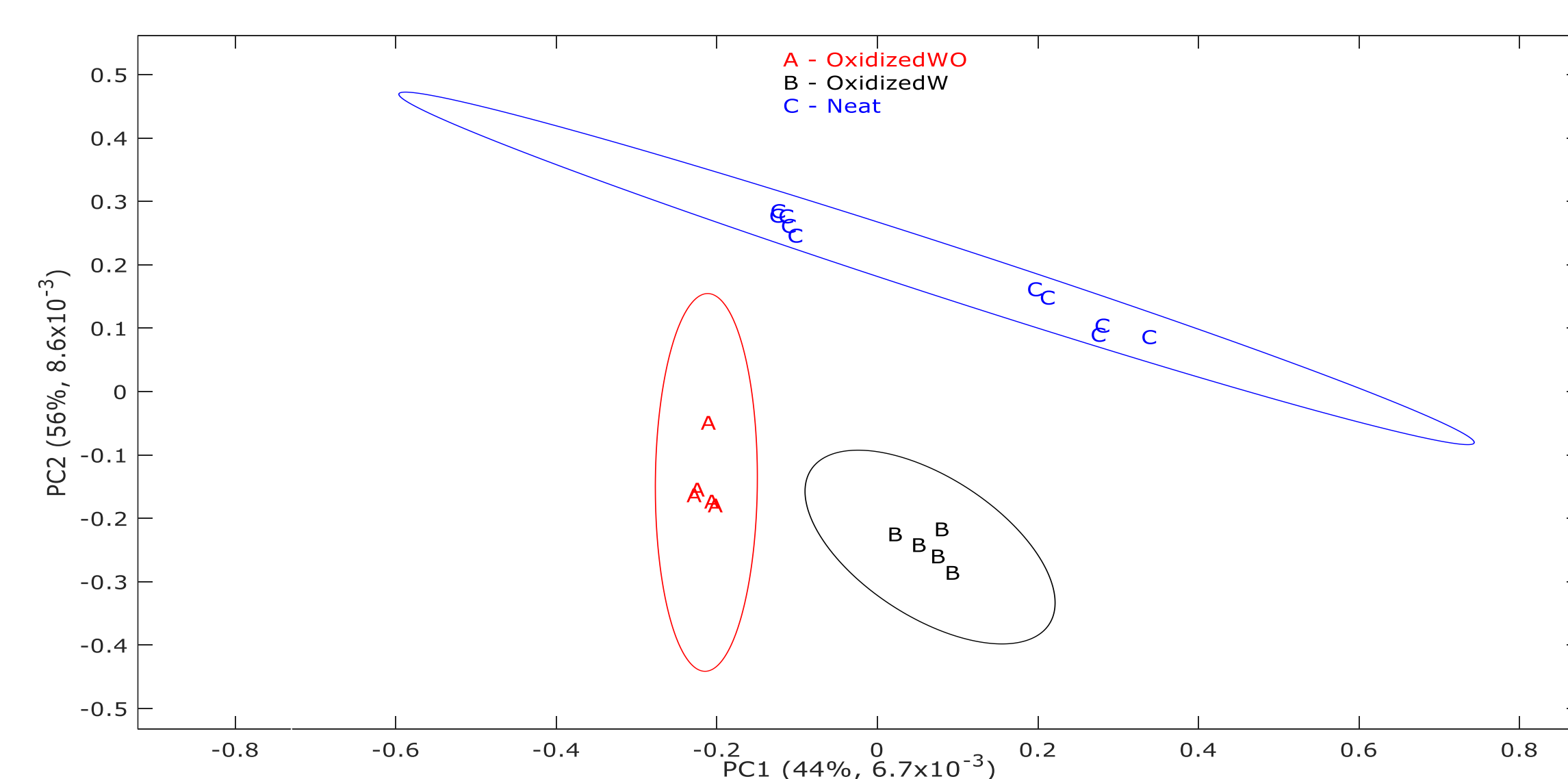


Figure 2. Factor analysis of the oxidized lignin samples (at 1.0 V vs. Hg/HgO) with the neat samples.

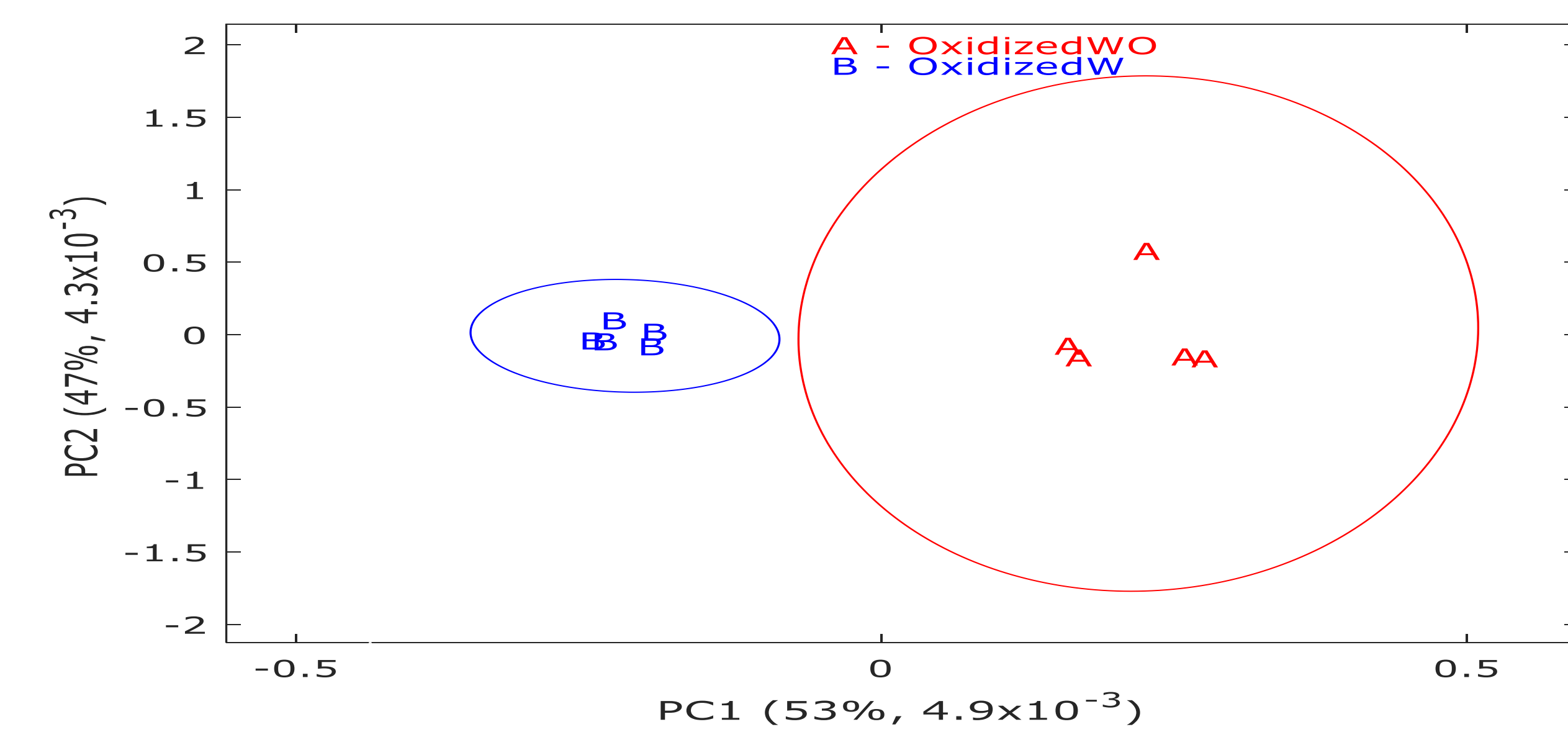


Figure 3. Factor analysis of the oxidized lignin samples (at 1.0 V vs. Hg/HgO) with (blue) and without (red) DMSO.

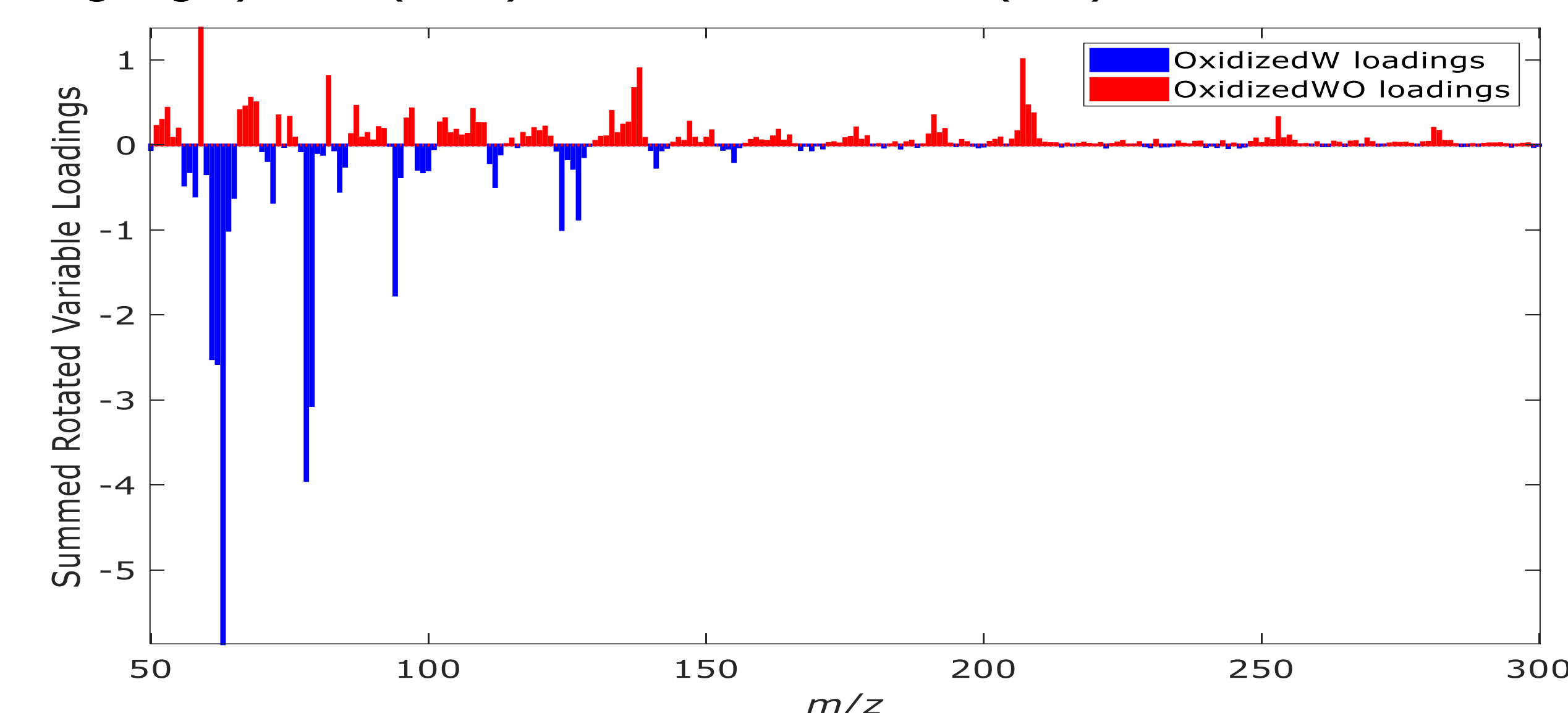


Figure 4. Mass spectral loadings to visualize the main difference between lignin samples oxidized (at 1.0 V vs. Hg/HgO) with (blue) and without (red) DMSO.

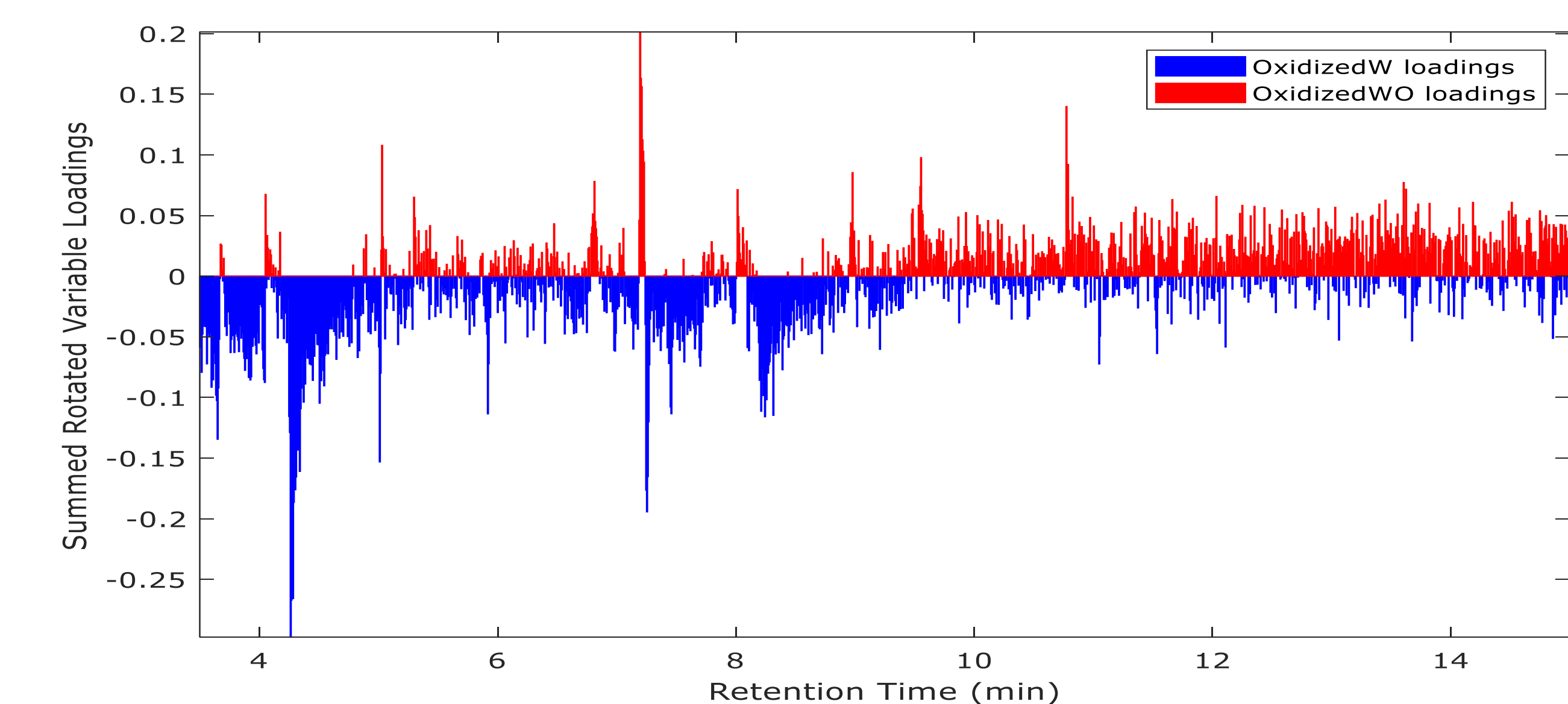


Figure 5. Retention time loadings to visualize the main difference between lignin samples oxidized (at 1.0 V vs. Hg/HgO) with (blue) and without (red) DMSO.

Table 2. Oxidation Products from Oxidized Lignin Samples (at 1.0 V vs. Hg/HgO) with DMSO.

Retention Time (min)	QRM (%)	Similarity	Compound Name
5.29	98.65	0.90	2,3-Dimethylpentane
8.01	5.36	1.00	Propanoic acid, 2-methyl-2,2-dimethyl-1-(2-hydroxy-1-methylethyl)-, propyl ester
8.14	100.00	0.96	Butanoic acid, 3-hydroxy-, 2,2-dimethylhexyl ester
8.38	48.20	1.00	2,4,7,9-Tetramethyl-5-decyn-4,7-diol
9.02	12.18	0.57	Phenol, 2,6-bis(1,1-dimethylethyl)-
9.54	31.46	0.98	Furan, 2-butyltetrahydro-
10.78	24.04	0.86	Isopropyl myristate
11.06	93.94	0.88	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester
11.54	96.01	1.00	1,2-Benzenedicarboxylic acid, butyl 2-ethylhexyl ester

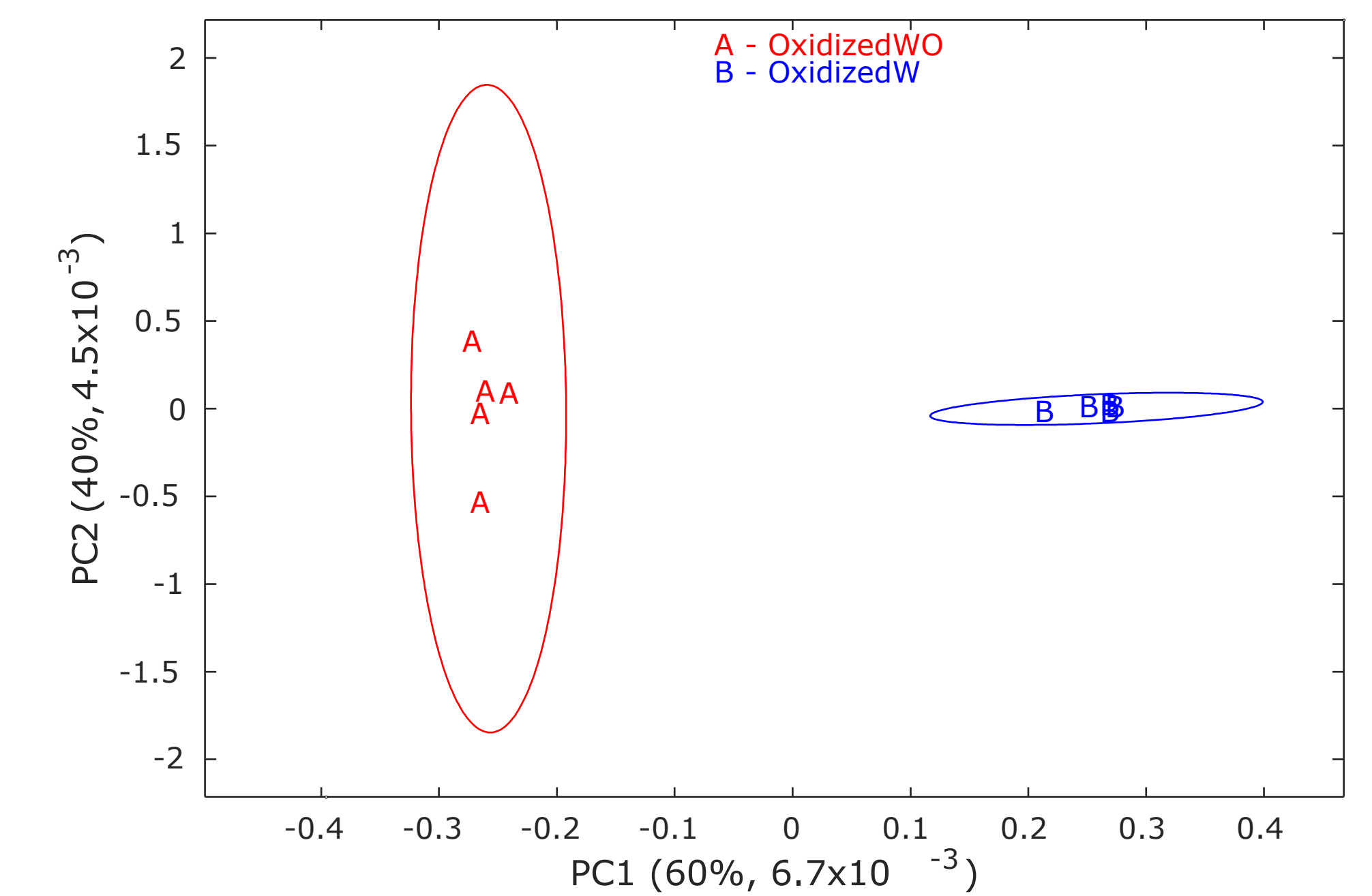


Figure 6. Factor analysis of the oxidized lignin samples (at 0.8 V vs. Hg/HgO) with (blue) and without (red) DMSO.

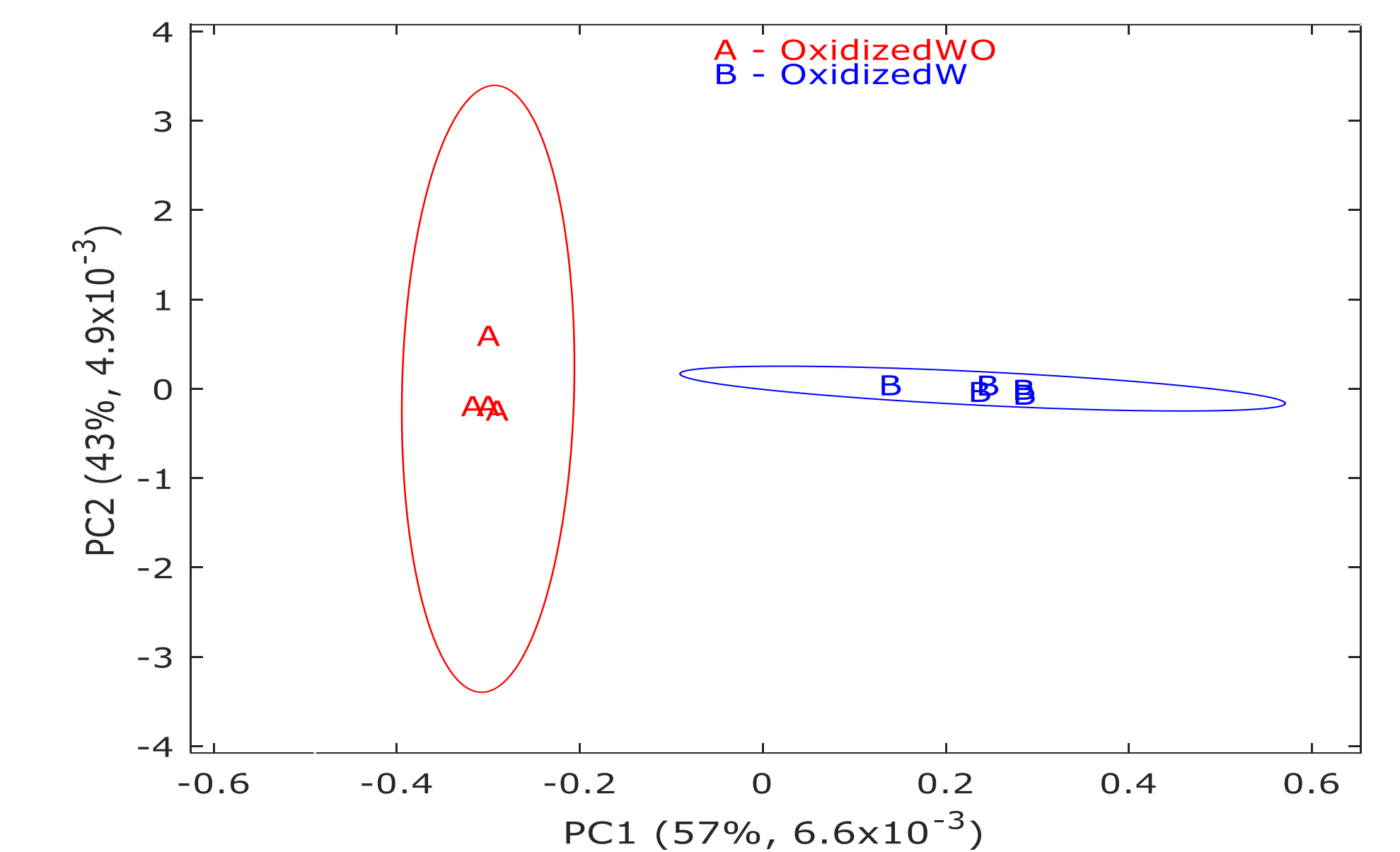


Figure 7. Factor analysis of the oxidized lignin samples (at 0.6 V vs. Hg/HgO) with (blue) and without (red) DMSO.

CONCLUSION

- Significant differences were observed between oxidized lignin samples with and without a radical scavenger (DMSO), indicating the involvement of the $\cdot\text{OH}$ radical in the electrochemical depolymerization of lignin.
- Oxidation of lignin without a radical scavenger resulted in oxidation products over a wide range of mass-to-charge ratios, indicating the electrochemical oxidation of lignin is driven by $\cdot\text{OH}$ radical attack.
- In the presence of DMSO, oxidation products within a narrow range of mass-to-charge ratio were observed indicating formation of lower molecular weight compound. The mechanism is driven by direct electrochemical oxidation.
- Both direct electrochemical oxidation at the electrode surface and $\cdot\text{OH}$ radical attack are involved in the depolymerization of lignin.

ACKNOWLEDGEMENT

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