

Development of Flow Reactor for Secondary Organic Aerosol Formation

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Keywords: secondary organic aerosol, flow reactor, Photo-oxidation, OH exposure.

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A substantial fraction of atmospheric fine particles are composed of secondary organic aerosol (SOA). SOA causes adverse health issues and affects radiative stability by absorbing and scattering solar radiation. Its physicochemical properties also affect cloud formation processes. Recently, compact flow reactors with wide oxidation exposure are being used as an additional tool to conventional smog chamber in SOA studies (Kang et al., 2007; Lambe et al., 2011). This study reports newly developed flow reactor for SOA researches. Residence time distribution (RTD), control of temperature and relative humidity (RH), and OH radical exposure were characterized for the reactor. SOA formations from dark ozonolysis and OH radical initiated photochemical reaction for representative organics were examined.

New flow reactor of this study includes reaction tube, radiation source, reactant injection system, and OH radical generation system. The reaction tube is made of 2 mil thick cylindrical FEP (ID 15 cm × L 70 cm). Four 32W UV lamps ($\lambda = 254$ nm) are used as radiation source. Two 480 W Peltier modules are used for cooling the reactor. Air stream heated by 530 W heating tape is used to evaporate reactants (e.g., organics and H₂O). O₃ is generated by the UV photolysis ($\lambda = 185$ nm) of high purify O₂. OH radical generation is instantly carried out by UV photolysis ($\lambda = 254$ nm) of the mixture of O₃ and H₂O in flow tube. Oxygen atom radical forms by photodissociation of O₃ and then reacts with H₂O to form OH radical

RTD was measured by injecting NO for 15 s into the reactor. Figure 1 shows measured RTD and those for ideal plug and laminar flow. Measured NO peak was ~0.6 times earlier relative to ideal plug flow. Actual RTD showed earlier arrival and longer tailing compared to ideal laminar flow. It might be due to non-ideal axial mixing in the reactor.

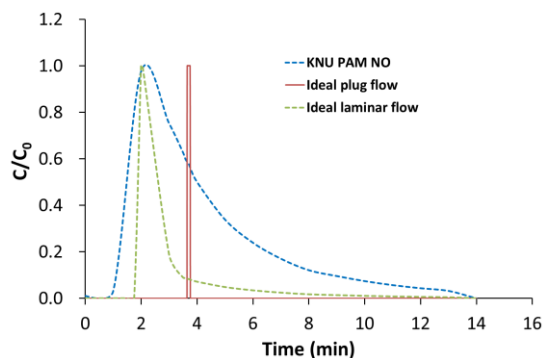


Figure 1. Residence time distribution of KNU flow reactor.

OH radical concentrations were estimated by photochemical decay of toluene that has well documented OH reaction rate constant and negligible reactivity to O₃. OH concentrations was calculated to be from 8.2×10^{10} to 7.2×10^{11} molecules cm⁻³ for O₃ and RH from 2000 to 8000 ppb and from 10 to 60%, respectively, by assuming first order decay of toluene by OH radical. Comparing to atmospheric OH concentration of 1.5×10^6 molecules cm⁻³, OH level in the reactor corresponds to atmospheric oxidation of ~0.5 to ~5 days.

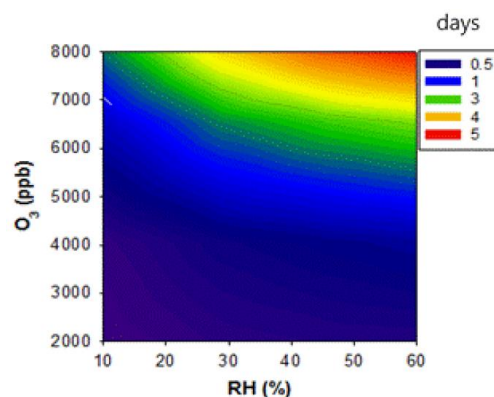


Figure 2. Contour plot of atmospheric aging time as a function of O₃ level and RH.

In this study, SOA yields of α -pinene dark ozonolysis at different temperature and RH were comparable to literature data. In OH initiated SOA formation, SOA yield decreased from 0.58 to 0.25 for α -pinene, 0.33 to 0.10 for Δ^3 -carene, 0.45 to 0.08 for toluene, and 0.65 to 0.06 for ethylbenzene with increase in OH exposure from 8.2×10^{10} to 7.2×10^{11} molecules cm⁻³ s⁻¹. Further details will be discussed in the presentation.

Kang, E., Root, M.J., Brune, W.H. (2007) *Atmos. Chem. Phys.* **7**, 9925–9972.

Lambe, T., Ahern, T., Williams, L.R., et al. (2011) *Atmos. Meas. Tech.* **4**, 445–461.