Summary:

I have reviewed the paper “Liquid-liquid phase separation in particles containing secondary organic material free of inorganic salts” by the authors M. Song, P. Liu, S. T. Martin, and A. K. Bertram, which was submitted to *Atmos. Chem. Phys. Discuss.* This paper expands on previous work in which Renbaum-Wolff et al. found that in particles composed of secondary organic material (SOM) generated from α-pinene, liquid-liquid phase separation (LLPS) could occur at very high relative humidities (RH > 90%) in the absence of salt. Such a result may explain discontinuities in hygroscopicity observed below and above water saturation. This paper extends this research to SOM generated from β–caryophyllene, limonene, and toluene. LLPS is observed for the first two compounds, and not for the third. Overall, the data in the paper are of interest to atmospheric chemists and will make a good contribution to this journal. I have several major and minor comments, as indicated below, which should be addressed prior to publication. Major comments are preceded by a “*”.

Abstract:

* O:C ranges overlap, which could be confusing to readers. Since only three systems are studied, it would be more accurate to state that you observed phase separation for BVOC oxidation products and not for toluene SOA. Plus, the O:C ratios obtained are averages over all SOA compounds formed in the experiment. LLPS may be observed due to a small concentration of compounds at very low O:C. To state a range may therefore be misleading.

Intro:

pg 2 line 8: Both low volatility and semivolatiles can partition to the particle phase

pg 2 line 24: LLPS can occur at O:C < 0.56 and does not occur at O:C > 0.8 according to your previous papers

pg 2 line 27: Peters is not cited. Perhaps you mean Petters et al.?

pg 2-3 lines 29,30,1: Change to “which could result in altered CCN properties” or similar, as the results from Renbaum-Wolff et al. are simulations of CCN data rather than experiments

pg 3 lines 1-4: The results of Hodas et al. ACP 2016, 16, 12767-12792 should be discussed here.

Materials and Methods:

The error for the hygrometer (2.0% RH) seems high. Can the authors comment further about where this error is coming from (e.g. rate of RH ramp)?

Results and Discussion:

* pg 6: More evidence is needed to support the claim that LLPS is occurring by spinodal decomposition. Comparing to the data in Ciobanu et al. 2009, both the results in this paper and Renbaum-Wolff et al. 2016 clearly look like nucleation and growth (formation of small inclusions), as no schlieren are observed.

* pg 6: It is reasonable to assume that the water-rich organic component is in the core of the particle and the more-insoluble organic is in the shell, but what evidence is there for this assignment?

* pg 6: It is important to note that while core-shell structures are observed for these systems, without the substrate, they could be either partially engulfed or core-shell. It is less clear that there would be an effect of LLPS on CCN for these systems if they are partially engulfed in morphology.

pg 7 line 4: The term "mixing" is more consistent with previous literature in this field (see for example Fig. 2 in the review from your group by You et al. in 2014). Later in this section, "MRH" is the mixing RH.

pg 7 line 8: Do you expect that particle mass concentrations will change O:C? Why is there a question that this will have an effect on LLPS?

pg 8 lines 15-23: SOA has a range of O:C values; the best that can be reported are average values. It could just be the very low O:C compounds that phase separate. It is therefore hard to understand how the systems used in this experiment can be compared to systems composed of only three components.

Implications:
pg 9 lines 9-13: The Hodas et al. reference mentioned above should be added here.

Table 1&2: It would be nice to list average O:C for these exact systems, if known.

* Table 3: This table shows the minimum and maximum O:C range observed in the literature for SOM derived from these species, rather than O:C from the experiment run in this study. This is not ideal, but it may be due to experimental limitations. I worry, however, that O:C will change dramatically depending on how a system is oxidized and for how long. Are these comparable techniques to what you used? Do the numbers represent both chamber and flow tube studies? More information is needed here or in the text to understand how to interpret this data. Plus, Table 3 & 4 are not consistent with one another (the highest O:C for alpha-pinene is 0.70 according to Table 4).

Figure 4: The first sentence of the legend is not clear. You are plotting SRH and MRH for the systems.