RESPONSES to REFEREE #2

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This manuscript presents measurements of single scattering albedo (SSA) of size-selected aerosols emitted from controlled combustion of African biomass fuels under three conditions: fresh emissions, dark aged aerosols and photo-chemically aged aerosols. Three types of wood fuels were combusted in a tube furnace at two different temperatures (500 C and 800 C) and an indoor smog chamber was used to age aerosols in clean and polluted (VOC rich) environments.

***AUTHOR RESPONSE**: We thank the reviewer for the time he/she took to provide us with valuable suggestions. The authors feel that the reviewer either misunderstood our descriptions and overlooked some aspects of the paper. We will show this is indeed true in our detailed responses with relevant references to each question and comment. We feel that there is rush to dismiss and devalue the work and undermine the paper instead of giving us a chance to respond and clarify our claims. We hope our responses and explanations will convince the referee to make a different final determination.*

The authors claim that the significance of their work lies in providing optical and chemical characterization of a previous unstudied group of fuels that contribute significantly to aerosol emissions in Africa. However, there are no novel findings reported in this study and claims of significance are greatly overstated. While the particular fuels in this study might not have been characterized, there is a robust body of literature regarding the effect of combustion conditions on optical properties of emitted aerosols in controlled (example: Chen and Bond, 2010, ACP; Saleh et al., 2018, ES&T) as well as representative household use (Roden et al., 2006, ES&T; Chen et al., 2012, ES&T) settings. This study was limited by a lack of chemical characterization and SSA measurements limited to mid-visible wavelengths, and therefore could only reiterate the well-known effect of combustion temperature on absorption efficiency.

***AUTHOR RESPONSE**.*

There is no doubt that emissions from African continent is a major source of atmospheric aerosol, but their optical properties are least studied compared to emissions from other regions. Even though there are several studies on the impact of burning conditions on optical properties, we don’t have full understanding as to why certain fuels burn with higher efficiency. For example, savannah grass fires tend to be of flaming type while boreal fires tend to be of smoldering type (Saleh et al., 2014). In addition, optical properties (such as absorption per mass) also show fuel dependency (Chen and Bond, 2010). All these facts suggest that we need more studies on different unstudied group of fuels. A recent critical review by Hodshire et al. (2019) recommends the following: “(1) More smoldering fires within the laboratory setting should be studied. As well, methods to more closely match field burns should be developed, such as burning more compact fuels/larger amounts… (2) A wider sampling of fuels as laboratory studies have been focused predominantly on fuels that may exist in North American fires.” This paper address both recommendations.

Regarding all the examples provided by the reviewer, work by Chen and Bond, 2010 was done at lower temperatures (max 360 °C) whereas Saleh et al. 2018 was done for propane not for *a biomass fuel. So, we think more studies are needed on biomass combustion. This work is presented as a two-part study, where this part focused on optical properties and chemical composition and characterization is presented in Part II, which is published in ACPD and we will refer the reviewer to the second part for a detailed discussion(Smith et al., 2020). Further integration of the two manuscripts will be done, and summaries from Part 2 will be incorporated into the revised manuscript.*

Following the paragraph contrasting eucalyptus and acacia combusted at 800^o C, the following text will be added to line 393:

"In the companion paper to this (Part 2), methanol extracts from BBA collected on Teflon filters were analyzed by ultra-performance liquid chromatography interfaced to both a diode array detector and an electrospray ionization high-resolution quadrupole time-of-flight mass spectrometer (UPLC/DAD-ESI-HR-QTOFMS) in negative ion mode. This was used to determine the relative abundance and light-absorption properties of biomass burning organic aerosol constituents. MS analysis of BBA extracts from combustion at 800 °C revealed very little difference between the two fuel types, suggesting that there are either very few BrC species produced for either fuel under these combustion conditions, or there are numerous species that are essentially the same between the samples. However, given that Eucalyptus has a higher SSA than Acacia, this would suggest that Eucalyptus has more non-absorbing OA, or at least less absorbing than BC. Since it is Acacia that appears to have many more low-abundant organic constituents, several possibilities exist to explain these differences in SSA, as explored in more depth in Part 2. It is likely that Eucalyptus combustion products are not captured by some aspect of the extraction and UPLC/DAD-ESI-HR-QTOFMS analyses, that the observed differences in SSA are due to morphology differences, or some combination thereof. One potential explanation would be the presence of significant amounts of eucalyptol in the BBA, which is a large fraction of Eucalyptus oil, and is a cyclic ether that lacks any basic functionality amiable for negative ion mode analysis, has good solubility in alcohols, and does not absorb in the UV and visible. An examination of the UV-Visible spectra from the DAD shows no absorbing species in either region."

The following paragraph will be included in the manuscript following the discussion of fresh emissions produced by combusted at 500^o C, added to line 410:

"Chemical analysis revealed that, when combusted at 500 °C, eucalyptus and acacia had a variety of compounds in common, such as lignin pyrolysis products, distillation products, and cellulose breakdown products. Several lignin pyrolysis products and distillation products are more prevalent in Eucalyptus than Acacia, while pyrolysis products of cellulose and at least one nitroaromatic species were more prevalent in Acacia. Given that these lignin pyrolysis and distillation products are known chromophores and are more prevalent in Eucalyptus than Acacia, while Acacia has a higher abundance of non-chromophores derived from sugars and cellulose, one would assume that Eucalyptus would be more absorbing in the visible (i.e. have a lower SSA) than Acacia. Despite the chemical analysis not capturing absolute amounts of OA, Acacia was found to have an SSA that is higher than Eucalyptus by 0.1 to 0.2, which is consistent with chemical measurements. This suggests that Acacia has either larger absolute amounts of non-chromophore compounds or Eucalyptus has a greater quantity of chromophores whose absorptive properties extend to the 500 – 570 nm region of the visible spectrum. An analysis of the chromatographically-integrated UV/Visible spectrum shows that there are chromophores whose absorption features

peak ~290 nm and extend into the 500 – 570 nm region, though a normalized spectrum does not appear to show drastic differences between species."

Contrary to the reviewers comment we believe that our claim is not overstated for several reasons.

(1) Most current optical properties measurements are limited to a single or a few selected wavelengths. The accurate measurement of aerosol optical properties over the <u>entire solar spectrum</u> is a technological challenge. ***Our system allows measurement of optical properties at a wide range of wavelengths over most of the solar spectrum to determine "featured" absorption cross sections as a function of wavelength.*** *While most of the example provided by reviewer are limited to single wavelength our study was done for 500-570 nm range, and it is within our capability to conduct extinction measurements from 400-800 nm at any wavelength interval by simply changing mirrors. This represents a significant effort with the current dataset and lets its novelty be its justification. We haven't come across any experimental set up for aerosol optical properties measurement that can accomplish this.*

*(2) We have more control of the combustion process. The tube furnace enables us to study different burning stages by controlling the temperature and speed of burning by adjusting the flow of air into the furnace. We have not come across aerosol optical measurement system that uses a tube furnace with so much control of the burning condition, as most studies simply burn an amount of fuel amenable for their measurement devices. The burn system closest to ours is the one reported by Chakrabarty's group (Sumlin et al., 2018b) where a heating coil is used to control temperature. The main difference is uniformity of the temperature throughout the furnace as opposed to a localized temperature in a coil and the control of the gas mixture flow during the burning***.*** *We have elected to present a range of combustion conditions to cover a range of combustion scenarios that could depend on different combustion circumstances (wildfires, land clearing, etc.).*

(3) Soot generation was done using a tube furnace, which was attached to an indoor chamber, and samples were directly fed into the optical properties measurement system to measure the optical properties as a function of aging. While smog chambers are not new, such an integrated system is not common.

We are surprised that the reviewer overlooked all the experimental features which alone are significant. Moreover, we disagree with the reviewer that our study does not have novel findings.

1) *There has never been a laboratory study of BB aerosols from biomass fuels in the region that we are aware of.*
2) *We showed that by just changing burning temperature, the SSA of emitted aerosol differ very significantly for the same BB fuel. This was different than Saleh et al. 2018, which was done for propane not biomass fuel. We showed that nighttime aging (dark aging) increase the SSA of aerosol, which we think this is one of the very few studies to report that.*

In that sense, this work represents attempt towards filling the gaps in our understanding of biomass burning aerosol optical properties in this under-sampled and ignored part of the world. Africa is *the single largest continental source of BB emissions, with recent studies estimating that it makes ~55% of the global contributions to BB aerosols (Ichoku et al., 2008;Roberts et al., 2009;Roberts and Wooster, 2008;Lamarque et al., 2010;van der Werf et al., 2010;Schultz et al., 2008). Measurement of optical properties of biomass fuels from the region is long overdue.*

The aging experiments show that both dark and photochemical aging reduce the absorption efficiency of size-selected aerosols (photochemical more so than dark) but no chemical properties were measured to illuminate the mechanism of absorption loss.

AUTHOR RESPONSE*: In the accompanying paper, we analyzed methanol extracts from Teflon filters, as detailed in the excerpt above. Given that this is the main subject of Part 2, it wouldn't be appropriate to go into significant depth here, and we would refer the referee to the accompanying paper that is on ACPD for a detailed discussion. While measurements of dark aged samples were not performed, a summary of results from Part 2 regarding the light aged BBA will be provided and incorporated into the manuscript. With regards to photochemical aging, the text will be amended at line 504, as described* ***two comments down from this.***

Further, the aging results are only presented for 500 C aerosols because (Line 471): "Therefore, due to the very low number concentration and highly absorbing nature of the particles, the scattering coefficient at 800 C was below the detection limit of our nephelometer during the aging experiments." The authors propose that future studies will include these missing measurements (performed by increasing the amount of fuel burnt) but I am puzzled why these changes were not made for this study.

AUTHOR RESPONSE*: We tried the aging experiment with higher load and were not successful due to the limitation in the amount of fuel we can burn in our system at a single time. Furthermore, our current setup prohibits bulk aerosol measurement. This work is focused on conducting measurements for size selected particles. It is possible to perform these measurements for the entire size distribution, but this brings its own challenges and other parameters, such as changes in the size distribution itself, become unconstrained.*

There are similar problems with aging experiments in a polluted environment (Line 505: "This is because we took our measurements after 12 hours of aging, which seems long enough to characterize the impact of the added VOC due to aging in UV. This fact suggests that a more carefully controlled study is needed to accurately simulate the impact of urban pollution on aerosol single scattering albedo") that indicate that the authors did not rigorously handle their motivating hypotheses, leaving glaring holes in their manuscript.

AUTHOR RESPONSE: *This is hardly the case, though the authors admit that this could be phrased better. Starting at line 504 with the sentence "We attempted…", the remainder of this paragraph and the next (after Figure 7) will be replaced with the following text:*

"Despite the use of anthropogenic VOCs, a concentration larger than those average values found in urban and suburban regions of South Africa, no distinct effect was observed for SSA

values of BBA produced during combustion at 500 °C. While it is possible that the relatively long aging time could obscure some of the effects due to the presence of VOCs, it is also possible that combustion products dominate molecular species and the effects of additional VOCs are insignificant. The later would suggest that anthropogenic pollution does not seem to affect the optical properties of BBA. Indeed, in examining the effects of aging on the chemical composition of BBA shows very few species that could be attributed to anthropogenic VOCs; specifically, only dihydroxyphthalic acid produced from xylene. For both Eucalyptus and Acacia, an isomer of dihydroxybenzene, such as resorcinol or catechol, was removed to the highest degree from the fresh BB aerosol upon photochemical aging. Generally, very few compounds were produced to a significant extent and both fuels were dominated by loss of chromatophoric lignin pyrolysis and distillation products. Not surprisingly, the associated absorbance from these chromophores, mostly from 200 – 350 nm, also attenuated with respect to age. This may be caused in part by the photo-bleaching effect created by irradiation of UV light for 12 hours, heterogeneous OH oxidation, and SOA formation of non-chromophores.

This fact suggests that a study with a higher temporal resolution is needed to simulate the impact of the VOCs on aerosol SSA, where continuous or much more frequent measurement are needed to determine impact of urban pollution on aerosol single scattering albedo. Such a study, using continuous measurements, is not possible for our setup when particles are also size selected. Like dark aged conditions, we were not able to estimate SSA for combustion at 800 ^oC due to the low particle concentration and highly absorbing nature of the aerosol. A chemical analysis of aged BBA produced at this temperature revealed very few changes, suggesting there are few molecular species produced by combustion at this temperature."

Indeed, this is substantiated later in the paper by the lack of OA enhancement from the presence of anthropogenic VOCs.

Aside from concerns about significance and study design, there are significant issues in how the manuscript is presented. Instances of grammatical errors and confusing sentence construction are far too many to enumerate but more importantly, several arguments/claims are not supported by findings in this study or citations from literature.

AUTHOR RESPONSE*: *We thank reviewer for constructive comment and pointing out the grammatical errors. There is indeed no excuse for this and we will thoroughly review the manuscript to fix the grammatical issues and clarify confusing sentences.

The authors establish that the fuels studied here are household fuels and acknowledge the potential differences between typical household use and controlled burning. They do not present any discussion of how findings from controlled combustion can be extended to a more realistic condition: this undermines the purported importance of their findings.

AUTHOR RESPONSE: *We thank reviewer for valuable comment. While laboratory studies provide opportunities for control over the environmental and chemical conditions, so we can examine the effect of changing single variable at a time, a limited number of fuel-specific comparisons can be made between the laboratory and field studies given the lack of adequate field studies in Africa. Recreating the atmospheric conditions of plumes in the field, is still a challenge though this is a long-term goal of our research group. We acknowledge that there are significant* *knowledge gaps that limit a full understanding of how field and laboratory observations can be reconciled. This should not be a reason not to do laboratory experiments, but rather the reason to do more of those so we can clearly understand the physics and chemistry that governs the observed variability. However, we added following discussion on L 98: "This study was done in more controlled environment and to extend the result from this kind of study to more realistic condition we apply our optical property result to previously proposed parameterization schemes."*

Further, they designate their 800 C burn condition as flaming (a reasonable assumption) and 500 C burn as smoldering (which is much higher than smoldering temperatures in literature). These assumptions are not substantiated with any further evidence. The SSA values reported for smoldering appear too low for pure smoldering combustion (eg. - those in (Sumlin et al., 2018a) and I am not convinced that the authors ensured that they are not from mixed combustion conditions.

AUTHOR RESPONSE: *We agree with reviewer. There is no clear single line that separates the smoldering and flaming fires, and it is likely that there is a gradient of conditions as a function of temperature. The designation was made based on the observed colors of the filter samples and measured MCE's. The latter is, of course, quantitative and enables the comparison of this work to others. Changes will be made throughout the manuscript with 800 ^{o}C described as "flaming-dominated burning" and 500 ^{o}C as "smoldering-dominated burning". As evident from the estimated MCE, flaming dominated and smoldering dominated are valid descriptions.*

Line 415 (comparing SSA values here with previous studies) states: "This could explain why our SSA calculations for BrC was lower than expected". All measurements in this study are for total aerosols, BrC is mentioned without any justification.

AUTHOR RESPONSE: *We appreciated reviewer comments. We will replace BrC with the phase "smoldering-dominated aerosol" throughout the manuscript. We agree that aerosol emissions at 500 ^{o}C have contributions from black carbon and other organic/inorganic components.*

Many hypotheses are presented for the aging observations however the study was not conducted in a way that allows any plausible claims about "night-time formation or aromatic nitrogen containing compounds", for example. SOA formation is presented as a hypothesis for SSA reduction (Line 492) during photochemical aging but fragmentation of absorbing aerosols is not considered.

AUTHOR RESPONSE*: We thank reviewer for constructive comments. The reason for making hypothesis for SOA formation during dark aging was that the SSA increase in those experiments was driven by an increase in scattering cross section with no evidence of changes in absorption cross section, as mentioned in the manuscript (L 455-458). There is lots of evidence of nighttime chemistry resulting in relatively high amounts of nitrogen containing SOA (Hartikainen et al., 2018;Tiitta et al., 2016;Li et al., 2015). That is the reason we made a statement about this possibility for our experiments. We acknowledge that this is a rich subject area, and there could be a variety of chemical transformations, such as acid-catalyzed reactions.*

Regarding reviewer comments on photochemical aging, we also talked about the possibility of fragmentation of absorbing aerosol. As stated on Line 494-95 "An increase in SSA is possible during photochemical aging due to degradation in brown carbon absorptivity (Sumlin et al., 2017). So, we think we were not sticking only to an SOA hypothesis. If the reviewer is referring to the physical fragmentation of aerosol, the authors are not familiar with this process, nor do we consider it very likely. If the reviewer is referring to "collapse" of aggregates into shapes that are more spherical, it's very unlikely that such large changes in SSA can be attributed to that process.

Finally, the choice of figure type for representing the results in figures 4, 6 and 7 is baffling to me: why are SSA values plotted over this very narrow range of wavelengths? Clearly, no wavelength dependence can be seen between 500 and 570 nm. I fail to see the purpose of multiple figures that contain a series of zigzagging flat lines.

AUTHOR RESPONSE: *Clearly, the purpose of those figures was to see the wavelength dependency, or lack thereof in this case. As previous studies (Sumlin et al., 2018a) showed that BrC has an impact on SSA with lower SSA at shorter wavelengths, though these measurements were performed at discrete wavelengths (like 405, 532, 600 etc.) and it was not quite clear that this range of wavelengths definitively shows a BrC effect on SSA. Most of the previous studies were limited to either 405, 532, 660, 780 nm measurements and the behaviors in between those wavelengths is typically assumed. Assuming something like a power-law dependence cannot realistically hold for a wide range of wavelengths. That's why we present whole range of SSA measurements between 500 to 570 nm which may appear as zigzag lines. Previous work in our laboratory shows that, even at this wavelength range, a wavelength-dependent SSA can be observed, and it should not be taken for granted or assumed that the range is too narrow for a wavelength-dependent conclusion to be made; only that the results are restricted to the most intense portion of the solar spectrum.*

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