

Interactive comment on “Characterization of aerosol photooxidation flow reactors: heterogeneous oxidation, secondary organic aerosol formation and cloud condensation nuclei activity measurements” by A. T. Lambe et al.

Anonymous Referee #2

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General Comments

The authors describe results of a comparison between the performance of two flow tube reactors used to form SOA and to oxidize organic particles. Comparisons are also made with previous SOA studies carried out in a smog chamber that are reported in the literature. The quantities compared include particle and gas transport through the flow tubes, the mass spectra and O/C ratios of organic aerosol measured with an AMS, and CCN activity, under different operating conditions. Attempts are made to explain

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the similarities and differences in the results based on the different properties of the reactors and their effects on reaction conditions. The study is technically sound and the results should be useful for future designs of aerosol reactors and the interpretations of results obtained with different systems. I am not aware of any such thorough previous evaluations of this kind. The manuscript is reasonably well written and I think will be suitable for publication in AMT after it is revised in response to the many significant comments and questions below:

Specific Comments

1. Page 5213, lines 19-21: Here and throughout the paper statements that particles had similar chemical composition cannot be made based on AMS measurements. Similar chemical composition means the particles are composed of similar chemical compounds, but the AMS does not measure chemical compounds. It measures a simple, highly fragmented mass spectrum that is influenced by chemical composition, but the information it gives is not chemical composition but a measure of oxidation state. This is why one can correlate m/z 44/43 ratios with O/C ratios. Instead of stating that measurements of chemical composition were made with the AMS, the authors should state that measurements of aerosol mass spectra and O/C ratios were made, which is technically correct. Furthermore, I suggest the authors note that when particles in different systems had similar AMS mass spectra or O/C ratios it does not necessarily mean they had similar chemical composition. Conversely, differences in mass spectra and O/C ratios are clear indications that two aerosols have different chemical composition.
2. Page 5213, lines 24-26: Is this the only possible explanation? Given the complexity of SOA formation and the limited amount of information gained from the measurements, the authors are more definitive than I would be.
3. I suggest that the authors write a short section on the similarities and differences one might expect to see in the results obtained from the two flow tubes and smog

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chamber. This could be placed at the beginning of the Results & Discussion section. The authors have sufficient knowledge about how differences in the reactor designs might influence wall loss, aerosol chemical composition, sulfuric acid and SOA yields, and CCN activity. This would allow the authors to educate readers in a clear and systematic way about the properties of these different systems before overwhelming them with their results, many of which have rather speculative explanations. This approach also gives the reader the sense that this is hypothesis-driven research, since some plausible expectations are presented first, followed by results.

4. Page 5218, lines 8-10: Please provide a more detailed description of the PAM design features that reduce wall loss. This is not clear from this simple sentence or the figure. One should not force the reader to go to another reference for this information. It is sufficiently important for this paper that it justifies a stand-alone explanation.

5. Page 5222 and Figure 3. I suggest adding results of the Hinds-type calculations of particle transmission efficiencies to the figure so that the reader can get a better sense of discrepancies.

6. Page 5222-5223, section 3.2: I suggest explicitly differentiating between H₂SO₄ vapor and H₂SO₄ particles in this discussion. As it is now I think H₂SO₄ refers sometimes to one or the other, and yet it is only the H₂SO₄ in particles that is measured.

7. Page 5222-5223, section 3.2: My interpretation of the discussion is that loss of H₂SO₄ particles to the walls is considered but not loss of H₂SO₄ vapor. This can also be estimated using Hinds-type calculations. How does the timescale for this loss of vapor to the walls compare with the timescale for condensation onto the particles? The discussion focuses entirely on loss of SO₂, so I get the sense that the authors are assuming that H₂SO₄ instantly condenses onto particles.

8. Page 5223-5224, section 3.3: Please provide the Reynolds Numbers for the TPOT and PAM flow conditions.

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9. Page 5225, lines 25-27: I would think that a factor of 4 difference between the measured AMS O/C ratio of BES of 0.15 and the true value of 0.04 would be cause for concern. I suggest some comments on the degree of confidence in the O/C measurements.

10. Sections 3.4 and 3.5: I suggest that when comparing AMS results on OA in the PAM, TPOT, and smog chamber that at least in some cases mass spectra are shown, not just O/C ratios. This will allow readers to get a better feel for how similar or different the OA mass spectra are in these systems and the information that is being used to distinguish differences.

11. Section 3.5: I suggest providing some estimates for possible time scales for loss of organic vapors to walls in the flow tubes and flow chambers and gas-particle partitioning. This can be done assuming maximum possible diffusion-limited rates. It is not enough to compare differences in particle mass loadings and assume gas-particle equilibrium, since the particles are competing with the walls for vapors. These time scales can be used to improve the comparisons of SOA formation in the systems.

12. Section 3.5: It should be kept in mind in this discussion that a major difference between the flow tubes and the smog chamber is that the much longer time available for reactions in the chamber will allow condensed phase oligomerization reactions to occur to an extent that will not happen on 100 s time scales. For both the SOA systems studied here it is known that in smog chambers oligomers contribute large fractions of the mass.

13. Page 5226, section 3.4.2: Why not use Kappa values to quantify the CCN activity of these systems, since these values can be more easily compared to the literature? Sc seems like a less useful quantity.

14. Page 5226, lines 24-26: Can't the explanation for the differences in CCN activity at low OH exposure be that there are significant differences in the chemical compositions of the oxidized BES particles (which is what determines CCN activity) that are not

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captured by a simple O/C ratio?

15. Page 5227, lines 27-28 through Page 5228, line 9: It seems that because the alpha-pinene reacts with O₃ before exposure to OH in the TPOT that the largest discrepancy in O/C ratios between the TPOT and PAM should be at low OH exposure, since the oxidation history is the most different in this case.

16. Page 5228, lines 16-18: What is the evidence that the SOA yields differed because of gas-phase wall losses?

17. Page 5228, lines 25-27 through Page 5229, line 2: It seems like the SOA yields being compared here are not statistically different. Why speculate on causes for possible differences that may not exist?

18. Page 5230, lines 17-19: Can the authors suggest possible materials that could be used instead of Pyrex that meet this criterion?

19. Page 5230, lines 23-25: Please be more specific about how to manipulate flows to avoid wall effects.

Technical Corrections

1. Page 5223, line 9: Should be Fig. 3 not Fig. 2.

2. Page 5224, line 15: "are times" should be "times are".

3. Figure 2 and 3 images should be switched; the captions are all right.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 5211, 2010.