

## ***Interactive comment on “Secondary organic aerosol formation from biomass burning intermediates: phenol and methoxyphenols” by L. D. Yee et al.***

**Anonymous Referee #3**

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This paper describes a series of environmental chamber experiments and gas/particle-phase chemical analysis performed in order to elucidate the mechanisms of SOA formation from biomass burning intermediates: phenol, guaiacol, and syringol under low NO<sub>x</sub> conditions. Time-profiles of signals observed by the CIMS, in comparison with SOA mass, suggested that ring-fragment carboxylic acids were in equilibrium with SOA. Although vapor pressure of syringol is much lower than those of phenol and guaiacol (~100 times lower than guaiacol), the SOA yield of syringol was significantly lower than the other two, which was ascribed to loss of carbon in methoxyphenol systems.

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This paper is clearly written and scientifically sound. I recommend publication after following points are addressed.

Major comments

1. Injection and quantification method of syringol needs to be evaluated. They stated “Guaiacol and syringol measurements obtained using the GC/FID were unreliable due to condensation loss in the sample loop; thus, the hydrocarbon concentration during these experiments was monitored using Chemical Ionization Mass Spectrometry (CIMS) in negative mode operation.” How was CIMS calibrated? Was the same 55L Teflon bag used? Is there any significant loss of syringol in the injection system or on chamber wall (e.g., Loza et al. 2010; Matsunaga et al. 2010) that may bias quantification? Reactant loss may lead to under-prediction of SOA yields, which may affect their major conclusion on low SOA yield from syringol. Since syringol is solid at room temperature, additional description on how syringol was introduced into the chamber would be useful for future studies.

2. It is an interesting observation that some ring-fragment carboxylic acids followed SOA growth (e.g., m/z 185 FRAG in Fig.3, m/z 149 FRAG in Fig.7) better than other products (e.g., -OH addition products). Although authentic standards are not available, is there any approximation for the concentration of gas-phase carboxylic acids? Although carboxylic acids are often observed in particle phase (e.g., Sato et al., 2012), they are not commonly reported from gas-phase product analysis of aromatics (e.g., Calvert et al., 2002; Birdsall et al., 2011). Is this because previous studies (not using CIMS) missed gas-phase carboxylic acid?

3. Although “Atmospheric relevance” section discusses the impact of NO, NO<sub>2</sub>, and O<sub>3</sub>, no discussion on NO<sub>3</sub> radical is given. Phenolic compounds react significantly with NO<sub>3</sub> even at the trace level of daytime NO<sub>3</sub> (e.g., Calvert et al., 2002, p.24, Figure 1-B-2: 86% of o-cresol in a polluted urban atmosphere reacts with NO<sub>3</sub> in daytime) and ~100% in nighttime. Although it may be reasonable to focus on low-NO<sub>x</sub> conditions in

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this paper, caution must be given in extrapolating this finding to atmospheric models, especially because biomass burning continues in nighttime as well.

4. P.3497 Line 13: They showed that SOA is in equilibrium with  $m/z$ 185 (Fig.3), which they propose to be the ring fragment  $C_4H_4O_3$ , a carboxylic acid that forms from the decomposition of the bicyclic radical from phenol + OH. However, the time-profile of  $m/z$ 185 seems unlikely for a 1st generation ring fragment;  $m/z$ 185 increases only after  $m/z$  211 (THB, 2nd generation product) started increasing. How come a 1st generation product increase after a 2nd generation product?

5. p.3498 Line 3: This paragraph needs more explanation. How does the time profiles of CIMS ions ( $m/z$  145,161, and 177) suggest that they are carboxylic acids? How does "prevalence of these products" explain the absence of a hydroperoxides  $C_6H_8O_4$ ?

Minor comments

6. P.3489 Line 21, correct particle volume unit:  $\mu m^3 cm^{-3}$

7. Ion trap is described in detail in the experimental section but results are not shown anywhere explicitly. If no results from the ion trap are used for this paper, remove the description from the experimental section.

8. Dealkylation of aromatic hydrocarbon was discussed by Noda et al. (2009) and Aschmann et al. (2010). Aschmann et al. did not observe dealkylation. Discussion on methoxy loss could be improved in the context of these studies.

Reference

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