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**Evolution of Size Distributions with condensation of sulfuric acid on particles**

As energy and environmental pressures increase, interests in biofuels such as biodiesel and ethanol continue to grow. The size distribution and composition of particles can be affect by different types of biofuels as well as engine combustion modes. The emissions from diesel engines have been shown to have a direct correlation to the chemical structure of the molecules in the fuel (Stevanovic et al., 2013). Particle size distributions from diesel engines running on biofuels increase nucleation mode particles relative to diesel (Su et al., 2013). This shift may be caused by more semi-volatile organic carbon in the exhaust causing an increase in nucleated particles. Dimethyl carbonate, which increases the mass of oxygen in biofuels, has also been shown to shift the geometric mean diameter of particles towards smaller size in comparison the diesel fuel (Zhu et al., 2011).

 In this project various size distributions of particle emissions from diesel engines running on biofuel are chosen to predict their growth from the condensation of sulfuric acid. The size distributions from *Su et al., 2013*, *Stevanovic et al., 2013* and *Zhu et al., 2011* represent the different size distributions of biofuel emissions and thus were chosen for this project. To simulate condensation of sulfuric acid onto particles the Condensation Size Distribution Model from http://aerosols.ucsd.edu/aerosolsinmotion.html was used to determine the growth of the three distributions. Included this model was the Condensation Rate Equation (Eq. 11.29 from Seinfeld and Pandis).

 *Stevanovic et al., 2013* and *Zhu et al., 2013* both had initial distributions predominantly in Aitken and accumulation mode (appx. diameter 0.1 μm). The condensation of sulfuric acid did not affect the diameter of the size distribution because the diameter was large relative to the amount of vapor condensed. *Su et al., 2013* measured particles in nucleation mode (diameter of 0.001-0.01 μm), thus the condensation of sulfuric acid had a greater affect on mean diameter.

Size distribution can give us a clearer idea of particle origin, either anthropogenic or biogenic, however, they cannot tell us the composition. Often particles evolve in the atmosphere and are affected by a number of chemical and physical mechanisms. For example, when a vapor condenses onto a particle it can change the composition and in some cases the mean diameter. *Coggon et al., 2012* measured marine aerosol and impacts of shipping emissions during the E-PEACE campaign. Measurements of in cloud aerosols contained almost a 1:1 ratio of sulfate to the organic component (47% sulfate). The particles in the size distributions chosen in this project were assumed to be composed of 100% organics and the Condensation Model was used to model the marine aerosols measured during E-PEACE.

 Particles <0.10 μm in diameter are composed of a larger fraction sulfuric acid than particles ≥0.10 μm in diameter. The particles in the accumulation mode and larger half of Aitken mode are less affected by the condensation of sulfuric acid than particles in nucleation mode. The nucleation mode particles measured in *Su et al., 2013* took approximately 8 days to grow the final particles to a 1:1 ratio of sulfuric acid to organic component. *Zhu et al., 2011* and *Stevanovic et al., 2013* measured particles dominantly in accumulation mode, however, even after the condensation of sulfuric acid persisted for over 24 days, the ratio of sulfuric acid to organics did not reach 1:1, but rather 0.65:1.

**References:**

Coggon, M. M. and Sorooshian, A. and Wang, Z. and Metcalf, A. R. and Frossard, A. A. and Lin, J. J. and Craven, J. S. and Nenes, A. and Jonsson, H. H. and Russell, L. M. and Flagan, R. C. and Seinfeld, J. H., Ship impacts on the marine atmosphere: insights into the contribution of shipping emissions to the properties of marine aerosol and clouds, Atmospheric Chemistry and Physics, Volume 12, June 2012, Pages 8439-8458.

Stevanovic, S. and Miljevic, B. and Surawski, N. C. and Fairfull-Smith, K. E. and Bottle, S. E. and Brown, R. and Ristovski, Z. D., Influence of Oxygenated Organic Aerosols (OOAs) on the Oxidative Potential of Diesel and Biodiesel Particulate Matter, Environmental Science & Technology, Volume 47, June 2013, Pages 7655-7662.

Su, J., Zhu, H., Bohac, S. V., Particulate matter emission comparison from conventional and premixed low temperature combustion with diesel, biodiesel and biodiesel–ethanol fuels, Fuel, Volume 113, November 2013, Pages 221-227.

Zhu, Ruijin, Cheung, C. S., Huang, Zuohua, Particulate Emission Characteristics of a Compression Ignition Engine Fueled with Diesel–DMC Blends, Aerosol Science and Technology, Volume 45, 2011, Pages 137-147.

As energy and environmental pressures increase, interests in biofuels such as biodiesel and ethanol continue to grow. The pollutant emissions from diesel engines has a direct correlation to the chemical structure of the molecules in the fuel (Stevanovic et al., 2013). and in particular the size and composition of particles, have been shown to change with different biofuels and engine combustion modes. Particles size distributions from diesel engines running on biofuel,increase nucleation mode particles relative to diesel (Su et al., 2013). This shift may be caused by more semivolatile organic carbon in the exhahust causeing an increase in the growth on particles nucleated from volatile species. More oxidized fewer particles emitted (higher soluable organic fraction). Dimethyl carbonate, which increases the mass of oxygen in biofuels had been show to shift the geometric mean dimater of particles towards smaller size in compartison the diesel fuel (Zhu et al., 2011). Interestingly, the total number of particles can be reduced with the use of diesel oxidation catalyst (DOC), reducing finer particles.
 In this project, various size distributions of pollutant emissions from diesel engines running on biodiesel fuel from *Su et al., 2013, Stevanovic et al., 2013* and *Zhu et al., 2011* are examined to predict their growth from the condensation of sulfuric acid. To simulate condensation of sulfuric acid onto particles the Condensation Size Distribution Model from <http://aerosols.ucsd.edu/aerosolsinmotion.html> was used to determine the growth of the three distributions. Included this model was the Condensation Rate Equation (Eq. 11.29 from Seinfeld and Pandis).

*Stevanovic et al., 2013* and *Zhu et al., 2013* both had initial distributions predominantly in Aitken and accumulation mode (appx. diameter 0.1 μm). The condensation of sulfuric acid did not affect the diameter of the size distribution relative to *Su et al., 2013* because the diameter was large relative to the amount of vapor condensed. *Su et al., 2013* measured particles in nucleation mode (diameter of 0.001-0.01 μm), thus the condensation of sulfuric acid had a greater affect on mean diameter size and the growth of particles can be seen in the *Su et al., 2013* graph.

Coggon et al., 2012 measured ship impacts on marine aerosol during the E-PEACE campaign. The organics, sulfate, and total OM were measured in the emissions. Measurements of in cloud aerosols contained 47% more sulfate than organics. The particles from initial size distributions were assumed to be composed of 100% organics and the Condensation Model was used to model the results.

Particles emitted at <0.10 μm in diameter are composed of a larger fraction sulfuric acid than particles ≥0.10 μm in diameter. The particles in the accumulation mode and larger half of Aitken mode are less affected by the condensation of sulfuric acid than particles in nucleation and the lower bound of Aitken mode. *Su et al., 2013* contained particles in nucleation and Aitken mode, thus it took a very short period of time to grow particles to a 1:1 ratio of sulfuric acid to organics; approximately 8 days. (more particles?) *Zhu et al., 2011 and Stevanovic et al., 2013* all contained particles in the upper bound of Aitken mode and accumulation mode and even after condensation of sulfuric acid persisted for over 24 days, the ratio of sulfuric acid to organics did not reach 1:1, but rather 0.65:1.

**The geometric mean diameter of the particles shirtfs towards smaller size in comparison with that of the diesel fuel.**

 such as a low temperature combustion (LTC) increases nucleation mode particles relative

The magnitude of pollutant emissions from diesel engines running on biodiesel fuel is coupled to the structure of the molecular structure of the fuel (Stevanovic et al., 2013) [diesel engine running on different biofuels Particulate emission measurements were performed on a Euro III Cummins diesel engine coupled to a water brake dynamometer. ]. Emissions from a diesel engine running on different biofuels were analyzd in detail to explore the role that different organic feactions play in…. Low emission diesel combustion modes, such as premxed low temperature combustion(LTC) are also of interst. On study examined particulate matter from a single cylinder rail diesel engine operated under conventaion and premixed LTC (Su et al., 2013) with diesel, biodesel and biodesil-ethoanol fules.

Generally, the magnitude of pollutant emissions from diesel engines running on biodiesel is related to the chemical structure of molecules in the fuel.

For premixed LTC, biodiesel shifts the accumulation mode size distribution curve upwards (i.e., more particles) and towards smaller size particles relative to diesel. The shift in size distribution for biodiesel may be caused by more semi-volatile organic carbon in the exhaust causing an increase in the growth of particles nucleated from volatile species, and less soot leading to a reduction in the number of large carbonaceous agglomerates.

Biodiesel increases LTC nucleation mode particles relative to diesel. Biodiesel-E20 increases the amount of small nucleation particles (<20 nm) and decreases the amount of large nucleation particles (20–50 nm) relative to diesel. Biodiesel-B20 produces the lowest soot and total particle number concentration, both at conventional and premixed LTC, demonstrating its potential as an alternative fuel for diesel engines.

Zhu et al., 2011 **compression-ignition engine fueled with Euro V diesel fuel blended with dimethyl carbonate (DMC) was investigated experimentally Blended fuels containing 4.48%, 9.07%, 13.78%, and 18.6% by volume of DMC, corresponding to 3%, 6%, 9%, and 12% by mass of oxygen in the blended fuels, were investigated.**

**Total number of particles of all reduced.**

**The geometric mean diameter of the particles shirtfs towards smaller size in comparison with that of the diesel fuel. The particulat mass concentration, can be reduced by the use of dielse oxidation catalyst (DOC). Particles shift towards larger geometric mean diamtere for each fuel. Indication that the DOC could reduce finer particles.**

**The articles are saying different things.?**