

Interactive
Comment

Interactive comment on “HO_x radical chemistry in oxidation flow reactors with low-pressure mercury lamps systematically examined by modeling” by Z. Peng et al.

Anonymous Referee #3

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Review of Peng et al.

The authors present a model of the chemistry that occurs within their oxidation flow reactor. This is an extension over previous work published by some of the co-authors. They discuss, importantly, the influence of OH suppression within the OFR, which complicates the relationship between light intensity and [OH]. This is an interesting work, although I have some concerns regarding the extent to which the model accurately simulates the system conditions, in particular the flow dynamics and timescales involved (the simulations assume plug flow, which is not correct for the OFR). It may very well be that this has no bearing on the conclusions, but as the conclusions are made quite

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strongly it is up to the authors to demonstrate that it is not an important limitation. That said, the authors do provide some relationships between various controlling factors ($[O_3]$, $[H_2O]$, UV) as well as some general insights into OFR behavior that will be of use to the burgeoning community of OFR users. I believe that this paper is certainly publishable once the address the comments provided here, as well as those of the other reviewers and commentators.

P3887/L9: It would be clearer to simply give an equation for the OHR_{ext} than the text that is written.

Flow: The authors assume plug flow. However, as discussed by Lambe in his comment, the flow in the OFR is not plug flow, but instead is more similar to a CSFTR, leading to a distribution of lifetimes and exposures. This would seem to me to be a major potential limitation of the model that is not addressed. I believe that the authors need to address issues related to the flow conditions of their OFR and how these would influence their conclusions. The equations describing the flow conditions in a CSFTR are known (Mason and Piret, 1950). The authors do note (p3891) that the assumption of plug flow should be the focus of future studies. However, given statements such as at the end of the abstract (“This study contributes to establishing a firm and systematic understanding of the gas-phase HO_x and O_x chemistry in these reactors, and enables better experiment planning and interpretation as well as improved design of future reactors.”) it would seem that consideration of this effect in particular is especially important in the current context.

I believe that the authors should carefully consider the questions posed by Lambe and co-workers in his comment.

P3890: I find the statement “although SO₂ is consumed by OH much more slowly than most primary VOCs, it is actually more realistic in terms of the decrease of total OH reactivity than using only the first generation reaction of a VOC, since the latter ignores the continuing reactivity of the products.” to be somewhat unclear in terms of

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how specifically using SO₂ actually captures the influence of “continuing reactivity of the products” that are missed if primary VOCs had been used. Is this simply saying that because SO₂ products do not react with OH, there are fewer complications?

P3894: Looking at Fig. 1, I am not certain the statement “Note that the production, consumption, and interconversion of HO_x have average rates on the same order of magnitude within each type of OFR.” Is fully justified. For example, the conversion flux given for O₃ going to OH is 8.3 for OFR185 but 171.2 for OFR254-70, which is a factor of nearly 20 different.

I find the statement(s) on P3895 regarding the sensitivity of OH_{exp} to the inputs to be somewhat ambiguous/difficult to understand specifically what is meant. I suggest that the authors clarify.

An entire section is pretty much written around a supplemental figure (Fig. S2), which suggests to me that this figure belongs in the main paper.

It seems to me that it would be simpler to include Figs. S5-S9 in Figs. 2-4 and the other associated figures. Is there a particular reason that the OH_{Rext} = 1000 1/s case was not included in the main graphs? If not, then I suggest that it is included. Alternatively, or perhaps in addition to, it seems that since the role of OH_{Rext} is a relatively major focus of this paper, it would be helpful to have some figure showing the dependence of e.g. OH_{exp} vs. OH_{Rext} for some fixed H₂O and UV. The authors could potentially have one axis as OH_{Rext} with complementary axes for equivalent concentrations of different reacting species (e.g. SO₂, NO, some favorite VOC) so as to give an idea of the concentration ranges over which one should be concerned. This would ultimately be more useful to experimentalists, who can easily control the concentrations (at least for things that are not naturally in the atmosphere, but at least for lab experiments) but for whom OH_{Rext} is a somewhat more abstract experimental variable.

It is somewhat unclear what is specifically meant by the statement at the end of P3899 that “Very high OH_{Rext} also results in much increased relative importance of non-OH

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driven reactions in both OFRs, which will be addressed in future work.” What reactions are being referred to?

For Fig. 5 and associated discussion, it should be noted that the lack of sensitivity (uncertainty) to the reaction rate of OH with some external species (e.g. SO₂, VOC) is because these were exactly specified in the model and thus do not have uncertainty. In a real system, where the identities and relative abundances of all reacting species may not be known, uncertainty in the OH_{exp} will also be important. This is sort of noted at the bottom of P3900, but it could be made clearer that this has the potential to be a major uncertainty.

P3901, Line 23: Technically, OH is produced by O(1D) + H₂O, not O₃ + 254 nm, although of course the O₃ photolysis is the primary source of the O(1D).

Figure 6: I find this figure could be clearer as to whether the authors are showing the “percentage of OH exposure” or the “Ratio of OH exposure to the base case”, as both are used (yet have different meanings). I believe they report only the “ratio”, in conflict with what is stated in the caption. Additionally, it is difficult to tell the upper limit of the color scale.

Figs. 6, S10 and S11: The authors keep switching between percent changes and ratios. They should pick one and use it consistently. It is otherwise a potential point of confusion to the reader.

P3904/Fig. S11: I do not agree that the overall effect of replacing SO₂ with a collision-rate limited reaction is “more dramatic”, in particular for the OFR254-70 case. In fact, the ratio there sits right around unity for nearly all conditions. Only very particular conditions lead to strong deviations. Of course, the behavior of OFR185 is much more complex.

P3905, Line 17: The qualitative word “minor” should be removed, as 40-80% change might be considered more than “minor” by some. 80% is nearly an order of magnitude.

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Fig. 8: It is not abundantly clear what “percentage of remaining OH after suppression” means. Is this some ratio to some base case? What is the “before suppression” case? When $\text{OHR}_{\text{ext}} = 0$?

Reference: D. R. Mason and E. L. Piret, *Ind. Eng. Chem.*, 1950, 42, 817–825.

Interactive comment on *Atmos. Meas. Tech. Discuss.*, 8, 3883, 2015.

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