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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Influence of fuel ethanol content on primary emissions and secondary aerosol formation potential for a modern flex-fuel gasoline vehicle" *by* Hilkka Timonen et al.

Anonymous Referee #1

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Timonen et al describe experiments using a flexible fuel vehicle operating on a dynamometer. They quantify the primary emissions of gases and particles, and investigate secondary PM formation using a potential aerosol mass (PAM) flow tube reactor. While the paper is topically relevant to ACP - indeed several similar papers (e.g., Chirico et al, Gordon et al, Platt et al) have been published in this journal - it is not ready for publication in its current form.

The paper is very poorly organized and presented. It reads more like a first-draft, "core dump" of all of the relevant data rather than a thoughtful analysis and discussion of the novel elements of this particular set of experiments. Furthermore, the authors have not sufficiently described the experimental setup and operation. Thus I have serious

concerns about how the data were collected and interpretation of the results that must be addressed in revision.

Specific comments:

1. Please define all abbreviations and acronyms upon first use. E.g., FFV in line 5, page 4 and THC on line 7 of the same page.

2. Page 5, Lines 15-17 - Including a time trace of the NEDC would be useful. Not all readers are familiar with the test cycle. (Upon further reading this time trace is presented in Figure 8, which is too late in the paper to be of much use to readers unless they plan to read the manuscript multiple times.)

3. How many experiments were conducted with each fuel? It seems like only one test was run per fuel, and I would argue that is not enough.

4. The methods section includes a long in-line list of measured VOCs. This information might be easier to interpret as a table that could also include information such as minimum detection limit or some of the measurement results.

5. How was the SP-AMS operated, and what data are presented? Do subsequent figures show rBC + NR-PM1 data from the laser + vaporizer configuration, or are rBC data from laser-on and the NR-PM1 data from laser-off operation? It is almost impossible for me to interpret the SP-AMS data without knowing exactly what data are being presented. Ionization efficiency from the two SP-AMS vaporization modes (thermal versus laser) is not necessarily identical (e.g., doi:10.5194/amt-2016-201), and thus it is important to know whether laser and/or thermal vaporizer data are presented.

6. Page 8, Line 18 - How was ammonia measured? It was not listed in the Methods.

7. Were any special precautions or preparations taken between experiments with different fuels? E.g., does the vehicle need to run for a certain number of kilometers on E85 after using E10 in order for the on-board oxygen sensor or other parameters to be reset? Similarly, was the vehicle certified to run on E100? The huge increase in

emissions for E100 versus E10 and E85 (Figure 1) might indicate operational problems.

8. Section 3.3.2 - rBC increased in the PAM for E10. The authors offer several possible explanations, but none seem particularly satisfying. Was there a separate measurement of BC (e.g., aethalometer) available for an independent measurement? The authors note that some of the apparent increase in rBC mass may be from growth of small particles with BC cores. While this may be the case, I would be more worried about changing particle collection and ionization efficiency in the laser-on mode (again, it would be very helpful to know how the SP-AMS was operated in this study). Did concentrations of inorganic ions (e.g., sulfate) also increase after the PAM for E10 operation? If the hypothesis that the increase in rBC comes from particle growth is correct, one might also expect to see higher sulfate from particle growth as well.

9. Section 3.4 - Wall losses in the PAM - the authors mention that wall losses may be an issue, but make no attempt to characterize or quantify them. Given that Jose Jimenez's group has recently published papers that consider PAM wall losses (e.g., doi:10.5194/acp-16-2943-2016), it seems incomplete for the authors to try and publish data without at least simple wall loss corrections.

10. Figures 2, 4, and 7 all show concentration rather than emission factor. I think plotting emission factor would be more instructive because it removes any differences in dilution between the separate experiments. In the end what is important are differences between fuels, and plotting concentration does communicate those differences, but it is hard to interpret, e.g., Fig 4, when the E10 bar is divided by 10 in the left panel but not the right. Using emission factor may help with the scaling.

11. Figure 3 and 5 would be easier to compare if the information was combined. The authors expect readers to compare O:C and H:C from fresh emissions to post-oxidation, but the figures may very well end up on different pages once typeset. It is much easier to compare adjacent bars than to look at one figure, remember the O:C, and compare it to another figure.

12. Figure 6 suggests that oxidation converts compounds that produce CxHy and CxHyO ions to compounds that produce ions with multiple oxygen. Can the authors suggest relevant chemistry that is happening? I was surprised to see that the CxHyO bar always seems to be depleted after the PAM relative to the fresh emissions. This seems like an important finding.

13. The comparison of primary versus secondary in Figure 8 is not like-versus-like. The PAM is not a perfect plug-flow apparatus. It operates more like a CSTR and there is mixing within the PAM. Thus the emissions become "smeared" over time, and this is evident from the smooth shape of the PAM output. Therefore trying to correlate the peak in PAM output to a specific point in the driving cycle seems to unwise (and perhaps impossible).

14. Likewise, the size distributions in Figure 10 likely tell you more about the gas-phase emissions entering the PAM than anything. The multiple "nucleation" events probably coincide with bursts of VOCs that can be converted to SOA.

15. In general, the discussion of the size distributions seems like a loose appendage. Section 3.7 and Figures 9 and 10 should either be expanded significantly or removed.

16. The manuscript needs a thorough edit for English grammar.

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