

Response to Referee 1

The authors present a new flow reactor designed for investigating multiphase chemistry in aerosols and cloud droplets. This is an interesting and technically challenging idea, which could potentially be an important tool to gain insights into these understudied processes. Care was taken in the design of the reactor to avoid temperature gradients due to the UV lamps, which would interfere with multiphase partitioning, to minimize losses of soluble gases, and to strictly control RH. They use a Spot sampler to generate cloud-like droplets from seed aerosol for study in the reactor. They present preliminary results for studies of the influence of aqueous processing on SOA formation in the lab and using ambient air. I believe the manuscript is publishable in AMT after some minor issues are addressed and the manuscript is revised accordingly.

- The article is too long, with 17 figures in the main text. Surely this can be tightened up, with some material moved to SI. At the same time the most interesting figure (the second Figure S2 - there are two Figure S2s) has been relegated to the SI.

We moved Figures 4, 10, and 16 to the supplement. That still leaves 14 figures, which we recognize is high, but we feel that all of those that remain are important for accompanying the text.

- The abstract is also too long. It's not immediately clear what "transmission efficiencies" are upon reading the abstract without first reading the manuscript.

We addressed both of these issues by deleting the following from the abstract: "The transmission efficiency of O₃ and CO₂ for all RH and of SO₂ for low RH exceeds 90 %, while it falls to about 70 % for SO₂ at 100 % RH. Particle transmission efficiency increases with increasing particle diameter from 0.67 for 0.050 μm particles to 0.98 at 0.20 μm, while that of the ~3.3 μm droplets formed on seed particles is greater than 80 %."

- Why is K₂SO₄ used instead of other particle types which may be more representative of atmospheric aerosol or more typical of laboratory studies of aerosol and cloud chemistry? I think the question is answered several pages later on line 496 but should also be acknowledged when this is first mentioned. Also note that "neutral" isn't really representative of ambient aerosol or cloudwater pH (cf. Pye et al. 2020)

It may be that the reviewer didn't notice the description accompanying the initial mention of K₂SO₄ starting on Line 210: "To date, most experiments have used potassium sulfate (K₂SO₄) seed particles because they are non-acidic, have a dynamic shape factor close to 1, and effloresce at an RH of about 60 % (Freney et al., 2009), which permits measurements without ALW at higher RH than would be possible with common aerosol types such as ammonium sulfate and sodium chloride."

- the size dependence of the particle transmission efficiency is mentioned, and compared with other studies, but no physical explanation for decreasing transmission for smaller particles is given. One would expect the opposite.

The original sentence: “The particle transmission efficiency increases with increasing particle size, from 0.67 for 0.050 μm particles, to 0.94 at 0.080 μm , and 0.98 at 0.20 μm .” was extended to (briefly) explain the size dependence: “As expected for the particle size range considered for which the dominant loss mechanisms are Brownian motion and electrostatic attraction to charged surfaces, the particle transmission efficiency increases with increasing particle size, from 0.67 for 0.050 μm particles, to 0.94 at 0.080 μm , and 0.98 at 0.20 μm .”

- The SO₂ transmission efficiency at high RH is low. Presumably studying SO₂ multiphase chemistry was one of the main intended purposes of this apparatus. Can the authors comment on how this issue may impact the design of future studies?

The experiments described in the manuscript in which SO₂ was injected and conversion to sulfate aerosol measured were meant to test the reactor with an extensively studied chemical system. The primary utility of the APPA is not for studying reaction of soluble gases that are directly injected, but rather further reaction of soluble products of gas phase oxidation of injected insoluble gases. Wall losses of those soluble products are expected to be lower simply because they will encounter a cloud of droplets in their path between where they form and the wall.

- line 444: 'described in by (Mitroo et al)'... clean that up

Now “described in Mitroo et al. (2018).”

- residence time distribution: why is there a distribution at all if the gases or particles are introduced in the same location and sampled in the same location (if this is not the case it's not possible to tell from the text)? How are three measurements sufficient to construct the whole RTD curve and detect the absence of a long tail?

Some smearing of an input pulse of particles or gases is unavoidable because the laminar velocity profile through the reactor is parabolic and not flat. The RTD tests are intended primarily to evaluate the contribution of things like mixing at the entrance and exit. The particle and gas measurements made at the outlet of the reactor were continuous and high time resolution, spanning the time between injection and several minutes later when concentrations had decreased to ~0. The “three” measurements were simply repeated tests of the same thing to ensure that the results were repeatable.

- line 490 - I would either delete or rephrase this. You are presumably introducing this apparatus for the first time in this manuscript, why are you making this statement about it not being applied very often to cloud chemistry studies when that is the most novel and unique application?

The sentence in question is “Though, like most OFRs, the APPA reactor is most often used to measure aerosol formation resulting from OH chemistry, conditions inside the reactor during cloud chemistry 490 experiments were first evaluated through the well-studied oxidation of dissolved SO₂ by O₃, leading to formation of sulfuric acid and growth of the particles on which the droplets formed.”

The intent of the sentence is not to suggest that the reactor will not often be used to study cloud chemistry, but rather that it will not often be used to study aqueous phase oxidation by ozone and not hydroxyl radical.

- Figure 9 and Figure S2. See my comment above about the second Figure S2. It is much more interesting than Figure 9. Figure 9 has been sufficiently described in the text lines 500-507. It could be made panel B of a figure which focuses on the data in Figure S2, moved to SI, or eliminated. How was the low SO₂ transmission efficiency dealt with in these calculations?

We wanted to include one figure that shows the change in particle size distribution resulting from addition of secondary aerosol. We felt that original Figure 14 (Figure 12 in revision) was a better choice because it shows the result of the type of experiment the APPA is primarily designed for. As noted above, the SO₂ to SO₄ conversion experiment was meant to test the reactor with a well-studied chemical system and, thus, it seems more important to include results that can help readers visually evaluate how similar the experimental results are to expectations. The figure in the supplement shows how the size distribution is altered, but does not allow a reader to evaluate the meaning of the extent of change.

The SO₂ concentration used in the calculations was determined based on a known concentration in gas mixture and a measured flow rate. No correction for wall loss was included. Though it may seem that this would result in a significant low bias based on original Figure 6, those transmission efficiency tests were done without introduced droplets. Thus, much of the SO₂ lost during the transmission efficiency tests will instead dissolve and react in the droplets.

- Is the relatively short residence time of APPA compared to a chamber experiment an issue when it comes to SOA studies?

Absolutely, but this is an issue that affects all OFRs and is discussed at length in other publications. Adding a discussion here would add even more to an already long manuscript.

- What is the reader supposed to take away from the SOA yield studies shown in Figure 15? Were these yields consistent with expectations?

The primary reason for including the discussion and figure was to show the clear influence of liquid water on the amount of secondary aerosol formed.

The following was added to provide some context for the measured yields: “The yield measured with no liquid water present is similar to the 0.18 – 0.28 range reported by Nakao et al. (2011), though the

comparison is indirect because of differences in OHexp and organic mass loading between the two studies.”

- funding acknowledgement seems to be missing.

The development of the APPA was supported by internal university funding sources and not a funding agency.

Response to Referee 2

Xu et al. present the evaluation of their “Accelerated Production and Processing of Aerosols” (APPA) OFR that is designed to enable aqueous-phase OH-initiated oxidative aging processes. The APPA OFR combines the authors’ PFA OFR with injected K₂SO₄ seed particles at the inlet and controlled humidification that enables control of the particle liquid water content (the range of RH discussed in this paper is 40 - 100% RH). The authors perform characterization studies of gas and particle transmission efficiencies, residence time distributions, droplet size distributions, and radiation/oxidant profiles. To demonstrate applications of the APPA OFR, they generated sulfuric acid from SO₂/O₃ reactions, benzene OH-SOA in the presence of dry/aqueous seeds and “cloud droplets”, and aged ambient aerosol.

Comments

While the APPA OFR appears to be capable of generating sulfuric acid from the aqueous-phase SO₂/O₃ reaction, its ability to initiate aqueous-phase OH oxidation chemistry was not conclusively demonstrated here. The authors did investigate SOA generated from gas-phase OH oxidation of benzene, followed by partitioning of OVOC/SOA into ALW/droplets. While this is a novel application that the APPA OFR seems to be well suited to, this is not a demonstration of aqSOA formation according to even the authors’ own definition: “water-soluble products of gas-phase chemistry [that] enter cloud droplets or aerosol liquid water and react in the aqueous phase with the hydroxyl radical (OH) or other oxidants” (L83-L86). In that regard, I think they should have used K₂SO₄ seed particles containing H₂O₂ and/or H₂O₂/FeSO₄ to initiate aqSOA formation (e.g. Nguyen et al., 2013; Daumit et al., 2016), then repeated the same experiments without H₂O₂/FeSO₄, and inferred the difference in aerosol loading and composition as aqSOA. It is not clear to me why this was not done here – this is what I would need to see to be convinced that the APPA OFR can be used to investigate aqSOA formation.

We certainly recognize that it is challenging to isolate the contribution of aqueous phase chemistry in a system in which it is occurring simultaneously with gas phase oxidation. But that is exactly the type of chemical system the APPA was developed to study. It is true that water soluble products of gas phase oxidation will preferentially partition into the aqueous aerosol and droplets, but without further

oxidation those species will evaporate with the water as the aerosol/droplets exit the reactor, pass through two Nafion driers, and travel through a few meters of stainless tubing prior to measurement in the SMPS or AMS. Though the precursor studied was different (isoprene), Lamkaddam et al. (2021) reported that the aqSOA formed in their wetted-wall flow reactor could not be explained as simply the result of dissolution of products of gas phase oxidation: "...the dissolution of isoprene oxidized vapors cannot explain the aqSOA production and provides strong evidence that aqSOA results from OH reactions of the dissolved species in the aqueous phase."

Adding H₂O₂ and/or H₂O₂/FeSO₄ would be challenging for this system. As is described, the seed particles/droplets are always produced through size classification of an atomized and dried aerosol. H₂O₂ from the atomizer solution would be lost to evaporation unless the aerosol were not dried below the ERH of K₂SO₄ of approximately 65%. Uncertainty in the calculated change in mass concentration of the aerosol following processing in the reactor would be substantially higher if a correction for the water content of the aerosol when initially classified is required. The alternative would be injection of gas-phase H₂O₂ into the reactor, but then estimating how much gets into the droplets and how much is lost to the walls would be difficult. Furthermore, even with H₂O₂/FeSO₄ in the aerosol/droplets, it is likely that the source of OH near their surface where more reactive species would be oxidized would still be that from the gas phase (which is needed to generate the oxidation products) and so interpretation of the with/without H₂O₂/FeSO₄ would be difficult.

Similarly, how did the authors conclude that aqueous phase OH oxidation was responsible for the increase in ambient OA oxidation state as RH was increased from 40%-->85%-->100% (Fig. 17 and related text)? Hypothetically, couldn't this change have been driven by the higher RH (and LWC) promoting more efficient partitioning of low-volatility gas-phase oxidation products into the aerosol? For the reasons mentioned in above comment, it is not clear to me that this evolution in OA oxidation state was in fact due to aqueous phase oxidative aging in the APPA OFR.

Similar to part of the response to the above comment, without subsequent oxidation in the aqueous phase, water-soluble products of the gas phase oxidation are expected to evaporate when the aerosol/droplets are dried prior to measurement in the SMPS and AMS. It is also unclear why preferential partitioning to the aqueous aerosol/droplets would be more pronounced for more oxidized (and presumably lower volatility) species.

Unless significant dilution flow is added downstream of the APPA OFR, its relatively low 1.5 L min⁻¹ sample flow capacity limits its application outside of measurements that can be made with particle counter(s) and instruments such as an AMS. What design changes would need to be made to increase this flow capacity to something in the range of 5-10 L min⁻¹ that is closer to other commonly used OFR techniques?

We do not intend to redesign the reactor to accommodate higher flow rate instruments. The reactor volume cannot easily be increased by increasing the length because of height restrictions in the lab and

any increase achieved through increasing the diameter would likely result in broadening of the RTD. The flow rate could easily be ~doubled to 3 L min⁻¹ if, as with reactors such as the PAM, a single outlet flow was used rather than subsampling just the core flow, but again at the expense of the RTD.

L25 and L230 - Quantify “low RH”

The sentence in which it was included on L25 was removed in response to a comment by Reviewer # 1 that the abstract was too long.

We could add (40%) in parentheses after “low RH”, but the exact value is unimportant and what matters is that it is low enough that there is no ALW (which is stated in the sentence).

L70 – Clarify which “new pathways” are being referred to here

We were referring to those described in studies such as Liu et al. (2020), but should have made the connection between that sentence and the following one clearer. We added “As just one example,” to the second sentence in the paragraph (“Liu et al. (2020) measured sulfate...).

L160 – Rather than “The APPA...is typically operated as a 254 nm-type OFR”, I suggest instead saying “the APPA reactor is typically operated in OFR254 mode”

We changed the text to “When used as an OFR, the APPA reactor is operated in OFR254 mode,” The suggested replacement could give the impression that it is sometimes operated in OFR185 mode (which it isn’t).

L376 – typo (“to a to a”)

Thank you. Fixed.

L446-L448 – Please indicate the relative humidity that was established in the APPA OFR when the RTD measurements were conducted, and please clarify if the lamps were on or off. Is there any humidity-dependence to the RTD?

The sentence “For both tests the RH was controlled to 40% and the UV lights were off.” was added after the sentence “The particle and CO₂ concentrations in the outlet-center flow were measured with the CPC and CO₂ analyzers identified in the previous section.”

Though we did not repeat the experiments at different RH, we do not believe that there should be a significant dependence for either particles or low solubility gases such as CO₂.

L450 – Why are the gas/particle RTD's in the APPA OFR narrower than in the PFA OFR when the two reactors are nominally the same design?

The biggest differences between the two reactors, and those we believe are responsible for the narrower RTD with the APPA are: i) an inlet that was redesigned to minimize development of a jet near the core of the reactor and ii) addition of a water jacket around the reactor that minimizes temperature gradients and the convective mixing they would promote.

L464 – I did not notice any explicit discussion of temperature control in the APPA OFR in this section.

Thank you. The section title has been changed to just “Droplet size distribution”

L492 - The experiments describing sulfuric acid formation from SO₂/O₃ were not clearly described. I assume sulfuric acid was generated from SO₂ + O₃ --> SO₃ + O₂ followed by SO₃ + H₂O --> H₂SO₄, but it would be useful to clarify this. How is the concentration of “dissolved” SO₂ controlled and measured? Is O₃ uptake onto the K₂SO₄ seed particles required to initiate this reaction?

The original introduction to this section included: “...first evaluated through the well-studied oxidation of dissolved SO₂ by O₃, leading to formation of sulfuric acid and growth of the particles on which the droplets formed.”

Which has now been expanded to “...first evaluated through the well-studied oxidation of dissolved SO₂ by O₃, leading to growth of the particles on which the droplets formed accompanying the formation of sulfuric acid through the generic reaction:



Where S(IV) represents the +4 oxidation state sulfur species SO₂ · H₂O, HSO₃⁻, and SO₃²⁻ that will not remain in the aerosol phase following evaporation of the droplet and S(VI) represents the +6 oxidation state sulfur species H₂SO₄, HSO₄⁻, and SO₄²⁻ that will remain in the aerosol phase.”

Regarding the amount of SO₂ and O₃ in the droplets, these are controlled only by the gas phase concentrations, the Henry's Law constants, and, for SO₂, the dissociation equilibrium coefficients. Those parameters and the reaction rate constants were used to calculate the expected increase in diameter shown in original Figure 9 (not Figure 8). Rather than including all of the details of those calculations, we referenced Caffrey et al. (2001), which includes a thorough description of the relevant chemistry and equations.

L583 – Typo (the)

We inserted “the” in front of GC-FID.

L608- Assuming that the authors are referring to the benzene/OH system here, I disagree that the “distribution of [benzene] oxidation products and their OH reaction constant(s) are generally unknown.” See, for example, Xu et al. (2020); Priestley et al. (2021).

You are correct. This statement is reasonable for some precursors, but not for benzene. We have removed the sentence.

L721. Please clarify the author contributions of C. Le and D. R. Cocker.

The author contributions has been updated to include C. Le and D. R. Cocker. “D. R. Collins designed the reactor and edited the paper. N. Xu performed the experiments and simulations, processed the data, and wrote the paper. C. Le and D. R. Cocker contributed to some of the experiments and data analysis.”

Some of the figures should be moved to the Supplement - in my opinion, Figures 4, 8, 9, 10, 12, 13, and 16 would be a better fit there.

We moved Figures 4, 10, and 16 to the Supplement. We feel that the others are needed for understanding the accompanying text in the manuscript and should be left there so that readers can view them more easily.

The KinSim mechanism and case files that were used here should be uploaded with the Supplement.

These will be included in the Supplement. The description provided in the manuscript has been changed to “The supplement includes a file with a table and several figures and a compressed folder that contains the KinSim mechanism and case files for the results shown in Figures 10 and 11.”

References

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