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Interactive comment on “Modeling of the chemistry in oxidation flow reactors with high initial NO” *by* Zhe Peng and Jose L. Jimenez

Anonymous Referee #2

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The current paper explores a chemical space extended to consider high NO concentrations within an OFR. Such a contribution, whilst of limited interest outside the immediate field, should be of considerable worth to users of such devices, particularly those looking to explore the emissions from high temperature combustion sources. However, to some degree, the paper is missing the same point that many previous theoretical characterisations of the devices also miss. The chemical space is just one element influencing the performance and atmospheric relevance of all PAM-type reactors (and the gas phase chemical space, just a subset of this). It is for this reason that I would hope that the current study is envisaged as one of a series of papers that will be extended to the dynamical, physical and condensed-phase chemical considerations. I will return to this below.

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Having said this, within the stated scope, this paper carries a large amount of good new work that will make it worthy of publication in ACP. The chemical modelling appears appropriate with most of the necessary rate constants relatively well-constrained. This allows the characterisation of "good", "risky" and "bad" conditions under both 185 and 254 nm photolysis, though with the same caveats to the earlier work relating to uncertainties in the photolysis cross-sections and product yields of all possible VOCs (particularly when considering complex mixtures as in combustion emissions). In general, I am in agreement with the other referee that the gas phase chemical modelling alone warrants publication in ACP, but would invite the authors to address two main points to establish the validity of the approach and one point relating to the contextualisation of their study.

i) Validity of the plug flow assumption: in section 3.1.3 it is stated that the uncertainties relating to kinetic parameters are relatively low compared to other factors including the plug flow assumption, referring to Peng et al., 2015. It would be useful for the authors to discuss whether the relative kinetic vs dynamic uncertainties under the high NOx conditions are of a comparable magnitude to those under low NOx conditions. There have been plenty of studies of axial and radial gradients in flow reactors, so some justification of the highly simplified modelling approach would be appropriate, given the biggest uncertainties are explicitly stated as being related to this assumption.

ii) Validity of separating the numerical treatment of gas phase and particle phase processes: there is no statement of any of the uncertainty in gas phase chemistry being attributable to multiphase processes. I find this rather curious, since the primary focus of most PAM chamber studies relates is particulate mass. Both radical and closed shell species may interact substantially with the particle phase. All the particulate material in SOA particles is, by definition, formed from the vapour phase. If the flow regime is anything near plug flow, then the particle number, condensation sink, mass and composition of the particulate will evolve with the gas phase species and hence mass transfer (in both directions, where there is oxidative fragmentation and functionalisation) will

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be changing temporally and spatially inside the reactor. There really should be some discussion of the potential impacts of these processes in the paper.

iii) My final point relates to the context of the study. If it is not envisaged that this second paper on the chemical characterisation of OFRs is to eventually be accompanied by a numerical study of the multiphase processes, then I think the paper requires quite a bit more contextualisation. The root of the missing material relates to the competition between processes (nucleation, condensation, evaporation, coagulation, condensed phase reaction) alluded to in point ii) above and relating to aerosol dynamical evolution that are highly dependent on the magnitudes of different moments of the aerosol distribution. Extrapolation to concentration regimes other than the dilutions under the operating conditions of the OFR is simply not possible without the adoption of substantial questionable assumptions or use of a highly complex model which has yet to be described. The current paper implicitly aims to limit its scope to gas phase oxidation of VOCs in the OFR, but this is seldom the purpose to which they are put. Indeed, the limited context for OFR studies explicitly points to their use for "...secondary organic aerosol (SOA) formation and aging [studies], in both the laboratory and the field", because of the perceived advantage of elevated oxidant levels. None of the disadvantages that are related directly to the inappropriate exptrapolation of all the multiphase processes of relevance to SOA formation and transformation are mentioned. This requires significant rebalancing, ideally quantitatively in a further detailed publication but at least qualitatively in the introduction of the current paper.

Related to the above, the previous findings of nitrogen being incorporated into SOA are very tricky to interpret. The recommendations for operation are made from the perspective of gas phase oxidation to ensure that the gas phase product distribution is not anomalous. Incorporation of the nitrogenous species into particles will be subject to multiphase processes leading to net mass transfer between the phases. The mass transfer rate will be proportional to not only the difference between the gaseous concentration and the equilibrium concentration above the particle, but also to the condensation sink provided by the particles. Extrapolation to the amount of a component or class of components in the SOA (e.g. nitrogen-containing ones) to ambient conditions should not only consider the equivalent oxidant dose and gas phase chemical regime, but also aim to establish some equivalence in terms of the mass transfer between phases.

So, in summary, I would suggest that the material contained in the paper is readily publishable, but requires both contextualisation and more discussion of the likely uncertainties surrounding the assumed dynamical framework and separation from the condensed phase processes.

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