

Response to Reviewer #2

General comments:

This work reports secondary organic aerosol (SOA) formation by OH radical oxidation of VOCs emitted from heated cooking oil using an oxidation flow reactor approach. Cooking emissions have been recognized as one of the major primary organic aerosol (POA) sources in urban environments. However, SOA formation potential of cooking emissions are largely unknown and hence this study is of great interest to the atmospheric community. Although the observations presented in this manuscript is qualitative due to their experimental limitations, this work clearly demonstrates SOA formation from cooking emissions that provide sufficient insight into future studies. The experiments are well performed in general but some clarifications are required, in particularly the relative importance of other oxidation chemistry in the flow tube reactor. The manuscript is well written and organized. I recommended this manuscript to be published in Atmospheric Chemistry and Physics after addressing the specific comments below:

Specific comments:

Q1: This manuscript focuses on discussing SOA production from OH radical oxidation chemistry. However, a recent modelling study by Peng et al. (2016) has illustrated potential significance of non-OH chemistry in oxidation flow reactors (OFR) for degradation of various SOA precursors. For example, some unsaturated VOCs such as monoterpenes might largely involve in the reaction with ozone depending on operating conditions of OFR. Since this manuscript demonstrates that mono- and poly-unsaturated fatty acids are important SOA precursors from heated cooking oils, it is necessary to comment on the relative importance of non-OH chemistry in the PAM reactor, especially for ozonolysis of unsaturated fatty acids, and how may this related to the observations reported in this manuscript. Control experiments of ozonolysis in the absence of OH radical may provide insight into this issue.

R1: As was also mentioned by Reviewer 1, it should be noted that the organic vapors studied here were not the specific fatty acids present in the raw oils, but the thermal

breakdown products of these fatty acids. According to Klein et al. (2016), emissions of VOCs from heating cooking oils were dominated by saturated and unsaturated aldehydes. In this study, the ratio of O₃ exposure to OH exposure ranged from 1.5×10⁵ to 1.9×10⁵, relatively lower than tropospheric values (Schmidt et al., 2014). At this O_{3exp}/OH_{exp}, ozonolysis of saturated and unsaturated aldehydes was negligible since the ratios of their ozonolysis rate constants to OH rate constants were in the range of 10⁻⁹ to 10⁻⁷. (Grosjean et al., 1993; Atkinson and Arey, 2003). Thus reactions with O₃ played a negligible role in this study. In addition, SOA formation in the absence of OH radicals was also tested. As shown in Fig. 3 in the revised manuscript, during the initial 10 min of heating, the mass concentration of organics was close to the detection limit of the instrument. During these periods of experiments, OH radicals were not present, indicating that ozone chemistry had a negligible influence on SOA formation in this study.

The following sentence has been added to the manuscript.

“Peng et al. (2016) found that non-OH chemistry, especially reactions with O₃, may play a role in the oxidation flow reactors for consumption of VOCs. According to Klein et al. (2016a), emissions of VOCs from heating cooking oils were dominated by saturated and unsaturated aldehydes. In this study, the ratio of O₃ exposure to OH exposure ranged from 1.5×10⁵ to 1.9×10⁵, relatively lower than tropospheric values (Schmidt et al., 2014). At this O_{3exp}/OH_{exp}, ozonolysis of saturated and unsaturated aldehydes was negligible since the ratios of their ozonolysis rate constants to OH rate constants were in the range of 10⁻⁹ to 10⁻⁷. (Grosjean et al., 1993; Atkinson and Arey, 2003). Thus reactions of VOCs with O₃ played a negligible role in this study.” (Line 99-107).

“During these periods of experiments where OH radicals were not present, we found that ozone chemistry had a negligible influence on SOA formation in this study.” (Line 205-207).

Q2: Line 88: What was the initial ozone concentration in the PAM reactor?

R2: The ozone concentration in the PAM reactor was adjusted to five different levels, ranging from 0.4 ppm to 2.7 ppm. This sentence has been added to the revised

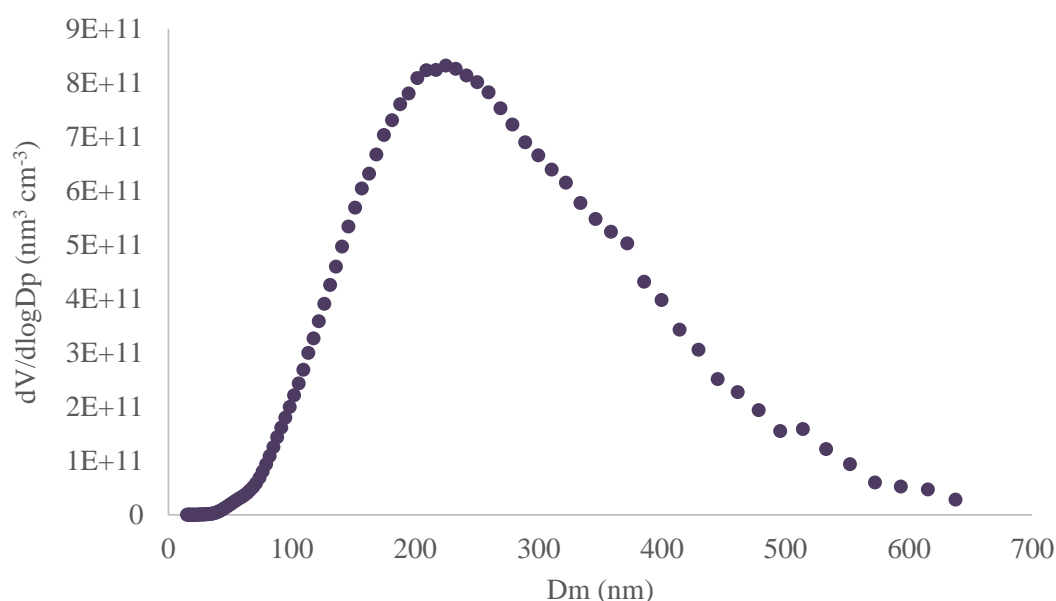
manuscript (Line 91-92).

Q3: Line 111: Was the Teflon line heated and temperature controlled to minimize wall loss of VOCs? Please clarify.

R3: This issue has been addressed in response to Q4 of Reviewer 1.

Q4: Particle mass determination from SMPS data: Line 131: In general, particle effective density of SOA can be estimated by comparing SMPS data and particle time-of-flight (PToF) measurements from AMS in laboratory experiments. Did the authors conduct this type of estimation to validate their assumption? Furthermore, Figure 1 illustrates that aerosol particles were not dried before SMPS measurements. Please discuss uncertainties of SOA mass calculation due to the presence of aerosol water content.

R4: The following figure shows the volume distribution of SOA measured by AMS for sunflower oil at an OH exposure of 1.7×10^{11} molecules cm^{-3} s. The mode diameter fell in the range of 210 nm to 230 nm. This variation of mode diameter might lead to large uncertainties in calculating the effective density. For instance, the effective density for sunflower oil SOA was estimated to be 1.55 ± 0.28 by comparing SMPS data and PToF measurements from AMS. The density of SOA for other oils was expected to be similar with that for sunflower oil, considering their similar H:C and O:C ratios. Taking considerations of the large uncertainty, the assumption of 1.4 g cm^{-3} is reasonable.



Lambe et al. (2011) investigated the cloud condensation nuclei activity of PAM-generated SOA and found that the hygroscopicity parameter κ_{org} was linearly correlated with O:C ratios. Based on their κ_{org} -to-O:C relationship, we estimated an upper limit of κ_{org} to be 0.089 in this study. The overestimate of SOA mass due to water uptake were thus determined to be less than 18%. The following sentences have been added to the revised manuscript.

“Note that particles were not dried prior to SMPS measurements, which might lead to an overestimate of SOA mass due to the uptake of water by organics. Lambe et al. (2011b) investigated the cloud condensation nuclei activity of PAM-generated SOA and found that the hygroscopicity parameter κ_{org} was linearly correlated with O:C ratios. Based on their κ_{org} -to-O:C relationship, we estimated an upper limit of κ_{org} to be 0.089 in this study. The overestimate of SOA mass due to water uptake were thus determined to be less than 18% (Petters and Kreidenweis, 2008; Pajunoja et al., 2015).” (Line 171-179).

Q5: Line 147: What was the collection efficiency (CE) for the SOA produced? Primary cooking organic aerosol is likely oil-like droplets that gives CE approximately equal to 1. Such information can provide insight into the viscosity of SOA produced from cooking emissions (i.e. particle bouncing on tungsten vaporizer increased with particle

viscosity).

R5: The CE varied from 0.38 to 0.78 in this study. Given that a diffusion dryer was used to remove water, which may change the morphology of SOA, we may not speculate on the viscosity of SOA.

The following sentence has been added to the manuscript.

“The value of CE varied from 0.38 to 0.78 in this study.” (Line 171).

Q6: SOA production rate: I agree that it is reasonable to define SOA production rate as SOA mass produced per minute due to the experimental limitations (i.e. no VOC measurements). However, considering emission rates of VOCs from oils at a given temperature can be different, an additional SOA production rate defined as SOA mass produced per volume of oil evaporated may be able to reduce one experimental variable for interpreting the data (e.g. line 195-196). It is recommended to perform such calculation if the evaporation rate of oils were measured (i.e. volume change of heated cooking oils before and after heating).

R6: The reviewer proposed a very good method to constrain the SOA production rate. But the evaporation rate of oils was not measured to perform such calculation in this study. Actually, it is difficult to measure the volume of cooking oils consumed as the oils became stickier after heating. We will adopt this method in the future study.

Q7: Lines 213-216: What were the emission rate of POA from heated cooking oils? Please include this information (if available) in the comparison.

R7: During the measurement of POA, the cooking oils were heated in a pan. We were not sure about the fraction of emissions introduced into the PAM reactor while all emissions were introduced to the PAM for SOA experiments. Thus, only mass spectra and elemental ratios of POA were discussed in the manuscript.

Q8: Lines 256-260: This argument is true if SOA is only a minor contributor to total COA mass because typical mass spectrum of COA factors have high m/z 41-to- m/z 43 ratios which are similar to the POA of heated cooking oil. Furthermore, typical diurnal patterns of COA show a strong peak during dinner time with extremely low OH radical concentration in the atmosphere. Of course, VOCs from cooking can react with other atmospheric oxidants but it is unclear if SOA produced by night time chemistry gives

the similar mass spectrum.

R8: This issue has been addressed in response to Q1 of Reviewer 1.

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