

Peng et al. conduct a modeling study to examine the importance of UV photolysis as well as O_3 , $O(^1D)$, and $O(^3P)$ reactions relative to OH reactions in oxidation flow reactors (OFRs). Overall, this manuscript addresses important issues regarding the application of oxidation flow reactors to examine OH oxidation chemistry in targeted laboratory and field studies. The authors examine a wide range of operating conditions in flow reactors and identify a subset of “optimal” and “pathological” conditions. Before the manuscript can be considered for publication in ACP, significant rewriting/reorganization is required to more clearly present and discuss the implications of the modeling work. Specific comments and suggestions are listed below.

1. F185, F254, $O(^1D)$ exposure, and $O(^3P)$ exposure are all correlated with OH exposure to some extent, yet the modeling work in this manuscript suggests it is possible to vary $F185/OH_{exp}$, $F254/OH_{exp}$, $O(^1D)_{exp}/OH_{exp}$, and $O(^3P)_{exp}/OH_{exp}$ over orders of magnitude range by varying the water vapor mixing ratio, photon flux, and external OH reactivity. To provide useful context/introduction to Figures 1-5, I suggest parameterizing these ratios as a function of input OFR conditions, because in its current form the manuscript mostly uses qualitative statements relating high $F185/OH_{exp}$, $F254/OH_{exp}$, $O(^1D)_{exp}/OH_{exp}$, and $O(^3P)_{exp}/OH_{exp}$ values to “pathological conditions”.

For example, plotting (i) $F185/OH_{exp}$ (ii) $F254/OH_{exp}$ (iii) $O(^1D)_{exp}/OH_{exp}$ (iv) $O(^3P)_{exp}/OH_{exp}$ versus $OHR_{ext}/[H_2O]$ – or a similar combination of input parameters that incorporate correlation of $F185/OH_{exp}$ with OHR_{ext} and anti-correlation with H_2O – over appropriate range of OHR_{ext} and $[H_2O]$. Individual traces could be shown corresponding to “L”, “M”, “H” photon fluxes displayed in Table 1 for “OFR185”, “OFR254-7” and “OFR254-70” as appropriate. These figures could allow for quantitative comparison of, for example: $[H_2O] = 2.3\%$ at $OHR_{ext} = 1000 s^{-1}$ versus $[H_2O] = 0.07\%$ at $OHR_{ext} = 0 s^{-1}$, as well as other intermediate conditions that are for the most part not considered in the manuscript. Presumably these plots can be derived from the model simulation data that has already been obtained, and perhaps consolidated into a single figure with a few subpanels.

2. Figures 1-5 are too difficult to read and interpret. There is too much data shown here – 28 compounds in Figure 1, 29 compounds in Figure 2, 9 compounds in Figure 3, 32 compounds in Figure 4, and 25 compounds in Figure 5 – making the figures overwhelming to the point of not being useful, especially with the histograms and insets that are also displayed in the figures.

3. The “fractional importance of X” ($X = F185, F254, O(^1D), O(^3P), O_3$) curves are derived from the literature rate constants and absorption cross sections that are summarized in Tables S1 and S2. Since they only serve as qualitative reference points to interpret the modeling results, it would be sufficient to show them only in Figures S1-S5 and reference as needed in the text, which could be cut back a bit. This might also make Figures 1-5 compact enough to consolidate into two figures, perhaps one with two subpanels ($F185/OH_{exp}$ and $F254/OH_{exp}$), and the other with three subpanels ($O(^1D)_{exp}/OH_{exp}$, $O(^3P)_{exp}/OH_{exp}$, O_3_{exp}/OH_{exp}).

4. It is not clear how to quantitatively interpret the CalNex, SOAS and BEACHON

histograms because they are shrunk to a minimal size to make room for the $X/(X + OH)$ curves. If they have a labeled ordinate, it is not clear to me what it is. Also, even though it is stated in the figure captions that “all curves, markers, and histograms share the same abscissa” (not the same ordinate) the natural tendency is to look at Figure 1, for example, and assume that $j_{185}/(j_{185} + k_{OH}[OH]) > 20\%$ for the field studies and $j_{185}/(j_{185} + k_{OH}[OH]) \sim 75\%$ for the source studies.

5. I would like to see more discussion of the characteristic features of the histograms displayed in Figures 1-5 and what causes them differ from one campaign to the next. For example, in Figure 1, there appears to be two distinct clusters of $F185/OH_{exp}$ in the SOAS campaign, whereas there is a wider band of $F185/OH_{exp}$ in CalNex. Then, in Figure 2, the SOAS dataset has a wider range of $F254/OH_{exp}$ than the CalNex dataset. What specific ambient or OFR conditions yield these results?

6. The results shown in Figure 6 would be more useful if displayed in a table format with columns: Species, Ambient photolysis %, OFR185 photolysis %, OFR254-70 photolysis %. Figure 6 is too busy/cluttered with all of the tags, and it is impossible to decipher the OFR photolysis percentages below the 1:100 and 1:1000 lines.

7. P23653 and Figure 8: “We use surrogate gas-phase species for the different functional groups as the cross sections of SOA-relevant species at these wavelengths are not available.” There are at least two literature studies reporting SOA absorption cross-sections down to $\lambda = 300$ nm (Updyke et al., 2012; Lambe et al. 2013; both of which report absorption Angstrom exponents that can be used to extrapolate down to $\lambda = 254$ nm), at least one study reporting SOA absorption cross sections down to $\lambda = 250$ nm (Romonosky et al., 2015), and at least two literature studies that report SOA absorption cross sections down to $\lambda = 220$ nm (Liu et al., 2013; Liu et al., 2015):

- Updyke et al., 2012: SOA generated from OH oxidation of naphthalene and cedar leaf oil
- Lambe et al., 2013: SOA generated from OH oxidation of α -pinene, tricyclo[5.2.1.0^{2,6}]decane, naphthalene, and guaiacol
- Romonosky et al., 2015: SOA generated from ozonolysis and OH oxidation of isoprene and α -pinene, and OH oxidation of *m*-xylene. There are 25 total SOA systems with reported absorption cross sections down to approx. $\lambda = 280$ nm).
- Liu et al., 2013: SOA generated from ozonolysis of α -pinene, limonene and catechol
- Liu et al., 2015: SOA generated from OH oxidation of toluene and *m*-xylene

All of these studies should be referenced in the Section 3.2 text, and a representative subset of the data should be incorporated into Figure 8.

8. Figure 8 and related discussion: aside from sulfuric acid, glyoxal, and nitric acid, virtually all of the individual compounds shown in this plot are either already presented on similar axes in Fig. 1, 2, S1 and S2, and/or are too volatile to participate in SOA formation processes. Thus, they are not relevant surrogate compounds for SOA. While it

is true that $\lambda = 185$ nm absorption cross sections are available for these compounds but not for SOA, the authors have already shown that the trends at $\lambda = 185$ nm and $\lambda = 254$ nm relative to OH_{exp} are similar. In this figure and related discussion, I suggest only showing relative photolysis rates at 254 nm for the SOA systems outlined in Comment #7, then if needed briefly mention in the text that the 185 nm results are expected to be similar.

9. Section 3.2: To supplement Figure 7, where the effects of (1) increasing RH from 3% to 60% in a laboratory SOA experiment and (2) diluting sample in two source measurements are shown, I would like to see an example of how humidifying an ambient sample to $[\text{H}_2\text{O}] = 2.3\%$ prior to introduction to the OFR influences the $\text{F185}/\text{OH}_{\text{exp}}$ and/or $\text{F254}/\text{OH}_{\text{exp}}$ histograms of one of the field studies shown in Figures 1-5. While the field measurements are generally not subject to “pathological conditions” as defined by the authors, this analysis would quantitatively demonstrate the efficacy of minimizing non-OH chemistry in OFRs using one of the suggested improvements in experiment design.

10. Water vapor concentrations are discussed in terms of both mixing ratio and relative humidity. It would be preferable to choose one or the other and stick with that throughout the manuscript.

11. P23545, L17: Quantify “low RH” and “high OHR_{ext} ”

12. P23545, L21: Quantify “low O_2 ”

13. P23545, L26-28: “*SOA photolysis is shown to be insignificant for most functional groups, except for nitrates and especially aromatics, which may be photolyzed at high UV flux settings.*” Quantify “insignificant”, “high UV flux”, and the extent of photolysis that is deemed significant at the high UV flux.

14. P23545-6, L28-2: “*The results allow improved OFR operation and experimental design, as well as guidance for the design of future reactors.*” Briefly summarize the suggested improvements, which include (1) maximizing $[\text{H}_2\text{O}]$ (2) minimizing OHR_{ext} through sample dilution and (3) operating OFR254 at $[\text{O}_3] \sim 70$ ppm rather than ~ 7 ppm. Also, while there is extensive discussion of how to improve OFR operation and experiment design, I did not notice any discussion in the manuscript about “guidance for the design of future reactors” – either delete this text or add specific suggestions for how to improve future reactor design.

15. P23548, L5: “...whose intensity can be rapidly computer-controlled.” This seems like extraneous detail to include - consider deleting.

16. P23549, L21: subscript “exp” in “ OH_{exp} ”

17. P23550, L16: suggested revision: “**estimate some parameters that are not specified or measured (e.g. UV) as needed**”

18. P23551, L3: “Photolysis of SOA, **a pathway ignored in previous OFR studies**, is also investigated.” SOA photolysis is considered in Lambe et al. (2013), which uses an OFR. Photolysis of α -pinene SOA generated in a flow cell is characterized by Epstein et al. (2014), and photolysis of several SOA types generated in a flow cell were characterized by Romonosky et al. (2015).
19. P23552, L24: Elsewhere in the manuscript, the “low” water vapor mixing ratio is represented as 0.07% rather than 0.0007.
20. P23558, L26: Replace “experimenter” with “experimentalist”
21. P23565, L7: Replace “faithfully” with “accurately”

References

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