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

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The authors would like to thank all referees for their helpful comments and suggestions for improving this manuscript. Responses to all referee comments are below and many revisions to the manuscript have been made. All references to specific sections, pages, and line numbers in author responses to the referee comments are based on those of the current discussion manuscript format.

Referee 3

This paper describes a series of environmental chamber experiments and

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gas/particlephase chemical analysis performed in order to elucidate the mechanisms of SOA formation from biomass burning intermediates: phenol, guaiacol, and syringol under low NOx 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 ($\sim$ 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.

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.

The authors have added the following description to clarify details on the calibration, “Calibrations of guaiacol and syringol on the CIMS were performed similar to those of phenol on the GC-FID by preparing 55 L Teflon chamber standards of varying concentrations of the methoxyphenol compounds. The LDL for guaiacol on the CIMS was established to be 100 ppt and that for syringol to be 500 ppt. While phenol was de-

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tected at both the transfer (m/z 113) and the cluster product (m/z 179), a calibration curve was not made because a photooxidation product in the phenol system interfered significantly at m/z 113."

We have also added the description to the experimental section after the description of hydrocarbon introduction into the chamber, "Gentle heat was applied to the glass bulb to support evaporation of syringol (solid) into the chamber."

The following paragraph has been added under the description of the yields: Syringol vapor-phase wall loss in the reactors are believed to be minimal. Lauraguais et al. (2012) found no vapor-phase wall loss of syringol and Coeur-Tourneur et al. (2010) found negligible losses for guaiacol and related methoxy and alkyl substituted benzenes. Assuming a first-order wall loss rate, kw $\sim$ 1 x 10$^{-5}s^{-1}$, a typical rate for previously tested compounds in our chamber (Loza et al. 2010), this would lead to roughly a quarter loss of syringol to the walls over the course of the experiment. Correcting for this by lowering ΔHC would lead to syringol SOA yields that are similar to those of guaiacol, but not significantly higher.

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?

Yes, the time profile comparisons of the gas and particle phases do provide insight for inferring the chemical development that is simultaneous with/responsible for aerosol growth. We keep in mind that many of these ions have contributions of isomeric, but often chemically similar compounds (based on the chemical ionization scheme).

For example, m/z 185 likely has contributions from the isomeric dicarbonyl (hydroxyl butenedial) as well as the carboxylic acid (depends on position of intial-OH attack). For this reason, we do not attempt quantification of these carbonyl components at this time. Yes, carboxylic acid formation is not generally attributed to gas-phase production from aromatics, though dicarbonyl fragments are. Some of these are isomeric, so it may be difficult to separate and not specifically looked for compared to more obvious assignments of larger functionalized aromatics.

3. Although “Atmospheric relevance” section discusses the impact of NO, NO2, and O3, no discussion on NO3 radical is given. Phenolic compounds react significantly with NO3 even at the trace level of daytime NO3 (e.g., Calvert et al., 2002, p.24, Figure 1-B-2: 86% of o-cresol in a polluted urban atmosphere reacts with NO3 in daytime) and $\sim$ 100% in nighttime. Although it may be reasonable to focus on low-NOx conditions in this paper, caution must be given in extrapolating this finding to atmospheric models, especially because biomass burning continues in nighttime as well.

Yes, that is true. We have added reference to the reaction with NO3 radical and we also agree that caution should be used in extrapolating the current findings to atmospheric models, especially in light of the interesting methoxy chemistry.

4. P.3497 Line 13: They showed that SOA is in equilibrium with m/z185 (Fig.3), which they propose to be the ring fragment C4H4O3, a carboxylic acid that forms from the decomposition of the bicyclic radical from phenol + OH. However, the time-profile of m/z185 seems unlikely for a 1st generation ring fragment; m/z185 increases only after m/z 211 (THB, 2nd generation product) started increasing. How come a 1st generation product increase after a 2nd generation product?

The compound at m/z 185 is actually likely to be the ring fragment coming from dihydroxybenzene because of the extent of its oxygenation. It also has contributions at the signal from dicarbonyl (hydroxybutenedial). Butenedial is known to be a first-generation ring fragment from phenol, but hydroxybutenedial would be the analogous second-generation ring fragment from dihydroxybenzene. Due to the confusion of the isomeric carboxylic acids (while definitely possible products) and the dicarbonyls (more well-known in aromatics chemistry as ring fragments), the authors made changes to the example isomer structures in Table 3 to show the dicarbonyls.

5. p.3498 Line 3: This paragraph needs more explanation. How does the time proïňĄles 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 $C_6H_8O_4$?

We have addressed this in Referee 1 Major Comment 1.

Minor Comments:

6. P.3489 Line 21, correct particle volume unit: μm3cm-3

Thank you for catching this. The correction has been made.

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.

This description has been removed.

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.

We have revised the discussion to reflect results of these studies, addressed in Referee 1, Major Comment 3.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 3485, 2013.