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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Nanoparticle formation in the exhaust of vehicles running onultra-low sulfur fuel" *by* Hua Du and Fangqun Yu

Anonymous Referee #1

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Review of “Nanoparticle formation in the exhaust of vehicles running on ultra-low sulfur fuel, by H. Du and F. Yu, submitted to Atmos. Chem. Phys. Discuss.

This paper discusses the modeling and comparison with data of nanoparticle evolution following exhaust from vehicles containing a particle trap and using low-sulfur fuel. The authors conclude that they can simulate such evolution by treating binary homogeneous nucleation of sulfuric acid/water, thus BHN is likely to be the main mechanism of nonoparticle formation in vehicles with a trap.

The study is novel and at first appears to make a convincing case. However, on closer inspection, the model used does not account for some important processes, and this reflects in some possibly incorrect results compared with data at small particle size

from studies not shown in the present paper. It is not clear whether such shortcomings affect the overall conclusion, but they may.

Specifically, the model does not treat Raoult’s law in the condensational growth equation; thus it does not account for this aspect of organic gas growth or evaporation that has been accounted for previously in nanoparticle evolution studies (e.g., Zhang et al., 2004; Jacobson et al., 2005 – both cited in the manuscript), Second, the model does not account for van der Waals forces or fractal geometry in the coagulation equation, so it underestimates the rate of coagulation in small particles, particularly those smaller than 10 nm. This results in Mode 1 concentration higher than they should be 45 s after emissions in Fig. 3a/3b. Jacobson and Seinfeld (2004, Atmospheric Environment, 38, 1839) found the coagulation due to these kernels may be important not only in reducing the mode but also in speeding the rate of reduction of the mode. At a minimum, the authors should acknowledge these shortcomings and perform a sensitivity test where they increase the coagulation kernel for small particles due to van der Waal’s forces, using, for example, enhancement factors provided in the study above.

Along the same lines, it is not clear from the simulations whether coagulation or growth is more important in the authors’ model. The authors should run separate simulations isolating the effects of nucleation, coagulation, and condensation.

The caption to Fig. 2a states that the conversion efficiency was tuned at each temperature to ensure the model matched the data. This renders the figure relatively useless. In particular, the fit derived appears to cross data from four different studies but not from any data consistently from the same study. The authors should show results in Fig. 2a for fits to each data set given in Fig. 2b (in addition to those results shown) and state in the text that the results from the tuned fit are somewhat inconsistent with any of the individual data set measurements.

Additional comments:

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1. How is Equation 1 solved. Is it solved with an ODE solver or operator split? In either case, what is the solution mechanism (provide original reference as well). Does the solution conserve properties (e.g., volume). Is it stable, positive definite?

2. Section 2.1. “It is important to note that previous theoretical studies…considered the latter two processes only and that the nucleation process was excluded from their models.” This statement should be clarified. Zhang et al. (2004) neglected coagulation in the model simulations. Jacobson et al. (2005) state on page 9487 that they treated homogeneous nucleation, coagulation, and condensation, thus the statement by the present authors appears to be incorrect. However, Jacobson et al. examined vehicles without traps rather than with traps. As the authors conclude, BHN is not so important in the absence of a trap. Thus, the difference in the present study is primarily that emissions with particle traps are examined and special attention is paid to conversion of sulfur due to the trap rather than other studies did not consider BHN, etc..

3. Section 2.2. “Although there are probably hundreds of organic species in the vehicular exhaust, they can be divided into the two distinct categories, and the characterization…should not largely affect the major conclusions concerning nanoparticle evolution.” Fig. 2b of Jacobson et al. (2005) shows that organics of different carbon number have significantly different effects as a function of particle size. It is probably not correct to say that selecting two distinct categories will have little effect in light of these results. The authors should at least discuss this issue a little more thoroughly in light of the variation of volatility with carbon number and acknowledge possible uncertainties.

4. Section 3.1. “..converts significantly more SO2 into SO3.” Are you certain that the pathway from SO2 to H2SO4 with a particle trap follows the mechanism given or is this your hypothesis based on what generally happens during ambient oxidation?

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5. Section 3.1. “Mode III consists mainly of soot agglomerates and ambient particles.” The emitted soot must dominate the ambient. This should be stated.

6. It is not clear in the text what the size distribution of emitted soot particles is. Are the emissions lognormally-distributed? If so, what are the lognormal parameters, including the mass emissions? Is the only source of nucleation-mode particles homogeneous nucleation, or were some particles emitted as with the soot mode?

7. A weakness of the present approach when examining results 90 m downwind is that the study does not account for 3-d transport (including vertical transport). This shortcoming should be acknowledged relative to other studies that have included such transport.

8. Summary and discussion. “A complete physical picture…” The authors need to modify this statement in light of the fact that the model does not account for 3-D effects, Raoult’s law, or several coagulation kernel terms.

9. Summary and discussion. “In addition, we have shown that instead of BHN, the non-volatile cores are the source of observed nucleation mode in California.” Please acknowledge that other studies have examined this issue in the absence of particle traps and come to similar conclusions about the importance of organics in the nucleation mode.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 2715, 2008.