Referee for Friebel and Mensah 2018
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Summary:

The authors provide a theoretical framework that introduces the concept of activation time, which is the reaction time necessary to produce an observable chance in an aerosol population's property (CCN ability in this case). This is done in an effort to interpret data from a reactor operated in continuous mode rather than batch mode, the case being made because of the increased use of OFRs and OFR-like reactors compared to environmental or smog chambers. They describe the entire reactor operation from fill-up to shut-down. They provide a mathematical description which, to my understanding, is a piecewise solution in time for activation fraction of aerosols in question (soot aerosols subject to heterogeneous ozonolysis). This manuscript is front-heavy with concepts of chemical reactor engineering (ideal reactors and their residence time distributions), and how these are used to develop analytical expressions for the time profiles. Then their expressions are overlaid to data from two experiments to observe model agreement. Finally, they depict a theoretical example based on preexisting data in the literature to show how their parameter t_{act} can be used to compare data from independent experiments, or even better, how future users chose to operate their reactors.

This is very important work that fits the scope of AMT; particularly the illustrative example in Fig. 7. However, I think the manuscript be improved. An in-depth revision of Sections 1-4 is necessary, mostly for emphasis on technical details and wording to reach a broader audience (that is, one unfamiliar with reactor design or operation). For example, the authors need to clarify what they mean by 'non-gradual' as soon as it is mentioned. Are they referring to fast reactions, e.g., heterogeneous nucleation? Or are they simply referring to non-steady state?

There is a bit of a disconnect between the theory and application. Probably because the nature of the subject is challenging. The authors are encouraged to make it clear in the Introduction that they are looking at CCN. Also, because t_{act} is yet to be explained, words like 'parameters' have no meaning thus far; they do eventually by the end, but I think not to confuse the reader a revision is necessary (I offer suggestions in the Major and Minor comments sections for the authors' considerations). From what I can tell, their data is centered on reactors operated in continuous mode, yet the word 'OFR' is mentioned only in Section 5, when the introduction is focused on the large batch reactors. For that matter, comparison of the mathematical framework to that of a PFR is not present. If so, I think some mention as to why should be made. It seems to me that PFR-like reactors (e.g., flow tubes) work well. Why are CSTRs preferred by the authors? Mathematically, it would appear to me you need an RTD, and the PFR has one (Delta function), so why not compare?

Major Comments:

Abstract: Details can be improved; I offer suggestions for the authors to consider in the Minor Comments.

1. Introduction: I strongly encourage the authors to be more precise in their sentences. It appears that what the authors communicate is not what they mean, and to reach a broader audience, I think details should be made clear. While Sections 5 and 6 are very clear and logical, at least in my view, Sections 1-4 are not. I encourage OFRs like the PAM (e.g., TPOT, CPOT, etc.) to be addressed early on. The authors can read more in Lambe et al. and Mitroo et al., already cited by them. Also what is not clear is whether the authors have a new CSTR design (different from that of conventional OFRs or Teflon chambers) or if they just develop a mathematical approach for data coming from a CSTR. Or both. Mention of the SAPHIR, in my view, belongs here.

2. Introduction to CSTR: This section is of course important for readers who are not familiar with environmental reactor engineering, however, is not only available in any chemical engineering textbook, but also summarized by Mitroo et al. (Appendix A). If the authors see fit, I would suggest renaming this section as ‘SAPHIR operation’ or something similar, and then have Filling, SS, and Flushing sections. It seems that from Sections 5-6, their math can be applied to non-CSTRs like the PAM and TPOT, so I wonder if when the authors say ‘CSTR’ they mean ‘non-batch’. Reactors operated in continuous mode range from CSTRs to PFRs, from a mixing perspective.

3. Introduction of the activation time (t_{act}) for non-gradual transitions: A major comment I have here that I alluded to prior to this section is to be explicit when talking about parameters. E.g., P6 L20 “If all other parameters stay constant…” what does this mean? Flow parameters? Temp and RH? If so, what is the parameter that is changing? I don’t think the reader thinks of AF by now. Also, P6 L24-26 seem to me like the crux of the study (unless I’m mistaken). Are the authors looking at a specific scenario where they keep RH constant but slowly react aerosol with (e.g, ozone for sake of argument) and there is a very small time window where enough reaction occurred to make the aerosols in the reactor cloud nuclei at that supersaturation? Is that time window what current reactors cannot accurately allow determination of, but this method does? Why can’t a PFR be used to detect that? If so, this concept needs to go in the introduction, with specific application to CCN if helpful. Finally, for the authors’ consideration, it appears they want to keep the x-axis uniform in their equations by introducing t_{switch} and t_{offset}. Seems to me like these are just substitutes for a Heaviside function. Would the authors consider using a Heaviside function instead to make the math simpler?

4. Application in first experiments: I don’t think this section header reflects the content. Maybe change to something else? Section 4.2 was described well. My only major comment here is why Figure 3 has a lag (noticed after seeing Table 2 and Figure 5) Why does the ‘step’ or ‘non-gaussian’ have a lag? Even in the filling regime a CSTR gives no lag. E.g., in P14 L10-13 I remain unconvinced that the blue line in Fig. 5 should have a lag. I think that assumption (P7 L7; see comments for Fig. 5) is highly questionable. I think that leads to an artifact in the calculation, and that is reflected by the stark difference in t_{act}-onset (Table 2). If the authors provide a counter, I’d be happy to know why.

5. Application to experimental data: No major comments here other than those that stem from the previous section.

6. Application of t_{act} to other continuous flow chambers: I think this section would be very useful for OFR users on how to use OFRs for CCN meaurements! Still, neither the PAM nor the TPOT

are CSTRs, so how have the authors applied t_{act} to their RTDs? Also, what if aerosol content is not well known (e.g., field sampling)? How is their mathematical framework applied? I am still unclear as to what parameters are needed experimentally.

7. Conclusion: No major comments here.

Minor Comments:

P1 L6: Consider changing “atmospheric” to “realistic”.

P1 L7: Arguably a small point, but I’d encourage a revision of “achieve extended observation times” to “obtain measurable reaction rates, due to long residence times” or words to that effect. I think owing to the small reactor design community there’s often scant attention paid to the details of a reactor and how it operates by the average reader; and this work has potential for a broad audience, so ensuring the readers become educated about reactor design and meaningful parameters to evaluate its performance is important in my opinion.

P1 L8-9: Change “…in a CSTR mode.” to “…as a CSTR.” Also, if the authors wish to introduce the concept of a CSTR this early on, perhaps the opening sentence could mention the use of environmental chambers as batch or semi-batch reactors.

P1 L9: Consider changing “…which…” to “…that…”.

P1 L9-10: Mean values of what? Perhaps ‘its mean value’, referring to the data.

P1 L10: Consider a colon, e.g.: “…metric: …”.

P1 L13: “Furthermore, we show…”

P1 L14: Are the authors referring to the PAM? Perhaps give an example.

P1 L14-15: Rephrase sentence. t_{act} explains or t_{act} helps explain? What are the different chambers? Are they smog chambers vs. OFRs? Are they aerosol flow tubes vs. OFRs?

P1 L17: This may apply throughout but “Aerosol particles” should be “Aerosols”.

P1 L17-18: Small detail, but stating aerosols are ‘emitted’ into the atmosphere implies they may not be generated by nucleation. The authors can consider the following rephrase: “Atmospheric aerosols undergo various reactions; the timescale for which depends on their lifetime.”

P1 L19: Citation for sea salt aerosol lifespan (textbooks are appropriate as well) please. Also, replace comma with ‘”whereas”.

P1 L21: Please check ‘aerosol particles’, as per my previous comment.

P1 L21-22: The authors can remove “…the fate of aerosol particles in the atmosphere and…”

P1 L22: I'd change 'parameter for' with 'process affecting'.

P1 L23: "task" should be plural; also, I'd change 'the investigation of aerosol' with 'understanding atmospheric aging'.

P1 L23-27: I'd encourage the authors to reword this section and not to gloss over how large reactor are 'technically' unfeasible, but instead be more explicit (e.g., wall losses, time dependencies, etc.). Also, I don't think the SAPHIR has a set 16 h operation time, so perhaps the authors can say '12-24h' to indicate a range.

P1 L28-29: This is a technical detail I would like not to be overlooked. "…in order to reduce the reaction time…" is not the objective; it is a consequence (advantageous, admittedly, for investigating physiochemical properties of SOA or LVOCs). The objective is to artificially augment the reaction rate. I believe the authors know this, but a reader may not, and I encourage the idea of having these details be clear. This is important work and should be presented as such!

P2 L4: Please consider adding a citation of Renbaum and Smith, doi: 10.5194/acp-11-6881-2011

P2 L6: In the engineering literature, CSTRs are well described, but the acronym is use as a general term for any well-mixed vessel. The authors choose to apply (or design?) a CSTR for their work in addition to the mathematical expression for t_{act}. Have I understood this correctly? Might I suggest them to give their reactor a more personalized name?

P2 L8: An ideal CSTR is perfectly mixed. A real CSTR is well-mixed.

P2 L9: Perhaps the authors can rephrase "…close to real processes in the atmosphere…" to "…mimics mixing in the free troposphere more accurately than [other reactors]". But more importantly, is the mixing state in this reactor important because it mimics atmospheric dynamics or because it allows more accurate data retrieval from laboratory experiments?

P2 L11-12: That's absolutely the case for a CSTR! At steady state, the distribution of ages is fixed, and is dependent only on reactor volume and flowrate. I think this needs to be clearer.

P2 L14: In addition to refining the sentence to make it sound less informal, I would encourage the authors to cite also Levenspiel's Omnibook (I think they cite it later, but it's missing in the Reference Section).

P2 L19: I'm confused, what do the authors mean when they say 'non-gradual' (see Major Comments)? Do they mean time-dependent? Do they mean non-steady state? This is a key concept in their work, so I would ask them to define it explicitly for the reader.

P3 L3-4: More than a physico-chemical (physio-chemical?) perspective, I'd say from a flow or mixing state perspective. Also, PFR can be placed in acronym in brackets (although PFRs can be mentioned in the introduction), and CSTR has already been spelled out earlier, so just the acronym should suffice here.

P3 L9: Can the authors make the case that environmental / smog chambers are batch-type reactors?

P3 L9: Again, I would urge the authors to be detailed. A PFR (which is the idealized reactor design on which flow tubes are built) allows no axial mixing (as the authors point out), but is perfectly mixed radially! The ADM (mentioned by Lambe et al.) allows for deviation from the PFR and is closer to describing flow tubes, but that discussion can be briefly mentioned, if needed at all.

P3 L17: Residence time of what? The large chambers?

P3 L19: Consider replacing "During a subsequent…" with "Following steady state, upon shut down, is the…"

P3 L20: To better illustrate their point, I think the authors can put an arbitrary schematic in the Supplement rather than alluding to a figure that has not yet been explained.

P3 L21: I don't think 'hydrodynamic' is necessary, but I could be wrong.

Equation (2): A suggestion to simplify notation, perhaps the subscript 'CSTR' can be removed, seen as it is implied. Also, (t) can be placed outside of the square brackets, as can the subscript 'feed-in', which I would also suggest be replaced with a subscript zero.

P4 L1: This is a good point by the authors! I would encourage a citation of Lambe et al., seen as what the authors are describing here is essentially the result of a tracer study (A is a chemically inert tracer essentially).

P4 L11: I would encourage a citation of Mitroo et al.

Equations (3-4): These are E and F-curves as described by Mitroo et al.; it may be worthwhile to mention.

P6 L16-19: This needs to go either at the end of the introduction, or at P2 L19 in my view.

P6 L20-21: This sentence needs to be rewritten as it is too handwavy and comes across as pseudo-science. "…a particle that undergoes changes that result in a non-gradual transition…" made no sense in my mind until I finished reading the manuscript. Could the authors come up with a physical example to help convey what change has been 'undergone' that resulted in a 'transition'? Or is the 'change' itself rapid (e.g., heterogeneous nucleation)? Are the authors implying they can model a process this fast as a function of time, and decouple it from other timescales within the reactor? Is a CSTR the best approach?

P10 L4: "aerosol particles"

P10 L6: "aerosol particles", but more importantly, what properties are distributed around a mean value? If they are physical (e.g., dpg, sigmag, etc.) maybe. If they are chemical (e.g., nitrate content) then not really.

P10 L7-9: I don't follow the logic here. If I understand correctly, the authors are saying that, due to multiplicity of charges on some aerosols, an aerosol population that follows a lognormal distribution if plotted by mobility diameter doesn't follow a lognormal distribution by aerodynamic diameter? I don't see how an aerosol population that is unimodal in mobility diameter can be multimodal in aerodynamic (or geometric) diameter.

P10 L15: Maybe "…has the potential to activate." instead of "…activates.", because after t=180 min, they don't all activate.

P10 L17: Why was 30 min chosen as standard deviation?

P14 L1: Unless I'm mistaken, t_{act}s don't really differ; only t_{act}-onset for $P_{Gaussian}$ differs.

P14 L12: Fix "tact", but more importantly, please address the Major Comment surrounding this sentence (the lag in Fig. 3 before t_{act}).

P14 L13: Fix "P(tact)"

P14 L15: Fix "Pstep(tact)".

P13 L5-6: Please provide appropriate citations.

P14 L21: I would appreciate either a description of the chamber or literature that describes it. I'd really like to know, as I think is important for the reader, if this chamber is indeed well mixed (does it have impellers, fans, baffles?) to where the equations can be applied to the data, or is this chamber not really well mixed? What about residence time in the tubing? The tracer data may require some convincing (see four comments down P15 L6).

P14 L22: For those not familiar with soot generation, what is a miniCAST, set point 6?

P14 L30-35: Would the authors see fit to put these two points at the end of the Introduction Section?

P14 L31: Again, I'd encourage the authors to refrain from using the word 'perfectly mixed' when talking about a real reactor. Might I suggest 'well-mixed'. More to my point: no RTD is available until Fig. 6; can a description of the chamber, or literature on it be presented?

P15 L6: Following the comment above: How the particles depict a CSTR would be more believable if the authors provide some way of showing it. Maybe plot an E-curve for the data and overlay that of an ideal CSTR over it? If I calculated it right, 2.78 m^3 / 25 LPM is ~111 min. Why is t_{act} more than twice that? In P7 L7 the authors claim t_{act} is one mean residence time for a CSTR. If their chamber is not as well mixed as believed that's OK, but it should be stated (and at least be better mixed than OFRs!).

Tables and Figures:

Figure 1: Please indicate a unit for the x-axis (I think it's seconds). Also, this figure is confusing because it should just be one curve representative of SS, but the authors mention in the caption "…while flushing the CSTR." I understand what the authors mean, but maybe the reader won't so this figure or its citation in the text should be made clearer.

Figure 2: No major comments.

Figure 3: No major comments here, other than the curiosity of how a graph like this would look like for a PFR.

Figure 4: No major comments.

Figure 5: Upon seeing Fig. 5, I struggle to now understand Fig. 3 (or, the blue line in Fig. 5). I was under the impression t_{act} is when reactants are introduced. If that is the case, why does the red line show AF > 0 at $t < t_{act}$? Or am I missing something? A CSTR has no lag by design; only PFRs have lags. Even in the 'filling regime'. I think the root of my misunderstanding can be traced back to P7 L7. Why is AF = 0 when t < tact? Even for a system with no Gaussian spread, purely based on CSTR design, at $t = 0^+$ AF (however small) is non-zero. If the authors can explain their assumption in P7 L7, I think it would clear this up (at least for me).

Table 1: No major comments.

Table 2: No major comments on the table itself (maybe capitalize the subscript 'gaussian'?); but I have comments on how the authors choose to explain the difference in values of t_{act}-onset for Step and Gaussian (see comment section).

Table 3: No major comments.

Figure 6: No major comments, but I do have a question: it's unclear how the authors' fit matches data well. Was it a fit? E.g., if instead of soot they used salt, what is needed experimentally to determine the blue dotted line in this Figure? Did I miss something in the text?

Figure 7: No major comments, but to be clear, is this illustrative? That $AF_{TPOT} > AF_{PAM}$ at high [OH], and the reverse for low [OH], is subject to experimental data, right?

References: