Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Radicals from the Gas-Phase Pyrolysis of Lignin Model Compounds.

p-Coumaryl Alcohol

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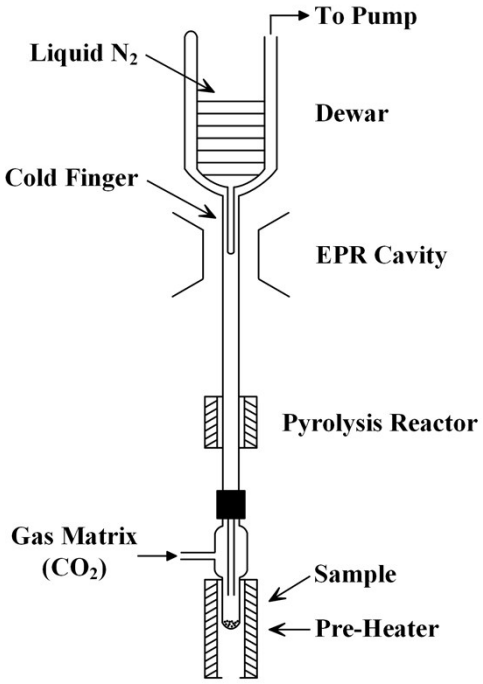

Figure S1. The system for gas-phase pyrolysis of *p*-CMA interfaced with LTMI-EPR

CPD radical

CPD radical has been identified previously from high temperature (>700 °C) pyrolysis of HQ, CT and phenol in a number of works [1-4] as well as recently from pyrolysis of diphenyl ether [5]. Regularly the CPD forms from the decomposition of phenoxyl radical by expulsion of carbon monoxide. It is important to note that the *p*-CMA contains the hydroxylphenyl moiety. Therefore, CPD may be formed during the high temperature gas-phase pyrolysis of *p*-CMA as it was predicted in our early DFT calculations. [6] Fig. S2 shows the comparison of EPR spectrum difference obtained during the annealing process of trapped radicals from gas-phase pyrolysis of *p*-CMA at 1000 °C and the spectrum of a reference CPD radical from the pyrolysis of η^5-C_2H_5-$Mn(CO)_3$ at 250 °C.[2] Note the characteristic peak at g = 1.9932 denoted by asterisk in Figure S2.

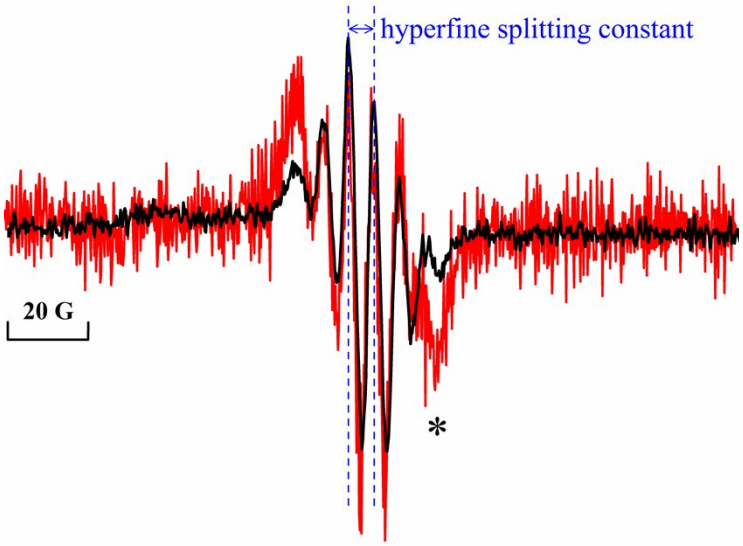

Figure S2. Comparison of EPR spectrum difference of radicals (red) from *p*-CMA pyrolysis at 1000 °C and a reference CPD radical (black) from our earlier data. [2]

Although the signal intensity of the resultant spectrum difference is less than 5% of the original one, it is similar to the spectrum that is characteristic of CPD radical, i.e., consisting of 6 lines, hyperfine splitting constant ~ 6.0 G and ΔHp-p ~ 3.0 G [2].

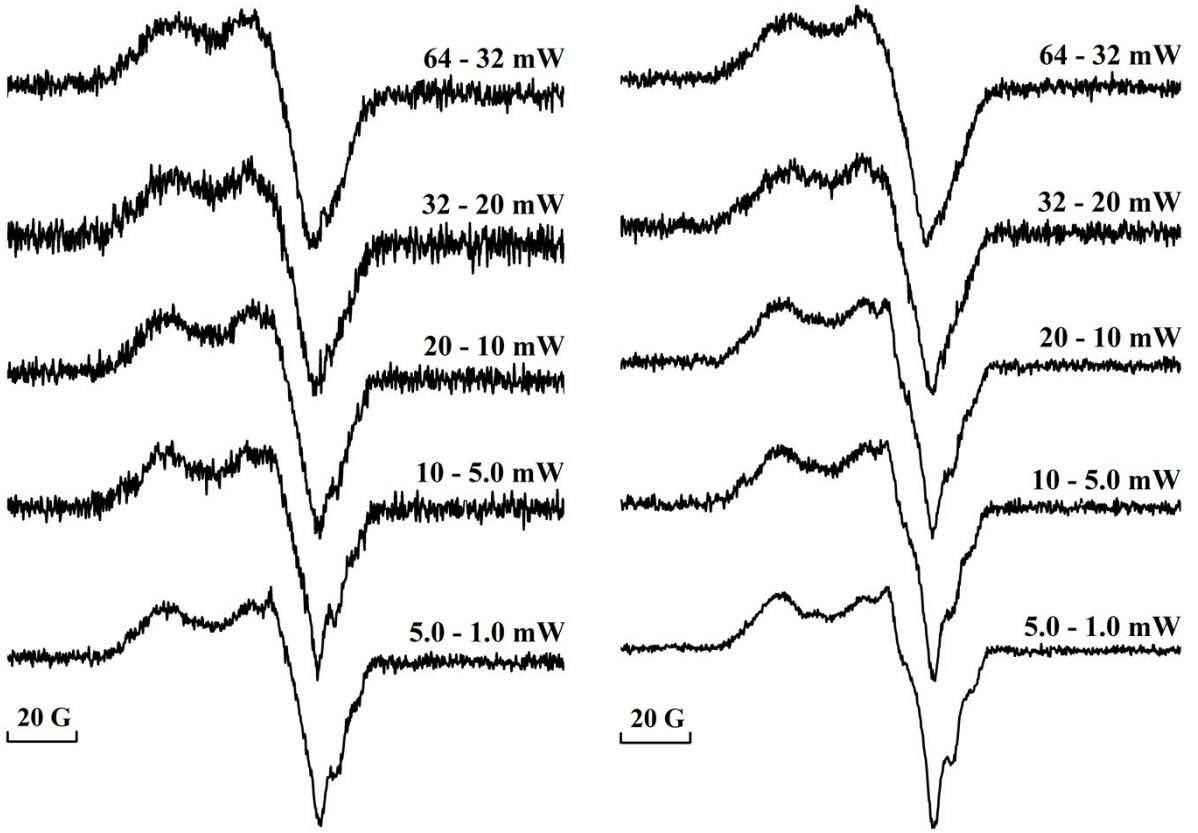

Figure S3. Radicals from pyrolysis of *p*-CMA at 850 °C (left) and 1000 °C (right): EPR spectra difference registered at various microwave power

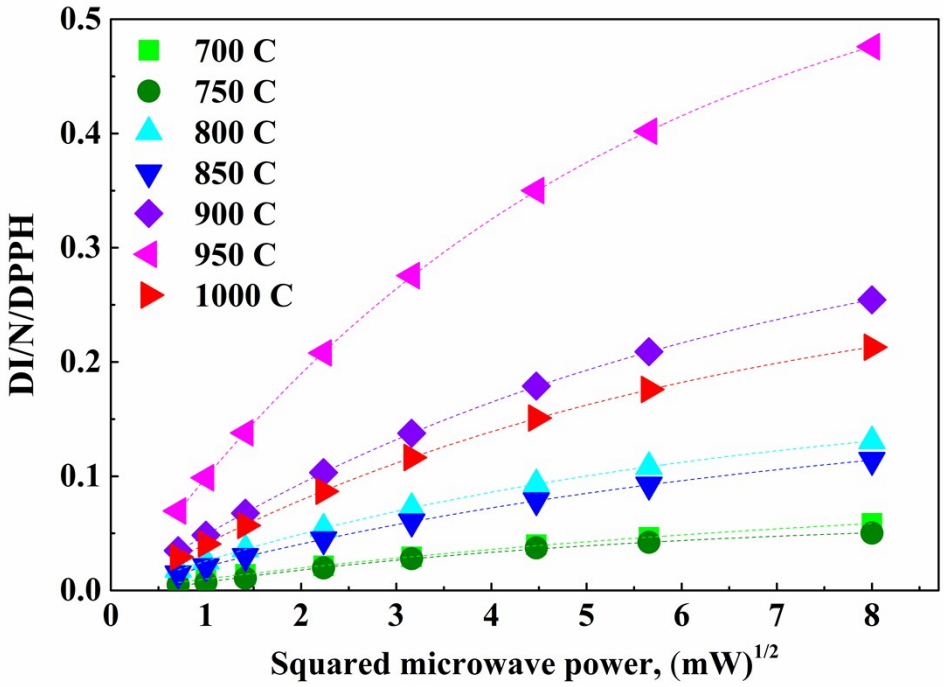

Figure S4. Microwave power dependence of the shoulder of EPR spectra from *p*-CMA pyrolysis

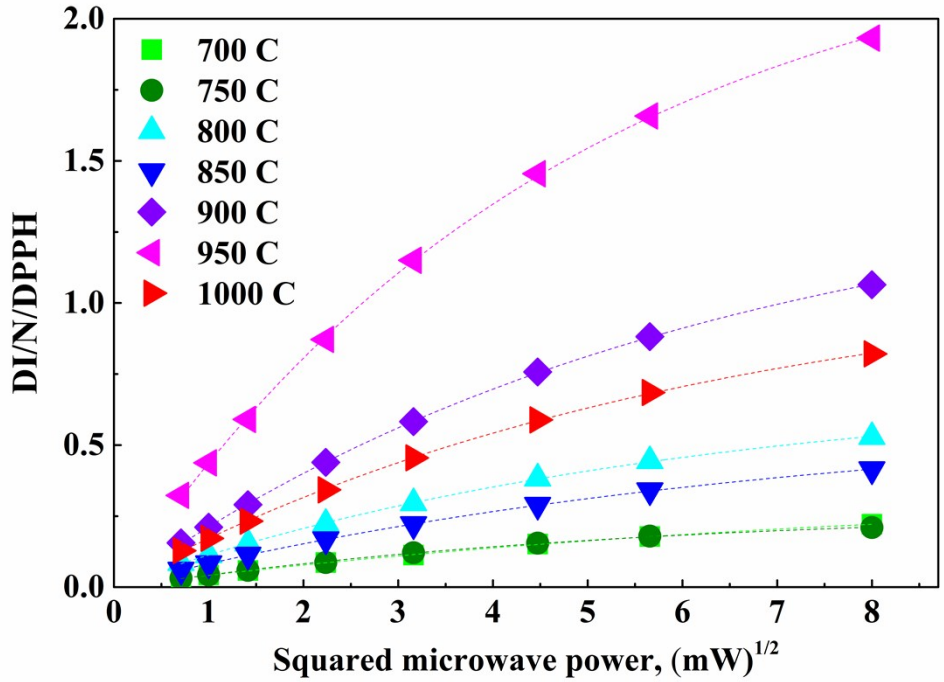

Figure S5. Microwave power dependence of the central line of EPR spectra from *p*-CMA pyrolysis

References

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