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Atmospheric Measurement Techniques Discussions



# *Interactive comment on* "The Caltech Photooxidation Flow Tube Reactor – I: Design and Fluid Dynamics" *by* Y. Huang et al.

**Anonymous Referee #1**

Received and published: 5 October 2016

Review of Huang et al., AMT

General comments:

Huang et al. presents a nice manuscript about the new CalTech Photooxidation Flow Tube Reactor (CPOT), which will enable them to join the dozens of research groups who have been using Oxidation Flow Reactors to study the secondary particles and their properties for oxidation times scales appropriate for the atmosphere for a decade. The manuscript is well written and well organized. It contains lots of nice color figures and drawings and solid analyses. However, there are some errors and omissions which must first be addressed, but when they are, the manuscript will be suitable for AMT.

Specific comments:

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When designing a flow reactor or chamber of any sort, the designer needs to consider how the flow reactor or chamber will be used. There are always compromises because there is no perfect flow reactor or chamber, particularly for atmospheric pressure. For instance, if you want to relate time in the reaction to reaction time, then you will have enhanced wall interactions because that is how this characteristic is achieved. For a flow tube that is at atmospheric pressure, you must have something to mix the different gases and particles to be studied completely into the carrier air flow. This mixing may be by shower heads or static mixers with lots of surface area, but then you will also have lots of possible surface interactions and losses for gases and particles before they even enter the main flow reactor.

If you want to study ambient aerosol particle chemistry or particle mass yields, then you will want to minimize wall effects and losses, which means minimizing wall interactions, but then the ability to relate time in the flow tube to reaction time may become difficult. If you want only to do laboratory studies, you still need to decide whether you want to look at chemical evolution (so that time in the reactor equals reaction time) or chemical properties that are distorted by wall interactions, such as SOA yields. Then that decision determines if you embrace wall interactions to give you laminar flow or you try to avoid walls and lose the ability to relate time in the chamber to reaction time. Which way the compromises are made depends entirely on the purpose. Of course you can decide to try to do both, and possibly compromise both.

The authors of this manuscript should have an introductory paragraph stating what they intend to study with this CPOT so that the reader can judge whether they have designed it appropriately for that purpose. They should also lay out the strengths and weaknesses of their approach for each type of study they intend to do (e.g., SOA mass yields, SOA chemical properties, time-dependent kinetic studies).

2.5 Computational Fluid Dynamics (CFD) Simulations page 4, line 20. Assuming isothermal flow is unrealistic, which the authors say later in the manuscript. The authors should say up front that they are going to try isothermal to see what they get and





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then will need to modify this assumption later in the manuscript.

3.1 Injection method. Page 5, line 8. The authors are wrong about the method of injecting air into the PAM chamber. The flow does enter through a tube in the middle, but is quickly diverted by a covered cap with holes drilled sideways to divert the flow toward the outer edges of the chamber. This air is then passed through a fine-mesh screen to break the larger eddies into smaller eddies inside the actual chamber. I suggest that the authors get in touch with the builders of the PAM chamber, so that they know and are thus able to give a correct description of the actual flow in the PAM chamber.

Page 5, line 16. This is not the dead volume to which Lambe et al., are referring. I recommend that the authors contact the designers of the PAM chamber to make sure they understand exactly what the PAM chamber design is, as well as the compromises that were made and why.

Page 5, line 18. The PAM chamber used in Ortega et al., is basically the same as the one used in Lambe et al.. The only difference is that the entrance plate with the flow diverter is removed so as to completely eliminate the loss of ambient particles and gases on the entrance plate and diverter by having the air flow into the chamber over almost its entire cross section. It is not to "reduce recirculation" in the reactor, as stated in this manuscript, although it might have improved the flow somewhat. The main result was that there was no longer any ambient particle loss in the PAM chamber.

Section 3.2. Page 6, Can the light from the reactor section get into the diffuser section? Is there ozone in the diffuser section? If so, then shouldn't the authors consider the diffuser section part of the reactor?

How does the lack of laminar flow in initial part of the diffuser section affect the particle formation/chemistry that the author may want to study since the diffuser is part of the reactor?





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Section 3.3. The authors did look at issues of convection due to the temperature gradients in CPOT, but not the convection due to “hot spots” along the walls, which are likely to be important, irregular, and possibly transient.

Did the authors measure the temperature distribution of the walls in the CPOT to within 0.1 C? I would assume that there will be hot spots with differences of as much as 0.2 C or more, even with the temperature-control jackets and especially when the lights are on. My guess is that assuming an axial temperature gradient in the non-isothermal case is the best case scenario and that reality will be quite a bit worse.

We could do the following analysis with the Richardson number, but we can illustrate the problem with an even simpler calculation. Simple buoyancy calculations would suggest that air warmed by these 0.2 C hot spots would stir the reactor vertically from bottom to top in less than 10 seconds, which is a much shorter time than the ∼20-minute residence time. And, because the reactor is a round tube, this vertical motion will get translated into horizontal motion as the rising air hits the top half of the tube. The stirring due to these hots spots is likely to be as important as any other flow considerations and is probably a major driving force in their eddy diffusion correction. Such eddy diffusion will do a great job of bringing the air in the chamber into close contact with the walls several times, thus increasing wall loss and exchange.

The temperature gradients that the authors determine are important are about the same as the 0.2 C difference used in this simple calculation. Thus, they have every right to be worried about thermal gradients and should include hot spots in their thinking about how convection is going to be a huge problem.

5. Results and Discussion 5.1 Measuring the initial value of the gases and particles downstream of the static mixer does not give a complete picture of particle and gas loss if those particles and gases will be added upstream of the static mixer during the experiments. How much of the gases and particles is lost on the static mixer? My guess is that a significant amount of the SO2 and the ammonium sulfate particles will





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be lost, as will some of the $H_2O_2$. Now, if the authors intend to measure the amounts of gases and particles downstream of the static mixer and use these values as their initial values, then this test would be valid. Is that their intent?

Also, what about any gases / particles that are modified by interactions with the static mixer? They could be important for the chemistry that occurs in the CPOT reaction section.

Even for the way this penetration study was done, my guess is that the authors had to wait a while for the surfaces to acclimate to $SO_2$ before they were able to get it all through. Did the authors have to wait?

Page14, line 8. This test does not provide evidence that there was negligible interaction with the walls for the gases. All the authors can really say is that there was negligible loss, which could mean that the surfaces were (temporarily?) passivated. How that would change with the lamps on and active chemistry is anyone's guess.

It would be good to know the penetration efficiency for both initial cases – before the static mixer and just after the static mixer. The authors should measure it and report the results in the next version of the manuscript.

Also, were these penetration efficiency tests done under dry conditions? If so, then these are "best case" values, especially for $SO_2$ and $H_2O_2$. Unless the authors intend to do all their experiments under dry conditions (which will greatly limit the maximum OH exposure in CPOT and the applicability of the results to the real atmosphere), they should do the penetration efficiency tests under the same conditions as they will use in the experiments. My guess is that the penetration efficiency for $SO_2$ and $H_2O_2$ will fall rather precipitously.

5.1.2. page 14, line 27. It is doubtful that the 20% particle loss is due to electrostatic loss to the quartz walls. Instead, it is likely that the loss is due to more active convection taking the particles closer to the wall more frequently in the CPOT than the authors



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think.

Page 16, line 19. Why are the eddy diffusivities for ozone and particles different? I would think that they should be the same for small particles.

Somewhere at the end of the discussion and results, the authors need to compare the characteristics of the CPOT to those of other flow tube reactors, such as the PAM chamber, TPOT, and the Irvine chamber. From the data provided here, CPOT appears to be not much better than any of these other existing chambers in terms of particle transmission or residence time distribution. If you look at the difference in the actual arrival time to that predicted by laminar flow and the full-width and also at the half-maximum of the actual peak to that of the laminar flow case, as in Figure 10, and compare those to what is achieved in TPOT and PAM in Lambe et al. Figure 3, you will see that the actual arrival time is about half that for the laminar case and the FWHM peak width is about double that of the laminar case for all three flow tubes.

Therefore, it is unclear to me if the authors have achieved their goal of having a flow tube that can be used for kinetic studies (in the sense of time in the chamber is equal to reaction time) any better than the existing flow reactors can.

Conclusions. The authors say in the conclusion that "The measured residence time distribution will enable correction for the unavoidable deviations that do occur." The only way this statement can be made credible is for the authors to add a section that shows how they are going to do this and then demonstrate that it works with real kinetics measurements. Then they need to do an error analysis to show what the uncertainty of their kinetic measurements will be. If they do not wish to do this work for this manuscript, then I suggest that they remove this sentence.

Conclusions. The second-to-last sentence in the manuscript says "Finally, the perturbations from strict laminar flow in the horizontal tube are a result of buoyancy effects." The authors recognize in this manuscript what other researchers have been saying for years – that buoyancy plays a dominant role in flow reactors with residence times of





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minutes to hours. They call it a perturbation, but there is nothing small about it, so I suggest that they call it "variations from strict laminar flow".

This point about buoyancy is important, so the authors should include a sentence about it in the abstract and not just in the conclusions.

Conclusions. I disagree with the last statement: "If it had been feasible to mount the flow tube vertically, these effects could have been largely eliminated." Mounting the flow tube vertically will not eliminate these buoyancy effects because it is impossible to eliminate "hot spots" that will drive the buoyancy. Instead, mounting the flow tube vertically will likely enhance the buoyancy effects. By luck or design, this enhancement can occur in a way that effectively isolates the center flow from the walls, although it greatly shortens the residence time. The flow reactor used for the Kang et al. papers was a vertical flow tube. The authors may want to contact the developers of the original PAM chamber to learn what they know about the flow characteristics in vertical flow reactors if they really want to retain this sentence in the manuscript.

Technical corrections / comments:

4. page 9, line 10. Please change "may" to "will".

Figure 11. Are the two dashed lines switched? I would think that the gravitational settling would cause a lower penetration efficiency for larger particles.

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