

Interactive comment on “Modeling the influence of precursor volatility and molecular structure on secondary organic aerosol formation using evaporated fuel experiments” by S. H. Jathar et al.

Anonymous Referee #1

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In this work, the authors applied different modelling frameworks to SOA formation from different fuels. This is a novel set of experiments, using a complex mixture as the starting precursor, and, as a result, represents the most atmospherically relevant emission source. This manuscript specifically evaluates how well each state-of-the-art modelling framework can reproduce the SOA data. The main lesson I drew from the analysis is that VBS represents the SOA formation well when there is a higher degree of complexity in the fuel composition, but molecular detail would be required when the composition is more homogeneous. My main critique is that this manuscript does not explicitly study molecular structure, so the authors should avoid giving that impression (see be-

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low comment). Otherwise, this manuscript is clearly written and the data analysis and modelling is novel and sound. I recommend this manuscript be published upon considering the following comments:

- In the title and in the introduction, the authors state quite clearly that they are investigating the effect of molecular structure on SOA formation. However, I was quite disappointed when I read that n-alkanes, isoalkanes and cycloalkanes end up being lumped into ALK4, ALK5 based on the SAPRC scheme. The volatility based scheme also does not account for molecular structure. In other words, the shift in volatility as a result of oxidation should depend on fragmentation mechanisms and molecular structure, but that effect is ignored when they are all lumped together. There is a differentiation between aromatics and alkanes, but not molecular structure of the backbone (degree and position alkyl branching, rings etc.). Therefore I do not believe that the manuscript in its current form is investigating molecular structures directly. I could be misunderstanding the authors, so I would like to see a clarification if I am mistaken. Currently, I believe the message is “molecular structure does not matter for SOA from complex fuels, but it does for fuels with simpler composition”. If so, I believe that is an important message to bring out, and the title should be changed to reflect that.
- One caveat of this study is that the results apply only to urban SOA formation, where reactivities are dominated by alkanes, simple alkenes, and aromatic compounds, or compounds of fossil fuel origins. Readers should be cautioned that the trends in SOA yields are unlikely to be the same for biogenic compounds, like isoprene, and monoterpenes, or biomass burning emissions. Therefore it is quite ambitious to say that volatility-based frameworks are sufficient for all CTMs, as stated in the last paragraph.
- The average OH rate constant is $1\text{E-}11$, which seems low. The species that will be primarily responsible for SOA formation will likely be larger alkanes or aromatics, which will have rate constants of at least 2 or $3\text{E-}11$ (naphthalene/heptadecane). So it would make sense to me that multiple generations are indeed more relevant. (For $3\text{E-}11$ rate

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constant, and OH exposure of $1.7E7$ molec cm^{-3} hr, that would be almost 2 lifetimes of oxidation.) Also, Ziemann et al. and the Caltech group showed that multiple generations are important for SOA formation. Therefore, one should take multiple generations into account. It is entirely reasonable to expect that the fractional bias and fractional error would be greater in such case (because the model will be more complex), but this is more realistic and accurate.

- In table S5, diesel seem to contain a disproportionately large amount of C9 aromatic (one order of magnitude higher than other species). That would suggest to me that SOA would be dominated by those from these C9 aromatics (trimethylbenzenes?). Is that common knowledge among scientists studying SOA formation? (There seem to a lot more focus on benzene/toluene/xylenes, judging from Ng et al., 2006).

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 24405, 2013.

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