

EPFRs character change and ability to induce OH formation under influence of light and water were studied to simulate the environmental fate of EPFRs in this research. EPFRs were characterized fully by many instrumental or fitting methods. The results are valuable. In general, after minor revision, the manuscript can be considered for publication on EGU sphere.

1. Have you verified that materials you used could not interfere the results during the experiment? Transition metals were reported to influence formation and stabilization of EPFRs. The disposable aluminum baking dish and aluminum foil used in this research might have influences. Please clarify that.

Response:

The aluminum baking dish was not in contact with the soot until after it had cooled, long after the formation period, so there is not likely to be an impact from it on the formation of combustion derived EPFRs.

Additionally, while we agree that there is a transition metal-mediated pathway toward formation of EPFR, there is also a pathway which involves the growth of organic matrices which stabilize the radicals formed within (Liao et al., 2014). Because of the fuel-source and controlled environment, the second pathway is governing here.

Lines 52-54 has been modified as follows:

*“The soot was collected from the funnel into a disposable aluminum baking dish (Reynolds KITCHENS® mini loaf pan) as soon as it was cool ~~enough to handle~~. The soot was transferred to the aluminum baking dishes only after it was fully cooled to prevent any interference from the foil on the EPFR structure.”*

2. Section 2.2, you mentioned there was a storage period of the EPFR samples. Considering the inevitable decay and high reactivity of free electron (even though in EPFRs), please provide the storage time of each sample and try to give evidence for not change of EPFRs during the storage.

Response:

EPFR samples were stored in a standard freezer from 2 to 7 days. EPR spectra are not statistically different for any of the samples, indicating that the aging of the EPFRs in the soot while under storage was insignificant. Additionally, we have a previous publication that shows very little change in any EPFR parameters of soot generated in the same manner after 30 days storage at room temperature (Runberg et al., 2020).

Lines 70-71 have been modified as follows:

*“All samples were stored in a freezer when not being analyzed, with storage times ranging from two to seven days (**Error! Reference source not found.**)”*

Additionally, Table A1 has been updated to include the storage times for each sample.

3. Line 134, though the g value in samples A-G showed no obvious change, it still could not conclude whether there was no radical type change. There was no hyperfine splitting information in the EPR spectra (Figure A1), making it difficult to deduce the structure of EPFRs. In addition, except for the influence of temperature, there were probably more than one kind of radical in each of the samples to give a single, broad peak. The sentence “Changes in g-factor indicate a change in radical type, which was not observed in this study.” was suggested to be modified.

Response:

We thank the Reviewer for this insightful comment. The composition of persistent radicals found in soot is a complex matrix of carbon and oxygen centered radicals. The EPR signal is, as the reviewer suggests, a superposition of the signals from all radical types within this matrix. This results in a signal with little to no hyperfine splitting.

Lines 136-139 have been modified as follows:

*“Because of the lack of hyperfine splitting in the EPR signal, it can be deduced that the soot is comprised of a large number of organic radicals which cannot be uniquely defined. Changes in g-factor indicate a change in radical type, for example, a shift from predominantly carbon-centered to predominantly oxygen-centered radicals, which was not observed in this study.”*

4. Line 145, please add discussion about possible composition change of samples based on the different  $\Delta B_{p-p}$  data.

Response:

The small decrease in  $\Delta B_{p-p}$  observed between dry and wetted soot samples is likely an artifact of the increase in Gaussian composition of the signal. Gaussian curves have a narrower profile than do Lorentzian curves with the same intensity (Sorin and Vlasova, 1973).

To clarify this to the reader, Lines 155-157 have been modified as follows:

*“This decrease in  $\Delta B_{p-p}$  is likely an artifact of the increase in Gaussian character of the lineshape for samples that had been submerged and agitated in water. This is discussed further in the next section.”*

5. Could you give possible EPFR structures based on the characterization data? And if possible, try to give the formation mechanism.

Response:

We thank the Reviewer for this suggestion. As there are many structures of EPFRs in soot, the mechanisms of EPFR formation are outside the scope of this study. More controlled

experiments are required to discern mechanisms. We have a parallel manuscript in review in the Journal of Physical Chemistry that further explores a more detailed formation mechanism. The focus here is the impact of environmental factors on changes to EPFR after formation occurs.