Response to the reviewer 2 (Manuscript Ref. NO.: acp-2021-649)

We would like to thank the reviewer for their time and considerate comments. Their comments are repeated below, followed by our response.

General comments:

The study at hand by Han and Jang deals with environmental chamber experiments at the UF-APHOR facility in Gainesville, Florida, which are interpreted using a high-level modelling framework (UNIPAR-CB6r3). The experiments look at the formation of secondary organic aerosol (SOA) from gasoline, and its hydrocarbon constituents individually. A primary focus is the importance of particle-phase chemistry in SOA formation, while a secondary focus is the treatment of gas-wall partitioning (GWP) of volatile vapors. These topics fit well within the scope of Atmospheric Chemistry and Physics.

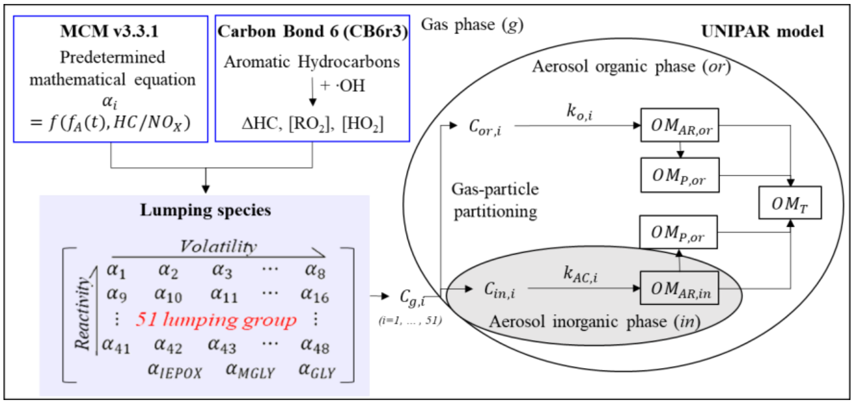
The authors find good correlation between the model and experiment. They find that a substantial amount of gasoline SOA is due to oligomers formed in the particle phase and GWP has a significant effect on model results. Both findings are very interesting, and I believe lots can be learned from their model. However, from reading this paper alone (and not also a wide range of previous publications), it is very hard for me to deduce what the fundamental parameters were in this model simulation and which parameters were optimized / fitted for this study. This makes it very hard to gauge the significance of the conclusions. Thus, before I can recommend this paper for publication within ACP, the authors must present their approach more clearly, with an emphasis on when and how coefficients / polynomials / fits to the data are obtained (if at all) and what the model is calibrated against.

Major Comments:

1. It did not become clear to me if fit parameters were used in this study to align the observed and modelled SOA mass concentrations. If I understand correctly, an important part of this modelling approach is the determination of the polynomial equation that led to all α_i. Line 138 states “These equations are mathematically derived by using explicit products predicted from MCM v3.3.1.” How is this done, as MCM does not specify an aerosol phase reactivity scale (L126)? Line 139 describes the parameters α_i as “dynamically predicted”, what does this mean? Is there fitting to the data happening?

   Response:
   The formation of oxygenated products is predicted by simulating the MCM v3.3.1 gas mechanism. The resulting oxygenated products are, then, classified into 51 lumping species based on their volatility and chemical reactivity. The stoichiometric coefficients (α_i) of 51 lumping species i are determined at varying HC/NO_x ratios and the different degree of gas aging, and dynamically constructed by using the mathematical equations based on the gas simulation with MCM v.3.3.1. The degree of aging is mathematically correlated with the concentration of RO_2 and HO_2, which are normalized with the initial concentration of hydrocarbons.
   To make it clear, the explanation of the creation of the dynamic α_i from gas mechanisms has been updated with detail description and Fig. 1 has been updated in the revised manuscript.

Fig. 1:



2. Figure S4 shows and it is stated throughout the manuscript that "OM_P", the organic mass attributed to gas-particle partitioning, is very low or even close to zero for some SOA precursors. In turn, this means that SOA mass must be almost exclusively (> 90 %) due to particle-phase reactivity (OM_{AR}). It is not entirely clear to me how solid the result is because I do not understand how the authors come to this conclusion. Is this just a result from the MCM-trained model, or does this rely on previous chamber experiments to optimize α_i parameterizations?

Response:
The α_i value was not optimized to the chamber data. As described in the response to comment 1, α_i is dynamically constructed by using the mathematical equations as a function of NO_x level and the degree of product aging based on the gas simulation with MCMv3.3.1 (Fig. 1). The α_i value with the HC consumption (ΔHC) enables the calculation of the concentration of lumping species. SOA forms via multiphase partitioning (gas, organic, and aqueous phases) and aerosol phase reactions (organic and aqueous phases). The OM_p contribution to the total SOA depends upon precursor types, NO_x levels, seed types and temperature. In general, the fraction of OM_P increases with decreasing temperature, decreasing NO_x levels, and decreasing aerosol acidity (Zhou et al., 2019). Additionally, aromatic SOA produces a higher OM_{AR} than terpene (Yu et al., 2021).

3. Given this result, it is surprising to me that Figure 6 shows that vapor pressures are the most relevant model parameters. Is that because low vapor pressure is a prerequisite to molecules being present in the particle phase where they undergo particle-phase chemistry?

Response:
Lowering vapor pressure can increase the gas-particle partitioning for both reactive and non-reactive organic species for aerosol phase reactions. Thus, both OM_P and OM_{AR} can increase. Relatively the OM_P fraction increases more than OM_{AR} similarly to the impact of temperature.

4. Does OM_{AR} mean that the product itself would not condense and only the particle-phase reactivity makes it stay in the particle phase? What types of reactions and products would this be that make up such a large share of SOA? I think my questions are inherently connected to point 1 above: have any of these parameters (α_i or $k_{o,i}$) been fitted for this study or does the model just naturally fit the data? My skepticism comes from the simulations results of gasoline, where particle-phase reactivity suddenly is of less importance (especially Figs. 3a,b,c). Why is that so?

Response:
OM_{AR} is estimated as a second order reaction product from condensed organics based on the assumption of a self-dimerization reaction of organic compounds in media.

α_i is created by using the predetermined mathematical equation by using the product distribution from gas mechanism.

SOA yields are affected by the rate constant ($k_{AC,i}$) in salted aqueous reactions. In our previous work (Jang et al., 2005;Jang et al., 2006), a 2nd order $k_{AC,i}$ (L mol^{-1} s^{-1}) was described via a rate determining step for polymerization to form polyacetal. The kinetic equation terms in $k_{AC,i}$ is related to both the molecular structure of an organic product (basicity of an organic compound in strong acid media and the hydration constant related to a reactivity scale); excess acidity (non-ideality of organic species in strong inorganic acid); and inorganic parameters (e.g., [H^+], FS, and aerosol water content). The coefficients of these model parameters in $k_{AC,i}$ were obtained via semiempirically fitting the equation to aerosol growth by heterogeneous acid-catalyzed reactions of various carbonyls with acidic inorganic aerosol using a flow reactor.

$k_{o,i}$ is determined by extrapolating $k_{AC,i}$. to the neutral condition (no acid) and in the absence of salted aqueous solution (organic phase) to process oligomerization in organic phase. Unlike aqueous reactions, $k_{o,i}$ is sensitive to the organic layer viscosity (De Schrijver and Smets, 1966;Reid et al., 2018). Thus, the additional term as a function of MW and O:C (Eq. 7) were introduced to express the sensitivity of SOA formation to organic viscosity and leveraged to numerous chamber data originating from three terpenes (α-pinene, β-pinene, and d-limonene), 10 aromatics (benzene, toluene, 3 xylene isomers, and 3 trimethylbenzene isomers), isoprene: nearly 120 data collected from the UF-APHOR large outdoor smog chamber for last 10 years) (Im et al., 2014;Beardsley and Jang, 2016;Zhou et al., 2019;Yu et al., 2021). Then, the resulting UNIPAR model and model parameters were applied to gasoline SOA of this study.

The importance of the OM_{AR} or OM_P is differed by meteorological and experimental conditions or the type of hydrocarbons. As mentioned as a response to the comment 2, the OM_P contribution to the total SOA depends upon precursor types, NO_x levels, seed types and temperature. In general, the fraction of OM_P increases with decreasing temperature, decreasing NO_x levels, and decreasing aerosol acidity (Zhou et al., 2019). Additionally, aromatic SOA produces a higher OM_{AR} than terpene (Yu et al., 2021).

5. The reaction rate $k_{o,i}$ must be a very influential parameter, given the high fraction of OM_{AR}. Why is its sensitivity in Fig. 6 (Fig.7 in the revised manuscript) so small? It follows a semi-empirical description. Is there a $k_{o,i}$ for every one of the 51 lumping species for each of the 10 hydrocarbons, so 510 individual parameters? How about cross-reactions between lumping species, how are these treated?

Response:

$k_{o,i}$ or $k_{AC,i}$ controls reaction rates. It depends on duration of chamber simulation (10-12 hours). Within chamber simulation time scales, it is hard to see the impact of aerosol rate constant. The reaction time scale of highly reactive organic species in VF and F group are very short ranging from second to minutes.

As shown in the Eq. 7, $k_{o,i}$ is determined based on the MW_{or} and $O:C$ of SOA, and the $pK_{BH_i^+}$ and R_i of lumping species i. Those $pK_{BH_i^+}$ and R_i of lumping species *i* is specific for the 51 lumping species which is unified for all the aromatic hydrocarbons. Thus, we have 51 individual parameters for the oxygenated products from 10 different aromatic HCs. The cross-reaction between lumping species is not considered in this study.

6. To me, the abstract seems very technical and does not reflect the discussion in the manuscript well. For example, OM_P and OM_{AR} are not mentioned there.

Response:

The abstract has been revised based on the comment.

7. It is not clear to me what role the inorganic particle phase reactions play for this study, can the authors comment on that in the manuscript?

   Response:
   The electrolytic inorganic particle can contain a significant amount of aerosol water above ERH or DRH. When the inorganic aerosol is wet, reactive organic species can heterogeneously react in aqueous phase and increase SOA mass.
   It has been added in the revised manuscript (L268).

8. Can it be calculated with the model which components of the gasoline HC mix form the most SOA?

   Response:
   No, the current UNIPAR-CB6r3 model cannot track the SOA formation form the individual aromatic hydrocarbons because 10 aromatic hydrocarbons use the unified array for physicochemical parameters. However, it is possible to modify the model to keep physicochemical parameters of individual aromatic hydrocarbons.

Minor and Technical Comments

1. 88 – It is not clear what CCl4 is used for in this work.

   Response:
   CCl_4 was injected and its concentration was monitored during the experiment to obtain the dilution factor of the chamber. The dilution factor obtained from CCl_4 measurement was applied to experimental data to correct the dilution during the experiment. It has been added in the revised manuscript.

2. Figure 2: Caption is missing what red and black markers are, respectively.

   Response:
   The Figure 2 has been revised based on this comment.

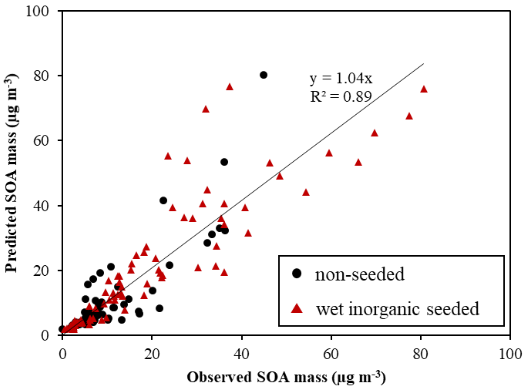


Figure 2. The linearity of predicted SOA mass (µg m^{-3}) using UNIPAR-CB6r3 and observed SOA mass (µg m^{-3}) in the absence and the presence of wet inorganic seed. SOA mass was produced via the photooxidation of various aromatic HCs (Table S2) in the UF-APHOR chamber.

3. Eq. 7 and L183: I cannot follow how with Eq.7 the impact of viscosity on oligomerization rate is considered. Why would viscosity affect chemical reaction rate?

   Response:
   The growth of organic particles can occur by in-particle chemistry; the rates of these reactions can be limited by slow bulk diffusion within a particle. It has been added in the revised manuscript L195 as:

   "Studies showed that viscosity can also influence chemical reaction rate, limited by slow bulk diffusion within a particle (De Schrijver and Smets, 1966;Reid et al., 2018)."

4. Fig. S4 and L232: The model lines for benzene OM_p are not visible in the figure.

   Response:
   Figure S4 has been revised based on this comment. Now, the dotted line represents the OM_{AR} instead of OM_P in Fig. S4.

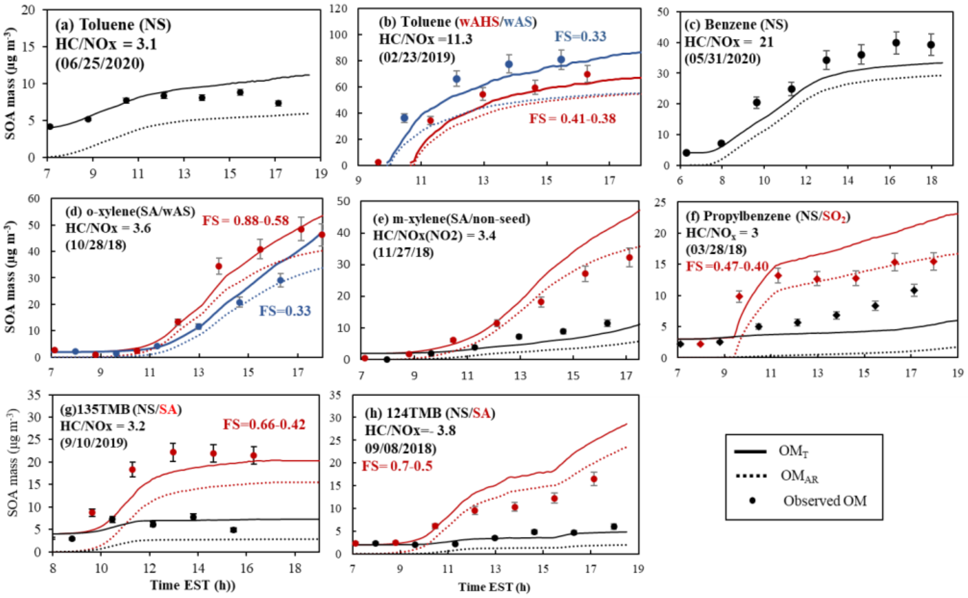


Figure S4. Observed (plot) and simulated (line) SOA mass in the chamber studies of aromatic HCs. The simulated OM_T (solid line) and OM_{AR} (dotted line) are illustrated. Particle loss of experimental data onto the chamber wall was corrected. The ranges of FS are presented for experiment under the acidic condition to indicate aerosol acidity over the course of the experiment. The error (9%) associated with SOA mass was estimated with the instrumental error originating from the OC/EC analyzer.

5. Fig. 3 and S4: It was confusing to me at first that the dotted lines stand for OM_P in Fig. S4 and for OM_{AR} in Fig. 3. I might be good to align this.

   Response:
   The manuscript has been revised based on this comment. Now, the dotted line represents the OM_{AR} instead of OM_P in Fig. S4. Please see the figure in the response for the minor and technical comment 4.

References

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